

**296.** *Studies on the Diels–Alder Reaction. Part II.\* The Reaction between Methylvinylcyclohexene and Benzoquinone.*

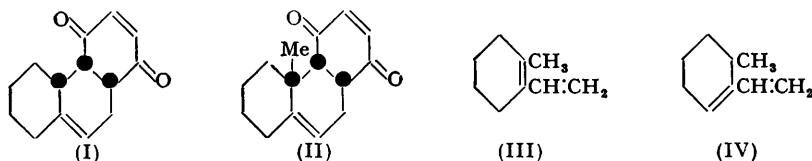
By P. A. ROBINS and JAMES WALKER.

Specimens of methylvinylcyclohexene, derived from the solid and liquid geometrically stereoisomeric forms of 1-ethynyl-2-methylcyclohexanol, appear to consist of mixtures of isomeric dienes, 1-methyl-2-vinyl- (III) and 3-methyl-2-vinyl-cyclohexene (IV), of which only the latter participates with benzoquinone in the Diels–Alder reaction, giving  $\Delta^{2:9(14)}$ -decahydro-1 : 4-diketo-8-methylphenanthrene (VII). The structure of (VII) was proved by conversion into 1-methyl- and 1 : 8-dimethyl-phenanthrene, and a number of reduction products are described.

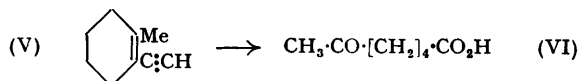
IN a previous paper \* we have described the Diels–Alder reaction between 1-vinylcyclohexene and benzoquinone, together with a study of the reduction, under a variety of conditions, of the resulting  $\Delta^{2:9(14)}$ -decahydro-1 : 4-diketophenanthrene (I). This work has now been extended with the intention of studying the 13-methyl homologue (II), which, however, we have not yet succeeded in obtaining. For the synthesis of (II), authentic 1-methyl-2-vinylcyclohexene (III) was required, and, notwithstanding the paucity of examples in the literature of the successful use of 1 : 1-disubstituted butadienes in the Diels–Alder reaction (cf. Kloetzel, *Org. Reactions*, **4**, 1; Holmes, *ibid.*, p. 60; Butz, *ibid.*, **5**, 136), there seemed good reason, in view of the seemingly convincing work of Wang

\* Part I, *J.*, 1952, 642.

and Hu (*J. Chinese Chem. Soc.*, 1943, 10, 1) discussed below, to believe that (II) would result from the Diels–Alder reaction between (III) and benzoquinone.

