benzene. The inner quartz surface was rubbed mechanically with glass wool in order to prevent the deposition of polymer films. Irradiation for 2 hr. gave a fulvene concentration of *ca.* 0·1 g./l., a figure not surprising in view of the obviously high endothermicity of the reaction. This proportion of fulvene was sufficient to impart a distinct yellow colour to the benzene. The fulvene co-distilled with the benzene through a column of *ca.* 10 plates, but a five-fold concentration was readily effected by fractional freezing. A higher-boiling yellow oil, probably fulvene polymers, was also always obtained.

Fulvene was identified by a comparison of its absorption spectrum and certain chemical properties with those of an authentic specimen prepared in dilute solution from *cyclo*pentadiene and formaldehyde by a modification of Thiele's method,[4] and also by comparison with Thiec and Wiemann's spectral data.[5] The characteristic peaks at 242 and *ca.* 365 mμ were observed. The latter peak is rather flat and moves as the fulvene polymerises: its tailing into the visible is responsible for the yellow colour. Thiec and Wiemann[5] found $\epsilon_{242}/\epsilon_{373} = 51{\cdot}3$ for freshly distilled material, and $\epsilon_{242}/\epsilon_{362} = 45{\cdot}7$ for material stored at −70° for three days in an inert atmosphere. We obtained values of $\epsilon_{242}/\epsilon_{365} = 48{\cdot}3$, 51·2, and 48·4. There was no spectral evidence for the formation of hexa-1:3-dien-5-yne[6] or hexa-1:5-dien-3-yne[6] (the open-chain isomers), and none for hexa-1:3:5-triene.[7] These hydrocarbons are colourless. The instability of fulvene, coupled with the difficulty of separating it from benzene, have so far prevented our examination of the infrared spectrum.

The present isomerised material was strongly unsaturated towards bromine in carbon tetrachloride and towards aqueous potassium permanganate. It was rapidly decolorised when warmed with maleic anhydride. It was instantly decolorised by piperidine and diethylamine, and more slowly by methylamine, benzylamine, or alcoholic sodium hydroxide, but was unaffected by triethylamine, pyridine, aniline, or mono- or di-methylaniline, except after several days. The colour was not discharged by ammoniacal cuprous chloride. Closely parallel results were obtained with the solution of authentic material.

Preliminary experiments indicate that benzene homologues undergo a similar rearrangement.

The authors thank Professor E. A. Guggenheim, F.R.S., for helpful comments on the manuscript. One of them (J.M.B.) thanks Messrs. Hanovia for a grant.

[*Received, September 9th*, 1957.]

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## The Use of Hydrazine Salts and the Influence of Catalysts in the Preparation of Borazole Derivatives

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IN experiments on the preparation of alkylated and halogenated borazoles, we found that, in Brown and Laubengayer's method[1] for the preparation of *BBB*-trichloroborazole from ammonium chloride and boron trichloride at elevated temperatures, the use of very pure ammonium chloride resulted in low yields. Cruder materials, on the other hand, which contained iron salts as the chief impurity, gave better results. Then it was found that a mixture of pure ammonium salts with a catalyst consisting of metallic iron, nickel, or cobalt supported on pumice gave complete reaction with boron trichloride below 120° and with a yield of 50—60%. Further, reaction of boron trichloride and methylamine hydrochloride occurred below 180° with the catalyst, and again the yield was of the order of 60%. In the catalysed reaction, much smaller quantities of non-volatile products resulted.

Improved yields of borazole have also been obtained by using hydrazine hydrochloride or alkylated hydrazine hydrochlorides in place of ammonium or amine salts. In these instances also the catalyst may be used to lower the reaction temperature and to improve yields. With hydrazine hydrobromide, for example, the following reaction occurred below 200° with the catalyst:

$$9N_2H_4,2HBr + 12BBr_3 \longrightarrow 4B_3N_3H_3Br_3 + 42HBr + 3N_2$$

It gave a yield of 40—45% of purified $B_3N_3H_3Br_3$. The quantity of catalyst normally employed was of the order of 10% by weight of the salt and it was prepared by calcining the nitrate on powdered pumice and reducing the resulting oxide with hydrogen. The catalyst and the salt were then thoroughly mixed in a dry-box. In the course of the reaction the catalyst was transformed, at least superficially, into halide.

(*Received, August 19th*, 1957.)

[1] Brown and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 3699.