

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at Manson House, Portland Place, London, W.1, on Wednesday, May 7, 1947, the Chair being taken by Mr H. C. Tett (Vice-President and Chairman of Council).

After the General Secretary (MR F. H. COE) had read the names of newly elected members, the Chairman said: It is now my pleasure to hand the meeting over to the Chairmanship of Dr A. Parker, C.B.E., the Director of the Fuel Research Station of the Department of Scientific and Industrial Research. Dr Parker is well known to us all, and we are very fortunate that he has agreed to occupy the Chair this evening. He was closely associated with Major Gordon in the work which resulted in this paper, and I am sure we could not wish for a better Chairman.

DR A. PARKER, having formally occupied the Chair, said: First I will strike a personal note and say how much I appreciate the invitation to occupy the Chair, as an outside Chairman, for the presentation by my old friend Major Gordon of his paper on the development of hydrogenation and Fischer-Tropsch processes in Germany.

It is my task to introduce Major Gordon, but I am certain he is so well known to everybody here that he really needs no introduction. You all know of his outstanding work, particularly at Billingham, in relation to coal hydrogenation, the hydrogenation of creosote, tars, and so on, and also his work in relation to the hydrogenation of certain petroleum fractions for the production of high-octane aviation spirit, which in large measure helped us to win the war. Without a spirit of that kind we certainly should not have won the Battle of Britain or have been able to proceed further.

I am not sure, however, that you know of Major Gordon's activities in relation to the investigation of the processes in Germany. Some will know; your Vice-President, Mr Tett, was one of the team, and there are others in the audience who took part in the investigations in Germany, which began in March or early April 1945 before the war was over.

In the paper Major Gordon has not stated how this was set up, because the paper deals with technical matters. But I would like to say that, at the instigation or suggestion of Sir Harold Hartley, in the autumn of 1944 the Ministry of Fuel and Power began to prepare for the time when we could go into Germany, within a few hours of works and plants being captured, in order to collect information with regard to the activities there, with the object of assisting to win the war. The Ministry decided to set up a body—I forget whether it was called a Working Party or a Group—which came to be known later as the Oil Mission, Major Gordon being Chairman. That Oil Mission included specialists in hydrogenation, the Fischer-Tropsch process, coal carbonization, gasification, petroleum refining, lubricating oil, and so on; and it was divided into a number of teams, with a leader responsible for each. Major Gordon and his colleagues at Billingham took full responsibility for collecting all the



information on hydrogenation, and the Fuel Research Station accepted responsibility for the Fischer-Tropsch process, whilst others took responsibility in connexion with refining, lubricating oil, and so on. An enormous amount of work was carried out. The various reports were written and many have been issued by H.M. Stationery Office as B.I.O.S. reports.

The next stage was to make an overall report dealing with processes as a whole—hydrogenation, Fischer-Tropsch, oil refining, tar refining, and so on. The various sections were written by individuals, and Major Gordon put in an enormous amount of work writing a summary of the whole lot. I am sorry that the printing has been so slow that it is not published yet; the work has got beyond the proof stage, but owing to the fuel crisis the printing has been delayed. When you see it I am confident you will agree that Major Gordon, as Chairman of the Oil Mission, leader of one of the teams and co-ordinator of the reports, has put in a tremendous amount of work.

That is a picture of how some of the information on what is happening in Germany has been obtained. Of course, we all became soldiers for the time being; we went over to Germany and were on the targets within a few hours of their capture. It was a rush job, because the assault on the Ruhr was very rapid once it did start.

MAJOR GORDON, in presenting the following paper, said : Dr Parker has given an indication of the conditions in which we examined the various plants in Germany, and I would take the opportunity to say what a very fine team of people was provided by the authorities concerned to make up these various missions into Germany. The position was a little complicated in that the investigation of the targets was a joint effort with the Americans. But I must say that I found the Americans very easy to get on with; the leader of their party, my various colleagues and I found no difficulty in co-operating and arranging who should go to which places, on the same sort of plane, though in a small way, as that on which Generals Montgomery and Eisenhower arranged who should be what.

Reference was made by Dr Parker to the document which gives a summary of the information contained in the reports written by the leaders of the various teams. A great deal of time had to be devoted to it in order to make everything consistent; and it is a very large document. I do not know what the Stationery Office will charge for it, but it is worth a lot of money, I think. I read the final proofs about a month ago.

When I was asked by this Institute to prepare a paper on the same subject it was rather difficult for me, as you will appreciate, to go over the same ground again. So that, rather than fill this paper with detailed scientific and statistical information, which would have made it very long, and having regard to the fact that the detailed report is being published, I felt that a brief summary of the position in Germany would be more acceptable and perhaps easier to read, drawing the attention of those interested to the various things they might like to follow up when the detailed report is available.

From the point of view of pure fuel technology we were all very dis-

appointed that not more knowledge was gained. So far as the hydrogenation process was concerned, of which I had a knowledge before the war of what was going on in Germany, the developments were completely negligible in the direction of new processes; there was the development of an enormous number of new plants, but there was no really new information beyond that which was known in 1938. I think the same remark applies to the Fischer-Tropsch process. I am not so familiar with that, but so far as I could make out there was really nothing new, and there was not in that case the very big development of output that had been effected in hydrogenation. In straight oil refining there was even less. There were some interesting developments of petroleum production in Germany, the Germans having found some new fields; that matter is dealt with in the report. There was also a very great deal of interesting chemical development on the border-line between petroleum technology and the chemical industry; some of that development is dealt with at greater length in the report.

DEVELOPMENT OF HYDROGENATION AND FISCHER-TROPSCH PROCESSES IN GERMANY.

By K. GORDON.*

GENERAL.

THE hydrogenation process was the more important of the two synthetic processes used in Germany from the point of view of the production of fuel. The first commercial plant was built at Leuna, and it was started in 1927. It was originally intended to operate with brown coal, but various difficulties caused this plan to be abandoned temporarily, and brown coal-tar was the raw material used until 1931, when the difficulties with brown coal were overcome.

By the outbreak of war the output at Leuna had reached 440,000 tons a year, and during the war the output increased to 600,000 tons a year.

The building of new hydrogenation plants was an important part of the five-year plan which was put into operation at the access of the Nazis to power. The first plants were at Böhlen and Magdeburg, and were combined brown coal carbonization and brown coal-tar hydrogenation plants. These plants added 300,000 tons a year to the capacity for home-produced oils in Germany.

The first plant built in Germany for the hydrogenation of bituminous coal was at Scholven. This plant was started up in 1937, and used a process similar to that employed at Billingham.

At the outbreak of the war the capacity of the plants completed was 1,400,000 tons a year, and actual output was at the rate of over 1,000,000 tons a year. More new plants were built, until the capacity of the installed plants was about 4,000,000 tons a year. The actual output reached a maximum rate corresponding to 3,600,000 tons a year early in 1944, when Allied bombing rapidly reduced production to a negligible amount.

* Imperial Chemical Industries, Ltd.

The hydrogenation plants were the most important of the German synthetic fuel plants, as they provided the whole of Germany's requirements of aviation fuel; nearly half the output of the hydrogenation plants was taken in this form.

The first plant employing the Fischer process was started by Ruhrchemie in 1936. In 1939 the rated capacity of the Fischer plants was 740,000 tons a year. There was little or no increase in this capacity during the war. The maximum output of the Fischer plants was at a rate of 570,000 tons a year, some 14 per cent of the total production of oil from coal.

The reason for the lack of development of this process compared with progress in hydrogenation is not difficult to find. The motor fuel produced is of very poor quality from the point of view of octane number, and is quite unsuitable for aviation fuel. The principal interest in the Fischer process was its use for supplying raw materials for chemical processes, and the pre-war scale of operation was ample to supply all the requirements in this field.

Table I, which is extracted from the "Report on Study of Liquid Fuel Processes in Germany," shortly to be published, gives a summary of the capacity for which the various processes were installed.

TABLE I.

	Annual rate of production, tons.					Total
	Hydrogenation.	Fischer-Tropsch synthesis plants.	Refining of German petroleum.	Brown coal and bit. coal-tar distillation.	Benzol.	
Aviation fuel .	1,900,000	—	—	—	50,000	1,950,000
Motor spirit .	350,000	270,000	160,000	35,000	330,000	1,145,000
Diesel oil .	680,000	135,000	700,000	110,000	—	1,625,000
Fuel oil .	240,000	—	70,000	750,000	—	1,060,000
Lubricating oil.	40,000	20,000	780,000	—	—	840,000
Miscellaneous .	40,000	160,000	90,000	50,000	—	340,000
	3,250,000	585,000	1,800,000	945,000	380,000	6,960,000

PRODUCTION OF SYNTHESIS GAS.

Synthesis gas is the term used for a mixture of carbon monoxide and hydrogen which is needed for the Fischer process directly or for the production of the pure hydrogen required for the hydrogenation process. To make 1 ton of Fischer product we need 11,000 m³ of synthesis gas. To make 1 ton of motor fuel by the hydrogenation process we need from 1000 to 3600 m³ of hydrogen, and hence synthesis gas, according to the raw material used, and the product made.

Coal Gasification.

Considering first of all a situation as in Germany where some form of coal is the only raw material, one is faced with the initial problem of gasification. The Fischer and the hydrogenation processes only differ in this

respect in degree. It is not proposed in this paper to give details of the various types of plant used. A large proportion of the output was made in conventional water-gas plants. Most of the developments were in the direction of the utilization of low grade solid fuel as the raw material for gasification. Oxygen was used both for this purpose and to make the process continuous.

Manufacture of Hydrogen from Hydrocarbons.

The development of processes, starting with hydrocarbon gas as the raw material, is of more interest to the oil industry. The first commercially operated plants for the production of hydrogen from natural gas cracked the natural gas thermally over red-hot brickwork to give "reformed gas," not dissimilar in composition to coke-oven gas. The hydrogen in this gas was then separated by liquefaction and distillation, employing the same process as is used to separate hydrogen from coke-oven gas.

A more attractive process was discovered by the I.G. Farbenindustrie, and was employed on a large scale for the first time by the Standard Oil Company. This goes by the name of the "methane-steam process." The gas is passed, together with steam, over a catalyst containing nickel, and the hydrocarbons are converted almost entirely to CO, CO₂, and H₂. There were considerable developments of this process by the I.C.I. in England. Details of the plants have recently been described in a paper by the writer to the Institute of Fuel entitled "Developments in the Hydrogenation of Coal and Tar."

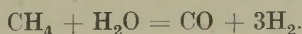
Two plants were built in Germany during the war, one at Wesseling on the Rhine, and one at Pöhlitz, near Stettin. The Wesseling plant was very similar to those built in Great Britain, and it does not call for any special comment. The raw material was the tail gas from the hydrogenation process, and producer gas made from brown coal briquettes was used as the fuel.

The hydrocarbon gas is first purified from sulphur compounds by passing at 420° C through chambers filled with iron oxide and zinc oxide. The reaction temperature is 750° C. The reaction is carried out in tubes in parallel made of Krupp's NCT6 alloy. The exit gas, after cooling in heat exchangers, goes over an iron chromium catalyst at a lower temperature for the conversion of the major part of the CO to CO₂ and H₂ by catalysis with steam.

KW Process.

Although the methane-steam process is at the same time simple in operation and low in capital cost, the Germans developed another process, known as the "KW Process," for the manufacture of synthesis gas from hydrocarbons. This process was developed at Oppau and it was intended to operate it on a much larger scale at new plants at Heidebreck, Waldeburg, Ausschwitz, and Linz. The heat of reaction for the conversion of the hydrocarbons to synthesis gas is provided by combustion of part of the gas with oxygen.

The reactions taking place in the methane-steam process can be represented by:—



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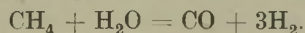
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The reactions taking place in the methane-steam process can be represented by:—



The reaction is endothermic, and the amount of fuel required corresponds to 37 per cent of the calorific value of the reacting gas.

In the KW process the reactant gas and oxygen are preheated and burned at high temperature; the hot gases pass directly over a nickel-containing catalyst. The overall reaction can be represented as follows :—



It will be seen that the gas produced is three-quarters of that made by the methane-steam process. As no additional fuel is required, the overall heat balances of the two processes are very similar. The KW process requires oxygen which involves capital expenditure and running costs.

Considerable precautions are necessary to avoid explosions in the burner. Because of the high temperature at which the gases leave the burner and pass to the nickel catalyst, 1200° C, nickel is lost as carbonyl and has to be replaced by introducing nickel nitrate in the combustion zone. Again on account of the high temperature, there is a small formation of carbon in the form of soot and this has to be filtered from the exit gas.

To give a proper comparison of this process with the methane-steam process an accurate economic study under comparable conditions would have to be made, but it is difficult to see what benefit the KW process offers over the methane-steam process. A possible reason for its adoption is to avoid the use of high chromium steel for reaction tubes, as this material was in short supply in Germany during the war.

Modification of the KW Process to Produce Acetylene.

A very interesting modification of the KW process was in the pilot plant stage in Germany. Oxygen was burned in the hydrocarbon gas in a similar way to that just described, but the reactants were preheated, the products were rapidly cooled, and no catalyst was used. Acetylene was produced in a proportion approximating to the equilibrium amount at the high temperature of the flame. No steam is, of course, added to the reacting gases.

In cases where both acetylene is required and the synthesis gas is needed for chemical purposes and not used as fuel, the process appears to offer some economic attractions. Approximately 25 per cent of the carbon in the hydrocarbon gases is converted into acetylene, and the balance is recovered as synthesis gas.

The reaction can be represented very approximately by the equation :—



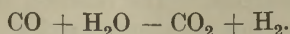
Using methane as the raw material the composition of the exit gas is :—

Acetylene	8 to 9 per cent.
Carbon dioxide	3 to 4 "
Methane	6 to 7 "
Carbon monoxide	24 to 26 "
Hydrogen	56 "

Acetylene and also CO_2 are removed from the gas mixture by compression to 18 atmospheres, and washing with water. The residual gas contains rather more methane than is desirable for both processes requiring synthesis, gas, and a second stage treatment would be desirable to remove it.

Operation of CO Conversion Under Pressure.

The only other noteworthy development in the production of synthesis gas was a pressure process for the reaction :—



This process operated at atmospheric pressure has long been known and is the conventional method of hydrogen manufacture for ammonia synthesis, for the hydrogenation process, and for adjusting the H_2 : CO ratio of gas for synthesis gas manufacture. An increase of pressure has no effect on the equilibrium, but it increases the velocity of reaction.

Since one volume of CO gives by this reaction one volume of CO_2 and one volume of hydrogen, compression costs are saved by carrying out the hydrogen reaction at as high a pressure as is practicable. It is, on the other hand, necessary to use high-pressure steam instead of low-pressure steam for the reaction.

In practice considerable difficulty was encountered by the Germans in operating this process. Whilst an atmospheric pressure plant can be built throughout of mild steel, and no particular corrosion problems are met, the use of high-pressure gases produces corrosion problems which are only overcome by the use of stainless steel.

As is the case with the KW process, it would appear doubtful whether this process would in fact give a substantial improvement over conventional methods.

THE HYDROGENATION PROCESS.

Table II gives a list of the German hydrogenation plants, their capacity and the raw materials employed :—

TABLE II.
German Hydrogenation Plants Operating in 1945.

Name of plant.	Main raw material.	Nominal capacity for production of total liquid products including liquefied gas (tons/year).
Leuna	Brown coal and brown coal-tar	620,000
Bohlen	Brown coal-tar	250,000
Magdeburg	Brown coal-tar	220,000
Zeitz	Brown coal-tar	250,000
Scholven	Bituminous coal	220,000
Gelsenberg	Bituminous coal	400,000
Welheim	Pitch and tar	130,000
Pölitx-Stettin	Bituminous coal, pitch, tar, and petroleum residues	700,000
Lützkendorf	Petroleum residues and tar	50,000
Wesseling	Rhine brown coal	200,000
Brüx	Brown coal-tar	400,000
Blechhammer	Bituminous coal	425,000

Hydrogenation of Bituminous Coal.

The first plant for hydrogenating bituminous coal was built at Billingham. The first plant in Germany was at Scholven, and formed an addition to an

existing ammonia plant. The Scholven plant employed substantially the same process as was used at Billingham, which has already been described.*

Coal is made into a 45 per cent coal paste; tin oxide and ammonium chloride are added as catalysts. The reaction takes place at 460°C and 300 atm pressure. The hot products leaving the main converter are neutralized with a suspension of alkali in oil to avoid corrosion through chlorine.

The throughput of coal at Scholven was 0.264 tons/m^3 reaction volume/hour. The yield of motor spirit and middle oil was 60 to 61 per cent of the ash- and moisture-free coal.

The sludge was treated for oil recovery by fugalling and carbonization in "kugelöfen" of the residue.

Later, coal hydrogenation plants were built at Gelsenberg, at Pölit, near Stettin, and at Blechhammer. In these plants it was decided to raise the reaction pressure at 700 atm. All other conditions being kept constant, the increased pressure would be expected to be accompanied by increase in yield and decrease in the reaction volume required. The main purpose of the increase in pressure in these plants appears not to have been to obtain this increased yield, but to simplify the operation by making unnecessary the use of maximum chloride and the subsequent neutralization of the hydrochloric acid in the vapours by alkali. It would indeed be impracticable to use the acid hydrogenation conditions with ammonium chloride at 700 atm pressure, since condensation of hydrochloric acid would take place even at the reaction temperature, and it would be impossible to avoid corrosion by the means adopted at 300 atm pressure. At 700 atm, 1.2 per cent of iron in the form of sulphate, together with 1.5 per cent by weight of "Bayermasse" (iron oxide), and 0.3 per cent by weight of sodium sulphide, was used as catalyst. A rather higher temperature, 480°C in place of 460°C , was employed.

At the plants at Gelsenberg and Pölit, coal hydrogenation was operated under approximately balanced conditions, so far as the production of heavy oil is concerned. The temperature and throughput are controlled so that the net formation of heavy oil just equals that lost in the treatment of the sludge.

At Blechhammer there was an interesting variation. A higher throughput was used, and gave excess of heavy oil which was disposed of as a fuel, under conditions involving the replacement of part of the heavy oil used for preparing the coal paste by middle oil.

It was the original intention of the Billingham plant to operate the coal hydrogenation stage in a similar way, but the object was not to make fuel oil, but to allow the heavy oil to be treated under more efficient conditions in a separate liquid-phase hydrogenation stage. Operation with excess of heavy oil had to be abandoned because at the pressure employed there was an excessive accumulation of asphalts in the circulating heavy oil system. Operation at 700 atm removes this limitation.

Table III gives the operating conditions of the coal stage at Scholven

* Gordon, K., "The Development of Coal Hydrogenation by Imperial Chemical Industries, Ltd.," *J. Inst. Fuel*, 1935, 9, 69; Gordon, K., "Progress in the Hydrogenation of Coal and Tar," *J. Inst. Fuel*, 1946, 20, 42.

TABLE III.

	Scholven.	Gelsenberg.	Blechhammer.
Operating pressure, atmospheres	300	700	700
Coal feed rate, ton/m ³ /hour	0.264	0.39	0.65
Hydrogen used, per cent	9 to 10	10.3	8
Yield of motor fuel plus middle oil, per cent	61	66.8	46.7
Fuel oil, per cent	nil	nil	21.5
Unconverted coal, per cent	8	4	4
Loss of oil, per cent	6.0	4.7	5.5
Hydrogen gases, per cent	25.0	20.5	29 to 20

and at Gelsenberg (these figures apply equally to Pölitze) and at Blechhammer.

The motor fuel and middle oil were then hydrogenated together by the vapour phase process, to be described later. In this way, separate acid treatment of liquid-phase motor fuel was avoided.

Hydrogenation of Middle-German Brown Coal.

This material was the first to be hydrogenated on a commercial scale and the process was operated at Leuna in the first instance in 1927. As already indicated, this operation ceased for a time but was restarted in 1931, and continued thereafter.

The operating pressure at Leuna is 230 atm, and this pressure was doubtless chosen to be in line with conditions employed for ammonia synthesis. A higher pressure is preferable, and in the brown coal plant built at Wesseling the pressure was increased to 700 atm. The raw material used in this plant differed from middle-German brown coal in being a more refractory material.

The dry brown coal was made into a paste with heavy oil and "Bayermasse" was added as the catalyst, in a concentration of 4 per cent by weight on the original coal. The paste contained 44 per cent coal and was hydrogenated with temperatures up to 490° C. Improved results were obtained by dropping the temperature of the last converter of the series to 475° C.

Operating conditions with brown coal at Leuna are given in Table IV.

TABLE IV.

Pressure	230 atm
Throughput	0.46 ton/m ³ /hour
Yield of motor fuel plus middle oil	50 per cent
Hydrocarbon gases	15.2 "
CO and CO ₂	10.6 "
Unconverted coal	1.5 "
Hydrogen absorbed	6.7 "

Hydrogenation of Brown Coal-Tar.

Brown coal-tar is a much more reactive and a lighter boiling material than tar from bituminous coal. On the plants at Böhlen, Magdeburg, Leuna, and Brück, the crude tar was first fuggled to remove solids, and then distilled into middle oil, for treatment in the vapour phase, and a heavy oil residue. The latter was hydrogenated at pressures in the region of

220 to 300 atm at a temperature of 460 to 480° C using as the catalyst finely divided brown coal coke impregnated with iron. The amount employed was 1 per cent of catalyst, containing 5 to 6 per cent of iron, on the tar.