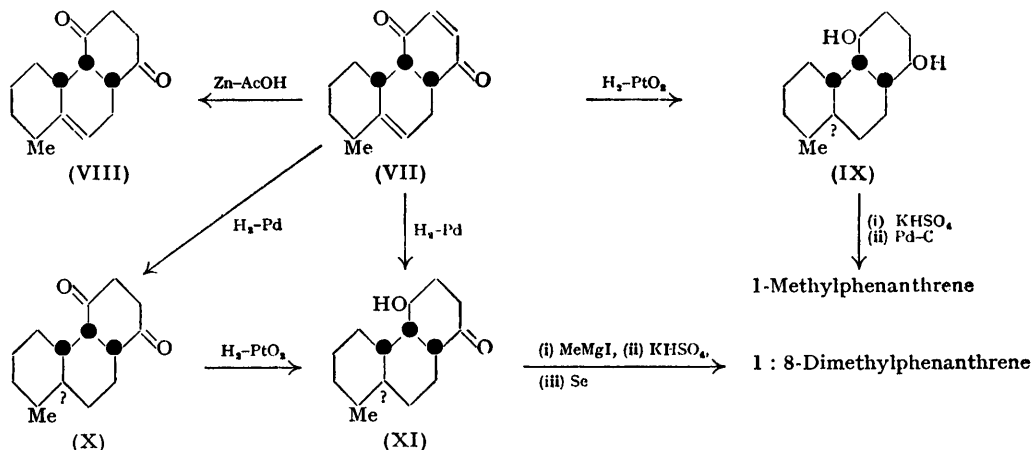


In addition to the experimental difficulties associated with obtaining pure specimens of vinylcyclohexene for use in the Diels–Alder reaction, discussed in our previous paper, the presence of the methyl substituent introduces a possibility of structural isomerism in the diene, which, as Wang and Hu indicated (*loc. cit.*), had previously been overlooked (cf. Cook and Lawrence, *J.*, 1938, 58). Two geometrically stereoisomeric forms are produced in the preparation of 1-ethynyl-2-methylcyclohexanol and these are relatively easily separated, since one is a solid and crystallises out (Wang and Hu, *loc. cit.*; Milas, MacDonald, and Black, *J. Amer. Chem. Soc.*, 1948, 70, 1829). On hydrogenation these two stereoisomerides afford stereoisomeric 2-methyl-1-vinylcyclohexanols, and these, on dehydration, give what may for convenience be termed methylvinylcyclohexene-*s* and methylvinylcyclohexene-*l* respectively, *s* and *l* denoting derivation respectively from solid and liquid stereoisomeric acetylenic alcohols. According to Wang and Hu (*loc. cit.*), these hydrocarbons, which they prepared by essentially the same method as we have used, yielded products with maleic anhydride which passed respectively on dehydrogenation into naphthalene-1 : 2-dicarboxylic anhydride and its 5-methyl derivative. From this evidence, methylvinylcyclohexene-*s* would appear to be 2-methyl-1-vinylcyclohexene (III) and methylvinylcyclohexene-*l* to be 3-methyl-2-vinylcyclohexene (IV), and, on the basis of *trans*-elimination of water, the solid acetylenic alcohol would thus appear to have the *trans*- and the liquid form the *cis*-structure. These configurations for the acetylenic alcohols are, however, contrary to those assigned by Milas *et al.* (*loc. cit.*) on the basis of the relative yields of the ethynylcyclohexenes obtained on dehydration over aluminium phosphate at 290–295°. Moreover, it may be noted that essentially the same ethynylmethylcyclohexene (V) was obtained by Milas and his collaborators from both alcohols since ozonolysis of enyne-*s* and of enyne-*l* gave in each case 6-ketoheptanoic acid (VI).



On allowing our methylvinylcyclohexene-*s* and -*l* to react with benzoquinone, we obtained comparable yields in the two cases of the same  $\Delta^{2:9(14)}$ -decahydro-1 : 4-diketomethylphenanthrene, which further study has conclusively shown to be the 8-methyl derivative (VII), and not (II), since it could be converted, as described below, into 1-methyl- and 1 : 8-dimethyl-phenanthrene. Furthermore, as only (VII) was obtained and no other decahydrodiketomethylphenanthrene could be isolated, it is obvious that, under the relatively standard conditions used, the specimens of methylvinylcyclohexene-*s* and -*l*, which we had obtained, were probably similar mixtures of (III) and (IV), of which only the latter participated readily in the Diels–Alder reaction with benzoquinone, giving (VII). In order to ascertain whether the 2-methyl-1-vinylcyclohexene (III) would react under more vigorous conditions, addition of benzoquinone to diene-*s* was carried out in boiling benzene : the sole product was (VII). Attempts to increase the vigour of the conditions, *e.g.*, by use of a benzene solution at 100° in a sealed vessel, gave only dark brown tarry products from which no recognisable material could be isolated. One may conclude therefore that, if benzoquinone is to be used to furnish ring c in a steroid synthesis, it will be essential to avoid the use of a 1 : 1-disubstituted diene in any Diels–Alder reaction intended for this purpose and to attach rings B and A, as well as, of course, ring D, in separate stages.

