Section A

Synthesis of a few polynuclear hydrocarbons.

Theoretical 1 - 13
Experimental 1 - 19
Interest in the chemistry of the polynuclear aromatic hydrocarbons was originally spurred by the discovery of the carcinogenic activity, associated with some of the derivatives of pyrene, particularly 3:4-benzpyrene (Cook & Hewett, J.Chem. Soc., 1933, 398). A series of polynuclear hydrocarbons and their derivatives has been isolated from coal-tar distillation products as well as from selenium dehydrogenation of complex naturally occurring substances, like terpenoids and steroids. The examples of chrysene and 1,2-cyclopentenophenanthrene serve as classical cases in organic chemistry. The isolation of Eudalene and Cadalene and of alkylated phenanthrenes from dehydrogenation of sesqui- and diterpenoids are too well-known. This technique has also proved to be of great assistance in the field of triterpenoids, where dehydrogenation experiments with selenium or palladised charcoal reveals the fundamental carbon-skeleton present in this class of compounds. Thus 1,8-dimethylpicene (I) and 2-hydroxy-1,8-dimethylpicene (II) are some of the products isolated from these studies and have proved the presence of the pentacyclic carbon-framework in a few members of the triterpenoids (Rodd, "Chemistry of Carbon Compounds," II B, p.741).
Apart from these studies, the importance of the polynuclear hydrocarbons also centres round their characteristic absorption properties in the ultra-violet region, aromatic resonance characteristics, amenable to considerable theoretical treatment, the peculiar tendency of forming molecular complexes particularly with polynitro-compounds and in the exhibition of high-order optical activity arising from the out-of-plane distortions of the aromatic rings, a new development in the field of molecular asymmetry (Newman, "Steric effects in Organic Chemistry" p. 471).

In the following pages, the present investigation describes a new synthesis of 3:4-benzpyrene (III), according to a method which has been developed in this laboratory (Saha & Bagchi, J.Org.Chem., 1955, 20, 1392) for the synthesis of pyrene (IV). Some of the intermediate steps in this synthesis have been significantly modified with a considerable improvement of the yield and shortening of the synthetic steps. There also exists a possibility of extension of this method for the synthesis of 3:4-benzpyrene and its alkyl analogues. A review of the various methods available for the synthesis of pyrene derivatives so far published, shows that these proceed mostly with phenanthrene and anthracene and aluminium chloride has been used in most of these synthetic methods. It is well-known that alkyl groups exhibit a tendency for migration or elimination on treatment with aluminium chloride at high temperature (Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry", p. 77-94). In one of the published synthetic
methods for picene derivatives, the loss of the methyl group on prolonged treatment of aluminium chloride has been definitely observed by Drake and his collaborators (J. Amer. Chem. Soc., 1939, 61, 1684). The biological importance of 3:4-benzpyrene arose in connection with the view that the carcinogenic action of polycyclic hydrocarbons is associated with metabolic oxidation at specific molecular centres. As a consequence, a series of publications have appeared during the last few years on the synthesis of 3:4-benzpyrene with methyl groups at different positions in the ring (Campbell, J. Chem. Soc., 1956, 1938; Adelfang & Daub, J. Amer. Chem. Soc., 1958, 80, 1405; Phillips & Chatterjee, J. Amer. Chem. Soc., 1958, 80, 4360; Doyle & Daub, J. Amer. Chem. Soc., 1958, 80, 5252; Comp & Daub, J. Amer. Chem. Soc., 1958, 80, 6049). Some of these methods are quite ingenious and novel with possibilities of wide applicability.
The \( \beta \)-keto-ester (V), (Chatterjee et al., J. Ind. Chem. Soc., 1947, 24, 169), which has been obtained through ring-opening and recyclisation of the condensation product from ethyl cyclohexanone 2-carboxylate and ethyl chloroacetate, is condensed with \( \beta \)-phenylethyl bromide to afford (VI) in an excellent yield. This was hydrolysed with hydrobromic acid-acetic acid mixture and the keto-acid (VII) is obtained. This is also one of the intermediate products of the Saha-Bagchi synthesis (loc. cit.) of pyrene, but they could not isolate it in an analytically pure form. This was cyclised with polyphosphoric acid (Saha & Bagchi, loc. cit.) to (VIII) which on dehydrogenation with palladised charcoal afforded pyrene (IV) in an excellent yield.