The feed rate was approximately 1 ton/m³/hour, the yield of motor fuel plus middle oil approximately 79 per cent, and the hydrogen consumption 3.8 per cent.

The products leaving the converter were separated in a catchpot maintained substantially at reaction temperature, and the liquid heavy oil recycled through the preheater to the first converter. Part of it must be let down in pressure continuously, to remove the accumulation of ash in the system. The purge is carbonized in similar rotary kilns to those used for coal hydrogenation product. The lighter products go overhead from the hot catchpot and are condensed in the coolers.

After separation from excess hydrogen, the pressure is released in stages. The product is normally distilled in the same plant as that employed for the distillation of the crude tar into middle oil and heavy oil. The latter is recycled.

The middle oil from the liquid-phase hydrogenation and the middle oil obtained directly by the distillation of tar were hydrogenated together in the vapour phase. Light oil recovered from the gases from brown coal carbonization was also included in the feed to the vapour phase.

The overall yield in the process from crude tar was 75 to 85 per cent by weight of motor spirit to about 70 per cent of aviation spirit.

At Zeitz there was an interesting variation of brown coal-tar hydrogenation. The tar, after fuggalling and filtering, was fed to converters filled with pelleted 5058 (tungsten sulphide) catalyst, at 300 atm and temperatures of 360 to 390° C.

The product is more saturated than that obtained by normal operation; indeed at the lower temperature some 10 per cent of lubricating oil base was obtained. The main product was diesel oil in a yield of 50 to 60 per cent.

Hydrogenation of Bituminous Coal-tar, Pitch, and Petroleum Residues.

These materials are all more refractory than brown coal products which formed such a large part of German production, and were treated at 700 atm at Stettin, Welheim, and Lutzkendorf. The process is the same as that described from brown coal-tar, except for the increase of pressure, and an increase of reaction temperature from 480 to 490° C. The catalyst was the same as that used for brown coal-tar.

The Welheim plant was of interest in having been built in the first place to treat coal extract made by the Pott Broche process. Difficulties with this process led to the plants being operated on pitch.

Welheim was started before the war, and was the first hydrogenation plant to work at 700 atm. The conditions for pitch hydrogenation at Welheim are given in Table V.

TABLE V.

Operating pressure	700 atm.
Feed rate	0.51 ton/m ³ /hour
Hydrogen used	7.1 per cent
Yield of motor fuel plus middle oil	28 "
Yield of fuel oil	45 "
Yield of hydrocarbon gases	9 "

According to information supplied by the I.G., a combination of pitch hydrogenation at 700 atm with hydrogenation of the middle oil resulting from this operation and that arising from the initial distillation of the tar, would give a final yield of 78 per cent of petrol with a hydrogen absorption of 13.7 per cent.

The 700-atm process was used at Stettin and Lützkendorf for the hydrogenation of residues resulting from petroleum cracking. Not much information is available. The same catalyst was used as for other liquid-phase hydrogenation processes. The feed rate was 0.63 ton/m³/hour, the hydrogen absorption 3.2 per cent, and the yield of motor fuel plus middle oil 86 per cent.

The petroleum residues were those resulting from cracking operations. Much improved results would be obtained from more carefully controlled hydrogenation of residues from distillation, in which cracking has been reduced to the minimum.

Vapor-Phase Hydrogenation.

The survey of the process as so far described for the treatment of coal, tar, and similar materials, has consisted of a combination of distillation and liquid-phase hydrogenation, giving as the products middle oil, motor fuel, and hydrocarbon gases. The first two were not normally separated in German practice.

The specification for the middle oil was fixed by the requirements of vapor-phase hydrogenation and normally calls for an end point of 325° C.

Vapor-phase hydrogenation is usually carried out at 250 to 300 atm pressure. There is normally no point in the higher pressures that have been used for liquid-phase hydrogenation. At Welheim and Lützkendorf, however, vapor-phase hydrogenation was worked at 700 atm. The reaction temperature was usually in the region of 400° C.

The oil was pumped to the required pressure and mixed immediately with hydrogen at the same pressure. The proportion was usually 2000 m³/ton of oil. The mixture of oil and hydrogen passed through tubular heat exchangers and then through a gas-fired or electrically heated tubular preheater. A unit may comprise one, two, or three converters in series, and each converter is divided into compartments. Each compartment is filled with solid pelleted or extruded catalyst, and the hydrogen and vaporized oil flow downwards over the catalyst. Between each two sections of the converter, cold hydrogen is introduced to control the temperature. On leaving the last converter the products are cooled, first in heat exchangers and finally in a water cooler. The mixed gaseous and liquid products from the cooler go to a high pressure separation vessel where the excess hydrogen is separated and recirculated to the plant.

The pressure is released, usually in three stages, to effect a degree of stabilization.

In vapor-phase hydrogenation the formation of light hydrocarbon gases is small relative to that found in liquid-phase hydrogenation. The solubility of hydrocarbon gases in the oil is such that the concentration of hydrocarbon gases does not rise above 10 per cent. In the liquid-phase, on the other hand, it is usually necessary to pass circulating hydrogen

through subsidiary columns, in which it is washed with circulating oil, to maintain the hydrocarbon concentration down to a reasonable maximum.

The original vapor-phase process was a single stage one. The liquid product contained some 50 to 70 per cent of motor fuel, and was distilled to give three fractions, excess butane and lighter hydrocarbon gases, motor fuel, and recycle middle oil. The last is returned to the process. The catalyst introduced by the I.G. in 1931 was tungsten sulphide (5058). It is extremely active, provided that a minimum concentration of sulphur is present in the total feed material. An improvement was developed in 1935. This consisted of the use of a catalyst (6434) containing 10 per cent of tungsten sulphide on activated earth. This catalyst is very active, gives a high yield, and works at rather lower temperature. It is very sensitive to nitrogen compounds, and when dealing with raw materials derived from coal-tar, and the like, it is necessary that the feed should have preliminary hydrogenation.

As the process was worked in Germany the first vapor-phase stage was operated with 5058 catalyst, giving some 30 per cent of motor fuel. The middle oil from this stage, amounting to nearly 70 per cent of the feed, then went to the 6434 unit for final conversion to motor fuel.

The yields obtained by the two-stage vapor-phase hydrogenation process varied from 95 per cent, in the case of motor spirit containing butane, down to some 80 per cent in the case of aviation spirit, in which no butane is permissible, and where the end point of the spirit is lower, so that a greater proportion of the crude product must be recycled.

The total average feed rate was in the region of 0.8 to 1.0 tons of feed per cubic metre of catalyst per hour. The average size of converter contained 8 m³ of catalyst, and usually three were operated in series.

The life of the 5058 catalyst was at least one, and frequently two, years. The 6434 catalyst also had a life of over a year, but care had to be taken to maintain its activity by excluding nitrogen compounds both from the liquid feed and the circulating gas.

At Welheim and Lützkendorf, vapor-phase hydrogenation was carried out at 700 atm pressure. This enabled 6434 catalyst to be used in a single stage operation at Lützkendorf. At Welheim a special catalyst operated at a good deal higher temperature was used (480° C) to produce a highly aromatic motor fuel. In both these cases the spirit yields were lower and gas yields higher than normal.

The properties of the motor fuel made depended upon the raw material and Table VI gives representative figures.

TABLE VI.

Raw material.	Motor spirit C.F.R. Octane No.	Aviation spirit C.F.R. Octane No. (Clear).	Aviation spirit leaded with 1.15 c.c./litre (5.2 c.c./gal) C.F.R. Octane No.
Brown coal	64	70	88
Brown coal-tar	62	68	86
Bituminous coal	68	72	90
Bituminous coal-tar	69	73	90

Hydroforming and Similar Processes.

The knock rating of hydrogenation motor spirit produced in Germany for aviation use was improved by one of two processes, of which the object was to dehydrogenate the six-ring naphthenes present to aromatic compounds. The first process, which was operated at Leuna and Moosbierbaum, was the hydroforming process, similar to that employed on a large scale in U.S.A.

The catalyst employed was ammonium molybdate on alumina, and the feed material was a naphtha with an initial boiling point of 90°C . The operating temperature was 510° to 520°C and the pressure 15 atm. The gas was recycled and the catalyst needed revivification with air every 6 to 12 hours.

A more commonly employed process was the so-called D.H.D. process, in which the feed material as before is a naphtha. The feed mixed with recycle gas containing hydrogen is heated to 500°C and passes through three or four converters arranged in series with intermediate heating coils.

The products after cooling by heat exchange to 300°C go through a final converter for separation of polymerizable components.

The operating pressure was about 75 to 80 atm. The catalyst was 8 to 10 per cent molybdic acid on activated alumina. Catalyst revivification in the unit was carried out approximately once per week.

The process gave a product approximately 80 octane number, which could be raised to rather over 90 by the addition of lead. The process in fact gave from petroleum and brown coal raw materials a motor fuel similar to that which could be obtained directly from coal.

FISCHER PROCESS.

General.

When CO and H_2 react together in the presence of a suitable catalyst at 200 atm pressure, they combine to form methanol. The reaction is practically quantitative, and by-products are negligible. By modifying the catalyst, higher alcohols appear in the product, but in the limit not more than 30 per cent of the product is in this form. The formation of these higher alcohols is accompanied by undesirable side reactions between the CO and H_2 to give methane and water.

When the CO and H_2 react at atmospheric pressure in the presence of catalysts of which the active ingredient is a carbonyl-forming metal, a mixture of gaseous, liquid, and solid aliphatic hydrocarbons is formed. The reaction temperature is in the region of 200°C and must be closely controlled.

The first commercial unit was started in 1935, and by 1939 there were nine units built in Germany with a rated output of 740,000 tons of oil a year.

As a result of research work an intermediate pressure process was devised operating in the region of 5 to 15 atm. The products were somewhat similar to those of the atmospheric process, but there was a tendency towards alcohol formation.

The plants in operation were worked with a cobalt catalyst. There was a good deal of development work on iron catalysts, but no large-scale operation.

During the war there was no increase in Fischer plant output, although research work continued unabated. The major part played by the Fischer plants in the German wartime economy was the production of raw materials for chemical manufacture.

Synthesis Gas Production.

Whilst in the hydrogenation process, only a part of the total coal consumption has to be gasified to give the necessary hydrogen, in the Fischer process the whole of the raw material must be turned into a mixture of CO and H_2 .

The Fischer plants in Germany employed a conventional water-gas process using coke as the raw material. The ratio of H_2 and CO, which are required in the proportion of 2 : 1, was adjusted either by reaction with steam over a catalyst to convert part of the CO to CO_2 and H_2 , or by introducing coke-oven gas to the water-gas generator.

It is necessary that the synthesis gas be highly purified, and the procedure was first to apply the conventional method of removing H_2S with iron oxide. The next step was to remove the organic sulphur by passing the gas through towers containing granules of a mixture of iron oxide and soda. The purity of the final gas varied from 0.05 to 0.2 gm of sulphur per 100 m^3 .

Fischer Synthesis.

The catalyst employed was a mixture of cobalt, thorium oxide, magnesium, and kieselguhr, in the ratio of 100 : 5 : 8 : 200.

Before putting to use, the catalyst is reduced with hydrogen at about 400° C to give a 60 per cent reduction of the cobalt to the metallic state.

The design of plant to carry out the synthesis reaction presents considerable chemical engineering difficulties. There is a very considerable catalyst volume, as the output of oil is only 0.008 tons per m^3 per hour, compared with 0.5 per m^3 per hour for vapor-phase hydrogenation. The heat of reaction is very great, approximately 600 kilocalories/ m^3 synthesis gas; in fact, approximately one-quarter of the heat of combustion of the same gas. This great heat of reaction must be removed without permitting a rise of temperature through the catalyst of more than about 10° C.

If the temperature is allowed to become excessive, then other reactions set in, such as the formation of methane and carbon.

This difficulty in removing the heat is accentuated by the fact that the process is operated at atmospheric pressure. At higher pressures, the greater heat conductivity of the gas makes the problem easier, and it was doubtless largely for this reason that the Germans developed the medium-pressure process.

In the plants designed for atmospheric pressure, the reaction vessels were rectangular steel chambers, 5 metres by 2.5 metres by 1.5 metre, containing horizontal tubes cooled by circulating water connected up to a steam drum. To increase the heat transfer surface, the tubes were expanded into vertical steel plates, and the catalyst was packed in the spaces between them.

Control of the pressure in the steam drum gives control of the temperature of the reaction.

In the case of the medium-pressure process, working at about 10 atm, a vertical cylindrical vessel was employed with tubes containing the catalyst expanded and welded between two tube plates. Generally, in place of the simple design of single tubes, concentric tubes were employed, with water at each side of the catalyst space.

In operating the atmospheric-pressure process, the gas passes through two sets of reaction vessels in series. Arrangements were made so that a suitable number of vessels could permanently be off-stream for reactivation, or replacement of catalyst.

The newly charged vessels were placed first on-stream in the second stage, and then transferred to the first stage.

The total catalyst life varied from 4 to 8 months. New catalyst would be put into operation at a temperature of 180° to 185° C, and the temperature gradually increased to 200° C.

The catalyst was from time to time revived *in situ* by washing with oil or by treatment with hydrogen, or both, with the object of removing high molecular weight hydrocarbons on the catalyst.

Operation with the medium-pressure process was generally carried out in three stages at a pressure of 10 atm. Similar arrangements were employed for treatment of the catalyst.

TABLE VII.
Comparison of Atmospheric and Pressure Fischer Synthesis.

Working pressure, atmospheres	1	10
H ₂ /CO ratio of gas: Stage 1	2:1	1.5:1
" 2	2:1	1.6:1
" 3	2:1	1.8:1
Average gas rate m ³ /hr/reactor, all stages	660	680
Reaction temperature, °C	180-200	180-200
Catalyst volume, m ³	10	10
Useful products (C ³ and over), gm/m ³ gas	150	155
" " " " kgm/hr/reactor	81	87
" " " " kg/hr/m ³ catalyst	6.75	8.7
" " " " tons/year/reactor	650	700
Shape of vessel	rectangular	cylindrical
Dimensions, metres	5 × 2.5 × 1.5	6.9 × 2.7 dia.
Number of tubes	600	2,100
Surface of tubes, m ²	400	2,100
Total cooling surface, m ²	4,000	2,100
Heat per m ³ gas converted, k.cals	600	600
Heat per reactor per hour, tonne cals	400	410
Heat transfer, k.cals/m ² /hour	100	195
Products (% by weight of total):		
C ₃ and C ₄	14 (45)	10 (40)
Light oil, 25-165° C	47 (37)	25 (24)
Middle oil, 165-230° C	17 (18)	
Heavy oil, 230-320° C	11 (8)	38 (9)
Soft wax, 320-460° C	8	15
Hard wax	3	14
(Figures in parentheses indicate olefin content of fraction.)		
Motor Fuel. Octane No. (165° C E.P.)	53	45
Middle Oil. Solid point	-40° C	-30° C
Cetane No.	78	55-48

In the normal-pressure process the gas leaving the converters was cooled directly with water, and then passed through active charcoal absorption plant for absorption of light hydrocarbons, which were recovered by steaming. In the medium-pressure process about one-third of the reaction product leaves the converters as liquids, and is collected in separators. The residual gas is cooled in tubular type condensers and is finally treated in active charcoal purifiers.

Table VII gives comparative average data for the two types of process. The motor fuel fraction, owing to its low octane number, could only be used as motor fuel by blending with benzol and lead. The middle oil was a valuable diesel oil blending agent, as is shown by its properties in Table VII.

The higher boiling liquid fraction, between 170° and 320° C, was originally also used as diesel fuel, but during the war it was used entirely for conversion into a synthetic detergent "Mersol" at the Leuna works.

The next fraction, the soft wax, was, in general, converted to fatty acids by oxidation, but it was used to some extent for the purposes to which paraffin wax is put. There were also recovered from the condensed products small amounts of fatty acids and alcohols, which were formed in the synthesis, particularly in the medium-pressure process.

CONCLUSION.

The large development of synthetic oil processes in Germany was undertaken as part of their war programme. Nothing was found by any of the investigating teams which revealed any developments from what was known before the war that affect appreciably the economic picture of synthetic oil processes.

The hydrogenation process was the best developed from the engineering point of view, and it is difficult to see how any substantial improvement could be made other than some radical discovery of new conditions for the hydrogenation of refractory materials such as coal.

The Fischer process on the other hand offers more scope for improvement. First of all when coal is the raw material, the manufacture of the synthesis gas by the present methods is both expensive and of not very high thermal efficiency. An improvement in gasification processes would be a big step forward. As synthesis gas accounts for something like 70 per cent of the total cost of the Fischer product, this would have a very substantial effect on the manufacturing cost.

The synthesis process itself is also obviously capable of great improvement. The Germans were working on alternatives to the tubular type of reactor, but had not advanced to the stage where anything was in large-scale operation. A big improvement to the process could be made at this stage, and it is possible that a satisfactory solution could be found by the use of the fluid catalyst technique developed for cracking processes.

In places where natural gas is available the economical processes already developed for the manufacture of synthesis gas would effect a very substantial reduction from the cost of the Fischer product in Germany.

DISCUSSION

THE CHAIRMAN: This paper is a very useful summary of what has been done in Germany on the hydrogenation and Fischer-Tropsch processes, and there is a comparison between the technique as known here and in Germany.

I would like to say how glad I am that Major Gordon has referred in his opening remarks to the fact that the teams in Germany were joint teams of British and American investigators. Even if there is not a great deal that is startlingly new in the information obtained in Germany, it is certainly valuable information; equally valuable, if not more valuable, are the close friendships we formed with our American colleagues, which friendships will last for many years. Any of us who go to America now feel that we are really going amongst friends. One excellent way of getting to know your colleagues is to live with them in the conditions we met in the Ruhr before the war was over; you really get to know your friends much better in that way than by meeting them at some luxury hotel for dinner, although I appreciate the value of such meetings. Conditions were not over-pleasant in Germany; but we got on very well together, sharing our K rations, C rations, and so on.

DR C. M. CAWLEY: It gives me a great deal of pleasure to add a few words in appreciation of Major Gordon's excellent paper and the most interesting manner in which he has delivered it. By investigating the production of synthetic oil in Germany, particularly by the hydrogenation process, Major Gordon and his organization have rendered a very valuable scientific service to the technical world; and now he has added to that service by giving the results of the investigations in this concise and useful paper.

We hear a lot nowadays about the use of the Fischer-Tropsch process for the production of chemicals and, as Major Gordon has said, some 30 per cent of the German production was being devoted to that purpose. We do not hear much about the hydrogenation process being used for that purpose, however, although it can be applied to the production of chemicals if we wish to do so; they would, of course, be chemicals of a different kind. Tar and benzole are the sources of aromatic raw materials for chemical industry; but anything we can get from tar can be obtained in greater yield from coal by hydrogenation. It has, for example, been stated that it is possible to produce ten to twenty times as much phenol from coal by hydrogenation as by carbonization. On the face of it, it would seem that the economics of the hydrogenation process might be improved if it were operated to give the maximum yield of chemicals, although the great bulk of the products would, of course, still be liquid fuels. The question I would like to ask Major Gordon is: Are the economics of the hydrogenation process much altered if the process is run to obtain the maximum credit for chemicals?

Another question concerns the Welheim catalyst. If I have followed Major Gordon correctly, the usual I.G. process for producing petrol during the war was by a three-stage vapour-phase process. The middle oil was treated over the 5058 catalyst, then the 6434 catalyst, and, finally, by the

D.H.D. process. At Welheim, however, a catalyst was developed to achieve the same result in one treatment. It would appear that the catalyst must be very resistant to poisoning, since presumably it had a long life. It might have many interesting applications, and it would be interesting if Major Gordon would give his assessment of the catalyst and the process developed at Welheim.

Thirdly, I would like to refer to future developments. In America in particular there are two major developments in connexion with the Fischer-Tropsch process. One concerns the use of natural gas as a source of synthesis gas; the second is the development in the operation of the Fischer-Tropsch process itself by the use of the fluid catalyst technique. Is there any possibility of any parallel far-reaching development taking place in hydrogenation? I ask this because the prevailing view in America seems to be that the relative positions of the two processes have been rather reversed. A few years ago I think it would have been generally acknowledged that hydrogenation was the best process by which to make motor fuel, and that the Fischer-Tropsch process was hardly in the picture there; to-day it would almost seem that, because of new developments, the position has completely changed. If I am right about the American modification of the Fischer-Tropsch process, it is now capable of producing about 80 per cent of 80-octane petrol. It would appear, therefore, that if you want to make motor spirit to-day, the Fischer-Tropsch synthesis might be preferable to hydrogenation. That would apply particularly to the use of natural gas, but not only to natural gas. I think the Americans also propose to make synthesis gas by the gasification of low-grade coal, and have quoted figures of the order of 9 cents per gallon for 80-octane petrol produced by the Fischer-Tropsch process from this raw material. It would be interesting to have Major Gordon's views on this development.

MAJOR GORDON : In the case of the hydrogenation process the Germans do not appear to have done anything at all about making use of any chemicals arising from the process; they did not even go to the trouble to extract the phenol from the middle oil, a fact which always impressed me as being very remarkable. The recovery of the phenol and other tar acids from the crude product, which are obtained in quite large proportions—phenol about 1 per cent on the coal and cresol about 3 per cent—is a valuable economic advantage to the process and one which we ourselves have not overlooked. Unfortunately, it is not possible to make the process pay on the strength of 1 per cent of a valuable product; if it were, we should start it again promptly at Billingham.

