36. *Reduced Cyclic Compounds. Part X.** *The Synthesis of* 1-1′-*Acetoxyvinyl*-3,4-*dihydronaphthalene and its Reactions with Some Dienophils.*

By M. F. ANSELL and G. T. BROOKS.

The preparation of 1-1′-acetoxyvinyl-3,4-dihydronaphthalene and its reactions with maleic anhydride, benzoquinone, and 2,6-xyloquinone are described.

THE preparation of 1-1′-acetoxyvinylcyclohexene and its reactions with dienophils have been described.[1] We now report a similar study with 1-1′-acetoxyvinyl-3,4-dihydronaphthalene which was prepared by the reaction sequence (I) ⟶ (V). The reduction [2] of 1-naphthoic acid (I) to 1,4-dihydronaphthoic acid (II) by addition of sodium to a solution of the acid and sodamide in liquid ammonia could not be repeated, and reduction was conveniently effected by addition of sodium to a solution of the acid in liquid ammonia containing ethanol (cf. the reduction of *o*-toluic acid [3]). There is little agreement (see Experimental section) among the recorded melting points of 1,4-dihydronaphthoic acid (II) and it is possible that the reduction product may contain some of the 3,4-dihydro-acid (III). Various procedures have been described [4] for the conversion of the 1,4- into the 3,4-dihydro-acid (III). It was found that use of boiling 10% potassium hydroxide solution gave an acid whose melting point (119—120° on small scale, 115—119° on 0·3-molar scale) was close to the most reliable recorded value [5] (121°). The 3,4-dihydro-acid was converted into the acid chloride by treatment with thionyl chloride. The melting point of the derived amide was considerably higher than that recorded by Birch and Robinson,[6] but agreed with that reported earlier by Ranedo.[7] The acid chloride was readily converted into 1-acetyl-3,4-dihydronaphthalene (IV), but methylcadmium was

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* Part IX, *J.*, 1960, 5219.

[1] (a) Ansell and Brooks, *J.*, 1956, 4518; (b) Nazarov, Kucherov, Andreev, and Segal, *Doklady Akad. Nauk S.S.S.R.*, 1955, **104**, 729; (c) Winternitz and Balmossière, *Tetrahedron*, 1958, **2**, 100.

[2] Birch, *J.*, 1944, 430.

[3] Birch, *J.*, 1950, 1551.

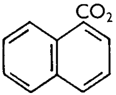
[4] Elsevier's "Encyclopedia of Organic Chemistry," Amsterdam, 1953, **12**, *B*, p. 4069.

[5] Fieser and Holmes, *J. Amer. Chem. Soc.*, 1936, **58**, 2319.

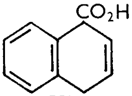
[6] Birch and Robinson, *J.*, 1944, 503.

[7] Ranedo, *Anales real Soc. españ. Fís. Quím.*, 1927, **25**, 429.

preferable to the dimethylzinc used by Birch and Robinson.[6] This ketone afforded a bright-red (characteristic of αβ-unsaturated ketones) 2,4-dinitrophenylhydrazone, different from that previously recorded [6] together with a small amount of an isomeric derivative. The latter was not identified, but may be a pyrazoline derivative.[8] The ultraviolet absorption spectrum of this ketone, which contains a cross-conjugated system, has a single maximum at 278 mμ. It is reported [9] that various 2-phenylcyclohex-2-enones which contain a similar cross-conjugated system, show absorption at 268—270 mμ. The more rigid chromophoric system in the ketone (IV) may explain the bathochromic shift in the ultraviolet absorption maximum of this ketone as compared with that of the 2-phenylcyclohex-2-enones. Treatment of 1-acetyl-3,4-dihydronaphthalene with isopropenyl acetate in the presence of toluene-*p*-sulphonic acid gave the expected 1-1′-acetoxyvinyl-3,4-dihydronaphthalene (V).



