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# THE PHOTOCHEMICAL REACTION OF TRIBUTYLBORANE WITH 4,4'-BISDIMETHYLAMINOBENZOTHIOPHENONE

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The facile reactivity of trialkylboranes with nitric oxide[1], nitrogen dioxide[2], and with oxygen[3], suggests that trialkylboranes might also react with other molecules containing one or more unpaired electrons such as free radicals and certain photoexcited molecules. Since thioketones have several absorption bands in the visible and near ultraviolet due to transitions which result in the unpairing of electrons[4], the photochemical reaction between 4,4'-bisdimethylaminobenzothiophenone and tributylborane was investigated. The absorption spectrum of a benzene solution of the thioketone was obtained and the data are given in Table 1. The absorption spectrum of this compound has been previously measured in ethanol[5]. The n ⟶ π* band is shifted to shorter wave length in going from benzene to the more polar ethanol whereas the π ⟶ π* band remains at the same frequency with the result that in ethanol the former band appears as a shoulder on the long wave length side of the latter band, while in benzene the two bands are clearly resolved.

TABLE I

Absorption Bands of 4,4'-bisdimethylaminobenzothiophenone in Benzene

| Transition | $\lambda_{max}$ | $\epsilon$ |
|---|---|---|
| $n - \pi^*$ | 573 | 1,190 |
| $\pi - \pi^*$ | 430 | 51,170 |
| | 323 | 3,580 |
| | 311 | 3,580 |

Irradiation by sunlight of 1.77 g (0.0063 mole) 4,4'-bisdimethylaminobenzothiophenone and 1.34 g. (0.0073 mole) tributylborane in 50 ml benzene in a Pyrex flask and a nitrogen atmosphere for 3 to 5 days resulted in the complete consumption of the thioketone. Evaporation of the solvent yielded a solid and a liquid product. Acid hydrolysis of the reaction mixture followed by steam distillation yielded dibutylhydroxyborane, $R_2BOH$, and butylmercaptan in the distillate indicating that the reaction product before hydrolysis contained the thioborinate, $R_2BSR$, which upon hydrolysis yields $R_2BOH$ and RSH. Neutralization of the acid hydrolysate yielded a precipitate which on the basis of melting point, infrared spectrum, and a comparison with an authentic sample was found to be tetrakis 4-dimethylaminotetraphenylethylene. The yield was almost quantitative. Thus the reaction can be depicted by the equation

$$2R_3B + 2(Me_2NC_6H_4)_2C{=}S \xrightarrow{h\nu} 2R_2BSR + (Me_2NC_6H_4)_2C{=}C(C_6H_4NMe_2)_2$$

To prove that the reaction was in fact photochemical a benzene solution of the reactants was allowed to stand in subdued light for a week. No reaction occurred. In another experiemnt the thioketone in benzene without the tributylborane was exposed to sunlight for five days. No reaction occurred showing that both light and borane are necessary for the consumption of the thioketone.

A possible pathway for this reaction which is consistent with the experimental observations is as follows:

$$Ar_2C{=}S \xrightarrow{h\nu} Ar_2\ C{=}S^*$$

$$Ar_2C{=}S^* + R_3B \longrightarrow Ar_2C{=}S\text{-}BR_3^*$$

$$2Ar_2C{=}S\text{-}BR_3^* \longrightarrow (Ar_2C{=}S\text{-}BR_3)_2 \longrightarrow Ar_2C{=}CAr_2 + 2R_2BSR$$

where Ar is p-dimethylaminophenyl, and R is n-butyl, and * indicates that the molecule is in an electronically excited state. The structure of the dimer which decomposes to give the final products is not known. The alternative mechanism in which the adduct formed in step 2 decomposes to give $R_2BSR$ and a diarylemthylene, $Ar_2C$, followed by dimerization of the latter seems unlikely since this highly reactive intermediate would be expected to react with the tributylborane to give products which are not found in the reaction mixture. An alternative sequence of steps which has been suggested by the referee is as follows:

$$2Ar_2C{=}S \rightleftharpoons Ar_2C{=}CAr_2 + 2S \text{ or } S_2$$

$$2R_3B + 2S \text{ or } S_2 \longrightarrow 2R_2BSR$$

The thioketone decomposes reversibly in sunlight as shown, the equilibrium lying far to the left in the above equation. In the absence of the borane little reaction is observed but in its presence there is a reaction between the sulfur and the borane thus shifting the equilibrium to the right. To test this hypothesis one needs atomic or diatomic sulfur which, of course, is not available. An experiment was carried out in which commercial sulfur was added to a benzene solution of tributylborane and exposed to sunlight for 5 days. The reaction mixture after hydrolysis produced no butyl mercaptan indicating that the above reaction does not occur with commercial sulfur. However the possibility that a reactive form of sulfur is an intermediate in the reaction cannot be ruled out. Further work on this and other photochemical reactions of boranes is in progress.

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