To extend this method to the synthesis of 3:4-benzpyrene, the \( \beta \)-keto-ester (V) is condensed with \( \beta \)-naphthyl-ethyl bromide to afford (IX). This was hydrolysed with hydrobromic acid-acetic acid mixture to the keto-acid (X) and this has been cyclised under identical conditions to the hydroxy-compound (XI). This was further characterised by an intense green colouration with ferric chloride solution. This was dehydrogenated to give 3:4-benzpyrene (III)
It may be emphasised that the advantage of this method is that the synthesis does not involve too many steps and the starting materials are easily available. Moreover the use of aluminium chloride has been avoided to minimise the chance of migration of alkyl groups during the synthesis. Because the knowledge of the positions of the methyl groups in 3:4-benzpyrene nucleus is of considerable importance in their physiological studies, this method bids fair to be of much use in the synthesis of polyalkylated 3:4-benzpyrenes.
In recent years introduction of a substituent at the \( \alpha \)-position of a carbonyl function has been rendered quite feasible in the presence of potassium tert-amylate in benzene solution, through the following system (cf. Conia, Bull. Soc. Chim., 1954, 690, 943).

\[
\begin{align*}
0 &= \text{C} - \text{C} = \text{C} - \text{C} < \\
\text{B'} &\quad \rightarrow \quad \text{OC} - \text{C} = \text{C} - \text{C} < \\
\text{RX} &\quad \rightarrow \quad \text{OC} - \text{C} = \text{C} - \text{C} <
\end{align*}
\]

This method has now been extensively employed in the field of steroids (Woodward et al., J. Amer. Chem. Soc., 1956, 78, 6278), and terpenoids (Stork et al., ibid., 1956, 78, 250), specially for the introduction of the gem-dimethyl group (Sondheimer et al., ibid., 1957, 79, 5545; unpublished work from this laboratory).

This method may be looked upon as complementary to the previous one i.e., alkylation of \( \beta \)-keto-esters, but it appears to be more useful in synthetic studies of complicated systems. During these studies, the method has been successfully employed for the synthesis of a series of polynuclear hydrocarbons, like chrysene, picene and two dimethylpicenes. These constitute, as mentioned earlier, some of the dehydrogenation products from a series of natural products. Consequently, this has stimulated a considerable volume of interest in the synthetic studies of the derivatives of picene with a view to locating the position of alkyl residues, particularly methyl, in the pentacyclic ring-systems characteristic of triterpenoids.
The simplest polycyclic system described here and synthesised according to this method is chrysene (XXX). The present synthesis is also capable of extension with a view to incorporating alkyl residues in the chrysene molecule. The complete carbon-skeleton has been built up by piecing together, in one step, the two components and in which wide variations in nature and position of the alkyl substituents are possible. Yield in each of the synthetic steps is quite good and the intermediate steps are well-defined and characterised, as a result of which the final products are easily available in a pure condition.
To build up the molecule of chrysene, the octalone (XII, Du Feu et al., J. Chem. Soc., 1937, 53) was prepared in a better yield through the condensation of \( \beta \)-chloroethyl methyl ketone with ethyl cyclohexanone-2-carboxylate. This condenses readily with \( \beta \)-phenylethyl bromide in presence of potassium tert-amylate in benzene solution to afford the unsaturated ketone (XIII). This underwent cyclisation with polyphosphoric acid leading to the formation of the tetracyclic compound (XIV) or its bond isomer (XV). This on dehydrogenation with palladised charcoal yielded chrysene (XXX) in an excellent yield. It was readily obtained in a pure condition and further identified through its characteristic ultra-violet spectra and the well-known trinitrofluorenone complex. In an identical manner, the synthesis of picene (XVI) has been achieved through the condensation of \( \beta \)-naphthylethyl bromide with octalone (XII) to afford (XVII). This underwent smooth cyclisation with polyphosphoric acid to afford the pentacyclic compound (XVIII) or its bond isomer (XIX). This readily underwent dehydrogenation with palladised charcoal to picene (XVI), characterised further through its ultra-violet absorption studies and the trinitrofluorenone complex.
As has been mentioned earlier, a dimethylpicene (I) and a hydroxy-dimethylpicene (II) have been isolated from the products of dehydrogenation of triterpenoids. It became necessary to synthesise some of the isomeric alkylated picenes so that they can be identified through direct comparison with those isolated from dehydrogenation experiments. This necessity stimulated considerable amount of synthetic studies in this field and particular mention may be made of the following compounds, which have been recently synthesised:


The experiments described below deal with the synthesis of 1,11-dimethylpicene (XX) and 1,8-dimethylpicene (I). For the synthesis of (XX) one of the components is methyloctalone (XXIII,Du Feu et al., loc.cit.). This has been obtained in a better yield through the condensation of morpholino derivative of o-methylcyclohexanone and formaldehyde (Downes et al., J.Amer. Chem.Soc., 1950, 72, 3464). The second component has been obtained through a series of steps which may be schematically represented below:
The Reformatsky product from 7-methyl-tetralin-1-one (Fieser & Dunn, J.Amer.Chem.Soc., 1936, 58, 575; Barnett & Sanders, J.Chem.Soc., 1933, 435) was dehydrated and subsequently dehydrogenated by heating with sulphur to the corresponding naphthalene derivative (XXIV). This was reduced with lithium aluminium hydride to the corresponding alcohol (XXV) in an excellent yield and the latter was readily converted to bromide (XXVI) with phosphorous tribromide. The bromide (XXVI) condensed readily with methyloctalone (XXIII) to afford (XXVII), which readily underwent cyclisation on treatment with polyphosphoric acid to give (XXVIII) or its bond isomer (XXIX), to be subsequently dehydrogenated to 1,11-dimethylpicene (XX) by heating with palladised-charcoal. This was again characterised through its trinitrofluorenone complex and ultraviolet studies.

