NOTE.

The Formation of Ketyls by the Action of Potassium on Benzpinacol. By TUDOR JOHN and SYDNEY T. BOWDEN.

SOME of the reactions of benzpinacol have been ascribed to slight dissociation into the radical $\cdot CPh_2\cdot OH$ and its subsequent transformation into benzophenone and benzhydrol (Thorner and Zincke, *Ber.*, 1877, **10**, 1474; Acree, *Amer. Chem. J.*, 1903, **29**, 588). There is, however, no direct evidence of the existence of this radical, and we have therefore compared the behaviour of benzpinacol with that of an equimolecular mixture of benzophenone and benzhydrol on treatment with metallic potassium.

When a solution of benzpinacol (5·3 g.) in xylene (50 c.c.) is treated under nitrogen with potassium (1·1 g.), the blue ketyl is rapidly formed at the surface of the metal. On raising the temperature to the m. p. of the metal, there is vigorous evolution of hydrogen and the solution passes through a series of colour changes ranging from green to blue. At this stage potassium benzhydryloxide is precipitated, and if now the solution is cooled, the above sequence of colour changes is reversed. Hydrolysis of the mixture yields benzhydrol (4·2 g.) and benzophenone (0·2 g.). An equimolecular mixture of benzhydrol (2·7 g.) and benzophenone (2·6 g.) behaves in a similar manner on treatment with potassium (1·1 g.) : the colour changes are closely duplicated and the products of hydrolysis are benzhydrol (4·6 g.) and benzophenone (0·2 g.). These results would seem to support the predissociation theory, but actually, preliminary experiments showed that the reaction with benzophenone alone is comparatively slow and that only 30% of the metal forms the ketyl after the mixture has been boiled for 5 hours. Under similar conditions, the metal reacts smoothly with benzhydrol to form the benzhydryloxide (J., 1939, 313).

The present experiments indicate that the hydroxyl hydrogen of benzpinacol is directly replaced by metal with formation of the mono- and the di-potassium derivative. The latter suffers partial dissociation into the unimolecular ketyl (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 1179; Doescher and Wheland, *ibid.*, 1934, **56**, 2011), and is then reduced to benzhydryloxide. As a further indication of the reactivity of benzpinacol, we find that it reacts almost instantaneously in the cold with potassium triphenylmethoxide to form the ketyl system and triphenylcarbinol (cf. Schlenk and Thal, *Ber.*, 1913, **46**, 2840). It is evident, therefore, that the formation of triphenylcarbinol from benzpinacol, bromobenzene, and sodium (Acree, *loc. cit.*) depends on the formation of ketyls through direct attack of metal and methoxide on the glycol.—UNIVERSITY COLLEGE, CARDIFF. [*Received, October 25th*, 1939.]