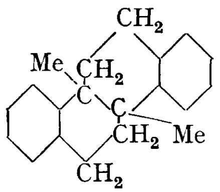
346. *Symmetrical Derivatives of Chrysene. Part II. Elimination of Methyl Groups during Dehydrogenation in an Attempt to Prepare* 1 : 10-*Dimethylchrysene.*

By W. Elwyn Jones and G. R. Ramage.

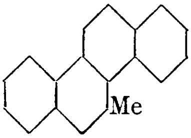
In an attempt to prepare homologues of chrysene it has been found that methyl groups attached to the 1- and 10-positions (numbering on III) in a reduced chrysene ring system are eliminated during selenium dehydrogenation, and therefore resemble groups in angle positions. This phenomenon is possibly related to R. D. Haworth's results in the phenanthrene series, in which a methyl group in an analogous position migrates to a vacant *p*-position. The compounds now examined are (X, R = H) and (X, R = Me), which were reduced by the Clemmensen method and on dehydrogenation gave chrysene and a small amount of a methylchrysene, m. p. 151° (possibly II).

For the examination of the products of the selenium dehydrogenation of *cis*- and *trans*-dimethylhexahydrochrysenes (I) referred to in Part I (this vol., p. 397), it was soon found that analytical data on the trinitrobenzene derivatives isolated would not serve to distinguish between monomethyl- and dimethyl-chrysenes of anticipated structures (II) and (III). Since the parent hydrocarbons could not be readily recovered, it was desirable to have available for comparison corresponding derivatives of synthetic specimens of these chrysene homologues.

It was considered that the symmetrical 1 : 10-dimethylchrysene (III) would be readily obtained by the method of double ring closure of the appropriately substituted diphenyladipic acids (J., 1933, 607). Unfortunately, an aluminium amalgam reduction of methyl α-methylcinnamate in ethereal solution was found to give methyl β-phenyl-α-methylpropionate almost quantitatively and none of the required bimolecular products. An alternative lay in reducing ethyl benzylidenemalonate, since Henle (*Annalen*, 1906, **348**, 29) noticed the formation of a bimolecular product and Vogel (J., 1928, 1019) separated this into ethyl *meso*- and *r*-βγ-diphenylbutane-ααδδ-tetracarboxylates, a substance, m. p. 88°, being then given the racemic configuration. Repeated attempts to methylate the crystalline ethyl ester with sodium or potassium ethoxide or sodamide in dry alcohol or benzene solution, and methyl iodide or methyl sulphate, failed. The tetracarboxylate was always recovered unchanged whatever the procedure, as shown by its m. p. and mixed m. p., and on one occasion the product was treated with 85% sulphuric acid, the ketone (V) obtained being identical with the *trans*-form previously described (J., 1933, 609), which confirms Oommen and Vogel's view (J., 1930, 2150) that the ester, m. p. 88°, must be the *meso*-form (IV) and brings this reduction into line with the formation of the methyl diphenyladipates, in which the *meso*-form of the ester is most readily isolated in a crystalline condition.



(I.)



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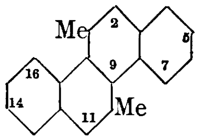

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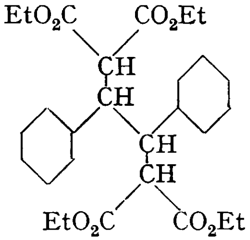

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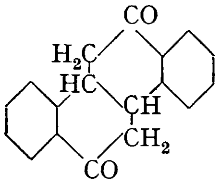

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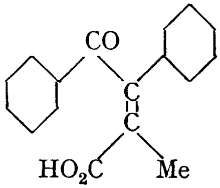
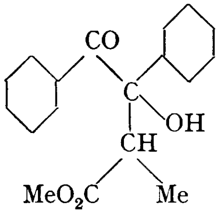


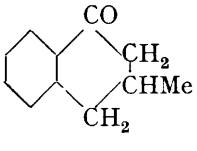
(VI.)