For the synthesis of 1,8-dimethylpicene (I), the condensation of 5-methyl-Δ^2-octalin-2-one (XXXI) with (XXVI) appeared to be the simplest route. For the synthesis of ketone (XXXI), the keto-ester (XXXII); Inhoffen et al., Chem.Ber., 1954, 87, 684) on catalytic hydrogenation and hydrolysis yielded the saturated keto-acid. The keto-acid was converted to the enol-lactone by boiling with acetic anhydride in presence of sodium acetate and the latter was allowed to react with methylmagnesium iodide. Subsequent alkaline treatment of the resulting product gave a ketonic material in a very poor yield (Woodward et al., J.Amer. Chem.Soc., 1952, 74, 4223). This was characterised by ultraviolet spectra and a red 2:4-dinitrophenylhydrazone. The extremely poor yield of the desired ketone prevented its use in subsequent
The ketone (XXXIII; Schinz et al., Helv. Chim. Acta, 1954, 37, 1230) has been prepared in a good yield in this laboratory (Mukherjee, unpublished work) and was condensed with the bromide (XXVI) in presence of potassium tert-amylate in toluene. The condensation product was obtained in a moderate yield which was directly ring-closed with polyphosphoric acid, and the resulting product (XXXIV) or its bond isomer was obtained as a well-defined crystalline solid. This on dehydrogenation with Pd-charcoal (10%) yielded the 1,8-dimethylpicene (I)
which was characterised by the mixed melting point with an authentic sample (by courtesy of Dr. D. Nasipuri) and the characteristic ultra-violet spectra.
**EXPERIMENTAL**

**Ethyl 6-carbethoxy-cyclohexanone-2-acetate (V).**

To sodium dust (6 g.) under dry benzene (150 c.c.), ethyl cyclohexanone-2-carboxylate (43 g.) was added slowly in the cold and left overnight. Ethyl chloroacetate (31 g.) was then added and the reaction mixture was refluxed for 6 hours. It was cooled and diluted with water and the benzene layer was separated, washed with water and dried. On removal of the solvent under reduced pressure, the product distilled mainly at 145-150° (6 mm.). Yield 45 g. Ethyl 2-carbethoxy-cyclohexanone-2-acetate (27 g.) was mixed with sodium ethoxide, prepared from sodium (0.5 g.) and absolute ethanol (11 c.c.) and the reaction mixture was heated on the waterbath for 2½ hours. The cooled solution was poured into mixture of ether and water containing some hydrochloric acid. The product distilling at 183-185° (8 mm.) was collected. Yield 25 g.

Ethyl hexane-1,2,6-tricarboxylate (19 g.) thus obtained was taken in benzene (50 c.c.) and was heated on the waterbath with sodium dust (3 g.) containing alcohol (1 c.c.) for 4 hours. The product was cooled, alcohol (10 c.c.) was added and the solution was acidified with dilute hydrochloric acid. The product was extracted with benzene, washed with cold dilute sodium carbonate solution and finally with water. The solvent was removed and the residue afforded a colourless liquid boiling at 168-170° (8 mm.). Yield 0 g.
Ethyl 2-carbethoxy-2-(β-phenylethyl) cyclohexanone-2-acetate (VI).

To a cooled suspension of powdered potassium (1.5 g.) under toluene (30 c.c.), the above keto-ester (10 g.) was added dropwise. The mixture was kept overnight and formation of the potassium derivative was completed by heating on a boiling waterbath for one hour. The mixture was cooled and treated with β-phenylethyl bromide (8 g.) and finally refluxed in an oil-bath for 40 hours. On cooling the product was diluted with water. The organic layer was separated, washed with water and dried over sodium sulphate. After removal of the solvent the residue was distilled when the major fraction boiled at 180-182° (0.4 mm.). Yield 8 g.

Calcd. for C_{21}H_{28}O_5: C, 70.00; H, 7.8%

Found: C, 69.9; H, 7.5%.

6-(β-Phenylethyl)-cyclohexanone-2-acetic acid (VII).

The above condensation product (10 g.) was refluxed with a mixture of glacial acetic acid (40 c.c.) and hydrobromic acid (50 c.c., 48%) in an oil-bath for 40 hours. Next hydrobromic acid and acetic acid were removed under suction. The product was cooled, diluted with water and extracted with ether. Ether was distilled off and the residue was boiled with a saturated sodium carbonate solution, cooled and the unhydrolysed ester was taken up in ether. The alkaline layer was acidified with dilute hydrochloric acid whereupon a semisolid mass separated. It was extracted with ether, washed with water dried over sodium
sulphate. After removal of the solvent, the residue was evaporatively distilled at 200-205° (0.5 mm.), when a glassy mass was obtained. Yield 3 g.