There are possibilities that products from the hydrogenation process will be valuable in chemical industry, and I am giving a certain amount of consideration to that matter at the present time. But I think that one will be able to use only part of the products in that way, and will still have to dispose of the major portion as fuel. That excludes from consideration a very large number of specialized hydrogenation reactions used in the chemical industry for specialized processes. However, that is not what Dr. Cawley had in mind.

The main point about the catalyst used at Welheim is that it worked at 700 atmospheres, and that high partial pressure of hydrogen enabled

the catalyst to stand up to much more severe conditions than at 300 atmospheres. That is the secret of the success of the catalyst. I do not suggest whether or not it is a paying proposition, because a 700 atmospheres plant is much more expensive than one at 300; 200 atmospheres is really enough. However, it was a very interesting development, and the Welheim management, who developed it further than did the I.G., were proud of themselves for having put it over.

The Fischer-Tropsch process is susceptible to considerable improvement, both from the points of view of the reaction itself and making synthesis gas. The Americans have made various statements about the cost of the gasoline, and I hope they will pardon me in saying they do not err on the side of pessimism when talking about it. The application of the fluid catalyst technique to the Fischer-Tropsch process will undoubtedly cheapen the synthesis step.

I have always felt in the past that one of the things to go after was the cheaper hydrogen in the hydrogenation process. That is why we paid so much attention to the methane-steam process. But I cannot see that a lot can be done in that way. What is really needed is some entirely new catalytic treatment for the coal itself. What it is, however, we do not know. I cannot think of anything corresponding to the fluid catalyst which is applicable to hydrogenation.

DR R. H. NAGEL: Have the Germans developed, in connexion with the Fischer-Tropsch process, any special method of separating the oxygenated products from the hydrocarbons or the aqueous phase?

MAJOR GORDON: So far as I know, they relied on the simple fact that oil and water do not mix; the alcohol, being the aqueous phase, separates out.

DR NAGEL: Both the water phase and the hydrocarbon phase contain various quantities of oxygenated products. Did the Germans find ways of extracting these bodies from either phase?

MAJOR GORDON: I have no details. Perhaps the Chairman could answer the question.

THE CHAIRMAN: I am afraid I cannot answer the question. At one stage there was a process of distillation on the alcohol side. The Germans put up a plant at the Ruhrchemie factory at Holten, for making and working up alcohols and making aldehydes; but just as the plant was ready for operation the Royal Air Force went over and smashed it, so that it was never operated. Thus it is not possible to give any detailed experience on that side. That was the position when we saw it; but a good deal of work had been done in the laboratory, and from the detailed records we should be able to answer, at least partially, the question Dr Nagel has asked.

I should like to comment a little on the paper. In connexion with the Fischer-Tropsch process Major Gordon has quite rightly referred to the question of cost and has pointed out that 70 per cent of the cost is in the

production of the synthesis gas. Although there may be considerable improvements on the catalyst side, any improvements that could be made, even if they halved the price, would not make a substantial difference to the cost of the Fischer-Tropsch process, starting with coal as the raw material, and with coal at the sort of price we have here, or even pre-war price.

Indeed, the position in Great Britain is that, with the Fischer-Tropsch process at the stage to which it was developed and used in Germany when we were there, the cost of the primary product from the process—with coal at £2 5s., *i.e.*, coke at £3—would be in the region of 2s. or 2s. 6d. per gallon; that product is not entirely ready for use, but has still to be worked up. If some cheaper method of making synthesis gas could be developed, the cost might be reduced considerably. There is definitely room for improvement on the catalytic side in the synthesis process. The chemical engineering side of the Fischer-Tropsch process was very poor because the rate of heat exchange was so low that large plants were required, and there was relatively low output in relation to the size of the plant used. In regard to gasification, the best way would be to use oxygen, if it were cheap enough. But I have yet to see figures indicating that oxygen is available at a sufficiently low price to make any substantial difference and to counteract the fact that water gas manufacture has a thermal efficiency somewhere in the region of only 60 per cent; further, inasmuch as the process is intermittent, the wear and tear on the lining of the generator and other parts of the equipment is heavy.

Again, the cost of the product from the hydrogenation of coal, with coal at our price, is high, being approximately the same as that of the product of the Fischer-Tropsch process. We hear of developments in America based largely on the use of natural gas, and there are claims for the great cheapening of the Fischer-Tropsch process by using the fluidized catalyst or moving bed. On that side I am certain great improvements could be effected; but time will tell whether the estimates of cost which have been put forward will be achieved.

There are some places in our Empire and throughout the world where coal can be obtained at prices in the region of 4s. per ton, instead of the £2 5s. per ton we pay here. There may be scope in circumstances of that kind, particularly if, for various reasons, the local price of motor spirit or petroleum is high. In many of those places, however, the coal available is not bituminous, it does not produce coke easily. We want more experience on gasifying those coals by some system which does not involve passage through a robust coke in order to produce water gas. Here, again, there is room for a considerable amount of work, possibly on gasifying those coals by a system very similar to the use of the fluid catalyst, *i.e.*, the particles of coal moving all the time while air and steam, or oxygen and steam (if oxygen is available cheaply), are passed through.

That is the position as I see it. But obviously the greatest scope at the moment lies in utilizing natural gas for making the synthesis gas, and then going on with the improved catalytic process for the conversion of the synthesis gas into the product.

The chemical side, which has also been mentioned, seemed to develop in the Fischer-Tropsch process later, because it could not compete with

the hydrogenation process in making high-octane spirit. They made soaps to some extent, and margarine. The soaps were unsatisfactory; they left an abominable odour on the hands after washing. Possibly that difficulty could be overcome; but in normal times I cannot imagine that side of it competing with the normal oils and fats for soap making. On the margarine side, I think I would rather have margarine from natural vegetable oils and fats. However, perhaps I am prejudiced and think that nature, at least so far as food is concerned, is usually better than the chemist—not always, but usually so.

We certainly look forward to the results of the experiments in America, and particularly the results from the large-scale plant which has been planned and which I understand is now being erected.

MAJOR W. H. CADMAN: I should like to ask whether shale oil has been treated in any of the hydrogenation plants. We know the Germans made a great effort to obtain all the shale oil they possibly could, first from the rich oil-shale deposits in Estonia and then from the less rich deposits in Germany. Did they try to hydrogenate shale oil and, if so, for what purpose?

I think the most remarkable piece of information we have had this afternoon is that the Germans made practically no war-time progress in the development of this process; they introduced practically nothing new. Indeed, the position at the end of the war seems to have been exactly as it was when I visited the Fischer-Tropsch plants in the Ruhr and the hydrogenation plant at Leuna before the war. That discovery must have come as a great surprise, and to some extent a disappointment to all members of the investigating teams.

MAJOR GORDON: The answer to Major Cadman's question is that I cannot recollect any mention of any shale oil being hydrogenated in any of these plants; indeed, I do not recollect any mention of shale oil at all in the report.

MR. V. BISKE: In connexion with costs, claims are made from time to time for the gasification of coal *in situ*. Is there a hope that there is anything in these claims?

MAJOR GORDON: I am afraid I am not an expert on the underground gasification of coal. It is a matter which is being given a good deal of attention by various people at the moment. Such gas could be used for the Fischer-Tropsch process, without doubt. It would mean that you would have to pump down oxygen, and not air, in order to produce a gas that was reasonably free from nitrogen; if you put down air and steam you would get a sort of low-grade producer gas which would not be of very much use, whereas if you put down oxygen I see no reason why you should not produce a gas suitable for treatment by the Fischer-Tropsch process or, for that matter, for making hydrogen for the other process.

DR K. G. MARGOSCHES: I would like to refer to the application of

variations of the Fischer-Tropsch process to natural gas for the purpose of obtaining liquid fuels.

Major Gordon has mentioned that in the United States processes using this technique are used also for making chemicals. In a plant using such a process, which is actually now in erection in the United States and which has also been mentioned during the previous part of this discussion, it has been planned to produce from 10 to 20 per cent of oxygenated compounds in relation to the hydrocarbons.

As to the production of liquid fuels from this source, however, A. C. Fieldner and W. C. Schroeder, of the Bureau of Mines (*Engineering Experiment Station News*, Ohio State University, April 1944) say that :

"In spite of attractive possibilities for the use of natural gas in this way, it is not desirable to encourage this development from the long-range national conservation viewpoint."

These authors give several reasons, on which they base this statement, such as not being able to supply the demand for liquid fuels for many years from this source, then because of its being a valuable chemical raw material, then because of its being used for specialized heating problems, where atmospheres must be carefully controlled, and in addition to this, because it cannot be imported in tankers or by railway to fill the needs.

The authors come to the conclusion :

"From that standpoint, it is even less desirable to exhaust our natural-gas reserves than our crude petroleum. This latter material at least can be imported if there is a source of supply abroad."

I should like to ask :

(a) Whether—in the opinion of Major Gordon—the application of the variations of the Fischer-Tropsch process in the case of natural gas as raw material is likely to shift towards its use mainly as a raw material for chemical compounds and towards reducing more and more its consumption for liquid fuel production? Its use as a gaseous fuel will probably continue.

(b) Whether as a result of this—in the opinion of Major Gordon—one will for the purpose of obtaining liquid hydrocarbon fuels mainly concentrate on the conversion of coal, oil shales, lignites, and other raw materials, which are in adequate supply, even at a time, when natural gas as raw material will still be available in large quantities? This question is being asked on the assumption that the cost of production from these other raw materials, be it with or without intermediate production of synthesis gas, is being made commercially economical, which assumption according to the recent technical press is, if not already, then certainly not far from being translated into a reality.

(c) How are the known crude oil resources likely to influence this trend?

MAJOR GORDON : First, I do not see that it matters very much whether in the United States they use up their natural gas resources or whether they use up their coal or their oil. The natural tendency would be to use the petroleum for so long as it was available, and then to use the next cheapest source of a substitute fuel; the next cheapest source is natural

gas, and that is why I think they are coming to use it. In the background, of course, there are still the coal resources, which are very much larger than any possible resources of oil. Nobody knows how long the oil deposits of the world will last; throughout the last twenty years we have been told that they would last for only fifteen years. We do know, on the other hand, that there is enough coal in the world to last for about 2000 years at the present rate of consumption. So that coal will come into its own eventually, and from the point of view of the Americans I do not think it matters which they use first. The obvious thing to do is to use the cheapest one.

As for crude oil refining, I think I indicated that I see the possibility of the production of crude oil or of the value of products from the field being enhanced in two possible ways. The natural gas which always accompanies the oil can be used for the Fischer-Tropsch process, or you can use it to make hydrogen to hydrogenate the heavy residues and produce distillate oils, of which there may be a shortage in a relatively short space of time.

MR H. C. TETT: I do not intend to contribute to the technical part of the discussion, but I would like to add my congratulations to Major Gordon on the way he has presented his paper. I would like to comment on the fact that, with two or three exceptions, those who have spoken at this meeting have been colleagues of Major Gordon in the work of collecting in Germany the information he has given. So that we have had a collection of old soldiers talking to us!

In that connexion I would comment on the Chairman's remarks concerning the discomforts which necessarily they had to face in Germany, and agree with him on the effect of those discomforts on the making of friendships. Some of us, I think all of us, quite enjoyed those trips; they were real fun, although uncomfortable, and most of those who took part felt that the experience was infinitely preferable to staying at home and being bombed. But although there was some fun in travelling about Germany and interrogating Germans, when we came to deal with the mass of information obtained it was not so funny. In the field for which I was responsible we brought back from one "target" 700 secret and confidential reports, each quite voluminous. We selected them with some care when we were on the "target." When we reached home three months afterwards those documents had to be sifted again and again, the important ones collected and translated by quite a large staff of translators, and, finally, the information was collated and written in the form of a report.

I want to emphasize that, because Major Gordon's very lucid summary of the highlights is wonderful, particularly when we realize that a terrific mass of information, much of it irrelevant, had to be dealt with in order to give us that summary.

There has been some mention of future developments of the Fischer-Tropsch and particularly the synthesis process. I feel quite confident that Mr Russell will touch on the American developments and possibly give us some more optimistic estimates when he delivers his Cadman Memorial Lecture on June 4.

It seems to me, from all that has been said concerning the economics of the hydrocarbon synthesis process, that so far as the United Kingdom is concerned the direction in which there is most room for improvement is in the price of coal !

Finally, I would like to express thanks on behalf of all of us to Major Gordon for the excellent talk he has given us, and also to thank Dr Parker for having presided so ably.

(The vote of thanks was accorded with enthusiasm.)

THE CHAIRMAN : It has been a source of great pleasure to me to occupy the Chair and to listen to this most interesting paper and discussion. I thank you very much, and I would express my thanks also to Major Gordon for his excellent paper.

MAJOR GORDON : I thank you very much for having listened so patiently, and would like to congratulate the Institute on having collected so large and so distinguished an audience.

IMPROVED METHOD FOR THE INTERPRETATION OF EXPERIMENTAL DATA OBTAINED IN MOLECULAR WEIGHT DETERMINATIONS OF PETROLEUM FRACTIONS.

BY J. G. REYNOLDS, F.R.I.C.

SUMMARY.

This communication describes a method of interpreting data, obtained with the Menzies-Wright ebullioscopic apparatus, or by the cryoscopic technique, which eliminates the effects of errors in the zero reading of the Menzies differential thermometer or in the value found for the freezing point of the pure solvent. Apparent changes in boiling point or freezing point are plotted against concentration of solute, resulting in linear relationships in all cases so far examined. This indicates that there is no substantial departure from ideality of solution within the limits of concentration covered by the experimental data. The molecular weight of the solute is calculated from the gradient of the line so obtained, whether or not the latter passes through the origin.

The method is illustrated by results obtained with a number of pure compounds, *e.g.*, diphenyl, fluorene, and dicyclohexylbenzene, from which the ebullioscopic and cryoscopic constants for *cyclohexane* are calculated.

Data obtained from the ebullioscopic and cryoscopic experiments on two oils are interpreted by the recommended method and also that involving extrapolation to zero concentration.

INTRODUCTION.

THE determination of molecular weights of substances dissolved in organic solvents, by the ebullioscopic method using the Menzies-Wright apparatus and by the Beckmann cryoscopic procedure has been discussed in previous publications.^{1, 2, 3}

A high precision in both methods is necessary for the purpose of the "type analysis" of petroleum fractions. Two analogous observations, namely, the zero reading of the Menzies-Wright differential thermometer and the apparent freezing point of the solvent, have been found to be sources of uncertainty in the final results obtained by the two methods. Error in such observations has the effect of causing extrapolation to infinite dilution of the plot of molecular weight against concentration to lead away from the correct value of the former instead of towards it. The error also leads to curvature in a graph which would otherwise have been rectilinear, thus increasing the uncertainty of extrapolation.

It is not only the variation about the mean of such "zero" readings that is of importance. A reading which is in all determinations consistently too high or too low in relation to corresponding readings after the addition of solute will lead to curved plots and erroneous extrapolations in exactly the same way as if the error were a random one. Our observations point to the possibility of such a systematic error in ebullioscopic measurements.

A Menzies-Wright boiling tube was constructed of slightly larger dimensions than usual, in order to allow more scope for vertical movement of the

differential thermometer without either raising the upper bulb into the neck of the inner cylinder or causing the lower bulb to become partially immersed. With steadily boiling *cyclohexane* in the apparatus the thermometer, with the Cottrell pump attached, was observed in a series of positions within the limits just indicated. It was found that for the lowest positions the zero readings varied in a random manner between about 1 cm and 1.4 cm of water, with no evident connexion between the result obtained and the position of the thermometer. With gradual raising of the latter, a point was reached at which the reading rapidly fell to 0.85 or 0.86 cm, remaining approximately constant thereafter over a considerable further upward change of position of the thermometer. It was noticed that the point at which the sudden diminution in the reading took place was also the point at which the Cottrell pump ceased to work owing to its excessive height above the liquid. A zero reading of the order of 0.85 cm had previously been observed, using the same thermometer in another Menzies-Wright apparatus, with the Cottrell pump working efficiently, and such a value apparently corresponded to equality of temperature of the upper and lower bulbs. There was thus clear evidence that the liquid delivered by the pump was at a temperature higher than that of the condensing vapour, in spite of the steadiness of boiling and the use of boiling-stones. The frequent occurrence of superheating of the pure solvent, with cessation or considerable diminution of this effect on addition of the oil sample, would account for the preponderance, among the plots of molecular weight against concentration, of curves having a negative slope and an upward concavity.

It was clearly of prime importance to devise a method of avoiding the effects of the errors in question. The following considerations have been developed from the point of view of ebullioscopic determinations, but they cover the analogous problem which arises in cryoscopic work.

EXPERIMENTAL.

(1) *Variation in Zero Reading with the Differential Thermometer Held in Different Positions.*

Zero readings were measured for four different positions of the differential thermometer in the Menzies-Wright apparatus employing *cyclohexane* as solvent. The positions chosen differed from each other with respect to the distance (d) from the top of the upper bulb of the thermometer to the top of the inner cylinder of the ebullioscopic apparatus.

The results are listed in Table I.

TABLE I.

Zero Readings for the Differential Thermometer Held in Different Positions.

Position	1	2	3	4
Distance (d) in cm	0.64	1.44	2.02	2.67
Zero reading in cm	1.470	1.647	1.500	1.848

(2) *Variation in Zero reading with the Differential Thermometer Held in One Position.*

The zero reading for this determination was measured for position 2 (Table I), which was chosen as giving adequate exposure of the upper bulb to condensing solvent vapour whilst keeping the lower bulb sufficiently above the boiling solution. After the first reading the apparatus was cooled, causing the water in the thermometer to collect in the lower bulb. The thermometer was then removed, shaken to shift the water from the lower bulb into the capillary, replaced as nearly as possible in the original position, and the zero reading re-determined. This process was repeated twice more, giving the results shown in Table II.

TABLE II.

Variation of Zero Reading for the Differential Thermometer Held in One Position.

Position number	2	2	2	2
Determination number	1	2	3	4
Zero reading in cm	1.514	1.318	1.358	1.336

(3) *Variation in the Zero Reading : Apparent Freezing Point of cyclo-Hexane.*

Four freezing point determinations were performed on one sample of cyclohexane using the same Beckmann thermometer for each series of observations. The results obtained, measured in degrees on the Beckmann thermometer scale, were 5.546, 5.521, 5.520, 5.529.

(4) *Purification of Solvent and Solute.*

cycloHexane. After oleum treatment and distillation, the solvent was further purified by fractional crystallization.

The crystallized cyclohexane, about 40 per cent of the original volume, melted between 5 and 6° C and had the following physical properties :—

Density d_4^{20}	0.77847 (literature value ⁵ 0.78310)
Refractive index n_D^{20}	1.42670 („ 1.42636)
Specific refraction	0.32960 („ 0.32743)
Melting point	5 to 6° C („ 6.4° C)

Benzil. Recrystallized from industrial ethanol, then from cyclohexane. M.p. 94.7 to 95.5° C (literature value ⁷ 95° C).

Dicyclohexylbenzene. Synthesized from cyclohexene and benzene using aluminium chloride as catalyst, purified by distillation *in vacuo*, and crystallized twice from acetone. M.p. 103° C (literature value ⁶ 102 to 103° C).

Tricyclohexylbenzene. Synthesized from cyclohexene and benzene using aluminium chloride as catalyst and purified by two crystallizations of the acetone-soluble fraction of the crude product. This was followed by removal of acetone from the crystals *in vacuo*. M.p. 68.5° to 69° C (literature value ⁶ 68.5 to 69° C).

Fluorene. British Drug Houses Lab. reagent grade, crystallized three

times from ethanol with activated charcoal. M.p. 113°C (literature values 8 113, 114, 115°C).

Diphenyl. British Drug Houses Lab. reagent grade, crystallized once from ethanol with activated charcoal. M.p. 69 to 69.5°C (literature value 7 71°C).

Phenanthrene. British Drug Houses Lab. reagent grade, crystallized from ethanol three times. M.p. 100°C (literature value 7 101°C).

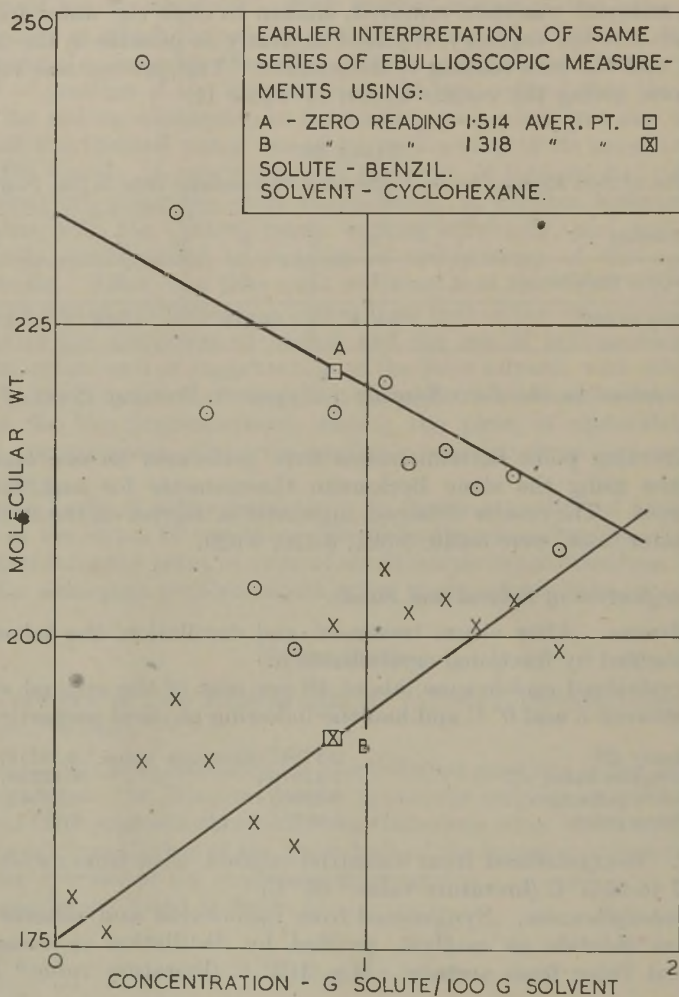


FIG. 1.