The Reformatsky reaction between benzil and methyl α-bromopropionate was investigated and two products were obtained. One, m. p. 235°, was an *acid* agreeing in properties and analysis with the formula (VI) and the second, m. p. 83°, was *methyl β-hydroxy-β-benzoyl-β-phenyl-α-methylpropionate* (VII), since it gave (VI) on dehydration with potassium hydrogen sulphate, followed by hydrolysis. The ease with which hydrolysis had occurred to give the acid is surprising, but the poor yields precluded any attempt at a second treatment to get the desired products.

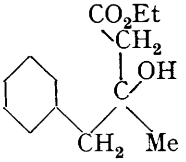
Finally, it was necessary to employ the general method of Rapson and Robinson (J., 1935, 1285) and the chrysene skeleton has been built up by condensing the sodio-derivative of 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (VIII) with *propionyl*cyclo*hexene*. The tetralone resulted from a Reformatsky reaction with ethyl bromoacetate on benzyl methyl ketone, giving the hydroxy-ester (IX), which was dehydrated, the product catalytically reduced to *ethyl β-benzyl*-n-*butyrate*, and this cyclised by 85% sulphuric acid. From the condensation, 2-*keto*-1 : 10-*dimethyl*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11-*decahydrochrysene* (X, R = Me) was obtained, m. p. 104°, and the product from a Clemmensen reduction, which was still unsaturated but was not obtained crystalline, was submitted to selenium dehydrogenation. After 72 hours at 280—300°, no solid product could be isolated, but at 360° a semi-solid gum was obtained; this was crystallised from benzene and found to be chrysene, m. p. 248° (trinitrobenzene derivative, m. p. 186°). From the mother-liquor, further amounts of chrysene first separated, followed by a methylchrysene, m. p. 151°, in very small amount. The total yield of material recovered from the dehydrogenation was surprisingly low, but could be increased by subliming the hydrocarbon under reduced pressure from the excess of selenium. It will be seen from the experimental section that chrysene is the only product readily isolated, and as analytically pure dimethylketone (X, R = Me) was employed, it is evident that methyl groups have been eliminated, although not in angle positions.



(VII.)

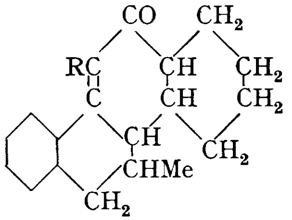


(VIII.)

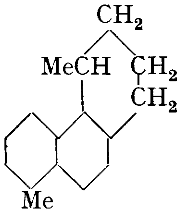


(IX.)

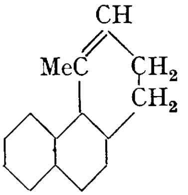
A similar result followed when the methyl-α-tetralone was condensed with acetyl*cyclo*hexene, a mixture of ketomethylchrysenes being isolated. By fractional crystallisation a homogeneous *ketone* (X, R = H), m. p. 132°, was found to be the principal component, and a second *isomer*, m. p. 165°, was obtained in small amount. The former was reduced by the Clemmensen method, and the product heated with selenium for three days to give chrysene and in much smaller amount the methylchrysene, m. p. 151°, obtained above. It is remarkable that during the treatment of the two hydrocarbons methyl groups should be eliminated and the problem is to be further investigated, particularly since Cook (J., 1930, 1088) has shown that α-methyl groups in the anthracene series are often split off by pyrolysis alone.



(X.)



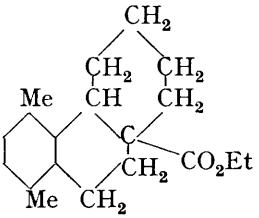
(XI.)

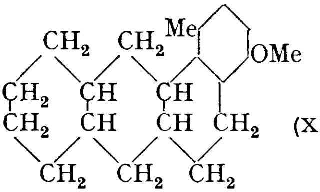


(XII.)

In this connection the work of Haworth on the alkylphenanthrenes (J., 1934, 454) shows the strong tendency of a methyl group in an analogous position to undergo migration to the *p*-position, *e.g.*, the dehydrogenation of (XI) gave 1 : 8-dimethylphenanthrene and very little of the expected 1 : 5-compound. Further, the absence of a hydrogen atom from the carbon carrying the methyl group produces stability, since (XII) was dehydrogenated smoothly to 4-methylphenanthrene; similarly, Bardhan and Sen-Gupta (J., 1932, 2522) dehydrogenated (XIII) to 1 : 4-dimethylphenanthrene.