Calcd. for C_{16}H_{20}O_{3}: C, 73.8; H, 7.7

Found: C, 74.3; H, 7.5%

6-Hydroxy-1,2,8,9,10,10a-hexahydropyrene (VIII).

The above acid (2 g.) was heated under stirring at 150-160° with polyphosphoric acid prepared from phosphorous pentoxide (10 g.) and phosphoric acid (9 c.c., 89%). The reaction product was cooled, diluted with ice-water and finally extracted with ether. The ethereal extract was thoroughly washed with sodium carbonate solution (5%) to remove any uncyclised acid, with water and finally dried over anhydrous sodium sulphate. On removal of the solvent the residue was evaporatively distilled at 160-165° (0.4 mm.), when a yellowish solid was obtained. On crystallisation from ethanol this afforded light-yellow needles melting at 129-130°. Yield 0.5 g.

Calcd. for C_{16}H_{16}O: C, 85.7; H, 7.2

Found: C, 85.5; H, 7.1%

Pyrene (IV).

The above cyclised compound (0.2 g.) was dehydrogenated with Pd-charcoal (40 mg., 20%) at 260-300° for 2 hours. The product was cooled, extracted with ether and dried over anhydrous sodium sulphate. On removal of the solvent, the
residue was evaporatively distilled at 160° (0.2 mm.), when a light-yellow crystalline product was obtained. This on crystallisation from absolute ethanol gave light yellow diamond-like plates; m.p. 149-150° (Lit. 151.3-151.5°).

Calcd. for C\textsubscript{16}H\textsubscript{10} : C, 95.0; H, 5.0

Found : C, 95.0; H, 5.0%

This formed a red picrate and it crystallised from rectified spirit in fine deep-red needles melting at 219-220° (Lit. 225-228°, corr.).

Calcd. for C\textsubscript{22}H\textsubscript{13}O\textsubscript{7}N\textsubscript{3} : N, 9.7

Found : N, 9.9%

\(\beta\)-(1-Naphthyl)-ethyl bromide.

\(\beta\)-(1-Naphthyl)ethanol was prepared in 75% yield from 1-naphthylmagnesium bromide and ethylene oxide. The reaction mixture was decomposed in the usual way and extracted with ether. The product distilling at 148-150° (1.5 mm.) was collected. A mixture of \(\beta\)-(1-naphthyl)-ethanol (150 g.) and hydrobromic acid (220 c.c., 48%) was refluxed for one hour and then distilled and the distillate was returned to the residue together with hydrobromic acid (60 c.c., 48%). After refluxing for one hour it was again distilled and a fraction (60 c.c.) was collected. The bromide layer was then separated, washed with water, sulphuric acid (80%) and finally distilled when the bromide (183 g.) boiling at 135-138° (1 mm.) was obtained.
Ethyl 6-carbethoxy-6-(β-1-naphthylethyl)-cyclohexanone-2-acetate (IX).

To a cooled suspension of potassium (1.5 g.) in dry toluene (50 c.c.), ethyl 6-carbethoxy-cyclohexone-2-acetate (10 g.) was added dropwise with constant shaking. The mixture was kept overnight and the formation of the potassium salt was completed by refluxing in an oil-bath for 1 hour more. The mixture was treated with β-(1-naphthyl)-ethyl bromide (10 g.) and refluxed in an oil-bath for 40 hours more. The mixture was then cooled and water was added. The toluene layer was separated, washed with water and dried. On removal of the solvent, the residue was distilled when the desired product was collected at 200-205° (0.4 mm.). Yield 6 g.

Calcd. for C_{25}H_{30}O_{5}: C, 73.1; H, 7.4

Found: C, 73.5; H, 7.5%.

6-(β-1-Naphthylethyl)-cyclohexanone-2-acetic acid (X).

The above condensation product (5 g.) was refluxed in an oil-bath for 40 hours with a mixture of glacial acetic acid (20 c.c.) and hydrobromic acid (25 c.c., 48%). Most of the hydrobromic acid and acetic acid was removed under suction and the residue was diluted with water and extracted with ether. The substance left on removal of ether was boiled with a saturated solution of sodium carbonate, cooled and extracted with ether
to remove any unhydrolysed ester. The alkaline layer was acidified with dilute hydrochloric acid, when a semisolid viscous mass separated out. It was extracted with ether, washed with water and dried over anhydrous sodium sulphate. On removal of the solvent, the residue was purified by sublimation under reduced pressure whereupon a yellowish solid was obtained at 220-225° (0.3 mm.). Yield 1.5 g. It crystallised from rectified spirit in white needles melting at 95-96°.

Calcd. for C_{20}H_{22}O_{3}: C, 77.4; H, 7.1

Found: C, 77.6; H, 7.2%

6-Hydroxy-1,2,8,9,10,10a-hexahydro-3:4-benzpyrene (XI).