Decalin. British Drug Houses micro-analytical reagent percolated through silica gel. Physical constants of the unadsorbed fraction:—

Density d_4^{20}	0.87145	(literature value 5 0.8865)
Refractive index n_D^{20}	1.46938	(" " 1.47950)
Specific refraction	0.31980	(" " 0.32017)

2. Interpretation of the Plot of ΔT Against Concentration.

In Fig. 2 the same two series of apparent elevations of boiling point ("observed" data of Table III) are plotted against the corresponding concentrations of benzil in *cyclohexane*. (A) is the "best" straight line through the points obtained using a zero reading of 1.514 and (B) using zero 1.318 cm. It is reasonable to assume that if there had been no

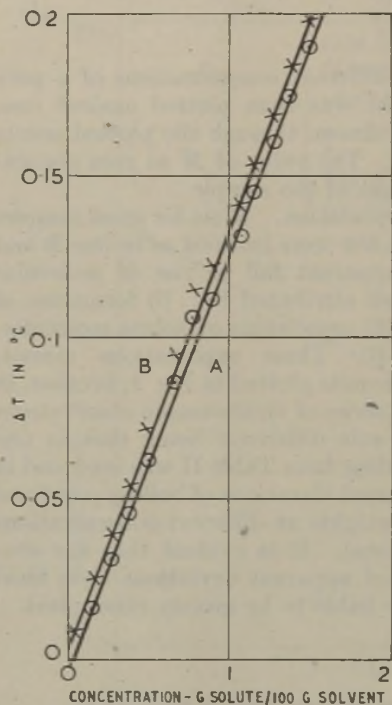


FIG. 2.

RELATIONSHIP BETWEEN ΔT AND CONCENTRATION FOR TWO DIFFERENT OBSERVED ZERO READINGS.

The series of observations shown were used to calculate the molecular weights plotted in Fig. 1. Solute: benzil. Solvent: *cyclohexane*.

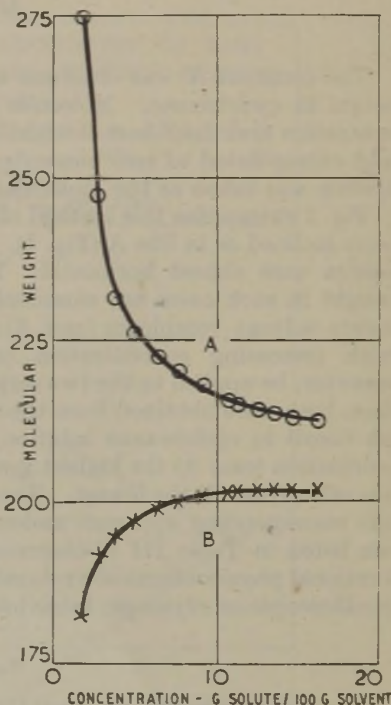


FIG. 3.

RELATIONSHIP BETWEEN CONCENTRATION AND MOLECULAR WEIGHT CALCULATED FROM THE VALUES OBTAINED FROM THE LINES IN FIG. 2.

Solute: benzil. Solvent: *cyclohexane*.

experimental error all the plotted points would have fallen on these lines according to their respective zero readings.

The ordinary ebullioscopic relationship between boiling point elevation (ΔT), concentration (C), and molecular weight (M) of the solute for ideal solutions can be written in the form

$$\Delta T = \frac{K}{M} \times C$$

where K is the ebullioscopic constant. Thus for an ideal solution the plot of ΔT against C is a straight line passing through the origin. In such a case

the molecular weight (M) can be calculated, K being known, from the gradient (K/M) of the line, without calculating values of M from pairs of values of ΔT and C . If the results obtained for ΔT are subject to a constant error of $\delta(\Delta T)$, then the plot of the apparent values ($\Delta T'$) of ΔT against C will be represented by:—

$$\Delta T' = \frac{K}{M} \cdot C + \delta(\Delta T) \quad . \quad . \quad . \quad (2)$$

and the line will no longer pass through the origin. It will, nevertheless, still have the same gradient, which can be used as before for calculating M .

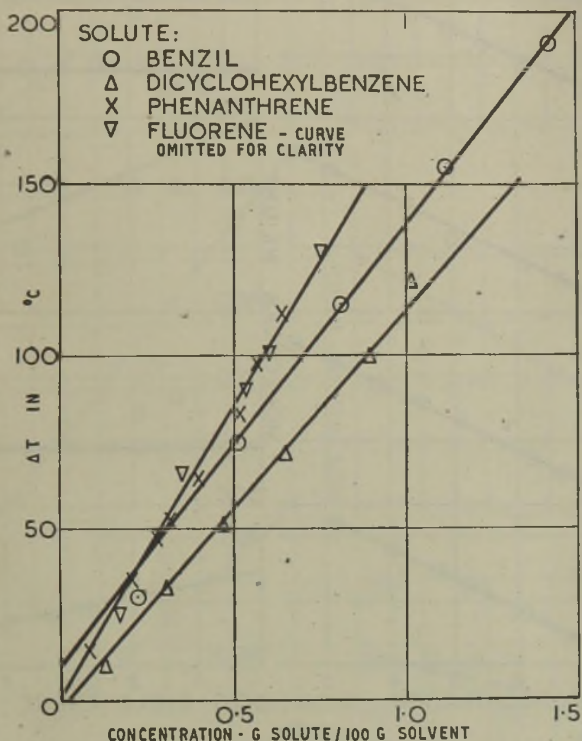


Fig. 4.

RELATIONSHIP BETWEEN ΔT AND C FOR ONE SERIES OF EBULLIOSCOPIC MEASUREMENTS WITH *cyclohexane* AS SOLVENT FOR VARIOUS SOLUTES.

Calculation of M by means of equation (1) from individual pairs of figures would in this case have given a series of incorrect values (M') of M , for

$$M' = \frac{KC}{\Delta T + \delta(\Delta T)}$$

and if $KC/\Delta T$ is constant and equal to M , the values of M' must not only differ from M but also increase or decrease with C . If ΔT is subject to a constant error there is thus an advantage in plotting ΔT against C and

calculating M from the gradient of the plot, instead of calculating separate values of M .

Fig. 3 represents two plots of molecular weight against concentration using molecular weights calculated not from experimental values of ΔT , but from values taken from Fig. 2, lines A and B (Table III "smoothed" data).

It will be seen, therefore, that the plots of Fig. 3, which, in fact, represent smoothed values corresponding to those in Fig. 1, are curves which cannot

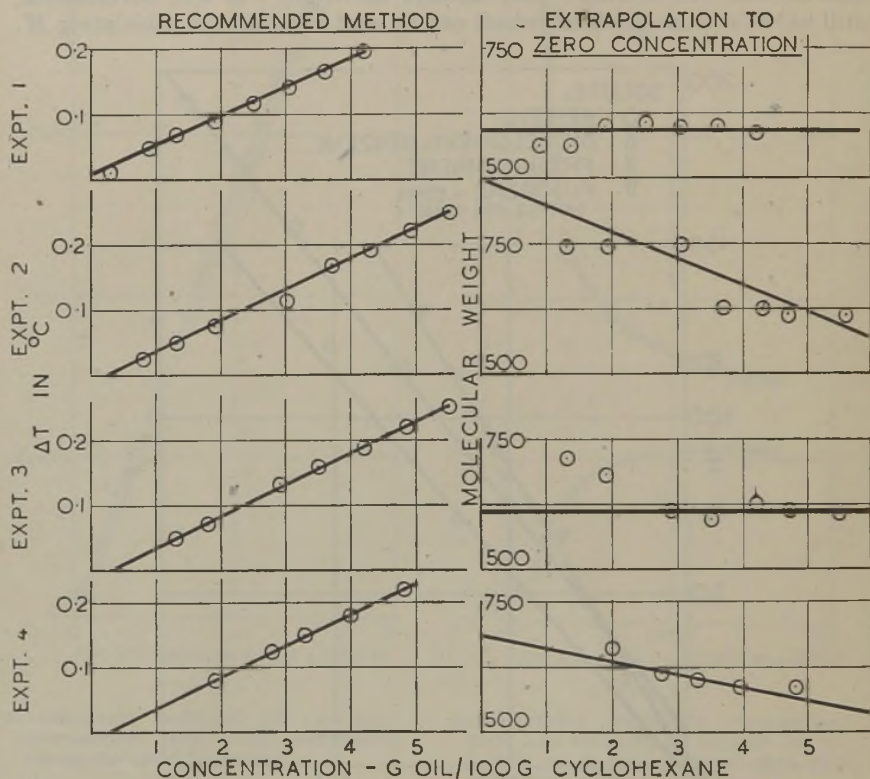


FIG. 5.

THE MOLECULAR WEIGHT OF OIL "A," DATA FROM FOUR EBULLIOSCOPIC EXPERIMENTS.

be extrapolated to zero concentrations as in the earlier interpretation. In Fig. 2, lines A and B are parallel and the only effect of calculating results using different zero readings is to transpose the plot bodily in a lateral direction. From this figure, the gradient of the "best straight line" through the plotted points can be obtained, being, in fact, the same for both plots obtained from the experimental results and practically independent of the zero reading chosen.

The plots of ΔT versus C for the substances listed in Table IV, as exemplified in Fig. 4, are substantially rectilinear; that is to say, any departure

of the data from the straight line relationship is not only small but is also, so far as can be seen, random. The solutions investigated may therefore be regarded to all intents and purposes as ideal. Further, in the applica-

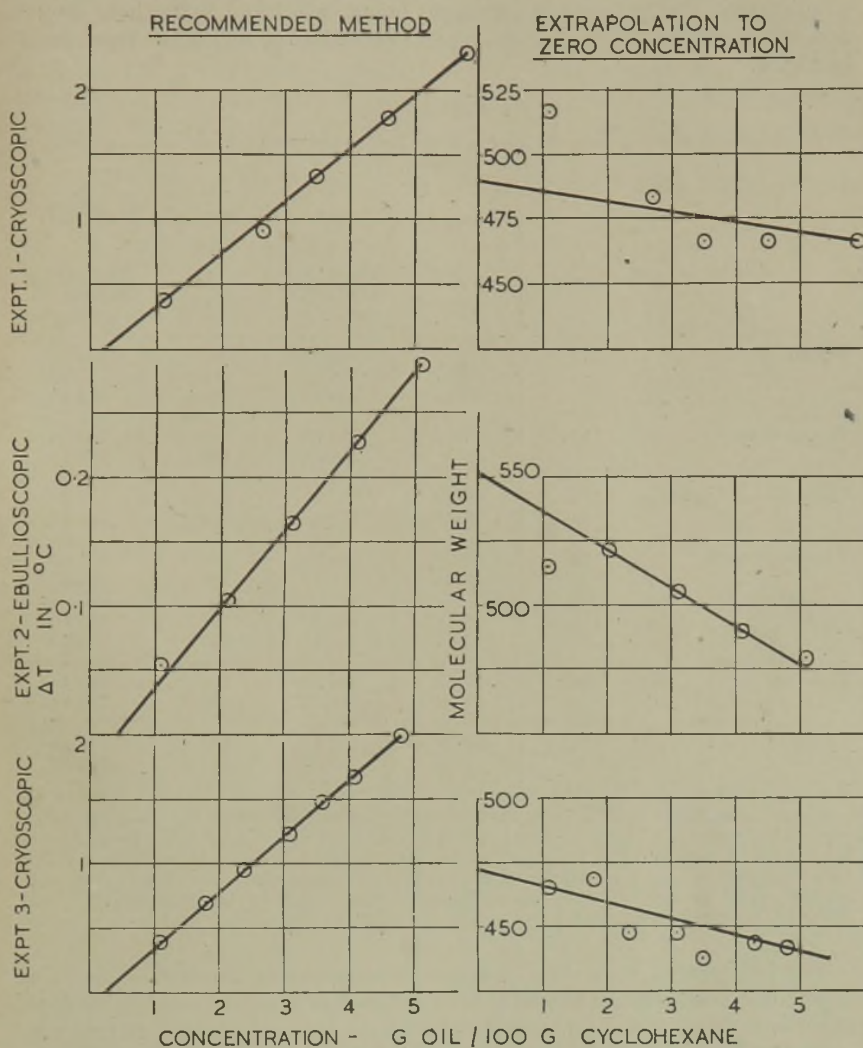


FIG. 6.

THE MOLECULAR WEIGHT OF OIL "B." DATA FROM EBULLIOSCOPIC AND CRYOSCOPIC EXPERIMENTS.

tion of the recommended method of plotting to ebullioscopic data already obtained for lubricating oils, no substantial departure from ideality of solution has so far been observed. Similar remarks apply to cryoscopic observations (Figs. 5 and 6).

M M

3. Application of the "Gradient" Interpretation to the Determination of Ebullioscopic and Cryoscopic Constants.

Table IV shows the theoretical molecular weights of the solutes used, the ebullioscopic and cryoscopic constants being calculated from these figures and the gradients of the graphs, typical examples of which are reproduced in Fig. 4.

TABLE IV.

Ebullioscopic and Cryoscopic Constants of Crystallized cycloHexane with Different Solutes.

Solute	M Theoret	Ebullioscopic method		Cryoscopic method	
		K (observed)	Corrected barometric pressure	K (observed)	Corrected barometric pressure
Benzil	210.2	27.85	759.42	192	758.24
	—	27.31	756.23	195	753.62
	—	27.47	756.49	196.4	752.90
Dicyclohexylbenzene	242	27.82	750.63	200	753.08
	—	28.3	751.88	196	753.10
Tricyclohexylbenzene	324	29.19	766.21	167.9	757.2
	—	29.58	760.96	174.2	761.45
Phenanthrene . .	178	28.26	750.56	189.3	757.93
	—	28.48	748.49	190.9	758.07
Diphenyl	154	28.79	762.29	195	757.45
	—	27.74	761.42	197	755.70
Fluorene	166	27.67	756.23	196.5	763.44
	—	27.0	761.56	195.3	762.24
Decalin	138	23.59	757.12	187.8	760.55
	—	—	—	191.6	760.55

From Table IV it will be seen that in each case the values of the constant agree reasonably closely. There is also good agreement between the respective constants for benzil, dicyclohexylbenzene, diphenyl, and fluorene. Tricyclohexylbenzene and decalin, however, gave rather lower cryoscopic constants than the above-mentioned solutes. The sample of tricyclohexylbenzene was found to be soluble only with difficulty in cold cyclohexane.

The influence of variations in atmospheric pressure on ebullioscopic and cryoscopic constants has usually been ignored in practice. While such an effect is to be expected on theoretical grounds, it is not possible to prove its existence from the results recorded in Table IV, for although figures can be selected from among these which may suggest the effect in question, the indications are not consistent enough to warrant drawing of any conclusions.

The values of *K* for cyclohexane given in Table IV agree reasonably well with the literature values quoted in Beilstein,⁴ which are :—

Ebullioscopic	26.9	27.53
Cryoscopic	200	203.3

4. Choice of a Standard Solute.

Benzil¹ appears to be suitable as an ebullioscopic standard and there seems no reason to abandon its use for this purpose, although in the cryoscopic method it tends to come out of solution on cooling if the concentration is above 1 per cent. Decalin, even after percolation, obviously comes under suspicion as a cryoscopic standard solute, and its tendency to become entrained by the boiling *cyclohexane* in the ebullioscopic method renders it of little use. If it is desired to use the same standard for both methods, *dicyclohexylbenzene*, *diphenyl*, and *fluorene* appear to be satisfactory.

The average constants using the benzil, *dicyclohexane*, *diphenyl*, and *fluorene* results are

Ebullioscopic	27.77
Cryoscopic	195.9

5. Recommended Method for Interpretation of Experimental Results.

It has been shown from general considerations that in the Menzies Wright ebullioscopic method of determining molecular weight, an error in the zero reading of the differential thermometer will lead, even in the case of ideal solutions, to curvature in the plot of apparent molecular weight against concentration of solute (see Fig. 3) and to error in the value found for molecular weight by extrapolation to zero concentration, unless it happens that an equal error is attached to subsequent thermometer readings. Analogous effects arise in the determination of the ebullioscopic constant using a solute of known molecular weight. Application of these considerations to actual experimental data proves that the magnitude of the resulting errors may be considerable, and illustrates the fact that they may be avoided by plotting the experimental results in a different form. Precisely similar considerations apply to the effect of the error in determining the freezing point of the pure solvent in cryoscopic molecular weight determinations.

It is therefore recommended that in all molecular weight determinations involving differences between thermometer readings—whatever type of thermometer is used—temperature differences (ΔT) should be plotted against solute concentrations (C) and the molecular weight of the solute calculated from the gradient of the plot. Unless the plot is obviously curvilinear, the straight line which best fits the data should be drawn, not necessarily through the origin. If $m = d(\Delta T)/dC$ is the gradient of this line, the molecular weight (M) of the solute should then be calculated from the formula

$$M = \frac{K}{m}$$

where K is the ebullioscopic or cryoscopic constant of the solvent. If the plot is curvilinear, the limiting value of its gradient as C approaches zero should be taken as the value of m .

In determining the ebullioscopic or cryoscopic constant using a solute of known molecular weight (M), the results should be plotted as described, and the constant calculated from the equation.

$$K = mM$$

6. The "Gradient" Interpretation Applied to Experimental Results.

Four ebullioscopic experiments were performed by one operator to determine the molecular weight of oil A. The data were interpreted both by the recommended method and by extrapolation to zero concentration (Fig. 5).

Two ebullioscopic experiments and one cryoscopic experiment were performed by different operators to determine the molecular weight of oil B, again, the data were interpreted by both methods (Fig. 6).

TABLE V.
Interpretation of Experimental Data for Two Oils.

Oil	Experimental method	Molecular weight	
		Calculated by recommended method	Calculated by extrapolation to zero conc
A	Ebullioscopic	583	590
	Ebullioscopic	570	860
	Ebullioscopic	570	615
	Ebullioscopic	557	680
B	Cryoscopic	432	490
	Ebullioscopic	434	552
	Cryoscopic	432	474

The molecular weights obtained are contrasted in Table V. It will be noted from Figs. 5 and 6 that the graphs involving extrapolation to zero concentration, only pass through a few of the plotted points in each case.

ACKNOWLEDGMENT.

The author's thanks are due to S. A. Bryant and C. N. Thompson, who collaborated, and to "Shell" Refining and Marketing Co. Ltd., for permission to publish this work.

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THE TEN DIMETHYLNAPHTHALENES, THEIR PHYSICAL PROPERTIES, MOLECULAR COMPOUNDS, AND ULTRA-VIOLET SPECTRA.

By A. S. BAILEY, K. C. BRYANT, R. A. HANCOCK, S. H. MORRELL,
and J. C. SMITH.

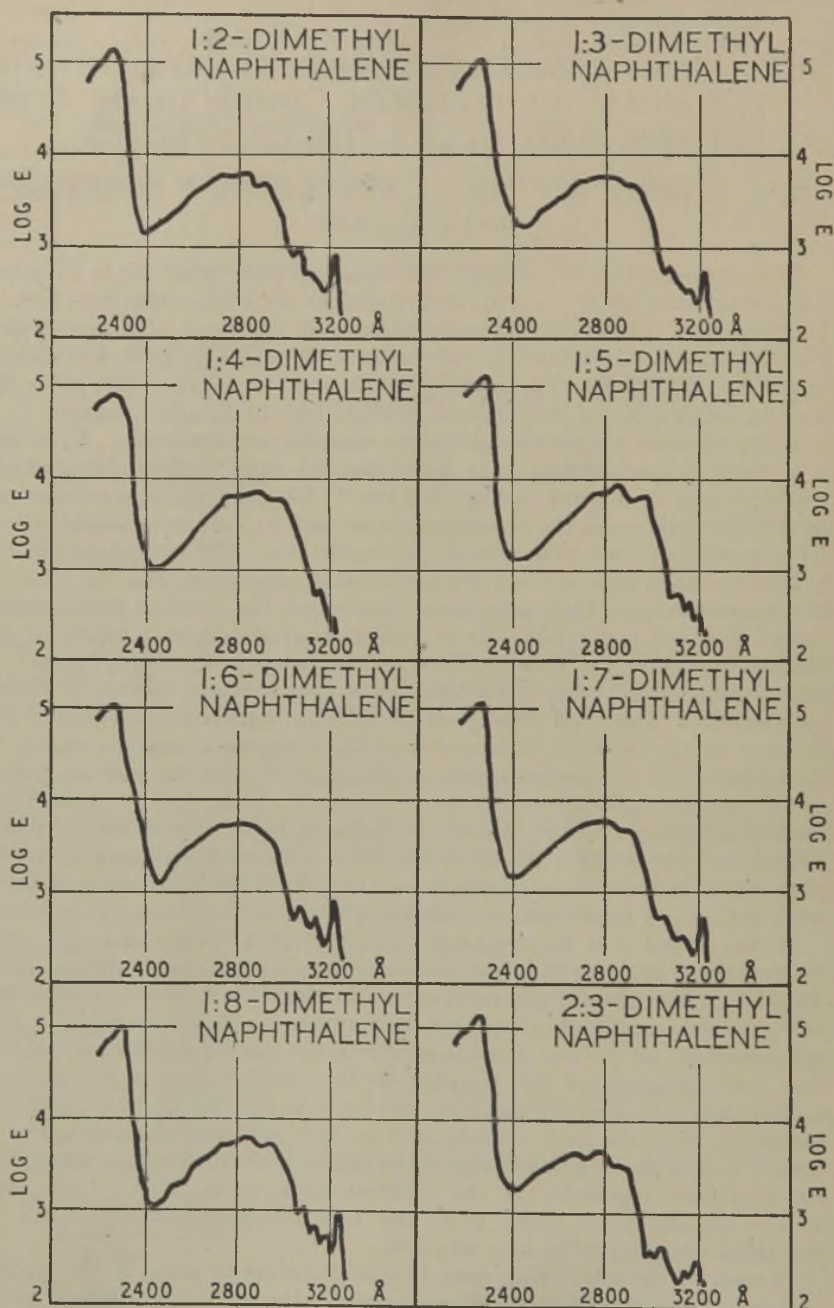
IN an investigation of the naphthalene homologues occurring in Trinidad petroleum, samples of the pure hydrocarbons for comparison had first to be prepared. The work of preparation and synthesis of these hydrocarbons, sponsored by the Colonial Products Research Council, was carried out in the Dyson Perrins Laboratory, Oxford, in collaboration with the Central Laboratory of Trinidad Leaseholds Ltd. at King's Langley.