By the techniques described in our previous paper, reduction of (VII) with zinc and acetic acid gave  $\Delta^9(14)$ -dodecahydro-1 : 4-diketo-8-methylphenanthrene (VIII), and perhydrogenation in the presence of Adams's catalyst yielded perhydro-1 : 4-dihydroxy-8-methylphenanthrene (IX), of which one pure stereoisomeric form has been isolated. Dehydration of the mixed stereoisomeric diols (IX) with potassium hydrogen sulphate, followed by dehydrogenation with palladised charcoal, yielded 1-methylphenanthrene, having characteristically the highest melting point among monomethylphenanthrenes,



Hydrogenation of (VII) in the presence of palladised strontium carbonate gave perhydro-1 : 4-diketo-8-methylphenanthrene (X), when stopped at the appropriate stage, or perhydro-4-hydroxy-1-keto-8-methylphenanthrene (XI), when prolonged until the appropriate volume of hydrogen had been absorbed. The hydroxy-ketone (XI) was, however, more conveniently prepared by hydrogenation of the diketone (X) in the presence of Adams's catalyst. The structure of (XI) was demonstrated by marking the position of the carbonyl group by the Grignard reagent, whereafter dehydration and dehydrogenation of the resulting perhydro-1 : 4-dihydroxy-1 : 8-dimethylphenanthrene afforded 1 : 8-dimethylphenanthrene, which, incidentally, has the highest melting point among the 17 dimethylphenanthrenes hitherto described.

#### EXPERIMENTAL

**2-Methylcyclohexanol.**—*o*-Cresol (500 g.), containing metallic sodium (0.3 g.), was hydrogenated at 80°/110 atm. (initial) in the presence of Raney nickel (*ca.* 20 g.) (cf. Ungnade and Nightingale, *J. Amer. Chem. Soc.*, 1944, **66**, 1218). Absorption of hydrogen was rapid and exothermic, the temperature rising to ~200°. The hydrogenated product, after dilution with benzene (500 c.c.), was filtered from the catalyst, washed once with 2*N*-sodium hydroxide, and fractionated, giving 2-methylcyclohexanol (485 g., 95%), b. p. 74–76°/20 mm.

**2-Methylcyclohexanone.**—2-Methylcyclohexanol (260 g.) was added slowly to a vigorously stirred solution of sodium dichromate (120 g.) and concentrated sulphuric acid (100 g.) in water (600 c.c.). A cooling-bath was used intermittently to keep the temperature of the reaction mixture below 50°. At the end of the reaction the mixture was stirred until cool and then extracted with ether. The ethereal solution was washed with 5% aqueous sodium hydroxide (3 × 200 c.c.), dried, and fractionated, giving 2-methylcyclohexanone (178 g., 70%), b. p. 62°/21 mm.,  $n_D^{20}$  1.4522 (lit., b. p. 59–60°/20 mm.,  $n_D^{15}$  1.450).

**1-Ethynyl-2-methylcyclohexanol.**—Condensation of 2-methylcyclohexanone and sodium acetylide in liquid ammonia as for 1-ethynylcyclohexanol (*J.*, 1952, 646) gave the alcohol (75–87%), b. p. 77°/13 mm. When kept at 0°, the distilled liquid partly solidified and filtration gave the solid isomer, which, after crystallisation from a small volume of light petroleum, had m. p. 56–58°; about 30% of the distilled material could be obtained as a solid. Milas *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 1829) record m. p. 61–61.5° for the solid stereoisomer obtained in 50% yield.

*Partial Hydrogenation of the Stereoisomeric 1-Ethynyl-2-methylcyclohexanols.*—1-Ethynyl-2-methylcyclohexanol (85 g.; m. p. 55°) was hydrogenated at room temperature and atmospheric pressure in methanol (1 l.) in the presence of 2% palladised strontium carbonate (5 g.), until the solution just failed to give a precipitate with alcoholic silver nitrate solution. After removal of the catalyst, fractionation afforded 2-methyl-1-vinylcyclohexanol-s (79 g.), b. p. 79–80°/15 mm.,  $n_D^{19}$  1.4830 (Found: C, 77.0; H, 11.4. Calc. for  $C_9H_{16}O$ : C, 77.2; H, 11.4%). Wang and Hu (*loc. cit.*) record b. p. 66–67°/10 mm.