(XIII.)





(XIV.)

In the dehydrogenation now described, the methyl groups are extremely labile, even in the dimethyl series when one group possibly adjoins a double bond. Further, the benzene nucleus rules out the possibility of elimination occurring through a migration to a *p*-position giving rise to an angle methyl group. With reference to the chrysene homologue isolated, it is most likely 1-methylchrysene (II), although the possibility of migration cannot be overlooked. Recently Cook and Robinson (this vol., p. 506) noticed that an attempted dehydrogenation of (XIV) gave a complex mixture of products, from which the only pure compound isolated, in small yield, was 1 : 2-benzanthracene, and it is possible that this represents the same phenomenon in operation with the methyl group again rendered labile under the influence of the methoxy-group.

EXPERIMENTAL.

Ethyl meso-*βγ-Diphenylbutane-ααδδ-tetracarboxylate* (IV).—Ethyl benzylidenemalonate (30 g.) on reduction gave ethyl benzylmalonate (21 g.), b. p. 129°/2 mm., which was removed by distillation, and the undistilled residue (6·2 g.) and ethyl alcohol (20 c.c.) deposited ethyl diphenylbutanetetracarboxylate (2·4 g.), which crystallised from alcohol in needles, m. p. 86° (Vogel records m. p. 88°).

trans-2 : 11-*Diketo*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene* (V).—The above ester (1·5 g.) was heated with sulphuric acid (85%) for 3 hours, and the *trans*-diketone precipitated with water; it crystallised from butyl alcohol in plates, m. p. 293°, identical with those previously described (J., 1933, 609).

Reformatsky Reaction.—A mixture of benzil (12 g.), methyl α-bromopropionate (15 g.), and zinc filings (11 g.) in dry benzene (45 c.c.) was refluxed on the water-bath, a trace of methylmagnesium iodide in ethereal solution being necessary to bring about reaction. After 3 hours' heating, the cooled mixture was treated with an excess of dilute sulphuric acid, and the benzene layer separated. On standing, *β-benzoyl-α-methylcinnamic acid* (2·2 g.) separated; it was crystallised from benzene, m. p. 235° (Found: C, 76·7; H, 5·2. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). The benzene was removed from the mother-liquor under reduced pressure, and the residual gum dissolved in a little methyl alcohol. *Methyl β-hydroxy-β-benzoyl-β-phenyl-α-methylpropionate* separated and crystallised from this solvent in needles, m. p. 83° (Found: C, 72·4; H, 6·0. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%). When the hydroxy-ester was dehydrated by heating with powdered potassium hydrogen sulphate and the resulting unsaturated ester was isolated and hydrolysed with alcoholic potassium hydroxide, β-benzoyl-α-methylcinnamic acid, m. p. 235°, identical with that described above, was obtained.

1-*Propionyl*cyclo*hexene.*—*cyclo*Hexene (21 g.) and propionyl chloride (24 g.) were mixed and added to a stirred solution of anhydrous stannic chloride (63 g.) in dry carbon disulphide (150 g.), the temperature being kept near − 10°. After standing over-night, ice-water was added, the carbon disulphide solution separated and dried, and the solvent distilled. The residue was heated with diethylaniline (24 g.) at 180° for 3 hours, cooled, shaken with an excess of dilute hydrochloric acid, and extracted with ether. On fractionation 1-*propionyl*cyclo*hexene* was obtained as a colourless oil (13 g.), b. p. 101—102°/14 mm. (Found: C, 78·0; H, 10·2. $C_9H_{14}O$ requires C, 78·3; H, 10·1%). The *oxime* crystallised in long colourless needles, m. p. 78° (Found: C, 70·3; H, 9·6. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%), and the *semicarbazone* in small colourless plates, m. p. 189° (Found: C, 61·9; H, 8·6. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·7%), both from alcohol. Wallach (*Annalen*, 1908, **360**, 57) claims to have isolated this ketone, b. p. 218°, semicarbazones, m. p. 160—170° and m. p. 179—180°, and Bergs (*Ber.*, 1934, **67**, 242) prepared the ketone and its oxime, m. p. 76°, but these workers record no analyses.