Eight of these dimethylnaphthalene samples are synthetic; 2:3- and 2:6-dimethylnaphthalene have been purified from commercial products readily available in good quality, but the 2:6-isomer was also synthesized on a small scale. All these compounds, except 2:7-dimethylnaphthalene, have previously been synthesized, but sometimes with conflicting results.

Now for each hydrocarbon the picrate, the styphnate, and the 1:3:5-trinitrobenzene complex have been made and the melting points taken under standard conditions. It is evident that the highest values of the melting points in the literature are not necessarily the correct ones: in some cases, the picrates of obviously less pure material melted at higher temperatures than did the picrates of the pure hydrocarbons. The styphnates are the least satisfactory of the complexes, as some appear to decompose near the melting point. For the first time the melting points of all the five liquid isomers (1:2-, 1:3-, 1:4-, 1:6-, and 1:7-dimethylnaphthalene) are recorded, and these constants, together with the refractive indices and the melting points of the three molecular compounds, should make much easier the identification of any dimethylnaphthalene isolated from coal-tar, or petroleum, or from the aromatization of natural products.

It was hoped that by means of the ultra-violet spectra not only pure hydrocarbons but also those present in mixtures could be identified. This would avoid the usually laborious separation by such methods as fractional sulphonation—methods which are difficult to make quantitative. But consideration of the ten spectra confirms the earlier finding of Gavāt¹ that "the spectra are not adapted to the identification of the methylnaphthalenes." This difficulty is partly due to the fact that the naturally occurring mixtures may contain also α - and β -ethylnaphthalene, but is mainly due to the close similarity of the ultra-violet curves of the dimethylnaphthalenes, especially of the $\alpha\beta$ -isomerides, 1:2-, 1:3-, 1:6-, and 1:7-. On the other hand, 2:6- and 1:8-dimethylnaphthalene can be identified unequivocally in a mixture.

In view of the conflicting data in the literature of some of the hydrocarbons it was necessary to choose carefully the synthetic methods to be employed. Some of the dimethylnaphthalenes were synthesized from pure α - or β -methylnaphthalene: the chloromethylation of β -methyl-



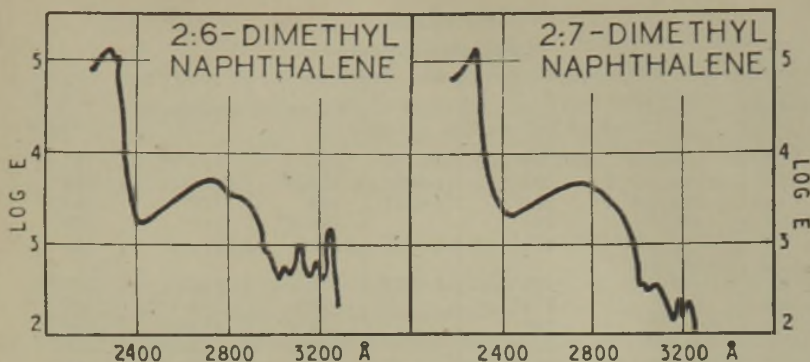


FIG. 1.

ULTRA-VIOLET ABSORPTION SPECTRA.

naphthalene yielded α -chloromethyl- β -methylnaphthalene, from which pure 1:2-dimethylnaphthalene was readily obtained by catalytic reduction. Chloromethylation of α -methylnaphthalene gave a mixture of 4- and of 5-chloromethyl-1-methylnaphthalene, from which the two dimethylnaphthalenes were isolated; but 1:5-dimethylnaphthalene was obtained more easily by chloromethylation of α -chloromethylnaphthalene or by bis-chloromethylation of naphthalene, followed by reduction. Introduction of a second methyl-group by the action of dimethyl sulphate on the Grignard reagent from 2-methyl-6-iodonaphthalene gave 2:6-dimethylnaphthalene.

Starting from a benzene nucleus three methods of building on the second ring were employed. (a) The succinic anhydride method on an alkylbenzene gave 1:3- and 1:7-dimethylnaphthalene; (b) tolylethyl bromide and the malonic ester synthesis gave the 1:6-, 2:7-, and 1:7-isomerides; (c) a Reformatsky reaction on *o*-methylacetophenone followed by chain-lengthening (Arndt-Eistert synthesis) led to 1:8-dimethylnaphthalene. Two of the points which now seem to be settled concern 1:7- and 1:8-dimethylnaphthalene. The 1:7-isomer was thought by Zelinsky² to melt at 107°, and Veseleý³ claimed that it melted at 84–85°; actually, there is no doubt that the substance is a liquid (m.p. –28.5° and –14° for the two forms): the succinic anhydride process applied to toluene by Barnett⁴ is an unambiguous synthesis. Veseleý⁵ claimed that 1:8-dimethylnaphthalene was a liquid, but Linstead,⁶ using process (c) listed above, obtained a solid melting at 63° and the latter result is confirmed in the present work.

Although the scale of these syntheses was not sufficiently large to ensure the highest purity of the final products, nevertheless, the samples obtained seemed to compare favourably with the best so far described. In Table I there are collected most of the data from the investigation.

The melting points of the five liquid hydrocarbons were taken with the thermometer in a tube of the slowly melting mush of solid and liquid. While the mush was stirred with the thermometer the tube was surrounded with cotton-wool.

For the molecular compounds the melting points were taken in capillary

TABLE I.
Dimethylnaphthalenes.

Isomer.	M. p.	B. p.	n_D^{20} .	Picrate.	Styphnate.	T.N.B. complex.
1 : 2	-1.6°	266°/760 mm.	1.6164	130°	143.5°	147-8°
1 : 3	-6 to -5°	263°	1.6078	116.5°	116-17°	135°
1 : 4	+5 to +6°	263°	1.6127	143°	126°	165-6°
1 : 5	81.5°	265°		138-9°	159°	158°
1 : 6	-17° to -15°	264°	1.6072	111°	121-2°	130-1°
1 : 7	-14° and -28.5°	263°	1.6072	118.5°	143°	137°
1 : 8	63.5°	270°		156°	160-1°	167°
2 : 3	104-5°	268°		123-4°	148.5°	136-7°
2 : 6	110-11°	261°		141-2°	157-8°	154°
2 : 7	96-97°	263°		136°	159°	152°

tubes in the usual manner : the temperature was raised at the rate of 1° per minute, all the stem from 0° upwards was exposed and no correction for stem-exposure was applied.

Boiling points were only approximate. They were taken on short-stem thermometers as the liquids distilled from small Claisen flasks.

TABLE II.
Band Maxima and Molecular Extinction Coefficients of Dimethylnaphthalenes.

1 : 2.		1 : 3.		1 : 4.		1 : 5.		1 : 6.	
λ .	Log E .	λ .	Log E .	λ .	Log E .	λ .	Log E .	λ .	Log E .
3220	2.90	3218	2.71	3212	2.46	3208	2.50	3220	2.96
3130	2.69	3170	2.49	3170	2.76	3170	2.69	3150	2.76
3080	2.95	3080	2.75	3145i	2.77	3115	2.75	3080	2.91
2930	3.68	2915	3.68	2995	3.73	3060i	3.15	2910	3.66
2855	3.77	2830	3.78	2890	3.88	2985	3.79	2815	3.80
2740	3.72	2760	3.76	2805	3.80	2870	3.96	2735	3.77
2620i	3.50	—	—	2690i	3.60	2765	3.85	—	—
2550i	3.33	2530	3.39	2600i	3.38	2675i	3.61	—	—
2280	5.12	2275	5.08	2270	4.91	2585	3.40	2270	5.07
2220i	4.95	2200i	4.90	2220i	4.78	2277	5.14	2230i	5.00

1 : 7.		1 : 8.		2 : 3.		2 : 6.		2 : 7.	
λ .	Log E .	λ .	Log E .	λ .	Log E .	λ .	Log E .	λ .	Log E .
3220	2.71	3227	2.99	3200	2.53	3240	3.14	3212	2.37
3175	2.47	3175	2.78	3155	2.43	3165	2.78	3175	2.41
3150	2.52	3125	2.86	3060	2.67	3100	2.98	3120i	2.41
3075	2.74	3080	3.03	3020	2.61	3030	2.73	3075	2.57
2915	3.67	2930	3.74	2885	3.53	2950	2.90	3025	2.57
—	—	2850	3.85	2785	3.71	2740	3.67	2750	3.69
—	—	2760	3.78	2685	3.69	—	—	—	—
—	—	2630i	3.55	—	—	—	—	—	—
—	—	2520i	3.30	—	—	—	—	—	—
2275	5.10	2290	5.02	2265	5.16	2270	5.15	2275	5.15
—	—	2240i	4.90	2200i	4.98	—	—	—	—

The letter "i" after a wavelength denotes an inflexion.

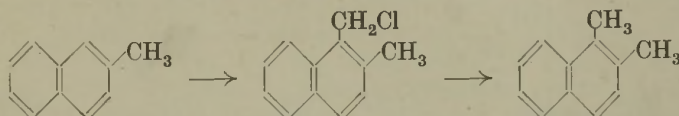
The effect of position of the substituents of the melting points of the hydrocarbons puts the values into three groups: the lowest-melting are the least symmetrically substituted, the $\alpha\beta$ -isomers and the melting points increase in the order 1:7, 1:6, 1:3, and 1:2; next come the $\alpha\alpha$ -isomers 1:4, 1:8, and 1:5; and the highest are the $\beta\beta$ -isomers, 2:7, 2:3, and 2:6. As might be expected, the higher-melting hydrocarbons usually yield the higher-melting molecular compounds.

ULTRA-VIOLET ABSORPTION SPECTRA.

For determining the ultra-violet absorption spectra, solutions of suitable concentrations of each dimethylnaphthalene were prepared in highly purified *isooctane*. The measurements were made using a Hilger E 498 Medium Quartz Spectrograph, with a Spekker spectrophotometer, the slit width being 0.015 mm and the cell length 1 cm. The source of radiation was a spark struck between two tungsten-steel electrodes.

Wavelengths were taken from a scale incorporated in the spectrograph, and hence may be slightly in error, particularly at long wavelengths, *e.g.*, the 3240 Å band of 2:6-dimethylnaphthalene, by comparison with earlier work.^{7, 8}

1:2-DIMETHYLNAPHTHALENE.



Of the methods reported^{9, 10, 11, 12, 14} for the synthesis of 1:2-dimethylnaphthalene that of Mayer and Sieglitz,¹⁰ by way of 2-methylnaphthalene and 1-bromo-2-methylnaphthalene, was first tried. The bromo-compound was readily converted into the Grignard reagent, but replacement of the MgBr group by methyl, using dimethyl sulphate, was incomplete and the product contained 2-methylnaphthalene. Following the route of Darzens and Lévy,¹² 2-methylnaphthalene was chloromethylated by the procedure of Grummitt and Buck¹³ and the purified 1-chloromethyl-2-methylnaphthalene was reduced catalytically.

A mixture of 71 g (0.5 mol) of 2-methylnaphthalene (m.p., 33.6 to 34.0°), 30 g of paraformaldehyde (equivalent to 1 mol of formaldehyde) 90 cc of conc hydrochloric acid, 65 cc of acetic acid and 42 cc of 85 per cent phosphoric acid was placed in a 2-litre, 3-necked flask fitted with a reflux condenser and a mercury-sealed stirrer and stirred for 6 hours at 80–85°. The warm product was poured into 1 litre of water and extracted immediately with benzene.

The benzene extract was washed with water until free from acid and then dried over potassium carbonate. After the benzene had been removed the residue, distilled from a Claisen flask, yielded 66 g of liquid, b.p. 148–165°/5 mm. This product was redistilled from a flask fitted with an 8-in Vigreux, electrically heated column, yielding 25 g of b.p. 158 to 160°/8 mm, m.p. 52–55°. The solid, crystallized from 50 cc of acetic acid, gave 16 g of m.p. 62° and recrystallization from 50 cc of alcohol gave 9 g of m.p. 64° (Found: Cl, 18.6 per cent. Calc: 18.7 per cent). Ziegler and

Tiemann¹⁶ state that 1-chloromethyl-2-methylnaphthalene melts at 61 to 63°, and Darzens and Lévy¹² give m.p. 65°.

Reduction.

Catalyst : A solution of 1 g of palladium chloride in 600 cc of water was stirred with 50 g of commercial strontium carbonate for 20 minutes, by which time the colour had left the solution. The solid was collected on a filter, washed well with water, then with alcohol, with acetone, dried, and bottled. It was added to the liquid in a 200-cc, low-pressure hydrogenator and readily formed metallic palladium when shaken with hydrogen (at 1 to 4 atm pressure) and the substance to be reduced.

TABLE III.
Dimethylnaphthalenes.

Isomer.	M. p., ° C.	B. p., ° C/760 mm.	n_D^{20}	Picrate, m. p., ° C.	Styphnate, m. p., ° C.	T.N.B. complex, m. p., ° C.
1:2-	- 1.6 - 3.5 ¹²	266 265 ⁴³ 264/749 mm. ¹¹ 265/770 mm. ¹² 144/22 mm. ¹³ 137/13 mm.	1.6164 1.6142 ¹⁰ 1.616 ¹⁸	130 128-129 ¹⁹ 129 ¹⁰ 130 ¹² 131 ⁸	143.5 140-141 ¹⁹ 141 ⁴ 142-143 ¹⁴	147-148 147-148 ^{14, 19}
1:3-	- 6 to - 5	263 126/13 mm. 107/1 mm. ⁴ 124-126/10 mm. ⁵⁰	1.6078	116.5 117-118 ¹⁴ 118 ⁴	116-117 116-118 ¹⁴ 132-133 ²¹	135
1:4-	5 to 6 5.5 to 6.5 ²⁸	263 264 ⁴ 265 ²³ 118/10 mm. ²⁸	1.6127 $n_D^{16.4} =$ 1.6157 ²³	143 139-140 ²⁵ 142 ⁶ 143-144 ^{28, 14} 144 ⁴	126 125 ⁶ 125-126 ¹⁴	165-166 165-166 ¹⁴
1:5-	81.5 77-78 ⁵ 79 ⁶ 80 ³³ 80-80.5 ²⁹ 82 ³⁰	265 265-266 ³⁰ 133-136/15 mm. ²⁹	—	138-139 137 ^{6, 33} 137-138 ⁶ 138-139 ²⁹ 140 ³⁰	159	158
:6-	- 17 to - 15	264 262-263 ^{34, 39} 130/14 mm. 126/13 mm. ⁴¹	1.6072 $n_D^{16.3} =$ 1.6089 ¹⁸	111 110-111 ⁴¹ 112 ³⁷ 113 ³⁹ 114 ³⁴	121-122 120 ³⁸ 121-122 ⁴¹	130-131 131-132 ⁴¹
:7-	- 14 and - 28.5	263 261-262 ⁴³ 147-149/15 mm. ⁴²	1.6072 1.6083 ⁴³	118.5 114-117 ³ 120 ⁴ 121 ⁴³ 123-124 ⁴²	143	137
1:8-	63-63.5 63 ⁶	270 128/8 mm. 140/18 mm. ⁶	—	156 148 ⁶ 143 ⁶	160-161 160 ⁶	167
2:3-	104-105 104 ⁴ 104-104.5 ⁶⁷	268 265-266 ⁶³	—	123-124 123-124 ⁶⁷	148.5	136-137 138 ⁶⁵
2:6-	110-110.5 110-111 ³⁴	261 261 ⁴³ 261-262 ³⁴	—	141-142 142-143 ^{69, 43}	157-158	154 154 ⁶⁵
2:7-	96-97 96-97 ³⁴ 96.5-97.5 ⁷⁰ 97-98 ⁷²	263 262 ³⁴	—	136 135-136 ³⁴ 135.5-136.5 ⁷⁰ 136-137 ⁷²	159 159-160 ^{70, 71}	152 151-152 ⁷⁴ 153 ⁶⁵

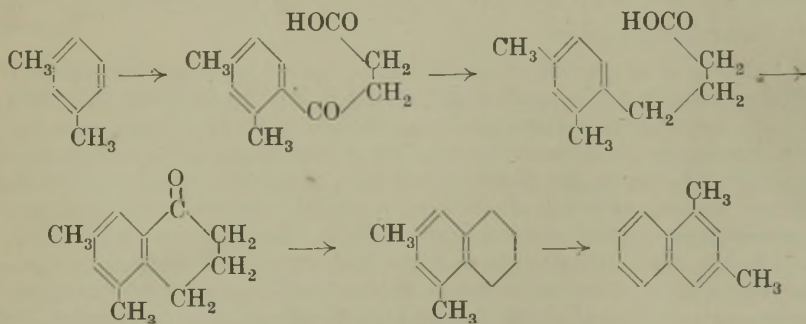
Data without superscripts are those obtained in this investigation.

The chloro-compound (14 g, 0.075 mol) was dissolved in warm alcohol (80 to 100 cc) and mixed with a solution of 2.0 g of sodium in 40 cc of alcohol. 4 Grams of catalyst were added, and the mixture shaken with hydrogen (at 3 to 4 atm) for half an hour, although the reduction seemed complete in a few minutes. The resulting liquid was filtered and the catalyst washed with warm alcohol; the combined filtrate and washings were evaporated to one-third of the bulk, ether added, and the ethereal solution washed repeatedly with water and then dried with calcium chloride. After evaporation of the ether the residual oil was distilled through a short column at 130 to 140°/15 mm, giving 11.5 g (95 per cent yield) of 1:2-dimethylnaphthalene, m.p. -2.5° . A second reduction also gave a 95 per cent yield of dimethylnaphthalene, m.p. -2.3° , b.p. 266° . Slow redistillation of these products gave a specimen of m.p. -2.0° , and 10 g of this were crystallized from 40 cc of 99 per cent alcohol at -50° , the crystals being collected on a cooled, sintered glass funnel.¹⁷ After the solvent had been removed at 100° *in vacuo* the hydrocarbon froze and also melted at -1.6° . Recrystallization from 60 cc of alcohol at -60° gave 5.5 g of well-formed crystals melting at -1.6° ; the liquid had n_D^{20} 1.6164, n_D^{25} 1.6140 and b.p. 265° /760 mm (Darzens¹² gives m.p. -3.5° ; von Auwers¹⁸ gives n_D^{20} 1.616).

The addition compounds were made and all were crystallized from ethyl alcohol. The orange picrate melted at 130° (literature,^{12, 14, 15, 19} 128 to 131°); the yellow-orange styphnate melted at 143.5° (Kloetzel¹⁴ gives 142 to 143°) (Found: N, 10.8 per cent. Calc: for $C_{12}H_{12} \cdot C_6H_3O_8N_3$, N, 10.5 per cent); the yellow 1:3:5-trinitrobenzene complex melted at 147 to 148° (literature,^{14, 19} 147 to 148°) (Found: N, 11.5 per cent. Calc: for $C_{12}H_{12} \cdot C_6H_3O_6N_3$, N, 11.4 per cent).

1:3-DIMETHYLNAPHTHALENE.

The synthesis of this hydrocarbon from *m*-xylene by the succinic anhydride- α -tetralone route⁴ is straightforward:—



β -2:4-Dimethylbenzoylpropionic Acid.

A specimen of pure *m*-xylene (b.p. 139.3° /760 mm, n_D^{20} 1.4970) was kindly supplied by Mr F. R. Buck, of Trinidad Leaseholds Ltd.

m-Xylene (47 g, 0.44 mol) was dissolved in 150 cc of carbon disulphide, 40 g (0.4 mol) of succinic anhydride were added and then 120 g (0.90 mol)

of aluminium chloride in small portions. The mixture stood at room temperature for 48 hours with occasional shaking. It was then poured into ice water and well stirred. The carbon disulphide layer was separated, and then extracted several times with sodium hydroxide solution; the alkaline extracts were acidified and then extracted with ether. From the ethereal solution a white powder was obtained which, crystallized from benzene, gave 61 g (75 per cent yield) of acid, m.p. 111 to 112° and on recrystallization from light petroleum gave 43 g of acid, m.p. 111.5 to 112.5°. Barnett and Sanders⁴ give 114° (but Krollpfeiffer and Schäfer²⁰ give 111 to 112°) as the m.p. of β -2:4-dimethylbenzoylpropionic acid. The melting points recorded by Barnett and Sanders⁴ throughout their paper appear to be 2° high.

