432. *Reaction of Anthracene with Free Radicals Derived from 2,2,4-Trimethylpentane (Iso-octane).*

By A. L. J. Beckwith.

C_8 radicals, produced by thermal decomposition of di-t-butyl peroxide in 2,2,4-trimethylpentane (iso-octane), react with anthracene to yield crystalline products, formulated as stereoisomers of 9,9′,10,10′-tetrahydro-10,10′-bis-(2,4,4-trimethylpentyl)-9,9′-bianthryl, and oily C_8 derivatives of 9,10-dihydroanthracene. More than 50% of the C_8 radicals formed are consumed by reaction with anthracene; no evidence for disproportionation of C_8 radicals was obtained. The bearing of these results on determination of " methyl affinities " is discussed.

Syntheses are described for 9,9′,10,10′-tetrahydro-10,10′-di-(1,1,3,3-tetramethylbutyl)-9,9′-bianthryl, 2,2,4- and 2,4,4-trimethylpentanoic acid, and related compounds.

Of the methods used to determine the rates of reaction of aromatic compounds with free radicals in solution, that developed by Szwarc and his collaborators has been the most extensively applied.[1,2] The radical source employed in the majority of Szwarc's experiments was acetyl peroxide. When heated in an iso-octane (2,2,4-trimethylpentane) solution of an aromatic hydrocarbon it decomposes into methyl radicals, which react by hydrogen-atom abstraction from solvent molecules (equation 1) or by addition to solute molecules (equation 2). Of the competing reactions (1) and (2), only the former results in the liberation of methane, and the ratio of the rate constants, k_1/k_2, can be calculated after analysis of the gaseous products.

$$\mathrm{Me{\cdot}CO{\cdot}O_2{\cdot}COMe} \longrightarrow \mathrm{2Me{\cdot}CO_2{\cdot}} \longrightarrow \mathrm{2Me{\cdot}} + \mathrm{2CO_2}$$

$$\mathrm{Me{\cdot}} + \mathrm{C_8H_{18}} \xrightarrow{k_1} \mathrm{C_8H_{17}{\cdot}} + \mathrm{MeH} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{Me{\cdot}} + \mathrm{ArH} \xrightarrow{k_2} \mathrm{Me{\cdot}ArH{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The accuracy of the method depends upon the validity of the assumption that methyl radicals are consumed only according to equations (1) and (2) and in their combination within a solvent cage to form ethane.[1] Direct evidence that methyl radicals do not take part in any other reactions has, in fact, not been forthcoming. However, it has been shown that no coupling occurs between methyl radicals and the $C_8H_{17}{\cdot}$ radicals derived from iso-octane.[1,3] This result has been put forward in support of the suggestion that methyl radicals do not react with the complex Me·ArH· radicals.[1]

The ultimate fates of the radicals produced according to equations (1) and (2) in

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[1] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.

[2] Szwarc and Binks, " Theoretical Organic Chemistry," Kekulé Symposium, Butterworths, London, 1958, p. 262; this review includes references to other papers on the subject by Szwarc and his co-workers.

[3] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1954, **76**, 5981.

Szwarc's experiments are not known. It has been suggested [1] that $C_8H_{17}\cdot$ may be destroyed by reacting in pairs, presumably to yield $C_{16}H_{34}$ by dimerisation, or C_8H_{16} and C_8H_{18} by disproportionation. There was some indication that thermal decomposition of acetyl peroxide in benzene yielded derivatives of cyclohexadiene but no pure products were isolated.[3,4] In a later study [5] the same reaction was found to yield toluene and 4,4'-dimethylbibenzyl. Similar products were obtained from attack of methyl radicals on toluene [5] and on chlorobenzene.[6] When acetyl peroxide was decomposed in ring-deuterated benzene or its alkyl derivatives deuteromethane was liberated, indicating that methyl radicals may abstract hydrogen from Me·ArH·.[5,7] However, no products have been isolated from reactions carried out under Szwarc's conditions, and his results have been criticised on this account.[8] Despite these uncertainties regarding their precise meaning, values of " methyl affinity " have been extensively used to evaluate the applicability of various theoretical quantities as indices of reactivity. Several satisfactory correlations have been noted.[2,9]

In order to investigate possible reactions between aromatic molecules and $C_8H_{17}\cdot$ radicals the thermal decomposition of di-t-butyl peroxide in an iso-octane solution of anthracene has now been studied. The reaction was conducted in a large excess of iso-octane at the boiling point. Decomposition of the peroxide under these conditions was extremely slow [10] and after fourteen days approximately 40% of it remained. Because of the relatively low reaction temperature it was expected that t-butoxy-radicals, formed by homolysis of the peroxide (equation 3), would react mainly by hydrogen-atom abstraction from iso-octane (equation 4) and that their rearrangement to acetone and methyl radicals (equation 5) would occur to a negligible extent. In fact, t-butyl alcohol was the only product derived directly from di-t-butyl peroxide which could be detected in the reaction mixture.

$$Bu^tO{\cdot}OBu^t \longrightarrow 2Bu^tO\cdot \qquad (3)$$

$$Bu^tO\cdot + C_8H_{18} \longrightarrow Bu^tOH + C_8H_{17}\cdot \qquad (4)$$

$$Bu^tO\cdot \longrightarrow Me_2CO + Me\cdot \qquad (5)$$

A variety of tests failed to detect unsaturated compounds in the iso-octane recovered after the reaction, indicating that $C_8H_{17}\cdot$ radicals derived from iso-octane do not undergo disproportionation. This conclusion is supported by the quantity of crude product isolated, which amounted to more than 90% of that theoretically obtainable. It may accordingly be calculated that less than 10% of the iso-octyl radicals formed underwent disproportionation to volatile products. Of the anthracene used, 34% was recovered. Since the conversion of one anthracene molecule into product requires its combination with one, or possibly two, iso-octyl radicals, this result indicates that at least 50% of the iso-octyl radicals formed reacted directly with anthracene. The assumption that all the iso-octyl radicals produced in Szwarc's experiments were destroyed by reaction in pairs is evidently incorrect.

