Products of the Reaction of Methylmagnesium Bromide with Benzophenone in Diethyl Ether

By STEPHEN E. RUDOLPH and STANLEY G. SMITH*
(*Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois* 61801)

Summary The reduction of benzophenone to benzhydrol in the reaction of benzophenone with methylmagnesium bromide in diethyl ether is reported and shown to involve reaction of a small, constant fraction of the Grignard reaction.

THE reaction of benzophenone with methylmagnesium bromide has been extensively investigated, in part because it involves a non-enolizable ketone and a Grignard reagent lacking β-hydrogens and is expected to give only an addition product. In spite of the apparent simplicity of such a ssytem, kinetic studies have shown this reaction to be complex.[1-6] Interpretation of available kinetic data is facilitated by a knowledge of the products of this reaction. Both diphenylethanol, the normal carbonyl addition product,[7] and benzopinacol have been found when an excess of Grignard reagent is used.[4] Ashby and his co-workers have recently verified this result and have reported[6] that benzopinacol formation is repressed by "ultra-pure" magnesium. We now report the formation of a third product, benzhydrol, in the reaction of MeMgBr with benzophenone in diethyl ether.

As summarized in the Table and illustrated in the Figure, the yield of benzhydrol increases with decreasing initial ketone concentration when a constant amount of MeMgBr is used. A 50% yield of benzhydrol was observed with a MeMgBr : Ph_2CO ratio of *ca.* 370. However, the absolute yield of benzhydrol is essentially constant, with *ca.* $1{\cdot}4 \times 10^{-3}$ moles of benzhydrol being formed per mole of MeMgBr, in this case. Apparently the reduction of benzophenone involves a low concentration of a reactive component in the Grignard reagent. Benzhydrol, identified by i.r., n.m.r., g.l.p.c., m.p., and mixed m.p., is formed both with a Grignard reagent prepared on a vacuum line with sublimed magnesium and with commercial samples of MeMgBr. The formation of benzhydrol is not influenced by the addition of magnesium metal, and control experiments indicate that this compound does not arise from benzopinacol, which is also formed in small amounts in these reactions. No Ph_2CDOH was detected (^2H n.m.r.) when CD_3MgBr was used; hydrolysis of reacted MeMgBr solutions with D_2O followed by H_2O work-up gave only Ph_2CHOH.

Products of the reaction of benzophenone with methylmagnesium bromide in diethyl ether at 0°

10^4 mol, Ph_2CO	10^2 mol, MeMgBr	% Yield benzhydrol	10^3 (Benzhydrol: MeMgBr)
0·83	3·48	54·5	1·30
1·32	3·38	33·0	1·29
1·63	3·38	29·0	1·40
1·92	3·70	25·4	1·32
2·43	3·31	19·9	1·53
2·93	3·18	15·0	1·38
3·22	3·36	15·1	1·45
3·72	3·58	15·0	1·56
4·50	3·01	10·4	1·55
5·35	3·18	7·4	1·25
5·91	3·16	8·5	1·59
		Average =	1·42

Side reactions such as that described above and benzopinacol formation may have an effect on measured kinetic parameters. Thus, for reaction of MeMgBr with benzophenone in diethyl ether at 25°, Ashby and his co-workers have reported[6] that elimination of benzopinacol formation results in a reduction of the curvature observed in their pseudo-first-order plots. To account for the remaining curvature in these plots, they suggest[6] that dimethylmagnesium, formed slowly,[8] is the reactive species in this reaction.[9] Previously they interpreted their data in terms of other mechanisms for Grignard addition reactions, including slow complexation of ketone and Grignard reagent followed by fast reaction of complex with a second Grignard,[10] fast complex formation followed by slow reaction with a second Grignard,[3] and two distinct mechanistic paths, depending on the stoicheiometry of the reaction.[11] Since conditions for obtaining first-order kinetics have been described[4,5] and illustrated with a sample run,[4] at this time the mechanism of the addition of MeMgBr to benzophenone in diethyl ether would seem to be described best by the schemes applicable to ketones for which more extensive kinetic and spectroscopic data are available.[4,12]

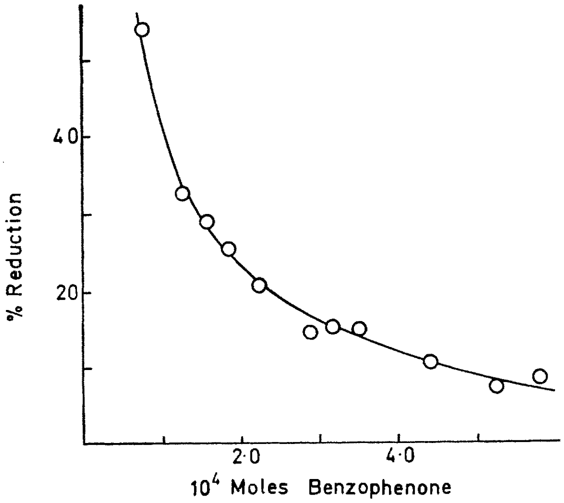

FIGURE. *Plot of % yield of benzhydrol in product* vs. *moles of benzophenone for reaction of* ca. $3{\cdot}3 \times 10^{-2}$ *moles of methylmagnesium bromide* (*as* 1·27 M *solutions in diethyl ether*) *with benzophenone at* ca. 0°.

We thank the National Science Foundation for support.

(*Received, July* 20*th,* 1970; *Com.* 1192.)

---

[1] N. M. Bikales and E. I. Becker, *Chem. and Ind.*, 1961, **45**, 1831; N. M. Bikales and E. I. Becker, *Canad. J. Chem.*, 1963, **41**, 1329.

[2] M. Anteunis, *J. Org. Chem.*, 1961, **26**, 4214.

[3] E. C. Ashby, R. B. Duke, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1967, **89**, 1964.

[4] J. Billet and S. G. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 4108.

[5] T. Holm, *Acta Chem. Scand.*, 1969, **23**, 579.

[6] E. C. Ashby, F. Walker, and H. M. Neumann, *Chem. Comm.*, 1970, 330.

[7] See M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N.Y., 1954, pp. 160—166.

[8] However, the currently available n.m.r. data (E. C. Ashby, G. Parris, and F. Walker, *Chem. Comm.*, 1969, 1464) suggest that the Schlenk equilibrium may be relatively fast at —100°.

[9] See, however, J. Billet and S. G. Smith, *Tetrahedron Letters*, 1969, 516, 4467.

[10] E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 4363.

[11] E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1968, **90**, 5179.

[12] S. G. Smith, *Tetrahedron Letters*, 1963, 409; S. G. Smith and G. Su, *J. Amer. Chem. Soc.*, 1964, **86**, 2750; S. G. Smith and G. Su, *ibid.*, 1966, **88**, 3995; S. G. Smith and J. Billet, *ibid.*, 1967, **89**, 6948.