γ -m-Xylylbutyric Acid.

Reduction of the keto-acid (20 g) by the Clemmensen method gave a product of m.p. 73 to 76°. Recrystallized from 50 per cent acetic acid this yielded colourless prisms (15 g), m.p. 76.5 to 77°, unchanged by further crystallization. (Barnett and Sanders⁴ give m.p. 79°, Krollpfeiffer and Schäfer²⁰ give m.p. 71°.)

5 : 7-Dimethyl- α -tetralone.

This was obtained in 60 per cent yield by heating the butyric acid (3 g) with conc sulphuric acid (15 cc) 1.5 hours on the water-bath. The product, b.p. 140°/0.4 mm, set to a mass of large crystals, m.p. 47.5 to 49°. Barnett and Sanders (who use 85 per cent sulphuric acid) claim only a 30 per cent yield and give m.p. 50°.

5 : 7-Dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene.

2.5 Grams of the tetralone on reduction (Clemmensen) and distillation gave 2.0 g of b.p. 132°/11 mm (75 per cent yield). The specimen, redistilled (b.p. 252°/742 mm), had n_D^{20} 1.539 (Found : C, 90.1; H, 10.1 per cent. $C_{12}H_{16}$ requires C, 90.0; H, 10.0 per cent).

1 : 3-Dimethylnaphthalene.

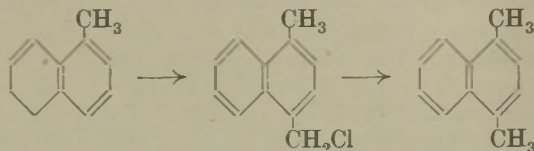
4.1 Grams of the tetrahydronaphthalene heated with selenium (9 g) at 340° for 41 hours gave a product (3.5 g) of b.p. 126°/13 mm, and n_D^{20} 1.5607. The low value of the refractive index showed that dehydrogenation had been incomplete. Accordingly, the 3.5 g were heated (in a wide tube surrounded by a paraffin bath) with 0.93 g of sulphur (two-thirds of the amount needed for 3.5 g of the pure tetralin). Evolution of hydrogen sulphide began at 200° and was rapid at 215°. The tube was kept at 210° for 3 hours, when the evolution of gas had ceased, and no more gas was evolved at 230°. The product was isolated with the aid of benzene, the benzene extract washed well with sodium hydroxide solution, with water, and then dried. It yielded 3.2 g of crude dimethylnaphthalene, b.p. 120 to 135°/12 mm, n_D^{20} 1.5954, which were converted into the picrate (4.0 g of orange-red needles, from alcohol), m.p. 116 to 116.5°. Recrystallized from alcohol the specimen still melted at 116 to 116.5° (Barnett and Sanders⁴ give m.p. 118°; Klotzel¹⁴ gives 117 to 118°). Regeneration of the hydrocarbon by adding the picrate gradually to a warm mixture of benzene and

sodium hydroxide solution gave 1:3-dimethylnaphthalene of b.p. 262 to 264° (corr.) and n_D^{20} 1.6078. It solidified readily and then melted at -6 to -5°. The styphnate crystallized from alcohol in yellow-orange needles melting at 116 to 117°, and the 1:3:5-trinitrobenzene complex formed yellow needles (from alcohol) of m.p. 135° (Found: N, 11.4 per cent. $C_{12}H_{12} \cdot C_6H_3O_6N_3$ requires N, 11.4 per cent.).

Kloetzel¹⁴ gives 116 to 118° as the m.p. of the styphnate, but Bogert²¹ records m.p. 132 to 133°.

1:4-DIMETHYLNAPHTHALENE.

There have been many syntheses of this hydrocarbon.^{4, 6, 12, 14, 22-25, 28} As we possessed a specimen of pure 1-methylnaphthalene we chose the chloromethylation process used by Darzens and Lévy.¹²



4-Chloromethyl-1-methylnaphthalene.

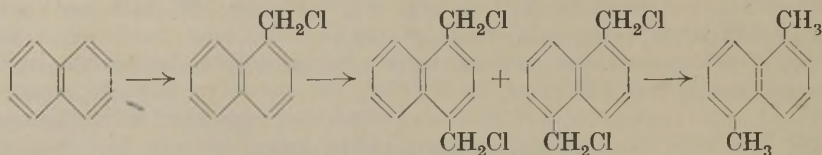
16 Grams (0.11 mol) of pure 1-methylnaphthalene (m.p. -30.7°, n_D^{20} 1.6168), 6.5 g of paraformaldehyde, 15 cc of acetic acid, 21 cc of hydrochloric acid, and 9.5 cc of syrupy phosphoric acid were heated and stirred for 2 hours on a water-bath (compare Grummitt and Buck¹³). The product was poured into 100 cc of water and this mixture was extracted with 100 cc of ether. From the ethereal extract after washing with potassium carbonate solution and drying over solid potassium carbonate there were obtained 13 g of semi-solid material of b.p. 125 to 145°/1.5 mm. Crystallization from ethyl alcohol gave 8 g of m.p. 59 to 60°, and recrystallization from alcohol yielded 3 g of m.p. 61 to 62°; a further 2 g of m.p. 60 to 61° were obtained by cooling the mother liquor to 0°. Darzens and Lévy¹² give b.p. 124 to 125°/2 mm and m.p. 62°; Vavon, Bolle, and Calin²⁷ give m.p. 57°.

Reduction.

A mixture of 3 g (0.016 mol) of 1-methyl-4-chloromethylnaphthalene (m.p. 61 to 62°) and 1 g of palladium-strontium carbonate catalyst in alcohol (50 cc) was added to a solution of sodium ethoxide (0.5 g of sodium and 20 cc of ethyl alcohol) in a low-pressure hydrogenator and shaken with hydrogen (4 atm). After half an hour the liquid was filtered from the catalyst and most of the alcohol distilled off. Water and ether were added, the ethereal extract washed with water, and then dried with calcium chloride. Distillation yielded 2.0 g of b.p. 140°/16 mm, 263°/760 mm, m.p. 5.5 to 6.0°, n_D^{20} 1.6127 (Robinson and Thompson²⁸ give m.p. 5.5 to 6.5°). The picrate formed orange-red needles, m.p. 143°; the styphnate, yellow-orange, was easily soluble in ethyl alcohol and melted at 126-127° to a red liquid and a yellow solid; the 1:3:5-trinitrobenzene complex, yellow needles, sparingly soluble in alcohol, melted at 165-166° (Found: N, 11.7 per cent. Calc for $C_{12}H_{12} \cdot C_6H_3O_6N_3$ N, 11.4 per cent.).

1 : 5-DIMETHYLNAPHTHALENE.

Several syntheses of 1 : 5-dimethylnaphthalene have been reported,^{5, 29, 32, 33} but the most direct is that of Anderson and Short²⁹ :—

*1-Chloromethylnaphthalene.*

256 Grams (2 mol) of naphthalene, 110 g of paraformaldehyde (3.7 mol of formaldehyde), 260 cc of glacial acetic acid, 362 cc of conc hydrochloric acid, and 165 cc of 85 per cent phosphoric acid were heated and stirred at 85° for 6 hours in a 3-litre, 3-necked flask fitted with a mercury-sealed stirrer and a reflux. The mixture yielded 182 g of 1-chloromethylnaphthalene, b.p. 130 to 180°/4 mm (mainly 130 to 135°), and m.p. 30°. A small higher fraction (b.p. 180 to 200°/4 mm) of *bis*-chloromethylnaphthalenes crystallized from acetic acid and melted at 138°.

1 : 5-Bis-chloromethylnaphthalene.

(a) 88 Grams (0.5 mol) of 1-chloromethylnaphthalene, 30 g of paraformaldehyde (1 mol of formaldehyde), 65 cc of glacial acetic acid, 90 cc of conc hydrochloric acid and 42 cc of 85 per cent phosphoric acid were heated and stirred at 100° for 8 hours. The solid which was deposited on cooling was filtered off, washed with water, and recrystallized from ethyl alcohol : 60 g of m.p. 95 to 102° were obtained. Recrystallization from acetic acid gave 22 g (20 per cent overall yield) of colourless crystals, m.p. 128°. Crystallization from alcohol gave a product of m.p. 130°, unchanged by recrystallization from ligroin or from ethyl acetate. Anderson and Short²⁹ obtained a product of m.p. 130 to 145° (Found : Cl, 30.8 per cent. C₁₂H₁₀Cl₂ required Cl, 30.6 per cent) and oxidation with potassium ferricyanide yielded naphthalene 1 : 5-dicarboxylic acid. Manske and Ledingham³¹ crystallized their *bis*-dichloromethylnaphthalene from benzene and obtained a specimen of m.p. 144°.

(b) By *di-chloromethylation of naphthalene*. As 1-chloromethylnaphthalene has unpleasant vesicant and lachrymatory properties we decided to avoid its isolation. 128 Grams (1 mol) of naphthalene, 110 g of paraform (3.7 mol of formaldehyde), 260 cc of glacial acetic acid, 362 cc of conc hydrochloric acid, and 165 cc of 85 per cent phosphoric acid were heated to 100° for 8 hours with stirring and left to stand overnight : 165 g of solid separated. On crystallization from acetic acid and then from ethyl alcohol this gave 80 g of crystals, m.p. 110 to 120°; recrystallized from acetic acid, these gave 30 g (13 per cent yield) of m.p. 132°. A second preparation yielded 200 g of crude product and 55 g (24 per cent yield) of crystals, m.p. 128°.

1 : 5-Dimethylnaphthalene.

A solution of 8.4 g (0.0375 mol) of *bis*-chloromethylnaphthalene, m.p. 130°, in 10 cc of dioxane was poured into 100 cc of ethyl alcohol in the

hydrogenator. Some of the chloro-compound crystallized. A solution of sodium ethoxide (1.9 g of sodium, 0.083 g atom, and 40 cc of alcohol) was added and then 4 g of palladium-strontium carbonate. With hydrogen at 4 atm pressure the chloro-compound was reduced in a few minutes. The liquid product, free from halogen, boiled at $164^{\circ}/40$ mm (yield 5.0 g, 88 per cent).

43 Grams of hydrocarbon mixture, obtained as described above, on crystallization from ethyl alcohol gave 6.5 g of m.p. 72 to 73° ; recrystallized from alcohol this gave 4.7 g of plates, m.p. 81° , b.p. 265° . Finally, a specimen of m.p. 81.5° was obtained. Anderson and Short²⁹ give m.p. 80.5° , Butz^{32,33} gives m.p. 80° , Kruber and Marx,³⁰ 82° . The picrate crystallized from alcohol in orange-red needles, m.p. 138 to 139° ; the *styphnate* formed yellow-orange prisms of m.p. 159° (Found: N, 10.2 per cent $C_{12}H_{12} \cdot C_6H_3O_6N_3$ requires N, 10.5 per cent) and the 1:3:5-trinitrobenzene complex, yellow needles, melted at 158° (Found: N, 11.6 per cent. $C_{12}H_{12} \cdot C_6H_3O_6N_3$ requires N, 11.4 per cent).

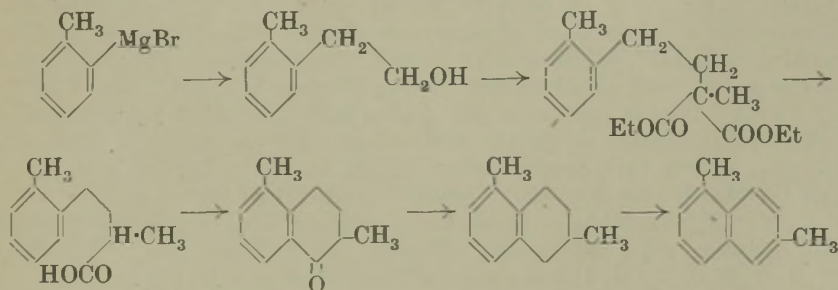
Isolation of 1:4-Dimethylnaphthalene.

When the mother-liquors from the crystallization of 1:5-dimethylnaphthalene were combined and cooled to -20° , crystals of m.p. -5 to $+20^{\circ}$ were obtained; at -60° a second crop of m.p. -2 to $+9^{\circ}$ followed, and at -75° a third crop, 2 g of m.p. $+2$ to $+3^{\circ}$ (picrate, m.p. 142 to 143°).

The first and second crops of hydrocarbon were mixed and converted into the picrate (m.p. 142 to 143°). Recrystallization gave orange-red needles of m.p. 142.5 to 143° . On decomposition with sodium hydroxide this picrate yielded 1:4-dimethylnaphthalene of m.p. $+5^{\circ}$.

1:6-DIMETHYLNAPHTHALENE.

Although this hydrocarbon has been isolated from coal-tar,³⁴ from petroleum,³⁵ from the sulphur dehydrogenation of ionone,^{36,37} and from the pyrolysis of vitamin-A,³⁸ there is recorded in the literature only one unambiguous synthesis, that of Kipping and Wild³⁹:-



Ethyl Methylmalonate.

The procedure of Lucas and Young⁴⁰ in which methyl bromide was allowed to react on ethyl sodiomalonate in alcoholic solution gave a product of b.p. 90 to $100^{\circ}/22$ mm. In order to remove unchanged ethyl malonate the ester was shaken for one minute with a cold, 25 per cent solution of

sodium hydroxide, washed with dilute sulphuric acid, with water, and dried. A fraction of b.p. 83 to 88°/16 mm was collected.

Methyl-β-o-tolylethylmalonic Acid.

The diethyl ester was obtained by the action of ethyl sodiomethylmalonate on *o*-tolylethyl bromide in alcoholic solution, but the yield was only 26 per cent (Kipping and Wild³⁹ give 33 per cent). When the methylmalonic ester and the bromide were added slowly in turn to a suspension of powdered sodium in toluene followed by heating to 100° the yield was raised to 50 per cent. Hydrolysis of the ester and crystallization of the product from benzene gave a 75 per cent yield of the malonic acid, m.p. 136.5°.

1 : 6-Dimethyltetralin.

γ -*o*-Tolyl- α -methylbutyric acid was obtained in yields of 61 to 85 per cent by heating the malonic acid under reduced pressure. It distilled at 160 to 165°/0.5 mm and melted at 25° (Equivalent, found by titration, 195; calc 192). Heating on the water-bath at 75 to 80° for half an hour with four times its weight of conc sulphuric acid cyclized the acid to the tetralone (2 : 5-dimethyltetral-1-one), b.p. 136 to 140°/3 mm and m.p. 42 to 44°. After crystallization from light petroleum, the substance melted at 45 to 46° (Kipping and Wild,³⁹ 47°).

Reduction, (a) by the Wolff-Kishner method. The tetralone only slowly formed a semicarbazone (m.p. 218 to 220°). 2.6 Grams of this, heated with sodium ethoxide solution (from 0.6 g of sodium and 9 cc of alcohol) for 24 hours at 195° gave 1.9 g (80 per cent yield) of 1 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, of b.p. 121–122°/19 mm and n_D^{20} 1.531; *(b)* the Clemmensen method was more convenient, giving over 70 per cent yields of the tetralin and little gummy material.

1 : 6-Dimethylnaphthalene.

Dehydrogenation with selenium at 340° for 40 hours gave products of n_D^{20} 1.56 to 1.57 (indicating incomplete dehydrogenation), and isolation of the naphthalene was accomplished through the picrate: 2.8 g of the tetralin gave 2.3 g of mixture having n_D^{20} 1.566. Conversion to the picrate and crystallization of this from alcohol gave 2.25 g of orange needles, m.p. 111°, unchanged by further crystallization. Decomposition of the picrate with alkali yielded the naphthalene b.p. 264°, m.p. –16°, n_D^{20} 1.6072. Impure specimens gave *higher* melting (112° or 113°) picrates.

The yellow-orange styphnate prepared in ethyl or isopropyl alcoholic solution melted with decomposition at 121 to 122°. Heilbron, Morton, and Webster³⁸ give m.p. 120°. Seidel⁴¹ gives 121 to 122°.

1 : 3 : 5-Trinitrobenzene in alcoholic solution gave yellow needles of the complex, m.p. 130 to 131° (Found: N, 11.1 per cent. Calc for $C_{12}H_{12} \cdot C_6H_3O_6N_3$, N, 11.4 per cent). Seidel⁴¹ gives m.p. 131 to 132°.

A sample of commercial (German) 1 : 6-dimethylnaphthalene, from coal-tar, distilled at 135 to 136°/20 mm. It yielded an orange-coloured picrate of m.p. 108 to 112°. After crystallization from alcohol the picrate melted at 111.5 to 112.5°; on decomposition with alkali it yielded a liquid of b.p. 262 to 264° and n_D^{20} 1.6066, but the m.p. was indefinite. The substance softened at –36° and finally melted at –27.5°.

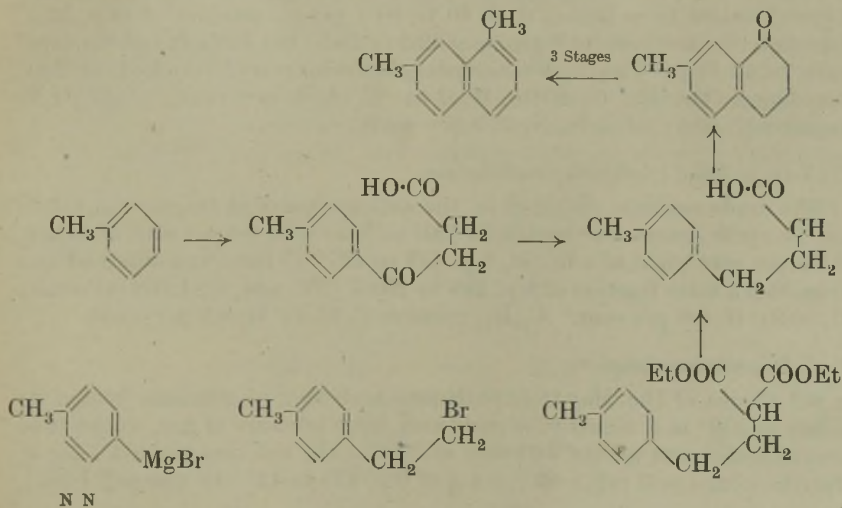
1 : 7-DIMETHYLNAPHTHALENE.

This hydrocarbon has had rather a chequered career. First, Zelinsky² considered that two hydrocarbons ($C_{12}H_{22}$) which he obtained by the action of zinc, hydrogen iodide, and acetic acid on 3 : 3'-dimethylcyclopentan-2-ol were respectively 1 : 7- and 2 : 7-dimethyldecalin. On dehydrogenation they yielded (a) a dimethylnaphthalene of m.p. 107° and picrate m.p. 143° (thought by Zelinsky to be 1 : 7-dimethylnaphthalene) and (b) a solid of m.p. 91°, picrate m.p. 130°, which was most likely 2 : 7-dimethylnaphthalene. In these experiments the dicyclopentyl structure becomes a decahydronaphthalene and, after examination of the rearrangement in models, we consider that the simplest process is the one in which the bond joining the two cyclopentyl rings becomes the central bond of the decalin. (Other processes lead to the formation of fused 5- and 7-membered rings.) The two decalins thus formed would be 2 : 7- and 2 : 6-dimethyldecalin; hydrogenation would yield 2 : 7-dimethylnaphthalene of m.p. 96-97° (picrate m.p. 136°), and 2 : 6-dimethylnaphthalene, m.p. 110° (picrate, m.p. 142°). Zelinsky's product of m.p. 107° (picrate, m.p. 143°) thus appears to be impure 2 : 6- and not the (liquid) 1 : 7-dimethylnaphthalene.

Next, Darzens and Heinz⁴² from a rather involved synthesis produced a liquid 1 : 7-dimethylnaphthalene (picrate, m.p. 123 to 124°) and Veseleý and Medvedeva³ followed with a synthesis from β -methylnaphthalene via 2 : 4-dinitro-7-methyl-1-chloronaphthalene and 2 : 4-dinitro-7-methyl-1-naphthylacetic acid : this led to a *solid*, m.p. 84 to 85° (picrate, m.p. 114 to 117°).

A satisfactory synthesis from toluene by the succinic anhydride method was carried out in 1933 by Barnett and Sanders :⁴ the product was a liquid (picrate, m.p. 120°). Kruber and Schade⁴³ isolated from coal-tar by fractional sulphonation a liquid dimethylnaphthalene, the picrate of which melted at 121°; on oxidation with alkaline ferricyanide it yielded naphthalene-1 : 7-dicarboxylic acid.

Our synthesis followed the lines of that of Barnett and Sanders:—



but we also made γ -*p*-tolylbutyric acid from *p*-bromotoluene via *p*-tolylethyl bromide.

γ -*p*-Tolylbutyric Acid.

(a) The action of ethylene oxide on *p*-tolylmagnesium bromide in ether solution gave a 51 per cent yield of β -*p*-tolylethyl alcohol, b.p. 124 to 130°/18 mm, n_D^{20} 1.528 (literature,^{44, 45} b.p. 115°/15 mm).