The isolation of pure products from the crude reaction mixture was difficult. The major fractions obtained by chromatography on alumina were weakly fluorescent oils which could not be separated further by chromatography on acetylated cellulose.[11] On the basis of their ultraviolet absorption spectra, their oxidation to anthraquinone, and their thermal decomposition (which yielded a volatile liquid tentatively identified as an

[4] Levy, Steinberg, and Szwarc, *J. Amer. Chem. Soc.*, 1954, **76**, 3439.

[5] Eliel, Rabindran, and Wilen, *J. Org. Chem.*, 1957, **22**, 859.

[6] Beckwith and Waters, *J.*, 1957, 1665.

[7] Wilen and Eliel, *J. Amer. Chem. Soc.*, 1958, **80**, 3309.

[8] Gould, " Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, Inc., New York, 1959, footnote on p. 718.

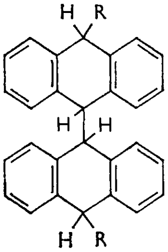
[9] Coulson, *J.*, 1955, 1435; Dewar, Mole, and Warford, *J.*, 1956, 3581; Pullman and Effinger, " Colloque International sur le Calcul des Fonctions d'Onde Moleculaires," C.N.R.S., Paris, 1958, p. 329.

[10] Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1958, **70**, 1336.

[11] Spotswood, *J. Chromatog.*, 1960, **3**, 101.

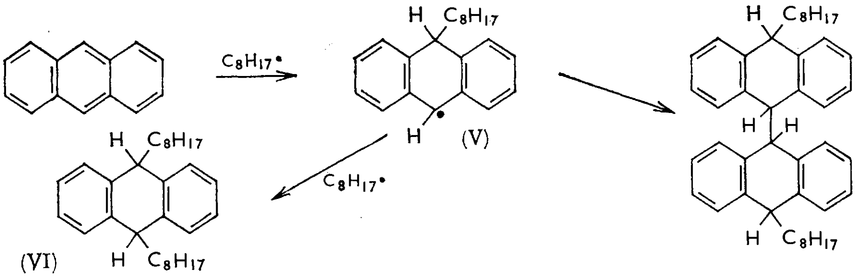
iso-octene), the oils are believed to be mixtures of mono- and of di-" iso-octyl " derivatives of 9,10-dihydroanthracene with isomeric $C_{16}H_{34}$ hydrocarbons formed by dimerisation of $C_8H_{17}\cdot$ radicals (dihydrodi-iso-octylanthracene of unspecified constitution or origin has been described as a viscous oil [12]).

Chromatography of the crude product also yielded three crystalline compounds, of m. p. 203°, 175°, and 153°. We are unable to suggest a structure for the last, which was isolated in very small amount. The properties of the other two compounds indicate that they are isomers of 9,9',10,10'-tetrahydro-10,10'-di-" iso-octyl "-9,9'-bianthryl (I). In view of the enhanced reactivity of tertiary positions towards hydrogen-atom abstraction by free radicals it was thought at first that one of the products was 9,9',10,10'-tetrahydro-10,10'-di-(1,1,3,3-tetramethylbutyl)-9,9'-bianthryl (II). However, synthesis of the authentic compound (II) showed that this was not so. Further information concerning the structures of the crystalline products was afforded by their oxidation with chromic acid which in both cases yielded anthraquinone and an aliphatic acid shown by paper chromatography to contain eight carbon atoms. The two possible structures are therefore those, (III) and (IV), which contain iso-octyl groups attached through primary positions to the anthracene nucleus. When the oxidation was conducted on a larger scale with a sample of the crude mixture of products it was possible to identify the acid as 2,4,4-trimethylpentanoic (XXI). Since no other acid was isolated it appears that the two crystalline compounds are most probably stereoisomers of 9,9',10,10'-tetrahydro-10,10'-di-(2,4,4-trimethylpentyl)-9,9'-bianthryl (IV). The fact that the two crystalline products have identical infrared absorption spectra suggests that they may be *meso*- and racemic forms.



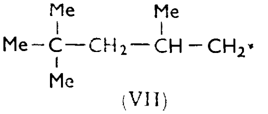
(I : R = C_8H_{17})
(II : R = $Me_3C{\cdot}CH_2{\cdot}CMe_2{-}$)
(III : R = $Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{-}$)
(IV : R = $Me_3C{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{-}$)

The identification of the crystalline products as derivatives of bianthryl with structures (IV) analogous to those obtained by attack of other free radicals, *e.g.*, methyl,[13] benzyl,[14] phenyl,[15] 2-cyano-2-propyl,[16] upon anthracene indicates that the mechanism is identical with that previously postulated for this type of reaction. The tentative formulation of the oily products as isomers of 9,10-dihydro-9,10-di-" iso-octyl "-anthracene (VI) accords with such a mechanism.

