CHEMISTRY LETTERS, pp. 1167-1168, 1972. Published by the Chemical Society of Japan

ON THE REACTION OF n-BUTYLLITHIUM WITH BENZOPHENONE

Hideo NAKAMURA, Hisashi YAMAMOTO, and Hitosi NOZAKI
Department of Industrial Chemistry
Kyoto University, Yosida, Kyoto

The title reaction at low temperature gives benzhydrol, whereas at higher temperature the normal adduct, 1,1-diphenyl-1-pentanol.

Although the reduction of ketones with Grignard reagent is a well established process[1] involving the β-hydrogen atom of the magnesium compound, none appears to have observed similar reaction with alkyllithium reagent. In fact, the amount of phenyllithium has sometimes been determined by the reaction with benzophenone on the assumption of quantitative formation of the carbinol.[2] We now wish to report that the treatment of benzophenone with n-butyllithium produced substantial amount of benzhydrol especially at low temperature.

Benzophenone in ether-pentane-tetrahydrofuran (1:1:4) was treated with an equivalent quantity of n-butyllithium at -130°C over a period of 10 min, and the mixture was stirred for an additional 5 hr at the same temperature to complete the reaction. In the early part of the reaction, the medium turned green, probably due to the ketyl radical of benzophenone. After usual work-up followed by preparative tlc purification, benzhydrol was obtained in 48% yield with a minor amount (33%) of 1,1-diphenyl-1-pentanol (I). The ratio between benzhydrol and the carbinol I was dependent on the temperature of reaction. Some results are summarized in Table 1.

When valerophenone was treated with phenyllithium under the similar reaction conditions, none of benzhydrol was present among the reaction product. This excludes the possibility that the lithium alkoxide of the carbinol I is an intermediate whose radical cleavage also could produce the benzophenone ketyl radical and therefore benzhydrol through dimerization followed by anionic cleavage.[3]

Table 1. Reaction of benzophenone with *n*-butyllithium

Reaction temperature[a] (°C)	Benzhydrol[b] (%)	1,1-Diphenyl-1-pentanol[b] (%)
25	11.2	62.5
0	24.0	57.9
-26	31.2	56.7
-78	42.0	45.5
-130	47.8	32.6

a) *n*-Butyllithium (in hexane) was added during 10 min, and the reaction mixture was stirred for 5 hr at the same temperature. The reaction was terminated by pouring into *aq*. hydrochloric acid.

b) After purification by preparative tlc (silica gel).

References

1. H. O. House and D. D. Traficante, *J. Org. Chem.*, **28**, 355 (1963); D. O. Cowan and H. S. Mosher, *ibid*., **27**, 1 (1962); C. G. Swain and H. B. Boyles, *J. Amer. Chem. Soc.*, **73**, 870 (1951); D. O. Cowan and H. S. Mosher, *J. Org. Chem.*, **28**, 204 (1963); R. MacLeod, F. J. Welch, and H. S. Mosher, *J. Amer. Chem. Soc.*, **82**, 876 (1941).
2. J. C. W. Evans and C. F. H. Allen, *Org. Syn. Coll. Vol. 2*, 517.
3. D. J. Cram, A. Langemann, W. Lwowski, and K. R. Kopecky, *J. Amer. Chem. Soc.*, **81**, 5752 (1959). See also D. J. Cram, "Fundamentals of Carbanion Chemistry", 1965, Academic Press, N. Y.

(Received October 6, 1972)