A solid residue left in the distilling flask crystallized from alcohol and melted at 121° (Found: C, 92.5; H, 7.4; mol. wt. 170. Calc for $C_{14}H_{14}$: C, 92.3; H, 7.7; mol. wt. 182). It was apparently 4:4'-dimethyldiphenyl. Bennett and Turner⁴⁶ and Gomberg⁴⁷ give m.p. 121°.

The tolylethyl alcohol was converted to the bromide,⁴⁴ which was condensed with ethyl sodiomalonate in benzene. In two experiments yields of 22 and 30 per cent respectively of ethyl β -*p*-tolylethylmalonate, b.p. 180 to 200°/9 mm, were obtained. Hydrolysis with alcoholic potash yielded the malonic acid, m.p. 135 to 136°, which when heated under reduced pressure at 140 to 160° lost carbon dioxide smoothly and gave a product of m.p. 57 to 58.5° (80 per cent yield) and 59 to 59.5° after crystallization from ligroin (b.p. 40 to 60°). Barnett and Sanders⁴ give 59° as the m.p. of γ -*p*-tolylbutyric acid; Martin⁴⁸ gives 61 to 62°. As the overall yield of the acid by this route was poor we then used the procedure of Barnett and Sanders⁴ and of Somerville and Allen.⁴⁹

(b) The β -*p*-toluypropionic acid was obtained in 90 per cent yield as a solid of m.p. 125 to 126°. Recrystallization gave a specimen of m.p. 127.5°. Limpricht⁵⁰ gave m.p. 127°; Barnett and Sanders⁴ gave 129°.

Reduction of this keto-acid by the Clemmensen method gave an 88 per cent yield of γ -*p*-tolylbutyric acid, m.p. 59° (60° after crystallization from benzene. Found: equivalent, 180, 179. Calc for $C_{11}H_{14}O_2$, equiv., 178).

7-Methyl-1-keto-1:2:3:4-tetrahydronaphthalene.

Cyclization of the butyric acid with 80 per cent of sulphuric acid⁴ gave a 90 per cent yield of crude ketone, b.p. 140 to 145°/16 mm, m.p. 31 to 32°. Crystallization from ligroin (b.p. 40 to 60°) gave a product of m.p. 33.5° (Krollpfeiffer and Schäfer²⁰ give m.p. 32.5 to 33.5°, but Barnett and Sanders⁴ give m.p. 35°). The 2:4-dinitrophenylhydrazone (red.) melted at 290° (decomp.) (Found: C, 60.0; H, 4.9; N, 16.3 per cent. $C_{17}H_{16}O_4N_4$ requires C, 60.0; H, 4.7; N, 16.5 per cent).

1:7-Dimethyl-3:4-dihydronaphthalene.

The crude carbinol obtained by the action of methyl magnesium iodide on the cyclic ketone was heated for half an hour with 0.5 per cent of iodine. A 70 per cent yield of a liquid, b.p. 117 to 127°/17 mm, was obtained and from this a main fraction of b.p. 248 to 250.5°/760 mm, n_D^{20} 1.5680 (Found: C, 90.8; H, 8.8 per cent. $C_{12}H_{14}$ requires C, 91.1; H, 8.9 per cent).

1:7-Dimethylnaphthalene.

8.2 Grams of the dihydronaphthalene and 10 g of selenium heated 24 hours at 310° in a sealed tube gave very little pressure of gas, so the tube was re-sealed and heated 44 hours at 330°. The reaction yielded 1.2 g of dihydro-compound (n_D^{20} 1.560), 5.1 g of b.p. 128 to 131°/18 mm (n_D^{20} 1.592),

and a fluorescent residue. The main fraction yielded a picrate of m.p. 118 to 120°. 6.3 Grams of this orange picrate, crystallized from alcohol, yielded 3.8 g of fine needles, m.p. 118 to 119°. Regeneration of the hydrocarbon with sodium hydroxide solution gave 1:7-dimethylnaphthalene, b.p. 262–263.5°, n_D^{20} 1.6068 and m.p. –15° to –14°.

Catalytic Dehydrogenation.

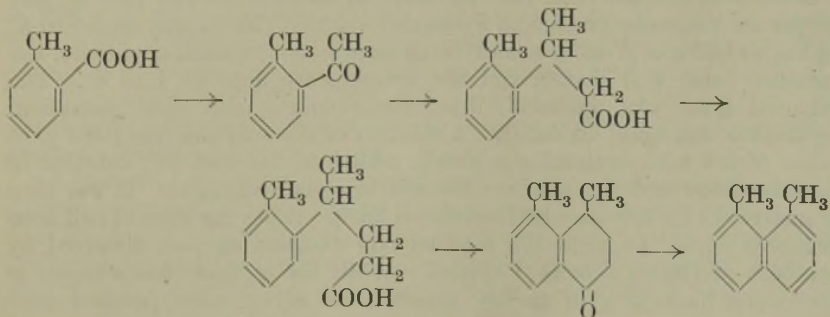
11.4 Grams of the dihydro-compound (n_D^{20} 1.569) and 0.9 g of palladium-charcoal dehydrogenation catalyst were placed in a 30 cc Claisen flask and the mixture gently boiled. Evolution of hydrogen was rapid at first, but was slow after an hour. A stream of carbon dioxide was bubbled through the boiling liquid for another hour, at the end of which a test showed that evolution of hydrogen had ceased and the boiling point had risen from 245° to 260°. The liquid was now distilled from the charcoal (finally heating *in vacuo*) and 9.7 g of crude dimethylnaphthalene were obtained. On fractional distillation this gave 2 g of b.p. 123 to 125°/11 mm, n_D^{20} 1.5920 (picrate, m.p. 118°) and 6 g of b.p. 125°/11 mm, n_D^{20} 1.6039 (picrate, yellow-orange needles, m.p. 118.5 to 118.8°). The residue in the distilling flask appeared to contain some higher-boiling by-product and it yielded a picrate of m.p. 119°.

From 10.1 g of the picrate, m.p. 118.5°, 3.4 g of 1:7-dimethylnaphthalene were recovered: the liquid had b.p. 261°/760 mm and n_D^{20} 1.6067. Refluxed with sodium and redistilled it had n_D^{20} 1.6072 and it froze readily, melting at –28.5°; but if the crystals were kept several hours at –40° they changed to a finer form, melting at –14°.

The *styphnate* crystallized as a fine yellow powder from alcohol and melted at 143° (Found: N, 10.5 per cent. $C_{12}H_{12} \cdot C_6H_3O_6N_3$ requires N, 10.5 per cent). The 1:3:5-trinitrobenzene complex crystallized in yellow needles, m.p. 137° (Found: N, 11.4 per cent. $C_{12}H_{12} \cdot C_6H_3O_6N_3$ requires N, 11.4 per cent).

1:8-DIMETHYLNAPHTHALENE.

Veseleý and Sturza⁵ made 1:8-dimethylnaphthalene by a synthesis which entailed difficult separations of isomerides and they described the final product as a liquid giving a picrate of m.p. 143°. Linstead and co-workers,⁶ by a synthesis which went through eleven clear-cut stages obtained a solid of m.p. 63° and yielding a picrate of m.p. 148°. We



modified the Linstead route considerably and obtained an obviously pure hydrocarbon of m.p. 63 to 63.5°. The picrate was obtained in two forms, orange and orange-red; both melted at 156° with no softening at 148°.

o-Methylacetophenone.

35 Grams (1 mol) of *o*-toluic acid (m.p. 101 to 103°) were dissolved in hot glacial acetic acid (75 g, 5 mol) and the warm solution allowed to drop at 1 drop/3 seconds into a tube containing thoria on pumice kept at 450°. A slow stream of carbon dioxide was passed through the apparatus.⁵¹ The condensate yielded 23 g (66 per cent yield) of ketone, b.p. 94 to 97°/16 mm, n_D^{20} 1.533 (Literature⁵² b.p. 93 to 95°/15 mm). 5 Grams of *o*-toluic acid were recovered.

β -*o*-Tolylbutyric Acid.

The Reformatsky reaction with ethyl bromoacetate converted the ketone into the β -hydroxy-ester which on distillation with iodine or with formic acid gave β -*o*-tolylcrotonic ester, b.p. 141 to 145°/17 mm, n_D^{20} 1.517 (yield 55 per cent) (Found : C, 76.5; H, 8.0 per cent. Calc for $C_{13}H_{16}O_2$, C, 76.5; H, 7.8 per cent).

Reduction of the crotonic ester (30 g) in dry ether (40 cc) with hydrogen and Raney nickel (4 g) at 50° and 50 atm pressure for 4 hours gave 27 g (90 per cent yield) of the *butyrate*, b.p. 136 to 138°/15 mm, n_D^{20} 1.4956 (Found : C, 75.7; H, 9.0 per cent. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.7 per cent).

Hydrolysis with alcoholic potash of 26 g of the ester gave 20 g (88 per cent yield) of the *acid*, b.p. 128 to 134°/0.2 mm, and m.p. 46 to 48°. After crystallization from ligroin (b.p. 40 to 60°) the substance melted at 48 to 49° (Found : C, 74.3; H, 8.1 per cent; equivalent by titration, 180. $C_{11}H_{14}O_2$ requires C, 74.2; H, 7.8 per cent; equiv. 178). The *amide* of this acid, crystallized from ligroin (b.p. 60 to 80°), melted at 109 to 110° (Found : C, 74.3; H, 8.6; N, 7.9 per cent. $C_{11}H_{15}ON$ requires C, 74.6; H, 8.5; N, 7.9 per cent); the *p*-phenylphenacyl ester had m.p. 70 to 72° (metastable form), and 128 to 129° (Found : C, 80.2; H, 6.4 per cent. $C_{25}H_{24}O_3$ requires C, 80.6; H, 6.4 per cent).

γ -*o*-Tolylvaleric Acid.—(Arndt-Eistert Synthesis.)

10 Grams of the acid and 10 cc of purified thionyl chloride yielded 10.5 g of the acid chloride (b.p. 121°/10 mm). A mixture of ether (250 cc) and 40 per cent aqueous potassium hydroxide solution (75 cc) was cooled to 5° in ice, and 25 g of *N*-nitrosomethylurea were added in small quantities, the mixture being well shaken and the temperature kept at 1 to 6°. The ethereal layer was decanted, dried for 4 hours with solid potassium hydroxide and again decanted. A solution of the acid chloride (10.5 g) in ether (dried with sodium) was slowly added to the cold (5°) solution of diazomethane and the mixture allowed to stand overnight. It was then transferred to a 500-cc, round-bottomed flask. After the solvent had been removed at 30° *in vacuo* the residual oily diazoketone was dissolved by addition of 120 cc of methyl alcohol. While the solution was warmed in the water-bath, 3 g of freshly precipitated silver oxide (washed with

methyl alcohol) was added in small portions. At one point the evolution of nitrogen became very vigorous; the mixture was heated for 4 hours. After the mixture had been filtered the ester, still in the methyl alcohol, was hydrolysed by refluxing for 8 hours with addition of 20 g of potassium hydroxide and 15 cc of water. The alcohol was removed, water added, and the aqueous solution, while alkaline, was extracted with ether; it was then acidified and the acid isolated with the aid of ether. 7.5 Grams of a viscous oil, b.p. 175°/9 mm (135°/0.1 mm), were obtained. The overall yield from the butyric acid to the valeric acid was 70 per cent, and, in a second experiment, 73 per cent. As the acid was a liquid full purification was deferred to the next crystalline stage.

4 : 5-Dimethyl-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene.

Cyclization to the tetralone was carried out (a) by heating in the water-bath for 1½ hours with 85 per cent sulphuric acid, which gave a 50 per cent yield of ketone, b.p. 140 to 150°/16 mm and m.p. 54 to 57°; (b) by the Friedel-Crafts method.⁶ To 9.5 g of powdered aluminium chloride in 20 cc of carbon disulphide 8.9 g of the acid chloride, b.p. 131 to 133°/10 mm, in 15 cc of carbon disulphide were gradually added with ice-cooling. Hydrogen chloride was evolved, and, at the finish, crystals separated. The mixture was heated to 40° for 10 minutes, then cooled and decomposed by addition of ice. From the carbon disulphide layer 7.2 g of crude ketone were obtained. It distilled at 171 to 173°/21 mm, giving 6.3 g of crystals, m.p. 56 to 58°. A total of 12.6 g of ketone was made and crystallized from ligroid (b.p. 60 to 80°), giving 4.0 g of hard, glistening prisms, m.p. 58°, and a second crop of 5.25 g, m.p. 57.5 to 58°. The 2 : 4-dinitrophenyl-hydrazone crystallized from xylene, melted at 239 to 240° (decomp.) (Found : C, 60.6; H, 5.0; N, 15.4 per cent. $C_{18}H_{18}O_4N_4$ requires C, 61.0; H, 5.1; N, 15.8 per cent).

1 : 8-Dimethylnaphthalene.

The tetralone was reduced to the tetralin by the Wolff-Kishner reaction. 8.75 Grams of tetralone gave a quantitative yield of semicarbazone (crude), m.p. 230°. Crystallized from *n*-propyl alcohol, it melted at 233 to 234° (Found : N, 18.4 per cent. $C_{13}H_{17}ON_3$ requires N, 18.2 per cent). 11.3 Grams of semicarbazone heated for 20 hours at 200° with sodium ethoxide solution (2.5 g of sodium in 30 cc of alcohol) gave 6.9 g (85 per cent yield) of 1 : 8-dimethyl-1 : 2 : 3 : 4-tetralin, b.p. 112 to 120°/10 to 12 mm. Fractional distillation gave a main fraction, b.p. 104 to 105°/9 mm, n_D^{20} 1.5399 (Found : C, 89.7; H, 10.2 per cent. $C_{12}H_{16}$ requires C, 90.0; H, 10.0 per cent. When 4.0 g of the tetralin were heated with 1.6 g of sulphur at 210 to 220° during 3½ hours the evolution of hydrogen sulphide gradually diminished, but the product, b.p. 245 to 265°, still contained much of the tetralin. It was therefore redistilled from sodium to remove sulphur and was dehydrogenated catalytically.

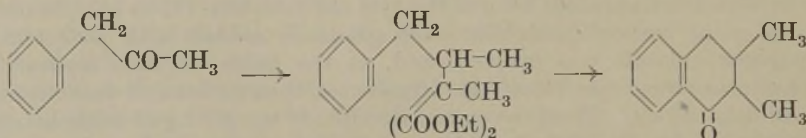
4.8 Grams of the tetralin, refluxed with 0.5 g of palladium-charcoal⁶ evolved hydrogen smoothly during 2 hours, while the b.p. rose to 260°. A slow current of carbon dioxide was passed while the liquid was refluxed 1 hour longer, and the product was then distilled from the reaction flask at 134°/16 mm. It solidified, and weighed 4.3 g. Crystallized from alcohol

the 1 : 8-dimethylnaphthalene melted at 62.5 to 63°, and recrystallized, at 63 to 63.5°. Linstead⁶ gives 63°. The b.p. was 270°/760 mm.

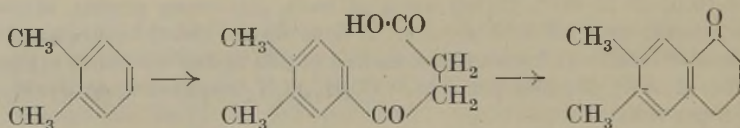
The best specimen gave an orange-red picrate, m.p. 155.5 to 156.5° (from alcohol. Found : N, 11.2. Calc., 10.9 per cent). Linstead states that the picrate is yellow-orange and melts at 148°. Some of the dimethylnaphthalene, m.p. 62.5 to 63°, yielded a yellow-orange picrate, m.p. 155 to 156°, with no change at 148°. The styphnate (yellow-orange) melted at 160° in agreement with Linstead, and the 1 : 3 : 5-trinitrobenzene complex formed yellow needles, m.p. 167° (Found : N, 11.5 per cent. $C_{12}H_{12} \cdot C_6H_3O_6N_3$ requires N, 11.4 per cent).

2 : 3-DIMETHYLNAPHTHALENE.

This hydrocarbon occurs in coal-tar,^{34, 53} and in Rumanian petroleum,⁵⁴ it is formed in the destructive distillation of guaiacum resin.⁵⁵⁻⁵⁷ The first synthesis⁵⁷ was from benzylmethyl ketone via 2 : 3-dimethyl-1 : 2 : 3 : 4-tetralone (twelve stages in all) :—



the second synthesis⁴ was by the succinic anhydride method :—



There is no doubt as to the structure of this hydrocarbon and it is easily obtained in an obviously pure state by crystallization of the commercial product. This is obtainable in large colourless plates, m.p. 101 to 102°, or higher. Systematic crystallization of 25-g batches from ethyl alcohol gave a product of constant melting point, 104° (literature, 103 to 105°) and b.p. 268°/759 mm. The picrate (orange) melted at 123 to 124°; the *styphnate* came out of ethyl alcohol as a yellow curd, but melted sharply at 148.5° (Found : N, 10.5 per cent, $C_{12}H_{12} \cdot C_6H_3O_8N_3$ requires N, 10.4 per cent); the yellow 1 : 3 : 5-trinitrobenzene complex melted at 136 to 137° (Found : N, 11.3 per cent. Calc, N, 11.4 per cent); the *trinitrotoluene* complex melted at 95 to 96° (Found : N, 11.2 per cent. $C_{12}H_{12} \cdot C_7H_5O_6N_3$ requires N, 11.0 per cent), and the α -quinone,⁵⁸ crystallized from methyl alcohol, melted at 126° (Kruber⁵³ gives m.p. 127°).

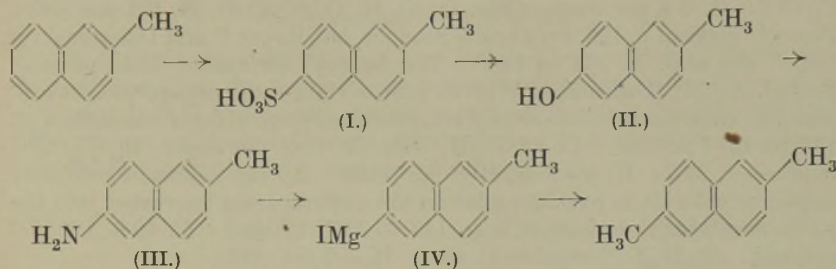
2 : 6-DIMETHYLNAPHTHALENE.

Baeyer and Villiger⁵⁹ first prepared this compound by a difficult route from ionene. It is easily isolated from coal-tar³⁴ as the sulphonic acid and, being the highest-melting of the dimethylnaphthalenes, it is readily purified. Careful fractional distillation of the 250 to 270° fraction of

Rumanium petroleum followed by cooling yielded 2 : 6-dimethylnaphthalene.^{54, 60} As stated on p. 515, the hydrocarbon isolated by Zelinski² from the dehydrogenation products of ring-systems was probably 2 : 6- and not 1 : 7-dimethylnaphthalene.

After the present investigation had been completed a synthesis (surprisingly, the first recorded) of the naphthalene was published by Royer.⁶¹ This author converted 2-methoxy-6-methylnaphthalene into 6-methyltetral-2-one by the method of Cornforth and Robinson⁶² and introduced the second methyl group by means of the Grignard reaction.

In the present investigation the hydrocarbon was synthesized from β -methylnaphthalene :—



Haworth⁶³ has shown that (I) is convertible into the same naphthalene dicarboxylic acid as is obtained from naphthalene-2 : 6-disulphonic acid via the dinitrile. Moreover, the structure of (III) was proved by Dziewoński⁶⁴ who showed that its acetyl derivative oxidized to 2-amino-6-naphthoic acid. The iodide is smoothly obtained from (III), but conversion of the Grignard compound (IV) into the dimethylnaphthalene gave only a moderate yield, as is usual with this reaction. Nevertheless, the product was easily freed from impurities and proved to be identical with the substance isolated from coal-tar.

2 : 6-Dimethylnaphthalene, from Coal-tar.

The commercial product (colourless plates, m.p. 109 to 110°) was repeatedly crystallized from ethyl alcohol (1 g in 35 cc), but the m.p. was constant at 110 to 110.5° after two crystallizations, and the b.p. was 261°. The orange-coloured picrate melted at 141 to 142°; the yellow styphnate at 157 to 158° (Found : N, 10.6 per cent. $C_{12}H_{12} \cdot C_6H_3O_8N_3$ requires N, 10.5 per cent); the yellow 1 : 3 : 5-trinitrobenzene complex at 153.5 to 154.5° (N, 11.5 per cent. Calc, N, 11.4 per cent). Triandaf⁶⁵ gives m.p. 154°.

Synthesis of 2 : 6-Dimethylnaphthalene.

Sodium 6-methylnaphthalene-2-sulphonate.—A well-stirred mixture of β -methylnaphthalene (m.p. 34°, 100 g) and conc sulphuric acid (75 cc) was heated on a boiling water-bath for 6 hours and then poured into water and the solution filtered. The filtrate was made alkaline by addition of a warm solution of sodium hydroxide (100 g) in water (150 cc) and the crude sodium salt was collected. It was crystallized from 1 litre of water with

the aid of 3 g of charcoal, giving 102 g (60 per cent yield) of crystals dried at 110°. The *p*-toluidine salt (long needles from water) melted at 250 to 252° (Fieser⁶⁶ reports m.p. 250 to 251°) and the *S*-benzyl-thiouronium salt⁶⁷ at 222 to 223° (Found: C, 58.7; H, 4.9; N, 7.0; S, 16.4 per cent. $C_{19}H_{20}O_3S_2N_2$ requires C, 58.7; H, 5.2; N, 7.2; S, 16.5 per cent).