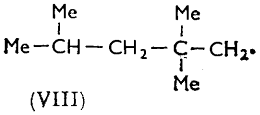


[12] Hugel, *Kolloid Z.*, 1953, **131**, 4.
[13] Beckwith and Waters, *J.*, 1956, 1108.
[14] Beckwith and Waters, *J.*, 1957, 1001.
[15] Norman and Waters, *J.*, 1958, 167.
[16] Bickel and Kooyman, *Rec. Trav. chim.*, 1953, **72**, 342.

The results of our experiments also suggest that of the isomeric $C_8H_{17}\cdot$ radicals those (VII, VIII) derived by hydrogen-atom abstraction from primary positions in 2,2,4-trimethylpentane are the most readily formed. A study of the autoxidation of iso-octane[17] led to similar results, which were interpreted as being due partly to the statistical factor in favour of the primary positions and partly to steric hindrance of the theoretically more reactive secondary and tertiary positions. Of the two possible primary radicals, 2,4,4- (VII) and 2,2,4-trimethylpentyl (VIII), the attack of the former on anthracene is less sterically hindered.


$\mathrm{Me{-}\overset{Me}{\underset{Me}{C}}{-}CH_2{-}\overset{Me}{C}H{-}CH_2\cdot}$

(VII)


$\mathrm{Me{-}\overset{Me}{C}H{-}CH_2{-}\overset{Me}{\underset{Me}{C}}{-}CH_2\cdot}$

(VIII)

The isolation of products arising by direct attack of iso-octyl radicals upon an aromatic hydrocarbon indicates that values of " methyl affinity " calculated by Szwarc's method, which does not allow for such a reaction, may be erroneous. In particular, the removal of an aromatic compound by its reaction with iso-octyl radicals may lead to an unexpected lowering of its concentration. Furthermore, there appears to be no reason why intermediate radicals of the type (V), whose stationary concentration must be relatively high, should not couple with methyl radicals if present. Such a reaction would directly affect values of " methyl affinity."

The observed linear relation[2,9] between the logarithm of methyl affinity and the appropriate maximum or minimum value of free-valence number, atom-localisation energy, and other calculated indices, does not necessarily invalidate the above criticism, because the rate of reaction of methyl radicals with $C_8H_{17}\cdot ArH\cdot$ will be proportional to the concentration of the latter, which in turn depends upon a variety of factors including the rate of attack of $C_8H_{17}\cdot$ radicals upon the aromatic substrate. Since the same electronic factors govern the rate of addition of any free radical to an aromatic molecule, the rate of reaction of $C_8H_{17}\cdot$ radicals will also be related to appropriate values of theoretical indices, and the linear relation noted above would be observed even if methyl radicals were consumed uniquely by coupling with $C_8H_{17}\cdot ArH\cdot$ radicals. The observation that the linear graphs of localisation energy, for a series of aromatic hydrocarbons, against the logarithms of methyl, ethyl, and propyl affinities have identical gradients[2] may, in fact, be explained on the supposition that the primary step in each reaction is the addition of iso-octyl radicals to the substrate.

A number of compounds were synthesised for comparison with the products from the above-mentioned reactions. Derivatives of 9,10-dihydroanthracene containing the 1,1,3,3-tetramethylbutyl group were prepared by treatment of sodium anthracenide with 2-chloro-2,4,4-trimethylpentane. The crude product was separated into anthracene, 9,10-dihydroanthracene, 9,10-dihydro-9-(1,1,3,3-tetramethylbutyl)anthracene (X), 9,10-dihydro-9,10-di-(1,1,3,3-tetramethylbutyl)anthracene (XI), and 9,9′,10′,10-tetrahydro-10,10′-di-(1,1,3,3-tetramethylbutyl)-9,9′-bianthryl (II). The isolation of a bianthryl derivative is in accord with the radical-ion structure (IX) of anthracene–metal adducts.[18,19] Formation of the other products may be explained by the reaction mechanism recently proposed.[18]

We had hoped to prepare anthracene derivatives (XII, XIII) containing the isopropyl-2,2-dimethylpropyl group by a similar reaction of sodium anthracenide with 3-chloro-2,2,4-trimethylpentane. However, all attempts to convert 2,2,4-trimethylpentan-3-ol into the required halide yielded 2,4,4-trimethylpent-2-ene. Alternative routes to the required anthracene derivatives were then investigated. 2,2,4-Trimethylpentan-3-one,

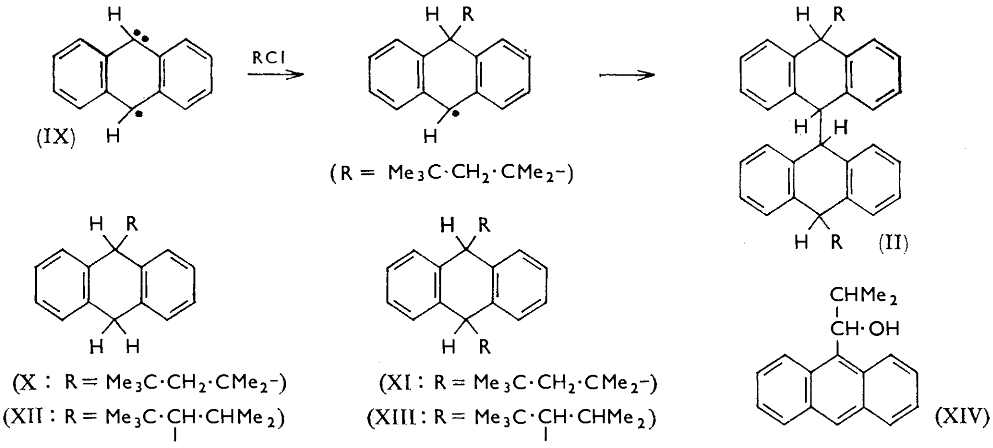
[17] Frank and Blackman, *Ind. Eng. Chem.*, 1954, **46**, 212.