(I)



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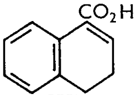

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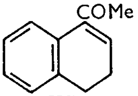

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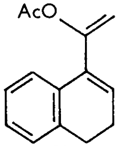

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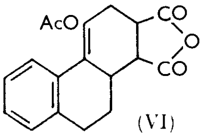

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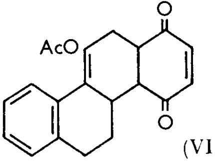

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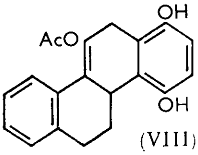
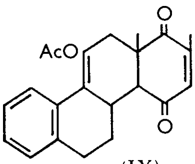
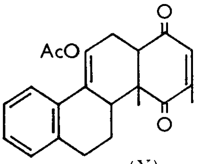


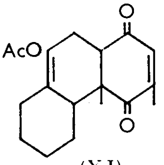
(VIII)



(IX)



(X)



(XI)

The diene (V) with maleic anhydride yielded 4-acetoxy-1,2,3,9,10,11-hexahydrophenanthrene-1,2-dicarboxylic anhydride (VI), which was hydrolysed by boiling water to the acid. The latter, as the dimethyl ester, formed a 2,4-dinitrophenylhydrazone, indicating the presence of a potential carbonyl group. The ultraviolet absorption spectrum of the free acid ($\lambda_{max.}$ 252 mμ in EtOH) resembles that recorded for β-methylstyrene [10] and 1-phenylcyclohexene [11] both of which contain a similar chromophore. Some similarity is also shown, with the expected hypsochromic shift due to the absence of the 7-methoxy-group, to the spectrum of 1,2,3,9,10,11-hexahydro-7-methoxyphenanthrene-1,2-dicarboxylic acid,[12] although the shoulder at long wavelength which has been used as a criterion of the presence of a 3,4-double bond is absent. There is no doubt, however, that the double bond is in this position, both from the conditions used to prepare the adduct and from the fact that the product forms a 2,4-dinitrophenylhydrazone.

With benzoquinone the diene (V) gave 11-acetoxy-1,4,5,6,10,13,14,15-octahydro-1,4-dioxochrysene (VII). The gross structure of this adduct was shown by its degradation to chrysene, and its detailed structure from its infrared absorption spectra which showed

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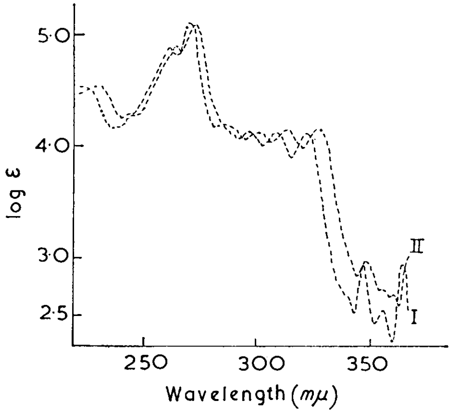
[8] Cf. Nazarov and Gurvich, *J. Gen. Chem. U.S.S.R.*, 1955, **25**, 1677.
[9] Bornstein, Pappo, and Szmuszkovicz, *Bull. Res. Council Israel*, 1952, **2**, 273.
[10] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," Chapman and Hall, London, 1951, spectrum no. 24.
[11] Carlin and Landerl, *J. Amer. Chem. Soc.*, 1953, **75**, 3969.
[12] Bachmann and Controulis, *J. Amer. Chem. Soc.*, 1951, **73**, 2636.

absorption at 5·7 μ, characteristic of the enol acetate group, together with the absence of absorption in the hydroxy-region [eliminating a structure such as (VIII)].

The Diels–Alder reaction of the diene (V) with 2,6-xyloquinone gave a single product, which existed in two polymorphic forms. This adduct may have either of the structures (IX) and (X), the latter being analogous to that (XI) of the adduct from 1-1′-acetoxyvinylcyclohexene and 2,6-xyloquinone. Degradation of the adduct (IX or X) by reduction with lithium aluminium hydride, followed by dehydration and dehydrogenation with selenium, did not give rise to either 2- or 3-methylchrysene (a synthesis of the latter is described), but to a substance whose ultraviolet spectrum shows a bathochromic shift of 4—5 mμ in the fine structure region as compared with 3-methylchrysene. Such a spectral shift is characteristic [13] of a dimethylchrysene (see Figure). The degradation product is not identical with any of the known dimethylchrysenes or with those subsequently synthesised.[14] These results although showing the tetracyclic skeleton of the Diels–Alder addition product from the diene (V) and 2,6-xyloquinone do not establish the position of the angular methyl group, which is tentatively assigned to the 14-position by analogy with the structure of the tricyclic adduct (XI).



