

Photolytic Boron–Carbon Scission as a Second Primary Photoprocess of (Benzylmethylamino)benzylphenylborane

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Summary Irradiation of (benzylmethylamino)benzylphenylborane in carbon tetrachloride results in homolysis of the boron–benzyl bond and formation of boron and alkyl radical recombination and solvent abstraction products.

(BENZYLMETHYLAMINO)BENZYLPHENYLBORANE (**1**)¹ has been reported to undergo a photochemical transformation

commonly observed in substituted styrenes, *viz.*, *trans-cis* photomerization.² We now report that it also undergoes a second photochemical reaction which has no precedent in styrene photochemistry: excited-state homolysis of the boron–benzyl bond.

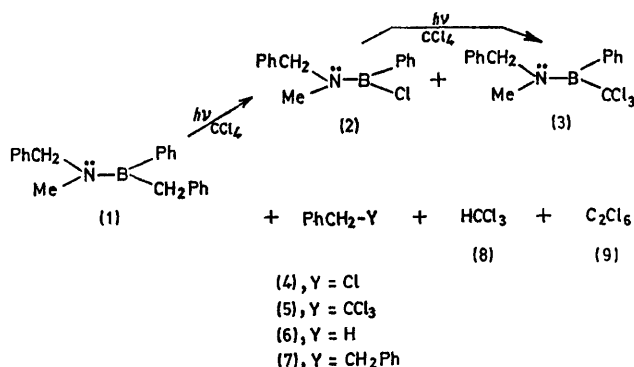
A thermally equilibrated, degassed *cis-trans* mixture of (**1**) in carbon tetrachloride was photolysed in a Rayonet reactor at 3000 Å and 35 °C. After 95 h, 80% of (**1**) was

destroyed. The following products were identified: (2), 51%; (3), 33%; (4), 8%; (5), 25%; (6), 8%; (7), 2%; (8), 40%; and (9), 8%. The relative amounts of boron-containing photoproducts (2) and (3) were dependent on the period of irradiation. Independent synthesis of (2)¹ followed by photolysis in carbon tetrachloride also gave (3). Similarly, (3) could be prepared by photolysis of (2) in either chloroform, hexachloroacetone, or a 0.7 M solution of trichloromethylsulphuryl chloride in benzene.³ Organic photoproducts were identified by comparison to authentic samples.

Since most of the possible radical recombination and solvent abstraction products have been identified, a mechanism involving photochemical cleavage of the boron-benzyl bond seems most plausible. The photochemical generation of such bi-co-ordinate aminoboryl radicals has been observed previously in the photolysis of 1,2-bis-(dimethylamino)-1,2-diphenyldiborane(4)⁴ and in the coupling reaction of chloro-bis(dimethylamino)borane with sodium.⁵

The photofragmentation reaction of (1) occurs with a quantum efficiency of 0.037 ± 0.004 . This relatively low quantum yield is consistent with the proposed homolysis mechanism. It is also in agreement with our previous finding² that photochemical geometrical isomerization of (1) functions at 35 °C as a hidden deactivation mechanism of high ($\Phi = 0.36$ at -22 °C) quantum efficiency.

Photochemical cleavage of the boron-carbon bond thus represents a second primary process available to amino-



borane excited states. However, whereas photoisomerization has a parallel in the photoreactivity of the isoelectronic and isosteric⁶ styrene analogues, B-C scission is a unique process, reflecting the polar nature of the B-N bond. Together, the two processes account for the chemical reactivity of *ca.* 40% of the excited states generated, the fates of the remainder being still unknown.

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