[18] Paul, Lipkin, and Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.

[19] Hoistink, de Boer, van der Meij, and Weijland, *Rec. Trav. chim.*, 1956, **75**, 487.

which was readily prepared by oxidation of the appropriate alcohol or by methylation of di-isopropyl ketone, failed to react with 9-anthryl-lithium or with 9,10-dihydro-9-anthryl-lithium. Nor were attempts to build up the required substituents more successful. 1-9′-Anthryl-2-methylpropan-1-ol (XIV), prepared by reaction of 9-anthryl-lithium with isobutyraldehyde, could not be oxidised to 9-isobutyrylanthracene. Attempts to prepare the latter by methylation of 9-acetylanthracene or by Friedel–Crafts synthesis also failed.

The preparation of 2,2,4-trimethylpentanoic acid (XVI) by a Grignard synthesis from 2-chloro-2,4-dimethylpentane occurred in small yield; other methods were therefore investigated. One attempted route, *via* 3-hydroxy-2,2,4-trimethylpentanoic acid, obtained by oxidation of isobutyraldol, proved impracticable. Successful methods are summarised in the Chart.



(IX)

($R = Me_3C\cdot CH_2\cdot CMe_2-$)

(II)

(X : $R = Me_3C\cdot CH_2\cdot CMe_2-$)
(XII : $R = Me_3C\cdot\underset{|}{CH}\cdot CHMe_2$)

(XI : $R = Me_3C\cdot CH_2\cdot CMe_2-$)
(XIII : $R = Me_3C\cdot\underset{|}{CH}\cdot CHMe_2$)

(XIV)

$$\begin{tikzcd}
{} & \mathrm{Me_2CH{\cdot}CH_2Br + Me_2CH{\cdot}COPh} \arrow[r, "\mathrm{NaNH_2}"] & \mathrm{Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}COPh} \arrow[d, "\mathrm{NaNH_2}"] \\
\mathrm{Me_2CH{\cdot}CH_2Br + Me_2CH{\cdot}CN} \arrow[r, "\mathrm{NaNH_2}"] & \mathrm{Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CN} \arrow[r, "\mathrm{H_2SO_4}"] & \mathrm{Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO{\cdot}NH_2} \arrow[d, "\mathrm{N_2O_3}"] \\
\underset{\text{(XV)}}{\mathrm{Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO{\cdot}CHMe_2}} \arrow[r, "\mathrm{NaNH_2}", "\mathrm{O_2}"'] & {} \arrow[r, "\mathrm{H_2SO_4}"] & \underset{\text{(XVI)}}{\mathrm{Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2H}}
\end{tikzcd}$$

Both the Haller reaction[20] and the nitrile synthesis gave high overall yields. The improvement over previously reported results[20] for the Haller reaction is attributed to the use of freshly prepared sodamide. The yield of acid obtained by autoxidation of the ketone (XV) with sodamide and oxygen was less satisfactory, but this method may prove useful for the synthesis of other tertiary acids. The mechanism probably involves acid-catalysed decomposition of the hydroperoxide (XVII). The acid (XVI) and its amide have physical constants in accord with those reported by Leers for the acid and its amide, obtained by oxidation of 3,3,5-trimethylhexan-2-one.[21]

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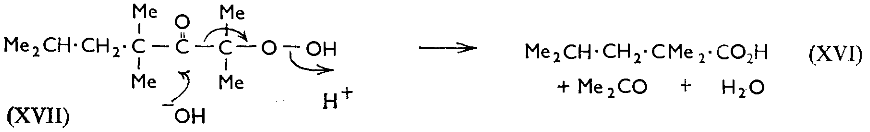
[20] Haller, *Compt. rend.*, 1909, **148**, 127; 1909, **149**, 5; Haller and Baur, *Ann. Chim.* (*France*), 1914, [9], **1**, 5; Birch and Robinson, *J.*, 1942, 488; Carter and Slater, *J.*, 1946, 130.

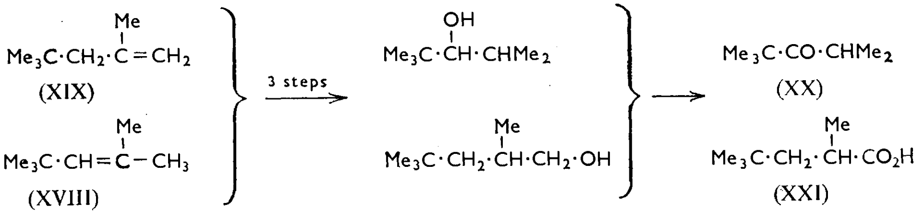
[21] Leers, *Bull. Soc. chim. France*, 1926, **39**, 653.

Reduction of the acid (XVI) with lithium aluminium hydride readily afforded 2,2,4-trimethylpentan-1-ol which was converted into its toluene-*p*-sulphonate. It was hoped that reaction of sodium anthracenide with the toluene-*p*-sulphonate would yield 2,2,4-trimethylpentyl derivatives of anthracene. However, no products of this type were isolated.

