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

By ALEXANDER SCHÖNBERG and AHMED MOSTAFA.

IT is known that benzophenone is reduced to benzpinacol by isopropyl 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:

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

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<sub>26</sub>H<sub>22</sub>O<sub>2</sub>: 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 the cooling is a solid separated by authority description of the cooling is a solid separated. The oily residue solidified on cooling; after crystallisation from the cooling is a solid separated by authority description of the cooling is a solid separated. hot ethyl alcohol it had m. p. 111°, not depressed by authentic isopropyl 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, isopropyl 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 I 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

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%).

FOUAD I UNIVERSITY, CAIRO, EGYPT.

[Received, March 3rd, 1943.]