Benzyl Methyl Ketone.—An intimate mixture of calcium phenylacetate (1 mol.) and calcium acetate (2 mols.) (Ludlam, J., 1902, **81**, 1185) was heated in a combustion tube in a nitrogen atmosphere. The distillate (from 108 g. of phenylacetic acid) on fractionation gave benzyl methyl ketone (46 g.), b. p. 105°/15 mm. The barium salts cannot be profitably substituted, since the mixture fuses too readily and the yield is considerably lower.

*Ethyl β-Benzyl-*n*-butyrate.*—The Reformatsky reaction with benzyl methyl ketone (10·5 g.) gave ethyl β-hydroxy-β-benzyl-*n*-butyrate (16 g.), b. p. 160—165°/15 mm. (Found: C, 70·1; H, 7·9. Calc.: C, 70·3; H, 8·1%) (Attwood, Stevenson, and Thorpe J., 1923, **123**, 1765). The corresponding *methyl* ester prepared from methyl bromoacetate had b. p. 151—152°/15 mm. (Found: C, 69·4; H, 7·6. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). Ethyl hydroxybenzylbutyrate (16 g.) was heated with powdered potassium hydrogen sulphate (20 g.) at 180° for 4 hours, water added, and the oil extracted with ether. After complete removal of the solvent the dehydration was repeated and the unsaturated *ethyl* ester (11·5 g.) was then isolated and fractionated, b. p. 155—157°/14 mm. (Found: C, 76·4; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). The corresponding unsaturated *methyl* ester, b. p. 140—141°/14 mm., was not so pure (Found: C, 75·0; H, 7·1. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). On reduction in absolute-alcoholic solution with palladium norit (2·0 g., 10%) the ethyl ester (11·5 g.) readily took up hydrogen at atmospheric pressure in the early stages, but the reduction proceeded to completion only slowly. After filtration, and distillation of the alcohol *ethyl* β-*benzyl*-n-*butyrate* (8·5 g.) distilled, b. p. 133°/12 mm. (Found: C, 75·3; H, 8·5. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

1-*Keto*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VIII).—Ethyl β-benzyl-*n*-butyrate (16 g.) was added to concentrated sulphuric acid (150 c.c.) and water (45 c.c.) and heated on the water-bath for 2 hours. After dilution with ice-water, the mixture was extracted with ether, and the extract fractionated, giving the methyltetralone (9·0 g.), b. p. 138°/11 mm. (Found: C, 82·1; H, 7·8. Calc.: C, 82·5; H, 7·5%). The semicarbazone crystallised from ethyl alcohol in rectangular plates, m. p. 189° (Found: C, 66·5; H, 6·9. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9%), and the 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate by addition of alcohol to the hot solution, which was then allowed to cool, or from *cyclo*hexyl acetate in bright red needles, m. p. 242° (Found: C, 59·9; H, 5·0. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·7%). Von Braun and Stuckenschmidt (*Ber.*, 1923, **61**, 1728) prepared this methyltetralone by an alternative route and record b. p. 127—128°/13 mm.; semicarbazone, m. p. 177°.

2-*Keto*-1 : 10-*dimethyl*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11-*decahydrochrysene* (X, R = Me).—The methyltetralone (7·5 g.) and powdered sodamide (2·2 g.) in dry ether (35 c.c.) were stirred for 6 hours, refluxed next day with stirring for 4 hours, and ice-cooled, and propionyl*cyclo*hexene (6·5 g.) in dry ether (10 c.c.) added dropwise. After being stirred for 12 hours, the mixture was refluxed for 4 hours, acidified with dilute sulphuric acid, and extracted with ether. The solvent and unchanged ketones were removed in steam and the non-volatile oil was extracted with ether, from which a brown oil (5·5 g.) was obtained which partly crystallised (3·5 g.) from ethyl alcohol and after several crystallisations gave a *ketodimethyldecahydrochrysene*, m. p. 104°, in large prisms (Found: C, 85·4; H, 8·8. $C_{20}H_{24}O$ requires C, 85·7; H, 8·6%). It was unchanged after boiling with semicarbazide acetate, but gave a 2 : 4-dinitrophenylhydrazone.