A recently reported method for the specific introduction of acyloxy-groups into the allylic positions of olefins[22] was employed for the synthesis of 2,4,4-trimethylpentanoic acid (XXI). Treatment of a large excess of di-isobutene, containing mainly 2,4,4-trimethylpent-2-ene (XVIII) with a small amount of 2,4,4-trimethylpent-1-ene (XIX), with t-butyl perbenzoate and a trace of cuprous bromide yielded a mixture of benzoates, which was hydrogenated and then hydrolysed. Oxidation of the resultant mixture of 2,4,4-trimethylpentan-1-ol and 2,4,4-trimethylpentan-3-ol gave the required acid (XXI) which was readily separated from the accompanying ketone (XX). When the acyloxylation step was carried out in acetic acid the product was a mixture of acetates which were somewhat easier to hydrogenate than the corresponding benzoates.



$Me_2CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2H + Me_2CO + H_2O$



EXPERIMENTAL

Materials.—2,2,4-Trimethylpentane was shaken with four portions of concentrated sulphuric acid, washed with aqueous sodium hydrogen carbonate and with water, and dried over sodium. Fractional distillation through a helix-packed column yielded the pure material, b. p. 99°. Di-t-butyl peroxide was fractionally distilled under a reduced pressure of nitrogen. The fraction, b. p. 50—52°/90 mm., was collected and used immediately.

Reaction of Anthracene with Di-t-butyl Peroxide in 2,2,4-Trimethylpentane.—Anthracene (10 g.) and di-t-butyl peroxide (10 g.) in 2,2,4-trimethylpentane (400 ml.) were boiled under reflux in nitrogen for 14 days. The mixture was then fractionally distilled. The first fraction, b. p. <95°, contained t-butyl alcohol (5·7 g.) and solvent; no acetone was detected by vapour-phase chromatography. The second fraction (200 ml.) was pure 2,2,4-trimethylpentane. It did not react with bromine or aqueous potassium permanganate and its infrared absorption spectrum contained no bands characteristic of the $C{=}C$ chromophore. Anthracene (3·4 g.), which crystallised from the cooled distillation residue, was collected, and the filtrate was evaporated under a reduced pressure of nitrogen. The infrared absorption of the distillate, when measured with pure 2,2,4-trimethylpentane in the reference cell, showed strong bands at 750, 875, and 1180 cm.$^{-1}$ characteristic of di-t-butyl peroxide. By comparison with standard solutions it was calculated that the distillate contained 4 g. of unchanged peroxide. A portion (7·0 g.) of the oily, pale yellow, distillation residue (14·8 g.) was chromatographed on alumina (Spence's type U.G.1.). The column was eluted with a gradient of benzene in light petroleum (b. p. 40—60°). The first fractions (total, 1·2 g.) were colourless oils with weak blue fluorescence. They showed weak light absorption at 265 and 275 mμ and had strong infrared absorption in

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[22] Kharasch, Sosnovsky, and Yang, *J. Amer. Chem. Soc.*, 1959, **81**, 5819.

the aliphatic C–H stretching region. Oxidation of two samples with chromium trioxide in acetic acid yielded anthraquinone. Attempted dehydrogenation of a sample with sulphur at 230° gave anthracene and an unsaturated liquid, b. p. 98—100°.

Later chromatographic fractions were separated by treatment with ether–methanol mixtures into amorphous solids (total, 1·47 g.) and soluble oils (2·2 g.) similar to those previously obtained. Repeated crystallisation of the combined solids from ether–methanol and from ethanol afforded an *isomer* (A) of (?) 9,9′,10,10′-tetrahydro-10,10′-di-(2,4,4,-trimethylpentyl)-9,9′-bianthryl (0·15 g.), needles, m. p. 203° [Found: C, 90·7; H, 9·5%; *M* (Rast), 510. $C_{44}H_{54}$ requires C, 90·65; H, 9·35%; *M* 582], a second *isomer* (B), needles (0·37 g.), m. p. 175° [Found: C, 90·4; H, 9·2%; *M* (Rast), 472], and a *substance* (40 mg.), m. p. 153—154° (Found: C, 91·5; H, 8·3. $C_{37}H_{40}$ requires C, 91·7; H, 8·3%). Later chromatographic fractions were intractable yellow oils.

Oxidation of reaction products. (*a*) Chromium trioxide (0·2 g.) was added slowly with shaking to a solution of product (A) (90 mg.) in acetic acid (5 ml.), and the mixture was then heated on the steam-bath for 30 min. Anthraquinone (46 mg.), collected by filtration of the cooled reaction mixture, was washed with cold methanol. The combined filtrates were copiously diluted with water and extracted with ether. The acidic portion (*ca.* 20 mg.) of the ethereal extract, when chromatographed on paper with the solvent system n-butanol–1·5N-ammonia (1 : 1), gave a strong spot with R_F 0·75, identical with that of octanoic acid.

(*b*) When product (B) (160 mg.) was oxidised by the foregoing method the products were anthraquinone (96 mg.) and an acid (*ca.* 30 mg.) which had R_F 0·75.

(*c*) A portion (3·9 g.) of the gum, when oxidised with chromium trioxide (3·5 g.) in acetic acid (25 ml.), yielded anthraquinone (0·95 g.). The neutral product (2·0 g.) was a viscous oil which failed to react with 2,4-dinitrophenylhydrazine. Treatment of the acid fraction (160 mg.) with 4-phenylphenacyl bromide gave 4-phenylphenacyl 2,4,4-trimethylpentanoate, which, after chromatography on alumina, had m. p. and mixed m. p. 83°.