Absorption spectra of (I) 3-*methylchrysene and* (II) *a degradation product* (? *a dimethylchrysene*) *in cyclohexane.*

Added in Proof.—Winternitz and Diaz (*Compt. rend.*, 1960, **250**, 3433; *Bull. Soc. chim. France*, 1959, **1444**) have reported the preparation of 1-1′-acetoxyvinyl-3,4-dihydronaphthalene from 1-acetyl-3,4-dihydronaphthalene obtained by a different route from that used by us. The ultraviolet spectrum of the diene is reported by Winternitz and Diaz to be at λ 233 (log ε 4·53) as compared with our value of λ 267 mμ (log ε 3·8). Absorption at λ 233 mμ is recorded [1] for the simple diene, 1-1′-acetoxyvinylcyclohexene, and in view of the discussion above it appears probable that cross conjugation with a phenyl group would alter this value, as the ultraviolet absorption maxima of the chromophores C=C–C=C and C=C–C=O are similar (cf. Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold and Sons, London, 1954).

EXPERIMENTAL

3,4-*Dihydro*-1-*naphthoic Acid.*—Sodium (35 g., 1·5 g.-atoms) was added in small pieces during 4 hr. to a stirred mixture of 1-naphthoic acid (86 g., 0·5 mole) in liquid ammonia (1200 ml.) and ethanol (78·2 g., 1·7 moles), contained in a Dewar vessel. The characteristic blue colour of sodium in liquid ammonia was not observed until towards the end of the addition. At this stage the reaction mixture became thick, and liquid ammonia was added to replace loss by evaporation. After being stirred for a further 3 hr. the mixture was left overnight under a stream of nitrogen. A solution of ammonium chloride (108 g.) in water (200 ml.) was then

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[13] Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 313.
[14] Ansell, Brooks, and Knights, *J.*, 1961, 212.

added and a fast stream of nitrogen passed through the mixture to expel excess of ammonia. 5N-Hydrochloric acid was added to bring the solution to pH 8, the hot solution was filtered (charcoal), the filtrate made strongly acid with hydrochloric acid, and the precipitated crude 1,4-dihydronaphthoic acid filtered off. The latter was dissolved in the minimum volume of dilute ammonia solution and treated with a saturated aqueous barium chloride until no further precipitation occurred. The precipitate (containing barium 1-naphthoate; cf. ref. 15) was filtered off and the filtrate, cooled in ice, was stirred and slowly acidified with 6N-hydrochloric acid. The granular buff-coloured precipitate was filtered off and washed with water. A sample of the acid, dried and recrystallised from light petroleum (b. p. 60—80°), had m. p. *ca.* 75° [recorded m. p.s for 1,4-dihydronaphthoic acid, 75° (ref. 3, 16), 91° (ref. 15, 17), and 86° (ref. 18)]. A solution of the remainder of the above acid 10% aqueous potassium hydroxide (850 ml.) was boiled for 1 hr. The cold solution was then filtered and adjusted to pH 8 by the addition of 6N-hydrochloric acid and filtered hot (charcoal). The filtrate, cooled in ice, was slowly acidified with 6N-hydrochloric acid. The precipitated solid was filtered off, washed with water, and dissolved in benzene. The residual water was separated from the benzene solution which was then evaporated to a small bulk. Addition of light petroleum (b. p. 60—80°) precipitated 3,4-dihydro-1-naphthoic acid (50 g.), m. p. 115—119°. Sowinski [16] and Birch [2] record m. p. 112°; Fieser [5] records m. p. 120—121°.

3,4-*Dihydro*-1-*naphthoyl Chloride*.—A mixture of 3,4-dihydro-2-naphthoic acid (155 g.) and thionyl chloride (250 ml.) was heated under reflux for 20 min. and then distilled to yield, after removal of excess of thionyl chloride, 3,4-dihydronaphthoyl chloride (159 g.), b. p. 113—114°/0·4 mm. The derived amide had m. p. 187—188° (after crystallisation from methanol) (Found: C, 76·0; H, 6·5; N, 8·2. Calc. for $C_{11}H_{11}NO$: C, 76·3; H, 6·4; N, 8·1%). Birch and Robinson [6] record b. p. 174°/14 mm., amide (not analysed) m. p. 128°. Ranedo [7] records b. p. 206°/65 mm., amide m. p. 185°.