The above acid (1 g.) was cyclised by heating at 140-150° under stirring with heterogeneous solution of phosphorous pentoxide (5 g.) in phosphoric acid (45 c.c., 89%) for 2 hours. On working up in the usual way, a glassy solid containing an oily matter was obtained which on crystallisation from ethanol melted at 110-112°. Yield 0.2 g.

Calcd. for C_{20}H_{18}O: C, 87.5; H, 6.6

Found: C, 87.0; H, 6.8%

3:4-Benzpyrene (III).

The above cyclised product (0.2 g.) was dehydrogenated with Pd-charcoal (40 mg., 20%) at 280-300° for 2 hours. On evaporative distillation at 160-165° (0.2 mm.) a yellowish solid was obtained, which crystallised from benzene in yellowish needles; m.p. 175-176° (Lit. 175°).
Calcd. for $C_{20}H_{12}$: C, 95.2; H, 4.8

Found: C, 95.0; H, 4.6\%

This readily furnishes a picrate, which crystallised from ethanol in dark-red needles melting at 198° (Lit. 197-198°).

Calcd. for $C_{26}H_{15}N_{3.07}$: N, 8.7

Found: N, 8.6\%

$4^{n}$-Octalin-2-one (XII).

Sodium-dust (9.96 g.) was taken under dry benzene (300 c.c.). To this was added with cooling ethyl/cyclohexanone-2-carboxylate (69 g.). Nextday the flask was cooled and freshly distilled β-chloro-ethyl methyl ketone (46 g.) added slowly to the sodium salt. The mixture was refluxed on a waterbath for 12 hours. It was decomposed with water and dilute acid and aqueous layer extracted with benzene. The combined benzene solution was washed with water and the solvent removed. The residue was treated with a cooled solution of potassium hydroxide (65 g.) dissolved in methyl alcohol (920 c.c.) and finally refluxed in an atmosphere of nitrogen for 12 hours. It was cooled, acidified with acetic acid and methyl alcohol (ca 500 c.c.) removed. The residue was poured into water, saturated with common salt and extracted with ether. The ethereal extract was washed with water and dried over anhydrous sodium sulphate. The solvent was removed and the residue distilled. The fraction boiling at 115-120° (7 mm.) was collected. Yield 26.3 g.
A higher boiling fraction (16 g.) boiling at 140-180° (7 mm.) was again hydrolysed affording a further amount (5.5 g.) of the octalone. A considerable amount of the polymeric product remained in the distillation flask.

1-((β-Phenylethyl)-1'-octalin-2-one (XIII).

Potassium (2 g.) was dissolved in dry tert-amyl alcohol (50 c.c.) and most of the alcohol removed under reduced pressure. To the residue dry thiophene-free benzene (50 c.c.) was added and the cooled suspension was treated with 1'-octalin-2-one (8 g.). The mixture was refluxed under nitrogen atmosphere for 1 hour, cooled and treated with β-phenylethyl bromide (10 g.) and again refluxed for 3 hours. Water was added to the cooled reaction product and acidified with dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted with benzene. The combined benzene extract was washed with water. After removal of the solvent the product distilled mainly at 172-175° (0.4 mm.). $\lambda_{\text{max}}^{\text{alc}} = 250 \text{ m} \mu$ (log $\varepsilon = 3.96$). Yield 4 g.

Calcd. for $C_{18}H_{22}O$: C, 85.0; H, 8.6

Found: C, 84.6; H, 8.6%

It did not give any 2:4-dinitrophenylhydrazone or a semicarbazone.

1,2,3,4,5,6,11,12-Octahydrochrysene (XIV) or its bond isomer (XV).

The above condensation product (3 g.) was heated with polyphosphoric acid prepared from phosphorous pentoxide (14 g.)
and phosphoric acid (12 c.c., 89%) at 140-150° for 2 hours. The reaction product was cooled and decomposed with ice-water. The oily mass separated was extracted with ether. The ethereal extract was washed with sodium carbonate solution (5%) and finally with water. The ethereal extract was dried with anhydrous sodium sulphate and the solvent distilled off. The residue distilled at 170-172° (0.4 mm.) whereupon a yellowish thick liquid was obtained. On crystallisation from ethanol-ethylacetate, white flakes m.p. 115-116° were obtained. Yield 1.1 g. \( \lambda_{\text{max}} \text{277 m} \mu; (\log \epsilon = 4.18).\)

Calcd. for \(\text{C}_{18}\text{H}_{20} : \text{C}, 91.5; \text{H}, 8.4\)

Found : C, 91.4; H, 8.3%.

Chrysene(XXX).

The above product (0.5 g.) was heated with Pd-charcoal (0.1 g., 10%) at 260-300° for 2 hours. The product was cooled, extracted with boiling benzene and the solvent removed. The residue on evaporative distillation under reduced pressure, a white solid was obtained at 200-210° (0.4 mm.). It was crystallised from benzene to afford white flakes melting at 250-251° (Lit. 247-249°).