Preparation of Reference Compounds.—Reaction of 2-*chloro*-2,4,4-*trimethylpentane with sodium anthracenide.* 2-Chloro-2,4,4-trimethylpentane,[23] b. p. 53°/32 mm., was added dropwise with stirring under N_2 to the complex obtained by shaking anthracene (4·6 g.) in ether (60 ml.) with sodium (2·3 g.) for 48 hr. When the blue colour changed to yellow the mixture was filtered through glass wool and water was added. The ethereal solution was separated and distilled, and the residue was dissolved in light petroleum. Anthracene (0·8 g.), which crystallised from the cooled solution, was collected, and the filtrate was chromatographed on alumina. Elution with benzene–light petroleum yielded: (i) 9,10-dihydroanthracene (1·6 g.), m. p. and mixed m. p. 108°; (ii) 9,10-*dihydro*-9-(1,1,3,3-*tetramethylbutyl*)*anthracene* (0·48 g.), needles (from methanol), m. p. 85° (Found: C, 90·4; H, 9·5. $C_{22}H_{28}$ requires C, 90·35; H, 9·65%); (iii) 9,10-*dihydro*-9,10-*di*-(1,1,3,3-*tetramethylbutyl*)*anthracene* (0·15 g.), prisms (from pentane), m .p. 174° (Found: C, 89·2; H, 11·2. $C_{30}H_{44}$ requires C, 89·05; H, 10·95%); (iv) 9,9′,10,10′-*tetrahydro*-10,10′-*di*-(1,1,3,3-*tetramethylbutyl*)-9,9′-*bianthryl* (0·48 g.), needles (from chloroform–ethanol), m. p. 182° (Found: C, 90·75; H, 9·3. $C_{44}H_{54}$ requires C, 90·65; H, 9·35%); and (v) anthracene (0·7 g.).

2,2,4-*Trimethylpentan*-3-*ol.* Treatment of isobutyraldehyde with t-butylmagnesium chloride[24] yielded the required alcohol, b. p. 148—152°. The 3,5-*dinitrobenzoate* crystallised from pentane in needles, m. p. 108° (Found: C, 55·6; H, 6·3; N, 8·35. $C_{15}H_{20}N_2O_6$ requires C, 55·55; H, 6·2; N, 8·6%). Treatment of the alcohol with toluene-*p*-sulphonyl chloride in pyridine yielded the crude toluene-*p*-sulphonate which decomposed into toluene-*p*-sulphonic acid and 2,4,4-trimethylpent-2-ene on attempted crystallisation. Dehydration of the alcohol also occurred on treatment with thionyl chloride or with hydrogen bromide in benzene.

2,2,4-*Trimethylpentan*-3-*one.* Di-isopropyl ketone (56 g.) was added to sodamide (from 9·1 g. of sodium) in liquid ammonia (250 ml.), and the mixture was stirred for 30 min. After addition of dry ether (150 ml.) the mixture was warmed until all the ammonia had evaporated. Methyl iodide (60 g.) was then added dropwise with stirring. When the vigorous reaction had subsided the mixture was boiled under reflux for 30 min., cooled, and washed with water. Fractional distillation of the ethereal solution yielded 2,2,4-trimethylpentan-3-one (48 g., 76%). The 2,4-dinitrophenylhydrazone had m. p. 160° (lit.,[25] m. p. 163—164°).

[23] Whitmore and Southgate, *J. Amer. Chem. Soc.*, 1938, **60**, 2571.

[24] Conant and Blatt, *J. Amer. Chem. Soc.*, 1929, **51**, 1227.

[25] Byers and Hickinbottom, *J.*, 1948, 284.

2,2,4-Trimethylpentan-3-one was also prepared, although in lower yield, by methylation of di-isopropyl ketone with methyl iodide and powdered sodamide in benzene, and by oxidation of 2,2,4-trimethylpentan-3-ol with chromium trioxide in acetone–sulphuric acid.[26]

When 2,2,4-trimethylpentan-3-one was added to 9-anthryl-lithium prepared from 9-bromoanthracene and phenyl-lithium, the only identifiable product was anthracene. The only product obtained on treatment of the ketone with 9,10-dihydroanthryl-lithium was 9,10-dihydroanthracene.

1-9′-*Anthryl*-2-*methylpropan*-1-*ol*. 9-Bromoanthracene (8 g.) was added to a solution of butyl-lithium (prepared from 5·0 g. of 1-chlorobutane) in ether, and the mixture was then stirred at room temperature for 10 min. Isobutyraldehyde (4·0 g.) in ether (50 ml.) was then added to the mixture, which was boiled under reflux for 2 hr., cooled, and poured into water. The ethereal solution was separated and evaporated. The residual *alcohol* crystallised from pentane in yellow prisms (5·2 g., 67%), m. p. 94° (Found: C, 86·75; H, 7·35. $C_{18}H_{18}O$ requires C 86·4; H. 7·25%) $\lambda_{max.}$ 255 (ε 187,000), 370 (ε 10,000), and 385 mμ (ε 9900). The 3,5-*dinitrobenzoate* formed yellow needles, m. p. 169° (Found: C, 67·2; H, 4·5. $C_{25}H_{20}N_2O_6$ requires C, 67·5; H, 4·5%).

