73. *Photo-reactions. Part VI. Formation of Benzpinacol by the Action of Acetone on Benzhydrol in Sunlight.*

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IT is known that benzophenone is reduced to benzpinacol by *iso*propyl alcohol in sunlight (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 394; *Org. Synth.*, Vol. 14, p. 8). We find that benzpinacol is also formed by the action of acetone (or methyl ethyl ketone) on benzhydrol in sunlight; the reaction proceeds rapidly and the product can be easily isolated:

$$2CHPh_2{\cdot}OH + COMe_2 \xrightarrow{\text{sunlight}} OH{\cdot}CPh_2{\cdot}CPh_2{\cdot}OH + CHMe_2{\cdot}OH$$

The preparation succeeds also in a sealed tube which does not contain oxygen and is therefore not due to partial oxidation of benzhydrol to benzophenone, which, as was found by Cohen (*Rec. Trav. chim.*, 1919, **38**, 113), reacts with benzhydrol to give benzpinacol.

EXPERIMENTAL.

Photo-reaction between Benzhydrol and Acetone.—A solution of benzhydrol (4 g.) in 20 c.c. of dry acetone (AnalaR) was exposed in a sealed Pyrex glass tube, in the absence of air, to direct sunlight for 8 hours (during May). The yellow solution was distilled in a vacuum (distillate A), and the crystalline residue recrystallised from absolute ethyl alcohol; it had m. p. 187°, not depressed by authentic benzpinacol (Bachmann, *loc. cit.*). The yield was about 50% (Found: C, 85·1; H, 6·1. Calc. for $C_{26}H_{22}O_2$: C, 85·2; H, 6·0%). A Monax glass vessel closed with a cork may be used if the absence of oxygen is not required. The experiment was repeated in winter time; after exposure for 10 days to direct sunlight (cloudy weather in December), the yield was about 70%.

The product was further identified by its interaction with pyridinium chloride to form tetraphenylglycolpyridinium chloride (Schönberg and Michaelis, J., 1936, 1571).

The distillate (A) was refluxed for 2 hours with an excess of *p*-nitrobenzoyl chloride; on cooling, a solid separated. The whole was dissolved in ether, and the solution washed with cold dilute aqueous sodium hydroxide, dried over anhydrous sodium sulphate, and distilled in a vacuum. The oily residue solidified on cooling; after crystallisation from hot ethyl alcohol it had m. p. 111°, not depressed by authentic *iso*propyl *p*-nitrobenzoate (Buchner and Meisenheimer, *Ber.*, 1905, **38**, 627). Yield, 2·5 g. When acetone was exposed to sunlight in the absence of air and treated with *p*-nitrobenzoyl chloride as described above, *iso*propyl *p*-nitrobenzoate was not detected.

Photo-reaction between Benzhydrol and Methyl Ethyl Ketone.—Benzhydrol (1 g.) and methyl ethyl ketone (1 mol.) in 20 c.c. of dry benzene (thiophen-free) were exposed in a sealed Pyrex glass tube to direct sunlight for 1 month (October—November). The benzene was removed in a vacuum, and the solid which separated from the residue on cooling was washed with benzene and crystallised from light petroleum (b. p. 100—110°); it had m. p. 187°, not depressed by authentic benzpinacol.

Photo-reaction between Benzhydrol and Benzophenone.—In a similar experiment, benzhydrol (1 g.) and benzophenone (1 mol.) were exposed to direct sunlight for 2 days (December). The benzene was driven off in a vacuum, and the crystalline residue recrystallised from absolute ethyl alcohol; it had m. p. 187°, not depressed by authentic benzpinacol. Yield, 80% (Found: C, 84·8; H, 6·1%).

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