Similar treatment of the stereoisomeric liquid 1-ethynyl-2-methylcyclohexanol (170 g.) afforded the stereoisomeric 2-methyl-1-vinylcyclohexanol-*l* (159 g.), b. p. 74–75°/11 mm.,  $n_D^{25}$  1.4760 (Found: C, 77.2; H, 11.6%). Wang and Hu (*loc. cit.*) record b. p. 75–76°/16 mm.

*Dehydration of the Stereoisomeric 2-Methyl-1-vinylcyclohexanols.*—2-Methyl-1-vinylcyclohexanol-s (30 g.) was slowly distilled in a stream of nitrogen from powdered anhydrous potassium hydrogen sulphate (5 g.), heated to 180° in an oil-bath. The distillate, separated from the aqueous layer and dried ( $K_2CO_3$ ), was redistilled from a little anhydrous potassium hydrogen sulphate, giving crude methylvinylcyclohexene-s (21 g., 80%), b. p. 156–157°,  $n_D^{19}$  1.4978. Careful fractionation of the crude diene showed that, although it distilled almost entirely over a very narrow temperature range, the refractive indices of the fractions varied considerably. The crude diene was therefore used without further investigation in the subsequent reaction with benzoquinone.

In a like manner, the stereoisomeric 2-methyl-1-vinylcyclohexanol-*l* (15 g.) was dehydrated, to give an inhomogeneous sample of methylvinylcyclohexene-*l* (11.7 g.), b. p. 155–157°,  $n_D^{19}$  1.4895.

$\Delta^{2:9(14)}$ -Decahydro-1:4-diketo-8-methylphenanthrene (VII).—Crude methylvinylcyclohexene-s (8.3 g.) in methanol (30 c.c.) was treated with benzoquinone (3 g., 0.38 mol.; the use of a molecular proportion of benzoquinone interfered with the subsequent isolation of the product). After swirling to effect dissolution of the benzoquinone, the reaction mixture became warm and a pale yellow crystalline solid separated. After 18 hours at room temperature, the reaction mixture was cooled to –5° and filtered, yielding  $\Delta^{2:9(14)}$ -decahydro-1:4-diketo-8-methylphenanthrene (VII) (3.9 g.), m. p. 125–126°, in the form of pale yellow leaflets; light absorption in ethanol,  $\lambda_{max}$ . 225, 290, 340 m $\mu$  ( $\log \epsilon = 4.08, 2.20, 1.90$ ) (Found: C, 78.3; H, 7.9.  $C_{15}H_{18}O_2$  requires C, 78.2; H, 7.9%). The observed light-absorption characteristics were practically identical with those recorded previously for the lower homologue (*J.*, 1952, 646).

Similar reaction of crude methylvinylcyclohexene-*l* (8.3 g.) in methanol (30 c.c.) with benzoquinone (3 g.) gave  $\Delta^{2:9(14)}$ -decahydro-1:4-diketo-8-methylphenanthrene (3.12 g.), identical with that described above.

Reaction of methylvinylcyclohexene-s (4.0 g.) with benzoquinone (3.0 g.) in boiling benzene (25 c.c.) for 2.5 hours gave, after evaporation of the solvent and removal of unchanged benzoquinone and diene at 100° *in vacuo*, almost pure  $\Delta^{2:9(14)}$ -decahydro-1:4-diketo-8-methylphenanthrene (1.70 g., 22.5% calc. on the diene). No other non-volatile product could be detected.

$\Delta^{9(14)}$ -Dodecahydro-1:4-diketo-8-methylphenanthrene (VIII).— $\Delta^{2:9(14)}$ -Decahydro-1:4-diketo-8-methylphenanthrene (1.0 g.) in glacial acetic acid (50 c.c.) was treated with zinc powder (1.0 g.), and the reaction mixture was stirred for 10 minutes at room temperature. Ether (50 c.c.) was added and the zinc acetate together with unused zinc removed by filtration. Evaporation of the filtrate under reduced pressure at below 50° gave a solid residue, which, on extraction with boiling light petroleum, afforded colourless prisms of  $\Delta^{9(14)}$ -dodecahydro-1:4-diketo-8-methylphenanthrene (VIII), m. p. 122–123° (Found: C, 77.9; H, 9.1.  $C_{15}H_{20}O_2$  requires C, 77.6; H, 8.7%).