1-*Acetyl*-3,4-*dihydronaphthalene*.—Anhydrous cadmium chloride (120 g.) was added to an ice-cold solution of methylmagnesium bromide (from magnesium 30 g.) in ether (500 ml.). The mixture was stirred and heated under reflux until it no longer gave a positive Gilman reaction (*ca.* 30 min.), and the ether then rapidly distilled off, leaving a partially solid residue. Dry benzene (500 ml.) was then added and distillation continued until the vapour temperature rose to *ca.* 70°. More benzene (50 ml.) was added and then to the vigorously stirred ice-cold solution was added during 10 min., a solution of 3,4-dihydro-1-naphthoyl chloride (155 g.) in benzene (200 ml.). After a short induction period the mixture became yellow and an exothermic reaction ensued, cooling being necessary to maintain a gentle reflux rate. Stirring was continued for 1¼ hr. after the exothermic reaction had ceased. The mixture was then poured on ice and 2N-hydrochloric acid, the benzene layer separated, and the aqueous layer extracted with ether. The combined organic solutions were washed with saturated brine and dried ($MgSO_4$). Distillation gave, after removal of the solvent, 1-acetyl-3,4-dihydronaphthalene (97 g.), b. p. 108—109°/0·09 mm., n_D^{17} 1·5891, $\lambda_{max.}$ 278 mμ (log ε 3·68) (Found: C, 83·4; H, 7·1. Calc for $C_{12}H_{12}O$: C, 83·7; H, 7·0%).

The derived 2,4-*dinitrophenylhydrazone* (red needles from benzene–alcohol) had m. p. 156—157°, $\lambda_{max.}$ (in cyclohexane) 360, 261 mμ (log ε 4·4 and 4·3) (Found: C, 61·3; H, 4·9; N, 15·9. $C_{18}H_{16}N_4O_4$ requires C, 61·4; H, 4·6; N, 15·9%). Chromatography of the residue from the mother-liquors from the foregoing crystallisation in benzene–light petroleum gave a further amount of the 2,4-dinitrophenylhydrazone, together with a small amount of an isomeric orange-yellow compound (prisms from benzene–light petroleum), m. p. 128—129°, $\lambda_{max.}$ (in cyclohexane) 352, 258 mμ (log ε 4·4, 4·3) (Found: C, 61·6; H, 4·5; N, 15·9%). The derived semicarbazone (needles from methanol) had m. p. 195—202°. The m. p. of this compound was dependent on the heating conditions, and the recorded value was obtained by heating from 180° (initial bath-temperature) at 2° per min. (Found: C, 68·1; H, 6·5; N, 18·3. Calc. for $C_{13}H_{15}N_3O$: C, 68·1; H, 6·6; N, 18·3%).

Birch and Robinson [6] record b. p. 165°/11 mm. [2,4-dinitrophenylhydrazone (not analysed), orange-red prisms, m. p. 119—120°; semicarbazone, m. p. 208°].

1-1′-*Acetoxyvinyl*-3,4-*dihydronaphthalene*.—1-Acetyl-3,4-dihydronaphthalene (92 g.) was

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[15] Baeyer, *Annalen*, 1891, **266**, 175.
[16] Sowinski, *Ber.*, 1891, **24**, 2355.
[17] Rupe, *Annalen*, 1903, **327**, 186.
[18] von Auwers and Möller, *J. prakt. Chem.*, 1925, **109**, 144.