Calcd. for \(\text{C}_{16}\text{H}_{12} : \text{C}, 94.7; \text{H}, 5.2\)

Found : C, 94.5; H, 4.9%.

2:4:7-Trinitrofluorenone complex.

Molar proportions of chrysene and T.N.F. were dissolved separately in a minimum quantity of boiling alcohol—
benzene mixture. The solutions were mixed together and heated for a minute or two and finally allowed to cool. An yellow solid separated, which on crystallisation from ethanol gave dull-yellow needles; m.p. 248-249° (Lit. 247.8-249°).

Calcd. for C_{31}H_{17}N_{3}O_{7}: C, 68.5; H, 3.1

Found: C, 68.4; H, 3.4%

1-((ß-1-Naphthylethyl)-octalin-4:9-2-one (XVII).

Potassium (2 g.) was dissolved in dry tert-amyl alcohol (50 c.c.). The alcohol was distilled off under reduced pressure and dry xylene (50 c.c.) was added. The reaction mixture was cooled and 4-octalin-2-one (8 g.) was added and refluxed for 1 hour. On cooling, (1-naphthyl)-ethyl bromide (14 g.) was added and the reaction mixture was refluxed for 3 hours more. It was cooled, diluted with water and the organic layer separated. The mother-liquor was extracted with benzene. Both the extracts were mixed and washed with water. After removal of the solvent, the product distilled at 210-215° (0.4 mm.). On crystallisation from ethanol, white needles separated; m.p. 131-132°. Yield 4 g. \( \lambda_{\text{max}} \) 252 m\( \mu \) (log(\( \epsilon \)) = 4.01).

Calcd. for C_{22}H_{24}O: C, 86.8; H, 7.9

Found: C, 87.2; H, 7.9%

It did not form any 2,4-dinitrophenylhydrazone or a semicarbazone.
1,2,3,4,4a,5,13,14-Octahydropicene(XVIII) or its bond isomer(XIX)

The above product (3 g.) was heated at 140-150° for 2 hours under stirring with polyphosphoric acid from phosphorous pentoxide (12 g.) and phosphoric acid (10 c.c., 89%). The reaction mixture was cooled and poured into ice-water and extracted with ether. The extract was washed with sodium carbonate solution (5%) and dried with anhydrous sodium sulphate. The solvent was removed and the residue distilled under reduced pressure when a yellowish glassy solid was obtained at 210-220° (0.3 mm.). On crystallisation from ethanol-ethylacetate it afforded a white crystalline solid melting at 179-180°.

$\lambda_{\text{max}}$ 280 m$\mu$ (log $\varepsilon$ = 4.2).

Calcd. for C$_{22}$H$_{22}$ : C, 92.3; H, 7.7

Found : C, 92.3; H, 7.6%.

Picene (XVI).

The above cyclised product (0.3 g.) was dehydrogenated with Pd-charcoal (50 mg., 10%) at 300-320° for 2 hours. The product was cooled and extracted with boiling benzene. Benzene was removed and the residue evaporatively distilled at 220-240° (0.4 mm.) when a white solid was obtained. This was crystallised from ethylacetate-pyridine to afford colourless flakes melting at 365° (Lit. 366-367°).

Calcd. for C$_{22}$H$_{14}$ : C, 94.9; H, 5.0

Found : C, 94.9; H, 5.1%.
It afforded a trinitrofluorenone complex, which crystallised from benzene in orange needles melting at 256-258° (Lit. 257-257.8°).

Calcd. for C_{35}H_{19}N_{3}O_{7}: C, 70.8; H, 3.2

Found: C, 70.5; H, 3.1%

7-Methyltetralin-1-one (XXII).

Finely powdered anhydrous aluminium chloride (60 g.) was slowly added with stirring to a mixture of succinic anhydride (20 g.), toluene (20 c.c.) and sym-tetrachloro-ethane (75 c.c.). On working up in the usual way it afforded the keto-acid (35 g.); m.p. 129° (Lit. 129-130°). The keto-acid (30 g.) was reduced with zinc-amalgam prepared from purified zinc-wool (40 g.), by refluxing with concentrated hydrochloric acid (250 c.c.) for 12 hours. On working up in the usual way the reduced acid distilled mainly at 150-155° (2 mm.). Yield 25 g. It solidified on cooling and melted at 57-58° (Lit. 59°). The acid (20 g.) was dissolved in thiophene-free dry benzene (100 c.c.) and slowly treated with phosphorous pentachloride (42 g.) under stirring. The reaction mixture was heated on a waterbath at 50° for 1 hour. The acid chloride thus prepared was cooled in an ice-bath and anhydrous aluminium chloride (30 g.) was slowly added. It was kept at room temperature for 2 to 3 hours and again heated on a waterbath at 50° for 2 hours. On working up in the usual way, the major fraction was collected at 120-124° (6 mm.). Yield 14 g.
Ethyl (7-methylnaphthyl-1)-acetate (XIV).