Attempted preparation of 9-*isobutyrylanthracene*. (*a*) Oxidation of the foregoing alcohol with chromium trioxide in acetone and aqueous sulphuric acid [26] yielded an intractable dark oil.

(*b*) When anthracene (4·2 g.) and isobutyryl chloride (18 ml.) in benzene (50 ml.) were treated with powdered aluminium chloride (7·2 g.) at 0° the products, isolated by chromatography on alumina, were 9,10-dichloroanthracene (350 mg.), m. p. 210° (Found: C, 68·3; H, 3·7. Calc. for $C_{14}H_8Cl_2$: C, 68·2; H, 3·3%), anthracene, and isobutyrophenone (2·2 g.), which was identified by preparation of the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 168°.

(*c*) Methylation of 9-acetylanthracene with methyl iodide and sodamide in liquid ammonia yielded no identifiable product.

2,2,4-*Trimethylpentanonitrile*. To a solution of sodamide (from 11·5 g. of sodium) in liquid ammonia (350 ml.) were added successively isobutyronitrile (35 g.) and 1-bromo-2-methylpropane (69 g.). After dilution with dry toluene (150 ml.) the mixture was warmed until the ammonia had evaporated and was then boiled under reflux for 2 hr. The cooled mixture was then poured into aqueous sulphuric acid, and the organic layer was washed with water, dried, and fractionally distilled. The required *nitrile* (39·5 g., 62%) had b. p. 75—77°/30 mm. and n_D^{20} 1·4134 (Found: C, 76·8; H, 12·05. $C_8H_{15}N$ requires C, 76·7; H, 12·1%).

2,2,4-*Trimethyl*-1-*phenylbutan*-1-*one*. Isobutyrylbenzene (55 g.) was alkylated with 1-bromo-2-methylpropane (55 g.) and sodamide (from 8·5 g. of sodium) in benzene (150 ml.) according to the method of the preceding experiment. Fractional distillation of the crude product yielded the required *ketone* (42 g., 55%), b. p. 96—98°/1·5 mm., n_D^{20} 1·5046 (Found: C, 82·3; H, 9·8. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%). The 2,4-*dinitrophenylhydrazone* crystallised from methanol in yellow laths, m. p. 112—113° (Found: N, 14·6. $C_{20}H_{24}N_4O_4$ requires N, 14·6%).

2,2,4-*Trimethylpentanamide*. (*a*) 2,2,4-Trimethyl-1-phenylbutan-1-one (23·5 g.) and toluene (100 ml.) were added successively to sodamide (from 5·5 g. of sodium) in liquid ammonia (150 ml.). After evaporation of the ammonia the mixture was boiled under reflux for 5 hr., cooled, and poured into water. The organic layer was washed with aqueous sulphuric acid, and the solvent was then removed under reduced pressure. The residue of 2,2,4-*trimethylpentanamide* (13·5 g., 82%), which solidified, crystallised from pentane in plates, m. p. 73° (Found: C, 67·2; H, 11·8; N, 10·0. $C_8H_{17}NO$ requires C, 67·1; H, 12·0; N, 9·8%).

(*b*) 2,2,4-Trimethylpentanonitrile (37 g.) in sulphuric acid (150 ml.) and water (30 ml.) was heated on the water-bath for 2 hr., cooled, and poured into water (1 l.). After neutralisation with sodium carbonate, the mixture was extracted with ether. Evaporation of the solvent and crystallisation of the residue from pentane yielded the required amide (38 g., 90%), m. p. and mixed m. p. 73°.

3-*Hydroxy*-2,2,4-*trimethylpentanoic acid*. 3-Hydroxy-2,2,4-trimethylpentanal (8·6 g., prepared in 28% yielded from isobutyraldehyde),[27] suspended in 5% aqueous potassium carbonate (100 ml.), was stirred while potassium permanganate (5·5 g) in water was added dropwise during 1 hr. The mixture was then extracted with ether, acidified, decolorised with sulphur dioxide, and extracted with ether once again. Evaporation of the second extract

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[26] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

[27] Saunders, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1943, **65**, 1714.

yielded the hydroxy-acid (4·6 g., 51%), which crystallised from hexane in prisms, m. p. 94° (lit.,[28] m. p. 92°) (Found: C, 60·3; H, 10·2. Calc. for $C_8H_{16}O_3$: C, 60·0; H, 10·1%). The 4-*phenylphenacyl ester* formed plates, m. p. 76—77° (Found: C, 74·5; H, 7·4. $C_{22}H_{26}O_4$ requires C, 74·55; H, 7·4%).

2,4,4,6-*Tetramethylheptan*-3-*one*. Di-isopropyl ketone (19 g.) and 1-bromo-2-methylpropane (25 g.) were added successively to sodamide (from 4·5 g. of sodium) in liquid ammonia (150 ml.). After addition of benzene (150 ml.) the ammonia was allowed to evaporate and the mixture was then heated under reflux for 6 hr., cooled, and treated with water. Fractional distillation of the organic phase yielded the required *ketone* (24 g., 84%), b. p. 82°/18 mm., n_D^{20} 1·4072 (Found: C, 77·6; H, 13·1. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%).