added to a boiling mixture of isopropenyl acetate (1050 ml.) and toluene-*p*-sulphonic acid (9·5 g.). The mixture was slowly distilled through a 36″ column packed with Fenske helices. After 4 hr. 27 g. of acetone had been removed, more isopropenyl acetate (100 ml.) was added, and the distillation was continued overnight. The residual liquid was then concentrated to half-bulk by distillation, cooled, and then diluted with an equal volume of ether, washed with 10% aqueous sodium hydrogen carbonate and saturated brine, and dried ($MgSO_4$). The solution was distilled under reduced pressure (vapour temperature up to 40°) and the residue distilled to yield, after a small forerun, 1-1′-*acetoxyvinyl*-3,4-*dihydronaphthalene* (80 g.), b. p. 116—118°/1 × 10^{-2} mm., n_D^{14} 1·5720, $\lambda_{max.}$ 219, 267 mμ (log ε 4·29, 3·8) (Found: C, 78·7; H, 6·8%; *M*, 198. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%; *M*, 214). Treatment with Brady's reagent gave a derivative identical with the " red " derivative obtained from the parent ketone.

4-*Acetoxy*-1,2,3,9,10,11-*hexahydrophenanthrene*-1,2-*dicarboxylic Anhydride*.—A solution of the above acetoxy-diene (2·2 g.) and maleic anhydride (1·0 g.) in dry thiophen-free benzene was left at room temperature for 4 days and then boiled under reflux for 1½ hr. and the solvent removed under reduced pressure. The residue readily solidified and was washed with ether and crystallised from ether–methylene chloride to yield 4-*acetoxy*-1,2,3,9,10,11-*hexahydrophenanthrene*-1,2-*dicarboxylic anhydride* (1·7 g.), m. p. 169—170° (Found: C, 69·2; H, 5·2%; *M*, 312. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%; *M*, 329). Hydrolysis of this anhydride with boiling water gave the parent *acid*, m. p. 220—227° (with effervescence) (bath initially at 210°), $\lambda_{max.}$ 252 mμ (log ε 4·1) (Found: C, 65·0; H, 5·4. $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·5%). Treatment of this acid with diazomethane in chloroform converted it into the methyl ester which with Brady's reagent (prepared in methanol) gave *dimethyl* 1,2,3,4,9,10,11,12-*octahydro*-4-*oxophenanthrene*-1,2-*dicarboxylate* 2,4-*dinitrophenylhydrazone* as yellow needles (from benzene), m. p. 209—210°, $\lambda_{max.}$ (in EtOH) 363, 263 mμ (log ε 4·2, 4·0) (Found: C, 58·2; H, 4·8; N, 11·3. $C_{24}H_{24}N_4O_8$ requires C, 58·1; H, 4·9; N, 11·3%).

11-*Acetoxy*-1,4,5,6,12,13,14,15-*octahydro*-1,4-*dioxochrysene*.—A solution of the acetoxydiene (8·8 g.) and *p*-benzoquinone (4·0 g.) in benzene (100 ml.) containing a little quinol was heated under reflux for 8 hr. after which the solvent was removed under reduced pressure. The residual solid (5·0 g.) was washed with a little ether and crystallised successively from benzene and methanol, to yield 11-*acetoxy*-1,4,5,6,12,13,14,15-*octahydro*-1,4-*dioxochrysene*, m. p. 175—185° (flocculent needles). Further recrystallisation did not improve the m. p. The product gave no colour with ethanolic ferric chloride, and its infrared spectrum showed no absorption in the hydroxyl region (Found: C, 74·3; H, 5·9%; *M*, 327. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%; *M*, 322).

Degradation of 11-*Acetoxy*-1,4,5,6,12,13,14,15-*octahydro*-1,4-*dioxochrysene*.—The above adduct (2 g.) was boiled with a 4 : 1 mixture (20 ml.) of ethanol and 10% hydrochloric acid for 8 hr. The mixture was then evaporated under reduced pressure, and the residue was heated with 5% palladium–charcoal (1 g.) at 320° for 5 hr. during which a small amount of chrysene sublimed. The whole of the reaction mixture was mixed with zinc powder (2 g.), sodium chloride (2 g.), and anhydrous zinc chloride (1 g.), and covered with an equal volume of zinc powder. The latter was heated to dull redness, and the mixture then heated to the same temperature. The sublimate which collected in the cool part of the tube was collected, boiled with dilute sodium hydroxide solution, and crystallised from benzene and aqueous acetic acid, giving chrysene (0·3 g.), m. p. and mixed m. p. 250—252° (recorded [19] m. p. 254).

