94. *The Addition of Bromine to αβ-Diphenyl-δ-methyl-Δ$^{\alpha\gamma}$-butadiene.*

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FOR reasons already explained (J., 1929, 2025), it was necessary to prepare butadienoid hydrocarbons of the type CHPh:CPh·CH:CHR (I), and to determine the structures of their bromine- and hydrogen-addition products. Circumstances have arisen which render unlikely a continuation of this work and it is therefore desired to place on record the few results so far obtained.

The synthesis of αβ-diphenyl-Δ$^{\alpha\gamma}$-butadiene (I, R = H) from α-phenylcinnamaldehyde and methylmagnesium iodide gave, under all the conditions tried, a product containing much unchanged aldehyde. The use of ethylmagnesium iodide, however, led to the isolation of *αβ-diphenyl-δ-methyl-Δ$^{\alpha\gamma}$-butadiene* (I, R = Me) as a low-melting solid which readily absorbed oxygen from the atmosphere either in alcoholic solution or in the solid state. Addition of bromine occurs in accordance with theory, that is, exclusively at the γδ-double bond. It has not been possible to isolate a definite product from attempted reductions with sodium and alcohol or with sodium amalgam in various media.

EXPERIMENTAL.

α-Phenylcinnamaldehyde.—The method of preparation described by Meerwein and Dott (*J. pr. Chem.*, 1918, **97**, 281) is laborious, and the yields recorded by these authors could not be obtained. A more convenient procedure is as follows. 20 C.c. of 5% methyl-alcoholic sodium methoxide are added gradually, with cooling, to a mixture of benzaldehyde (53 g.) and phenylacetaldehyde (60 g.); the mixture, after being kept over-night, is neutralised with glacial acetic acid and fractionated. Redistillation of the fraction, b. p. 150—

210°/18 mm., gives 20—32 g. of a straw-coloured oil, b. p. 196—201°/16 mm., which solidifies almost completely on cooling. Crystallisation of the solid from alcohol gives the aldehyde, m. p. 94—95° after softening at 90° (Found: C, 86·4; H, 5·9. Calc.: C, 86·5; H, 5·8%). This product is sufficiently pure for most purposes; it is contaminated with a small amount of a higher-melting substance, which can be separated by fractional crystallisation from alcohol.

The phenylhydrazone separates from alcohol in pale yellow needles, m. p. 140—141° (Found: C, 84·2; H, 5·9. Calc.: C, 84·6; H, 6·0%); Meerwein and Dott (*loc. cit.*) give m. p. 125—126°. The p-*nitrophenylhydrazone* crystallises from acetic acid in dark red needles, m. p. 205—206° (Found: C, 73·1; H, 4·95. $C_{21}H_{17}O_2N_3$ requires C, 73·5; H, 4·95%). The *semicarbazone* separates from alcohol in clusters of needles, m. p. 194—195°; a satisfactory analysis was not accomplished (compare Bryant and Clemo, J., 1931, 2080) (Found: C, 70·45; H, 6·0. $C_{16}H_{15}ON_3$ requires C, 72·45; H, 5·7%).

αβ-*Diphenyl-δ-methyl-*$\Delta^{\alpha\gamma}$-*butadiene* (I; R = Me).—A solution of α-phenylcinnamaldehyde (20·8 g.) in benzene (125 c.c.) was added with stirring to the Grignard reagent prepared by the method of Gilman and McCracken (*J. Amer. Chem. Soc.*, 1923, **45**, 2463) from magnesium (4·8 g.), ethyl iodide (31·2 g.), and ether (100 c.c.). The mixture was boiled for 18 hours and then decomposed with ice and saturated ammonium chloride solution. The residue from the dried ether–benzene extract distilled almost completely at 158—160°/5—6 mm., and partly crystallised when cooled in ice. The distillate (19·5 g.) dissolved almost completely in hot alcohol, giving a faintly opalescent solution which, when filtered rapidly and then cooled in a freezing mixture, deposited crystalline material; rapid filtration of the solid and drying on porous earthenware in a vacuum desiccator over sulphuric acid gave 7·5 g. of the *hydrocarbon*, m. p. 48—49° (Found: C, 92·6; H, 7·45. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%).

If, during the above crystallisation process, the operations are not carried out rapidly, the hot alcoholic solution rapidly becomes turbid and an oil separates. This solidifies on cooling and the solid contains a smaller proportion of carbon (Found: C, 88·9; H, 7·1%) than does the hydrocarbon, showing that oxidation has occurred. The hydrocarbon is stable as long as it is kept in a vacuum, but when it is kept in dry air, it absorbs oxygen [Found: (after 24 hours) C, 89·4; H, 7·25; (after 3 days) C, 86·9; H, 6·9%]. The oxidised product has a strong smell of benzaldehyde and is sparingly soluble in hot alcohol.

Addition of Bromine to αβ-*Diphenyl-δ-methyl-*$\Delta^{\alpha\gamma}$-*butadiene.*—A solution of the hydrocarbon (3·4 g.) in cold carbon tetrachloride was treated with bromine (2·56 g.) (a slight excess), also dissolved in

carbon tetrachloride. Evaporation of the solvent in a vacuum left 5·8 g. of a viscous oil (Found: C, 53·8; H, 4·0. $C_{17}H_{16}Br_2$ requires C, 53·7; H, 4·2%) which showed no tendency to crystallise. A solution of the oil in chloroform was treated with ozonised oxygen for 36 hours, and the ozonide decomposed with boiling water for 2 hours; no volatile aldehyde (Schiff's reagent) was evolved, thus demonstrating the non-occurrence of any αβ-addition. Subsequent oxidation with hydrogen peroxide (20 vol.; 25 c.c.) gave benzoic acid in very good yield (90% of the theoretical) as the only acidic product, identified by mixed m. p., and a neutral bromine-containing oil which could not be induced to crystallise.

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