Synthesis of Carbon–Boron Bonds with Small Carbon Molecules

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A METHOD of producing useful quantities of carbon vapour for organic syntheses has been pioneered by Skell and his co-workers.[1] Recently atomic silicon and trimethylsilane have been shown to afford a trisilane as the major product.[2]

It would appear that atomic carbon might be used to prepare novel organo-metallic and -metalloidal compounds, and we have initiated a programme to test this idea by studying the reaction of carbon vapour with diboron tetrachloride using essentially the same apparatus and procedure described by Skell *et al.*[1] Multiple runs were carried out using approximately 25 g. samples of B_2Cl_4. Each run consumed about 4 g. of diboron tetrachloride and afforded approximately 0·6 g. of volatile products, which were isolated and purified by conventional high-vacuum techniques. The major product (about 400 mg. obtained per run) was a white crystalline, extremely moisture-sensitive, solid (I), m.p. 66—68°, which is thermally stable at room temperature for periods of at least several weeks. A complete elemental analysis and a molecular weight determination in boron trichloride solution established CB_4Cl_8 as the molecular formula. The ^{11}B n.m.r. spectrum consisted of a broad but symmetrical singlet at $-57{\cdot}0$ p.p.m., relative to $Et_2O^{11}BF_3$ as external standard. These results suggest that (I) is tetrakisdichloroborylmethane, $C(BCl_2)_4$, and the mass spectrum confirms this. The most intense peaks in the mass spectrum occur at *m/e* 80—85 corresponding to BCl_2^+ ions; on the basis of the isotopes present the envelope of peaks expected for these ions is 80—85. An exceedingly weak envelope, probably due to the molecular ion occurs in the region *m/e* 330—334 and there are very strong envelopes of peaks at *m/e* 298—311 ($CB_4Cl_7^+$), 217—228 ($CB_3Cl_5^+$), 183—193 ($CB_3Cl_4^+$) and 137—145 ($CB_2Cl_3^+$). Further details of the spectrum will be given subsequently.

Other products from the reaction between carbon vapour and diboron tetrachloride are $(Cl_2B)_3CCl$ (II) (m.p. $-72°$) and $(Cl_2B)_2CCl_2$ (III) (m.p. $-82°$), both of which afford BCl_3 and oily residues on standing. Trisdichloroborylchloromethane and bisdichloroboryldichloromethane can be obtained in higher yield from the reaction between carbon vapour and boron trichloride. This reaction also affords a compound of formula $C_2B_2Cl_6$ (IV) (m.p. $-10°$) the infrared spectrum of which shows a band at 1550 cm.$^{-1}$, characteristic of a C:C·B group,[3] suggesting that (IV) is *cis*-$Cl(Cl_2B)C:C(BCl_2)Cl$.

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