

PHOTOCHEMISTRY OF TRIBENZYLBORANE AND ITS AMMONIA COMPLEX  
 —HETEROLYTIC CLEAVAGE OF BENZYL CARBON—BORON BOND

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Irradiation of tribenzylborane-ammonia complex in protic solvent produced toluene in a 262% yield. Irradiation of tribenzylborane also produced toluene as a major product. Formation of toluene was elucidated by a protonation of benzyl anion which resulted from heterolytic cleavage of the benzyl carbon-boron bond.

The carbon-boron bond of trialkylborane is susceptible to homolytic cleavage leading to alkyl radical under irradiation, or in the presence of oxygen or a radical initiator.<sup>1)</sup> However, in the course of study on a di- $\pi$ -alkane photoisomerization<sup>2)</sup> of the compounds involving a central boron atom, we discovered a heterolytic cleavage of the benzyl carbon-boron bond of tribenzylborane and its ammonia complex under irradiation. Heterolytic cleavages of the benzyl carbon-heteroatom bond have been reported in the photochemical reactions of benzyl ammonium salts,<sup>3)</sup> sulfonium salts<sup>4)</sup> and phosphonium salts,<sup>5)</sup> all of which produced benzyl cations as an intermediate. In this communication, we wish to report the first example of the formation of a benzyl anion by photochemical cleavage of the benzyl carbon-boron bond.

Irradiation of tribenzylborane<sup>6)</sup> in ether under an argon or nitrogen atmosphere produced toluene and bibenzyl in a 38% and 15% yields, respectively.<sup>7,8)</sup> Irradiation of the ammonia complex of tribenzylborane<sup>6)</sup> also produced toluene and a trace of bibenzyl. Results under various conditions are summarized in Table 1. The yield of toluene was increased when alcoholic solution was employed. In particular, when the ammonia complex was irradiated in THF-methanol solvent, a 262% yield of toluene was produced.<sup>7)</sup> Similarly, a high yield of toluene was obtained even when t-butyl alcohol, having no  $\alpha$ -hydrogen atom, was employed in place of methanol. Reaction of alcoholic solution of tribenzylborane and its ammonia complex in the dark did not produce toluene. The results mentioned above suggest that a heterolytic cleavage of the benzyl carbon-boron bond may occur in these photochemical reactions. This was further clarified from the fact that deuterated toluene was exclusively produced when tribenzylborane and its ammonia complex was irradiated in THF-methanol-d. From nmr and mass spectra, contents of deuterated toluene were determined to be 85% and 80%, respectively. Such a heterolytic cleavage of the benzyl carbon-boron bond

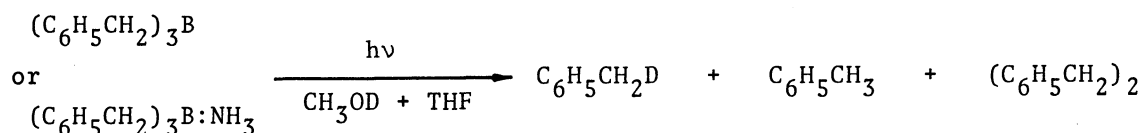


Table 1. Photochemistry of tribenzylborane and its ammonia complex<sup>a)</sup>

Substrate	Solvent	Irradiation		Conversion of borane (%) <sup>b)</sup>	Yield of products (%) <sup>b)</sup>	
		Time	(hr)		$C_6H_5CH_3$	$(C_6H_5CH_2)_2$
$(C_6H_5CH_2)_3B$	$Et_2O$	20		78	38	15
	$Et_2O + MeOH$	20		62	50	12
	"	40		79	82	10
	" c)	(70)		13	0	10
$(C_6H_5CH_2)_3B:NH_3$	$Et_2O$	40		67	64	trace
	THF	40		33	74	"
	THF + MeOH	20		98	262	"
	THF + t-BuOH	20		—	227	"
	THF + MeOH <sup>c)</sup>	(120)		31	1	"

a) Irradiated with a 500 W high pressure mercury vapor lamp under an argon or nitrogen atmosphere. Concentration of borane was 0.1 M.

b) Based upon benzylborane and its ammonia complex employed.

c) Kept in the dark at room temperature.

leading to benzyl anion may have resulted from the increasing electron density of the boron atom due to a coordination of ammonia, or perhaps of alcohol in the case of tribenzylborane, to a vacant p-orbital of boron.

#### REFERENCES AND NOTES

- 1) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca and London (1972), p.410.
- 2) a) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, Chem. Revs., 73, 531 (1973).  
b) R. W. Binkley and W. C. Schumann, J. Amer. Chem. Soc., 94, 1770 (1972).
- 3) a) M. A. Ratcliff, Jr., and J. K. Kochi, J. Org. Chem., 36, 3112 (1971).  
b) D. C. Appleton, D. C. Bull, R. S. Givens, V. Lillis, J. McKenna, J. M. McKenna, and A. R. Walley, J. C. S., Chem. Commun., 473 (1974).
- 4) A. L. Maycock and G. A. Berchtold, J. Org. Chem., 35, 2532 (1970).
- 5) C. E. Griffin and M. L. Kaufman, Tetrahedron Lett., 773 (1965).
- 6) B. G. Ramsey and N. K. Das, J. Amer. Chem. Soc., 94, 4227 (1972).
- 7) Yields and conversions in the photoreactions of tribenzylborane and its ammonia complex were determined by glpc analyses after treatment with alkaline hydrogen peroxide or the deamination with HCl gas followed by oxidation with alkaline hydrogen peroxide, respectively. Both treatments did not produce any effect on the yields of toluene. Yields are based upon the starting borane or its ammonia complex employed.
- 8) Bibenzyl may be resulted from an oxidation of tribenzylborane by a small amount of oxygen dissolved in solvent.<sup>6)</sup> Irradiation of an ethereal solution of tribenzylborane for 20 hr under exposure to air resulted in the increase of the yield of bibenzyl (20%) but a slightly decreased yield of toluene (35%).

(Received November 25, 1975)