*Perhydrogenation of  $\Delta^{2:9(14)}$ -Decahydro-1:4-diketo-8-methylphenanthrene (VII) in Ethyl Acetate Solution.* *Perhydro-1:4-dihydroxy-8-methylphenanthrene (IX).*—A solution of the decahydrodiketomethylphenanthrene (VII) (1.0 g.) in ethyl acetate (80 c.c.) containing perchloric acid (2 drops of 70%) was shaken with Adams's platinum oxide catalyst (50 mg.) in hydrogen at atmospheric pressure and room temperature until absorption of hydrogen ceased (8 hours for 4.5 mols.). After removal of the catalyst the solution was concentrated to small bulk and addition of much light petroleum then gave a white crystalline solid. Recrystallisation from benzene–ethanol afforded fine colourless needles (0.12 g.) of *perhydro-1:4-dihydroxy-8-methylphenanthrene (IX)*, m. p. 195° (Found: C, 75.9; H, 10.6.  $C_{15}H_{26}O_2$  requires C, 75.6; H, 11.0%). No further solid product could be isolated.

*Degradation of (VII) to 1-Methylphenanthrene.*— $\Delta^{2:9(14)}$ -Decahydro-1:4-diketo-8-methylphenanthrene (VII) (2 g.) was hydrogenated at atmospheric pressure and room temperature in glacial acetic acid in the presence of Adams's platinum oxide catalyst (0.2 g.). After 5½ hours

absorption of hydrogen had ceased, approximately 3.6 mols. having been absorbed. Removal of the catalyst and evaporation gave a clear gum consisting essentially of a mixture of stereoisomeric perhydro-1:4-dihydroxy-8-methylphenanthrenes. The gum was mixed with powdered anhydrous potassium hydrogen sulphate (8 g.) and the mixture was heated in an atmosphere of nitrogen to 180–200° for 45 minutes. After cooling, the reaction mixture was distributed between water and low-boiling light petroleum, and the organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and allowed to percolate down a short column of activated alumina (Peter Spence and Sons, type H). The effluent, together with low-boiling light petroleum washings, was evaporated to dryness, to give a pale yellow mobile oil (1.3 g.) which gave a strong brown colour with tetranitromethane.

The oil (0.7 g.) was heated with 5% palladised charcoal (1 g.) in boiling diphenylamine (5 g.) until no further evolution of gas took place, about 5 hours being required. After cooling, the reaction mixture was taken up in ether and filtered to remove the catalyst. The filtrate was saturated with dry hydrogen chloride, and the precipitated diphenylamine hydrochloride was collected and washed with ether. On evaporation of the filtrate and washings to dryness, the residue, which solidified readily but still contained traces of diphenylamine, was taken up in low-boiling light petroleum and allowed to percolate through a short column of activated alumina. The effluent and washings, on evaporation, gave a solid residue, which, after one recrystallisation from methanol, afforded shining colourless plates of 1-methylphenanthrene (0.36 g.), m. p. 118–119° (styphnate, m. p. 149–150°). Haworth (*J.*, 1932, 1125) records 1-methylphenanthrene, m. p. 118°, and its styphnate, m. p. 149–150°.

*Perhydro-1:4-diketo-8-methylphenanthrene* (X).—A solution of  $\Delta^{2:9(14)}$ -decahydro-1:4-diketo-8-methylphenanthrene (VII) (500 mg.) in methanol (100 c.c.) was shaken with 2% palladised strontium carbonate (0.5 g.) in hydrogen at atmospheric temperature and pressure until two molecular proportions of hydrogen had been absorbed, 70 minutes being required. After filtration and removal of the solvent, the residue, crystallised from aqueous methanol, gave colourless needles (280 mg.) of *perhydro-1:4-diketo-8-methylphenanthrene* (X), m. p. 140–141° (Found: C, 76.9; H, 9.2.  $\text{C}_{15}\text{H}_{22}\text{O}_2$  requires C, 77.1; H, 9.5%).