2,2,4-*Trimethylpentanoic acid*. (*a*) Nitrogen trioxide, prepared from arsenious oxide (40 g.) and nitric acid,[29] was bubbled during 2 hr. into a solution of 2,2,4-trimethylpentanamide (30 g.) in acetic acid (100 ml.), cooled in ice. The mixture became warm and there was a vigorous evolution of gas. After 5 hr. at room temperature the mixture was heated on the steam-bath for a further 2 hr. The solvent was then distilled off under reduced pressure and the residue was dissolved in aqueous sodium hydroxide and washed with ether. After acidification of the aqueous layer it was extracted with ether. Fractional distillation of the extract yielded 2,2,4-*trimethylpentanoic acid* (26·5 g., 88%), b. p. 75—76°/6 mm., n_D^{20} 1·4290 (Found: C, 60·9; H, 11·1. $C_8H_{16}O_2$ requires C, 66·6; H, 11·2%). The 4-*phenylphenacyl ester* crystallised from hexane in plates, m. p. 81° (Found: C, 78·0; H, 7·75. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%).

(*b*) 2,4,4,6-Tetramethylheptan-3-one (6·0 g.) and 1,2-dimethoxyethane (50 ml.) were added successively with stirring to sodamide (from 1·0 g. of sodium) in liquid ammonia (50 ml.). After removal of the ammonia in a stream of nitrogen, the mixture was cooled to −10° and shaken under oxygen. There was a rapid absorption of gas (800 ml.). 10% Aqueous sulphuric acid (50 ml.) was then added dropwise and the mixture was slowly distilled until all the dimethoxyethane was removed. The cooled residue was extracted with ether, and the extract was separated into neutral and acid fractions. The latter (1·8 g., 35%) was identified as 2,2,4-trimethylpentanoic acid by preparation of the 4-phenylphenacyl ester, m. p. and mixed m. p. 81°.

2,2,4-*Trimethylpentan*-1-*ol*. The foregoing acid (23 g.) was boiled under reflux with lithium aluminium hydride (6 g.) in ether (200 ml.) for 2 hr. The required *alcohol*, which was isolated in the usual way, had b. p. 99°/55 mm., n_D^{20} 1·4310 (Found: C, 73·50; H, 13·9. $C_8H_{18}O$ requires C, 73·8; H, 13·9%). The 3,5-*dinitrobenzoate* crystallised from pentane in plates, m. p. 56° (Found: C, 55·3; H, 6·4. $C_{15}H_{20}N_2O_6$ requires C, 55·55; H, 6·2%).

When treated with toluene-*p*-sulphonyl chloride and pyridine in benzene the alcohol was converted into its *toluene*-p-*sulphonate*, which crystallised from methanol or pentane in plates, m. p. 29—30° (Found: C, 63·4; H, 8·5. $C_{15}H_{24}O_3S$ requires C, 63·4; H, 8·5%).

2,4,4-*Trimethylpentanoic acid*. A suspension of cuprous bromide (0·3 g.) in di-isobutene (250 ml.) was boiled under reflux (nitrogen) while t-butyl perbenzoate (50 g.) was added dropwise, with stirring, during 1 hr., and the mixture was then boiled for a further 3 hr. Benzoic acid (14 g.) was extracted from the cooled, filtered, mixture with aqueous sodium carbonate. Distillation of the organic layer yielded a mixture (39 g., 65%) of " iso-octenyl " benzoates, b. p. 79—85°/0·2 mm. A sample (30 g.) of the mixed benzoates in ethanol (150 ml.) was hydrogenated over Raney nickel at 60°/100 atm. After filtration the solution was evaporated and the residual crude mixture of " iso-octyl " benzoates was hydrolysed with potassium hydroxide (15 g.) in methanol (100 ml.). A mixture (13·4 g., 78%), b. p. 66—72°/15 mm., of 2,4,4-trimethylpentan-1-ol and 2,2,4-trimethylpentan-3-ol was obtained by fractional distillation of the crude product.

A solution of chromium trioxide (3 g.) in water (12·5 ml.) and sulphuric acid (5 ml.) was added dropwise, with stirring, to a sample (6·0 g.) of the mixed alcohols in acetone (25 ml.) until a permanent brown colour developed. The mixture was set aside at room temperature for 1 hr., then poured into water. Ether-extraction yielded neutral and acid fractions. Fractional distillation of the latter gave 2,4,4-trimethylpentanoic acid (3·4 g.), b. p. 118—120°/18 mm., n_D^{20} 1·4260 (lit.,[30] b. p. 109°/14 mm., n_D^{20} 1·4233) (Found: C, 67·0; H, 10·9. Calc. for $C_8H_{16}O_2$: C, 66·6; H, 11·2%). The amide crystallised from hexane in needles, m. p. 122° (lit.,[30] m. p.

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[28] Reformatsky, *Ber.*, 1895, **28**, 2842.

[29] Dox, *Org. Synth.*, 1925, **4**, 27.

[30] Whitmore, Noll, Heyd, and Surmantis, *J. Amer. Chem. Soc.*, 1941, **63**, 2028.

123°) (Found: C, 66·9; H, 11·8. Calc. for $C_8H_{17}NO$: C, 67·1; H, 12·0%). The *4-phenylphenacyl ester* formed needles from pentane, m. p. 83° (Found: C, 77·9; H, 7·7. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%).

When the first step in the synthesis was repeated with t-butyl perbenzoate (40 g.), cuprous bromide (0·3 g.), and di-isobutene (100 ml.) in acetic acid (100 ml.) the products were "iso-octenyl" acetates (22 g., 62%), b. p. 90—98°/30 mm., and benzoic acid (25 g.).

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