To a solution of the above ketone (27 g.) and ethyl bromoacetate (20 c.c.) in anhydrous benzene (60 c.c.) was added purified zinc-wool (12 g.) and the reaction mixture was heated on a waterbath. After 2 to 3 hours' reflux, fresh zinc-wool (5 g.) and ethyl bromoacetate (6 c.c.) were added followed by further refluxing for 3 hours. The reaction mixture was cooled and decomposed with ice-cold sulphuric acid (10%). It was extracted several times with benzene, the benzene extract washed with water, dilute ammonium hydroxide solution and finally with water. On distillation it passed over at 150-165°C (6 mm.). Yield 32 g. This was heated in an oil-bath with freshly fused potassium bisulphate (40 g.) at 120-130°C for 3 hours in nitrogen atmosphere. The reaction mixture was cooled, diluted with water and extracted with benzene. The extract was washed with water and then distilled. The distillate was collected at 146-148°C (2 mm.). Yield 25 g. A mixture of the dihydro-ester (25 g.) and powdered sulphur (6 g.) was heated at 230-260°C for 6 hours. On cooling it was extracted with benzene and the extract was washed with water, dried and the solvent was distilled off. The residue was taken in dry benzene (80 c.c.) and was refluxed with freshly precipitated copper-powder (13 g.) for 6 hours. The reaction mixture was cooled, filtered and the solid residue washed with dry benzene. The solvent was distilled off and the fraction coming at 162-164°C (5 mm.) was collected. Yield 21 g.
Calcd. for C_{15}H_{16}O_2: C, 78.9; H, 7.0
Found: C, 78.7; H, 7.2%.

\( \beta \)-(7-Methylnaphthyl-1)-ethanol (XXV).

Lithium aluminium hydride (3.5 g.) was covered with dry ether (100 c.c.) and the above ester (20 g.) added dropwise while the reaction mixture was kept under stirring. After the completion of addition, the reaction mixture was kept at room temperature for 1 hour. It was then refluxed on the waterbath for another hour. The reaction mixture was cooled and the excess of lithium aluminium hydride was decomposed with ethylacetate followed by a saturated solution of sodium sulphate and finally with an ice-cold solution of hydrochloric acid (5%). The product was extracted with ether and the ethereal extract washed thoroughly with water and dried. On removal of the solvent the residue boiled mainly at 155-157\(^\circ\) (1 mm.). Yield 14.5 g.

Calcd. for C_{13}H_{14}O: C, 83.8; H, 7.6
Found: C, 83.5; H, 7.3%.

\( \beta \)-(7-Methylnaphthyl-1)ethyl bromide (XXVI)

The above alcohol (14 g.) was taken in a three-necked flask (250 c.c.) fitted with a stirrer, condenser and a dropping funnel. The flask was cooled in an ice-bath. Phosphorous tribromide (22 g.) was added dropwise while the reaction mixture was kept under stirring. After complete addition of phosphorous tribromide the product was refluxed on a waterbath for 2 hours.
On cooling it was poured into ice-water. The organic layer was separated, washed with sulphuric acid (80%), finally with water and dried. On removal of ether, the residue was distilled under reduced pressure affording the bromide (14.5 g.); b.p. 162-164° (5 mm.).

8-Methyl-\(\Delta^1\)-octalin-2-one(XXIII).

2-methylcyclohexanone (28 g.), morpholin hydrochloride (31 g.) and paraformaldehyde (8 g.) were added to absolute ethanol (60 c.c.) and the mixture was refluxed in nitrogen atmosphere for 6 hours. After 2 hours, more of paraformaldehyde (2 g.) was added. The reaction mixture was cooled and diluted with ice-water and extracted with ether to remove the unreacted ketone. The aqueous portion was cooled with crushed ice and made alkaline with sodium hydroxide solution (10%) and finally potassium carbonate was added to saturate the reaction mixture. It was extracted with ether 6 times and the extract was washed with brine solution and dried. The solvent was removed and the residue distilled under reduced pressure. The product distilled mainly at 140-150° (6 mm.). Yield 35 g.

The Mannich's base so prepared was cooled, mixed with methyl iodide (12 c.c.), thoroughly shaken and left overnight in the refrigerator. The methiodide was washed with dry ether and the solvent decanted off to remove excess of methyl iodide. The methiodide was dissolved in a minimum quantity of absolute ethanol and the solution added to ethyl alcohol containing
ethyl acetoacetate (20 g.) and sodium (3.5 g.). The reaction mixture was refluxed for 4 hours. The product was cooled, diluted with water and the neutral product was isolated with ether and finally distilled under reduced pressure whereupon the main bulk (25 g.) distilled at 130-160° (6 mm.). This was again refluxed with potassium hydroxide solution (120 c.c., 15%) in nitrogen atmosphere for 12 hours. The reaction mixture was cooled and thoroughly extracted with ether. The ethereal extract was washed with water, dried and finally distilled. The lower boiling fraction (6 g.) distilled at 116-116° (8 mm.). Yield 6 g. It afforded a 2:4-dinitrophenylhydrazone, which on crystallisation from ethylacetate-ethanol separated in dark-red needles melting at 170-171° (Lit. 171-172°).