*Perhydro-4-hydroxy-1-keto-8-methylphenanthrene* (XI).—*Perhydro-1:4-diketo-8-methylphenanthrene* (X) (1.95 g.) in methanol (100 c.c.) was shaken in hydrogen at atmospheric pressure and room temperature with Adams's platinum oxide catalyst (100 mg.) for 42 hours, one mol. of hydrogen being absorbed. After removal of the catalyst and evaporation of the solvent, recrystallisation of the residue from light petroleum-ethyl acetate gave fine colourless needles of *perhydro-4-hydroxy-1-keto-8-methylphenanthrene* (XI) (1.50 g.), m. p. 125–126° (Found: C, 76.5; H, 10.2.  $\text{C}_{15}\text{H}_{24}\text{O}_2$  requires C, 76.2; H, 10.2%).

The 2:4-dinitrophenylhydrazone separated from toluene in orange needles, m. p. 190–193° (Found: C, 60.8; H, 6.8; N, 13.2.  $\text{C}_{21}\text{H}_{20}\text{O}_5\text{N}_4$  requires C, 60.5; H, 6.8; N, 13.5%).

The hydroxy-ketone (XI) could also be obtained in 56% yield by hydrogenation of (VII) in methanol in the presence of palladised strontium carbonate but the uptake of hydrogen became extremely slow at the last stage.

*Perhydro-1:4-dihydroxy-1:8-dimethylphenanthrene*.—The above hydroxy-ketone (XI) (1.0 g.) was added in dry benzene (40 c.c.) to a boiling stirred solution of methylmagnesium iodide (from 2.0 g. of magnesium and 11.5 g. of methyl iodide) in benzene (100 c.c.). After being stirred under reflux for 5 hours, the reaction mixture was cooled in ice and decomposed with 2N-sulphuric acid (80 c.c.). The organic layer was separated and the aqueous phase was extracted once with ether. The combined organic layers were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. The residue, which solidified spontaneously, was recrystallised from ethyl acetate-light petroleum, affording colourless prisms (0.55 g.) of *perhydro-1:4-dihydroxy-1:8-dimethylphenanthrene*, m. p. 155–156° (Found, on a sample dried at 140°/20 mm.: C, 76.2; H, 11.2.  $\text{C}_{16}\text{H}_{24}\text{O}_2$  requires C, 76.1; H, 11.2%).

*1:8-Dimethylphenanthrene*.—The above *perhydro-1:4-dihydroxy-1:8-dimethylphenanthrene* (0.52 g.), mixed with powdered anhydrous potassium hydrogen sulphate (5 g.), was heated at *ca.* 180° under nitrogen for 45 minutes. After cooling and addition of water, the organic material was extracted with low-boiling light petroleum. The petroleum solution was dried ( $\text{Na}_2\text{SO}_4$ ) and allowed to percolate down a short column of activated alumina, and effluent and washings on evaporation yielded a colourless oil (0.4 g.), giving a strong brown colour with tetranitromethane.

The oil was heated in a sealed tube with selenium (1.2 g.) at 345° for 42 hours. After cooling, the tube was cautiously opened in view of the internal pressure and the contents were washed out with much ether. Evaporation of the filtered ethereal solution afforded a solid residue, m. p. 140–160°, which was sublimed at 180–200°/20 mm. Five crystallisations from glacial

acetic acid afforded glittering plates of 1 : 8-dimethylphenanthrene (100 mg.), m. p. 187—190°, not depressed on admixture with an authentic specimen, m. p. 190—191°, kindly provided by Professor R. D. Haworth, F.R.S. (cf. Haworth, Mavin, and Sheldrick, *J.*, 1934, 454) (Found : C, 93·4; H, 6·8. Calc. for  $C_{16}H_{14}$  : C, 93·2; H, 6·8%).

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