Selenium Dehydrogenation of the Dimethyldecahydrochrysene.—The above ketone (2 g.) was reduced by the Clemmensen method after 12 hours' boiling, the hydrocarbon being recovered with benzene and the solvent removed (under reduced pressure in final stages), leaving an unsaturated non-ketonic residue, to which selenium (4 g.) was added. Dehydrogenation proceeded on heating at 280°, raised to 320°, and was finally completed at 360°, the mixture being kept for 24 hours at each temperature. The upper part of the tube was occasionally heated to keep the material in contact with the selenium, but only in the later stages was there any evidence of crystallisation. Finally, the product was extracted with benzene, the selenium being repeatedly melted under reduced pressure to allow a complete recovery of hydrocarbon. The solvent was removed from the combined benzene extracts, and the residue (0·8 g.) distilled under reduced pressure from sodium and dissolved in a little benzene. The material which separated on cooling was filtered off, crystallised, and found to be chrysene, m. p. and mixed m. p. 248° (Found: C, 94·5; H, 5·4. Calc.: C, 94·7; H, 5·3%); trinitrobenzene derivative, m. p. 186°. The benzene was removed from the original mother-liquor, the oil dissolved in alcohol, the solution cooled, and a further quantity of chrysene filtered off. On concentration of the mother-liquor needles separated; after several crystallisations this substance had m. p. 151° and was identical with the methylchrysene described below.

2-*Keto*-10-*methyl*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11-*decahydrochrysene* (X, R = H).—1-Acetyl-*cyclo*hexene (6·0 g.) was substituted for the propionyl*cyclo*hexene in the preparation of the ketodimethyldecahydrochrysene, and the mixture stirred for 12 hours but not refluxed. The residue, after steam distillation, proved to be a mixture of ketones (3·9 g.), usually m. p. about 120°, which, on repeated crystallisation from alcohol, gave a homogeneous *ketomethyldecahydrochrysene* (2·5 g.), m. p. 132°, as needles (Found: C, 85·4; H, 8·2. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%). The *semicarbazone* was readily prepared and crystallised from alcohol, m. p. 227° (Found: C, 74·1; H, 8·1. $C_{20}H_{25}ON_3$ requires C, 74·3; H, 7·7%), and the 2 : 4-*dinitrophenylhydrazone* crystallised from *cyclo*hexyl acetate in needles, m. p. 210° (Found: C, 67·1; H, 6·1. $C_{25}H_{26}O_4N_4$ requires C, 67·3; H, 5·8%). By fractional crystallisation of the ketone mother-liquor a second *isomer* was obtained pure in small amount and crystallised in prisms, m. p. 165° (Found: C, 85·3; H, 8·2. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%), but a considerable fraction was never satisfactorily separated. It was found that refluxing the ethereal solution during the condensation increased the yield (5·0 g.), but the mixture was difficult to separate, giving only 1·3 g. of ketone, m. p. 132°.

Selenium Dehydrogenation of Methyldecahydrochrysene.—The pure ketone (4·0 g.), m. p

132°, was reduced by the Clemmensen method, and the product dehydrogenated with selenium exactly as described above. The hydrocarbon (1·2 g.) recovered was distilled from sodium and on fractional crystallisation gave chrysene (0·7 g.), a methylchrysene (0·1 g.), and non-crystallisable material (0·3 g.). The *methylchrysene* crystallised in fine needles, m. p. 151°, from alcohol, the solution showing a slight purple fluorescence (Found: C, 94·3; H, 5·7. $C_{19}H_{14}$ requires C, 94·2; H, 5·8%). The *trinitrobenzene* derivative crystallised from alcohol in bright yellow needles, m. p. 184—185° (Found: C, 66·4; H, 3·9. $C_{19}H_{14},C_6H_3O_6N_3$ requires C, 65·9; H, 3·7%), and the picrate was prepared in alcohol solution as fine orange needles, m. p. 162°, but on attempted crystallisation the hydrocarbon was recovered; a styphnate was not formed.

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