Reaction of 1-1′-*Acetoxyvinyl*-3,4-*dihydronaphthalene with* 2,6-*Xyloquinone*.—A solution of the diene (17·1 g.), 2,6-xyloquinone (8·0 g.), and quinol (0·12 g.) in absolute ethanol (120 ml.) was heated under reflux for 24 hr., and then evaporated at 15 mm. The residue, on treatment with light petroleum (b. p. 60—80°) and ether, gave 11-*acetoxy*-1,4,4a,4b,5,6,12,12a-*octahydro*-xx-*dimethyl*-1,4-*dioxochrysene* (5·5 g.), m. p. 121—122·5°. Heating for 50 hr. did not improve the yield, and a lower yield was obtained with benzene as the solvent. The product exists in two forms; in some experiments the crude material had m. p. 146—149°. Recrystallisation of either form gave pale yellow needles, m. p. 123—125°, $\lambda_{max.}$ (in cyclohexane) 241 mμ (log ε 4·4) (Found: C, 75·3; H, 6·4%; *M*, 330. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%; *M*, 350).

Degradation of the above adduct. The above adduct (4·7 g.) was reduced twice with lithium aluminium hydride (1·3 g.), and the product heated with potassium hydrogen sulphate (11 g.) as described [1a] for 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-1,4-dioxophenanthrene. The dehydrated material (3·0 g.) was heated with selenium (13 g.) at 350° for 24 hr. The cold residue was extracted

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[19] Baxter and Hale, *J. Amer. Chem. Soc.*, 1937, **59**, 506.

with benzene, and the extract filtered through a short column of alumina (Peter Spence Type H) and then evaporated. The residual oil (2 g.), on treatment with benzene and alcohol, partially solidified. The solid was filtered off. The liquid product on treatment with a saturated alcoholic solution of picric acid gave a red picrate (m. p. 170—176° after recrystallisation), which on treatment with ammonia gave the parent hydrocarbon which was combined with the solid previously obtained. Recrystallisation of this material from ethanol and then light petroleum gave a compound, m. p. 173—175° (mixed m. p. with 3-methylchrysene 161—168°) which from its ultraviolet absorption spectrum is considered to be a *dimethylchrysene* (Found: C, 92·6; H, 6·2. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%).

4-*Methyl*-1-(2-1′-*naphthylethyl*)*cyclohexanol*.—A solution of 4-methylcyclohexanone (31 g.) in ether (30 ml.) was added slowly to a stirred ice-cold solution of the Grignard reagent prepared from 2-1′-naphthylethyl chloride (48 g.) and magnesium (6 g.) in ether (130 ml.). After the addition the mixture was stirred for 1 hr. at room temperature, left overnight, and then poured on ice and ammonium chloride. The aqueous layer was extracted with ether. Evaporation, at 100°/14 mm., of the dried ($MgSO_4$) combined extracts gave crude 4-*methyl*-1-(2-1′-*naphthylethyl*)*cyclohexanol* (47 g.). A redistilled sample (b. p. 198—200°/0·5 mm.) solidified and had m. p. 68—69° after crystallisation from light petroleum (b. p. $<40°$) (Found: C, 84·4; H, 8·7. $C_{19}H_{24}O$ requires C, 85·0; H, 9·0%).

3-*Methylchrysene*.—The above crude alcohol was heated with glacial acetic acid (200 ml.) and concentrated sulphuric acid (20 ml.) on a steam-bath for 1 hr. with stirring, cooled, diluted with water, and extracted with benzene. The extract was washed with 85% sulphuric acid and then 10% sodium carbonate solution, dried ($MgSO_4$), and evaporated. Distillation of the residue (from sodium) at 0·5 mm. gave a colourless syrup (11 g.). A portion (4 g.) of the latter was heated with selenium (10 g.) at 300—310° for 12 hr. The cold residue was extracted with benzene. The residue obtained on evaporation of the solvent was crystallised from benzene–alcohol and sublimed (220°/0·5 mm.), to yield 3-methylchrysene, m. p. 173·5—174·5°. The derived picrate (orange needles from alcohol) had m. p. 165—166°. Wilds [20] records m. p.s 172·5—173·5° and 166—167·5° respectively.

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[20] Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469.