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

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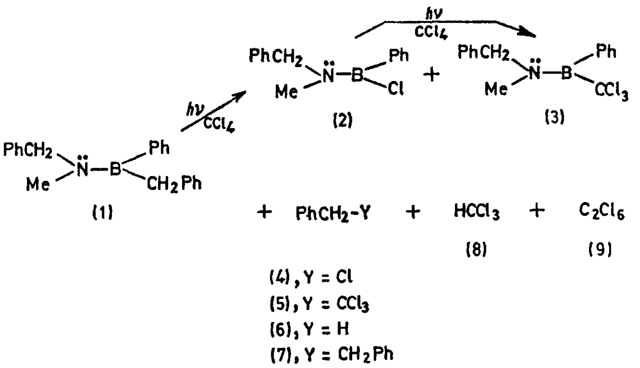
Summary Irradiation of (benzylmethylamino)benzylphenylborane in carbon tetrachloride results in homolysis of the boron–benzyl bond and formation of boron and alkyl radical recombination and solvent abstraction products.

(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 $0{\cdot}037 \pm 0{\cdot}004$. This relatively low quantum yield is consistent with the proposed homolysis mechanism. It is also in agreement with our previous finding[2] that photochemical geometrical isomerization of (**1**) functions at 35 °C as a hidden deactivation mechanism of high ($\Phi = 0{\cdot}36$ at -22 °C) quantum efficiency.



Photochemical cleavage of the boron-carbon bond thus represents a second primary process available to aminoborane excited states. However, whereas photoisomerization has a parallel in the photoreactivity of the isoelectronic and isosteric[6] 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.

We acknowledge financial support from the Petroleum Research Fund of the American Chemical Society, the Research Corporation, and the University of California.

(*Received*, 8*th June* 1972; *Com.* 981.)

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