6-Methyl-2-Naphthol.

Fusion of the sulphonate (30 g) at 280 to 300° with potassium hydroxide (98 g) and water (1.5 cc) gave 13 g (68 per cent yield) of naphthol, b.p. 295 to 300°, and m.p. 118 to 120°. Recrystallization from aqueous alcohol gave a product of m.p. 121 to 122°, unchanged by recrystallization (Found: C, 83.2; H, 6.4 per cent. Calc. for $C_{11}H_{10}O$, C, 83.6; H, 6.3 per cent). Fieser⁶⁶ gives m.p. 123° for a crude product, but Royer⁶¹ and Dziewoński⁶⁴ record the m.p. as 128 to 129°. The benzoyl derivative, from alcohol, melted at 127° (Dziewoński⁶⁴ gives 128 to 129°); the orange *picrate* prepared in chloroform solution and recrystallized from chloroform melted at 136 to 137° (Found: C, 52.6; H, 3.2; N, 10.8 per cent. $C_{17}H_{13}O_8N_3$ requires C, 52.7; H, 3.4; N, 10.8 per cent). By the action of *p*-toluenesulphonic chloride in pyridine solution the naphthol was converted into the *p*-toluenesulphonyl derivative, m.p. 142 to 143° (Found: C, 69.0; H, 5.3 per cent. $C_{18}H_{16}O_3S$ requires C, 69.2; H, 5.1 per cent).

6-Methyl-2-naphthylamine.

6-Methyl-2-naphthol (20 g) and conc ammonium sulphite solution⁶⁸ (100 cc) heated and stirred in an autoclave for 8 hours at 150 to 160° yielded 18 g (90 per cent) of a pale tan powder, m.p. 123 to 125°. Crystallization from ligroin (b.p. 80 to 100°) gave a product of m.p. 127° (Found: N, 9.0 per cent. Calc for $C_{11}H_{11}N$: N, 8.9 per cent). (Dziewoński⁶⁴ records m.p. 129 to 130°). The acetyl derivative crystallized from aqueous alcohol and then from ligroin (b.p. 100 to 120°), melted at 154 to 156° (Dziewoński⁶⁴ gives m.p. 155 to 156°); the benzoyl derivative, from alcohol, melted at 177 to 179° (Found: C, 82.4; H, 5.6; N, 5.4 per cent. $C_{18}H_{15}ON$ requires C, 82.8; H, 5.7; N, 5.4 per cent). The yellow *picrate*, formed in ethyl alcohol and recrystallized from ethyl alcohol, melted at 194 to 196° (Found: C, 52.8; H, 3.6 per cent. $C_{17}H_{14}O_7N_4$ requires C, 52.8; H, 3.6 per cent). A 1 : 3 : 5-trinitrobenzene complex, formed in alcohol, crystallized in long, dark-red needles, m.p. 165 to 166° (Found: N, 15.2 per cent. $C_{17}H_{14}O_6N_4$ requires N, 15.1 per cent).

2 : 6-Dimethylnaphthalene.

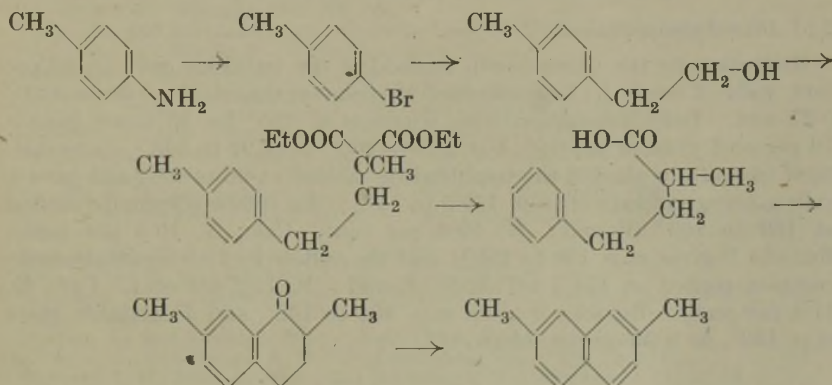
The amine was converted through the diazo-reaction into 6-methyl-2-iodonaphthalene, m.p. 145 to 146° (Found: C, 49.2; H, 3.3; I, 47.6 per cent. $C_{11}H_9I$ requires C, 49.2; H, 3.4; I, 47.4 per cent) and the iodide then made into the Grignard reagent, running the reaction concurrently with the preparation of methylmagnesium iodide.

Magnesium (1.5 g, 2 atm), methyl iodide (3.5 g, 1 mol), 6-methyl-2-iodonaphthalene (7 g, 1 mol), ether (50 cc) and benzene (50 cc) were placed in a 3-necked flask fitted with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser. A crystal of iodine was added and the mixture heated

on a water-bath until the reaction started; heating and stirring were continued for 2 hours after the reaction had subsided. Dimethyl sulphate (21 g, 5.0 mol) in benzene (50 cc) was then added and 60 cc of the liquid (mainly ether) distilled off; the mixture was then refluxed for 24 hours. After the flask had been cooled in ice, 20 cc of water were added and then dilute sulphuric acid. The benzene layer yielded 2.2 g of b.p. 240 to 265° (smelling of β -methylnaphthalene) which solidified. Crystallized twice from alcohol it melted at 109 to 111° and, mixed with 2:6-dimethylnaphthalene, m.p. 110 to 110.5° (from coal-tar) at 109.5 to 110.5°; the picrate melted at 140°.

2:7-DIMETHYLNAPHTHALENE.

Although this hydrocarbon has been isolated from coal-tar,³⁴ from petroleum³⁵ and from the degradation products of several naturally occurring compounds⁶⁹⁻⁷² it does not appear previously to have been synthesized. The present synthesis follows in outline that of 1:6-dimethylnaphthalene, the starting-point being *p*- instead of *o*-toluidine.



Pure *p*-toluidine was converted into *p*-bromotoluene,⁷³ and the bromo-compound (70 g) mixed with methyl iodide (6 g) in 50 cc of dry ether was added slowly to 11 g of magnesium covered with dry ether. The methyl iodide promoted the reaction and kept it going smoothly. After the mixture had been stirred under reflux for 6 hours all the magnesium had dissolved; the solution was cooled with ice-water while ethylene oxide (20 g) was passed in. The resulting *p*-tolylethyl alcohol boiled at 140 to 145°/40 mm (yield 27 g, 47 per cent). Shoesmith and Connor⁴⁴ give b.p. 116 to 118°; the urethane melted at 114° (Speer and Hill⁴⁵ give m.p. 112°).

Methyl- β -p-tolylethylmalonic Acid.

Sodium (2.5 g) was powdered under toluene and ethyl methylmalonate (20 g) was slowly added as in the synthesis of 1:6-dimethylnaphthalene. The reaction was completed by warming on the water-bath and then 26 g of β -*p*-tolylethyl bromide (b.p. 127 to 132°/23 mm; see Shoesmith and

Connor ⁴⁴) were slowly added. The mixture was heated on a boiling water-bath for 2½ hours and then poured into water. Working up with the aid of ether gave 17 g of ester, b.p. 218°/26 mm (39 per cent yield). Hydrolysis with alcoholic potassium hydroxide solution of 48 g of this ester yielded 30.5 g (78 per cent) of solid acid, m.p. 154 to 158°. After crystallization from ligroin and then from toluene the substance melted at 161.5° (Found : C, 65.5; H, 6.8 per cent; equivalent, by titration, 122. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8 per cent; equiv. 118).

2 : 7-Dimethyltetralone.

The malonic acid on heating to 160 to 170° gave an almost theoretical yield of γ -p-tolyl- α -methylbutyric acid, b.p. 150°/0.8 mm and m.p. 50 to 51° (Found : equiv., by titration 192. $C_{12}H_{16}O_2$ requires 192). When this acid was heated with four times its weight of conc sulphuric acid at 90° for half an hour it gave a 70 per cent yield of an oil, b.p. 122°/0.5 mm. This tetralone failed to solidify; it gave a 2 : 4-dinitrophenylhydrazone which, crystallized from toluene, melted at 251° (Found : C, 61.1; H, 5.3; N, 15.6 per cent. $C_{18}H_{16}O_4N_4$ requires C, 61.0; H, 5.1; N, 15.8 per cent).

2 : 7-Dimethylnaphthalene.

Reduction by the Clemmensen method of the tetralone gave an 85 per cent yield of crude 2 : 7-dimethyltetrahydronaphthalene, b.p. 95 to 110°/0.27 mm. Dehydrogenation with selenium at 340° for 40 hours gave a 70 per cent yield of product, b.p. 260 to 266°, m.p. 92 to 94°. Recrystallized twice from alcohol the naphthalene melted at 96 to 97°, and gave a yellow-orange picrate of m.p. 135.5 to 136°; the yellow styphnate melted at 159 to 160° (Found : N, 10.6 per cent. Calc, N, 10.5 per cent). Ruzicka ⁷⁴ gives m.p. 158 to 159°; and the yellow 1 : 3 : 5-trinitrobenzene complex melted at 151.5 to 152.5° (Found : N, 11.2 per cent. Calc, N, 11.4 per cent). Ruzicka ⁷⁴ gives m.p. 151 to 152°, and Triandaf ⁶⁵ gives m.p. 153°, on a Maquenne block.

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SOME NEW EXTREME PRESSURE (E.P.) LUBRICATING OIL ADDITIVES CONTAINING CHLORINE AND SULPHUR.

By W. DAVEY, B.Sc., Ph.D., F.R.I.C.

SUMMARY.

The condensation of chloral with mercaptans, in presence of acid, gives trichloro-thioacetals which show marked E.P. properties when blended in mineral oil. These compounds are active at low concentrations and the good E.P. properties shown are due to the presence of a $\text{Cl}_3\cdot\text{C}$ group. The E.P. properties of the compounds have been assessed by the Four-Ball Machine.

INTRODUCTION.

It has been shown ¹ that the presence of a $\text{Cl}_3\cdot\text{C}$ group in a compound, e.g., chloroform, benzo-trichloride, imparts useful E.P. properties when such a compound is blended in mineral oil, and that whilst such compounds have good E.P. properties by themselves these properties are enhanced by the addition of free sulphur or reactive sulphur compounds.^{2,3} Mercaptans condense smoothly with aldehydes and ketones in presence of a little mineral acid to give thio-acetals or mercaptoles, and by the use of chloral $\text{Cl}_3\cdot\text{C}\cdot\text{CHO}$ and mercaptans reactive chlorine and sulphur are obtained in the form of a single additive. Such compounds, prepared from chloral or chloral hydrate, by condensation with various mercaptans, have been tested in the Four-Ball Machine and found to possess good E.P. properties. The ease of preparation of these compounds and availability of mercaptans from petroleum sources will be of interest.

EXPERIMENTAL.

Preparation of Additives.

In the preliminary experiments anhydrous chloral was used for the condensations, but it was found that the reaction proceeded just as readily when chloral hydrate was used, and the solid hydrate was therefore employed in the subsequent preparations.

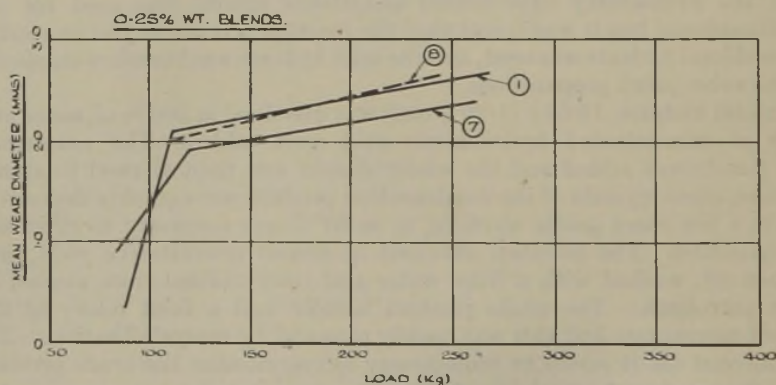
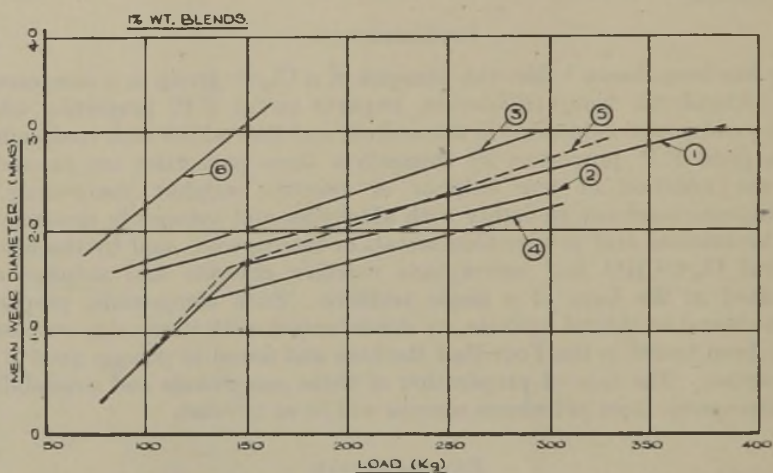
Chloral hydrate, 16.55 g (1/10 g-mol) was dissolved in 200 cc of water and 5 cc of concentrated hydrochloric acid were added. The mercaptan (0.2 g-mol) was added and the whole shaken and then allowed to stand. In most cases crystals of the condensation product were quickly deposited, but in a few cases gentle warming to ca 60° C was necessary to effect the condensation. The product, obtained in almost quantitative yield, was filtered off, washed with a little water and recrystallized from alcohol or light petroleum. The crude product usually had a faint odour of the parent mercaptan, but this was readily removed by recrystallization. For commercial use it would be unnecessary to recrystallize the crude product since it was almost invariably of over 90 per cent purity.

The properties and analyses of the compounds prepared are given in Table I:—

TABLE I.

Ref. No.	Mercaptan used	Appearance of product	Melting point °C	% Sulphur		% Chlorine		Solubility in oil
				Found	Calc	Found	Calc	
1	Ethyl	White needles	61	25.2	25.2	42.0	42.0	Readily
2	n-Butyl	" "	55	20.6	20.7	34.3	34.4	"
3	iso-Butyl	" "	46	20.7	20.7	34.4	34.4	"
4	Phenyl	" "	82	18.4	18.3	30.4	30.5	"
5	Benzyl	" "	80	16.9	16.9	28.0	28.2	"
6	Thioglycollic Acid	Thick syrup	—	20.0	20.2	34.0	34.2	Very spar. sol. <0.2%
7	Thiosalicylic Acid	White needles	165	14.7	14.6	24.2	24.3	" "
8	Mixture A	" "	45	22.1	—	38.4	—	Readily
9	Mixture B	" "	50	20.0	—	34.0	—	"

Note.—Mixture A consisted of a mixture of mercaptans from petroleum of boiling range 20 to 44° C and Mixture B of mercaptans of boiling range 44 to 50° C.



- KEY:-
- | | | | | |
|---|------------|--|---|--|
| ① | COMPOUND 1 | $\text{Cl}_3\text{CCH}(\text{SC}_2\text{H}_5)_2$ | ⑤ | $\text{CH}_3\text{CH}(\text{SC}_2\text{H}_5)_2$ |
| ② | " | 2. $\text{Cl}_3\text{CCH}(\text{S}-n\text{-butyl})_2$ | ⑦ | COMPOUND 8. $\text{Cl}_3\text{CCH}(\text{SR})_2$ |
| ③ | " | 4. $\text{Cl}_2\text{CCH}(\text{SC}_6\text{H}_5)_2$ | ⑧ | " |
| ④ | " | 5. $\text{Cl}_3\text{CCH}(\text{SCH}_2\text{C}_6\text{H}_5)_2$ | ⑨ | $\text{Cl}_3\text{CCH}(\text{SR}_2)_2$ |
| ⑤ | | $\text{Cl}_3\text{CCH}(\text{OC}_2\text{H}_5)_2$ | | |

FIG. 1.
WEAR-LOAD DIAGRAMS.

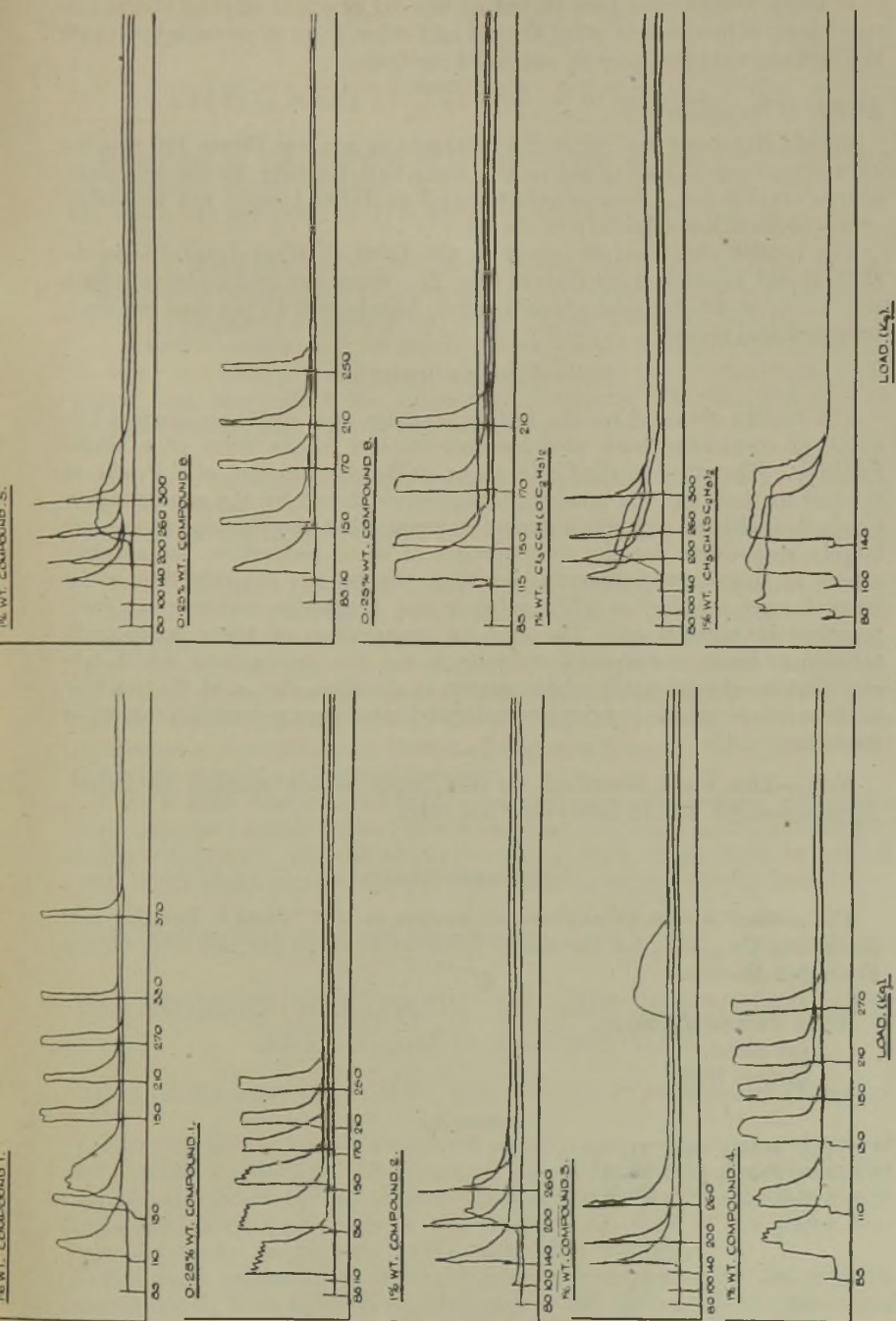


FIG. 2.

Friction-time curves. Scale: 0.5 cm vertical = 0.086 (coefficient of friction), 0.5 cm horizontal = 3.2 sec.

In order to study the part played by the chlorine and sulphur atoms the condensation products of ethyl alcohol and chloral and of acetaldehyde and mercaptans were prepared by standard methods.

Testing of the Additives.

Blends of 1.0 per cent wt of the additives in genuine Penna 150 neutral oil were prepared and tested in the Four-Ball Machine by the standard short-duration test. Compounds 6 and 7 in Table I could not be tested owing to their low solubility in the oil.

The results obtained are given in the form of Wear-Load Diagrams (Fig. 1) and Friction-Time Curves (Fig. 2). Since the first additive tested was active in 1.0 per cent concentration, blends of 0.25 per cent wt were prepared and tested.

DISCUSSION OF RESULTS.

The results obtained on the testing of these new additives suggest the value of combining both chlorine and sulphur in the form of a single additive. The effect of the $\text{Cl}_3\text{C-}$ group in the development of E.P. effects is most marked and the good E.P. properties shown by the condensation product of chloral and ethyl alcohol indicates that the chlorine atoms are largely responsible for the development of these properties, the sulphur atoms in the other compounds enabling the ferrous chloride film to be formed more readily, as when sulphur and a chlorine additive are used together in mineral oil. The ease of preparation of these compounds from petroleum mercaptans suggests a use for mercaptans which are regarded as objectionable when present in gasoline, etc., and the activity of these compounds in low concentration indicates their potential commercial usefulness.

Note.—The work described in this paper is the subject of Patent Application No. 22,173 dated July 25, 1946.

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