\[1-(\text{7-Methyl-}\beta-1\text{-naphthylethyl})-8\text{-methyl-4:9-octalin-2-one(XXVII)}\]

Condensation of the above octalone (8 g.) with \(\beta-(\text{7-methylnaphthyl})\)-ethyl bromide (14 g.) was carried out by refluxing for 3 hours in dry xylene (50 c.c.) in presence of potassium tert-amylate prepared from potassium (2 g.) under the experimental conditions described earlier. The condensation product distilled at 210-220° (0.4 mm.) as a highly viscous glassy mass. Yield 4 g. \(\lambda_{\text{max}}^{\text{alc}} = 250\ \mu\) (log \(\varepsilon = 4.01\) \\

Calcd. for C\(_{24}\)H\(_{28}\)O: C, 86.7; H, 8.4 \\
Found: C, 87.2; H, 8.2%.
Ring-closure was effected with the above condensation product (3 g.) by heating with polyphosphoric acid from phosphorous pentoxide (12 g.) and phosphoric acid (10 c.c., 89%) under stirring at 140-150° for 2 hours. On working up in the usual way, the product was evaporatively distilled at 215-220° (0.3 mm.), when a hard and brittle solid mass was obtained which crystallised from ethanol-ethylacetate; m.p. 190-191°. Yield 1 g. \( \lambda_{\text{max}}^\text{alc} \) 280 m\( \mu \) (log\( \varepsilon \) = 4.2).

Calcd. for C\(_{24}\)H\(_{26}\) : C, 91.7; H, 8.2
Found : C, 91.6; H, 8.4%

1,11-Dimethylpicene (XX).

The cyclised product (0.2 g.) was heated with Pd-charcoal (50 mg., 10%) at 300-320° for 2 hours. The product was cooled and was taken up in boiling ethylacetate. The solvent was removed and the residue was evaporatively distilled at 220-230° (0.3 mm.) yielding a yellowish white solid. On crystallisation from ethylacetate-pyridine, colourless, flowery crystals separated; m.p. 301-302°.

Calcd. for C\(_{24}\)H\(_{18}\) : C, 94.1; H, 5.9
Found : C, 94.5; H, 5.5%

This formed a trinitrofluorenone complex which crystallised from benzene in deep-red needles melting at 264-265°.
1,1,8-Trimethyl-1,2,3,4,5,6,13,14-octahydropicene (XXXIV) or its bond isomer (XXXV).

To a suspension of dry potassium tert-amylate (prepared from 2.4 g. of potassium) in dry toluene (50 c.c.) the ketone (XXXIII, 5 g.) was added with shaking, whereupon the solution turned deep-red. The mixture was heated on a steam-bath for half-an-hour. To the ice-cold swirling mixture a solution of the bromide (XXVI, 11 g.) was added dropwise and left as such for half-an-hour. On refluxing for 6 hours the colour of the reaction mixture turned light yellow with separation of potassium bromide. The reaction product was decomposed with ice-cold water containing hydrochloric acid. The toluene layer was separated and the aqueous layer extracted once with toluene. The combined organic extract was washed with sodium carbonate solution (5%) and then with water. The residue after evaporation of the solvent under reduced pressure, yielded on distillation two fractions, a low boiling fraction b.p. upto 180° (0.5 mm.) containing mostly the unreacted products and a thick yellowish gummy mass (1.6 g.) b.p. 210-220° (0.5 mm.).

The gummy product (1.6 g.) was stirred for 1½ hours at 130-140° with polyphosphoric acid (prepared from phosphoric anhydride (7.5 g.) and phosphoric acid (89%/w/w, 9 c.c.) The colour of the reaction mass initially turned orange and finally deep-brown; it was decomposed with ice-water and
extracted with ether. The ethereal extract was washed with sodium hydroxide solution (2%), with water and finally dried over sodium sulphate. After evaporation of the solvent, the residue on evaporative distillation yielded a glassy solid (1 g.) at 195-205° (0.4 mm.) which on trituration with petroleum ether (40-60°) yielded a white crystalline mass (500 mg.). It crystallised from petroleum ether as shining needles; m.p. 165-167°.

Calcd. for C_{25}H_{28}: C, 91.4; H, 8.6

Found: C, 90.9; H, 8.3%.

1,8-Dimethylpicene (I).

A mixture of the above product (100 mg.) and Pd-charcoal (25 mg., 10%) was heated at 260-280° for half-an-hour and at 310-320° for another 1½ hours. The resulting product was taken up in benzene and was passed through a column of alumina, when the desired hydrocarbon was obtained as shining crystalline flakes (30 mg.), m.p. 299-300° (uncorrected) alone or mixed with an authentic sample.