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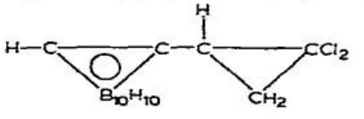
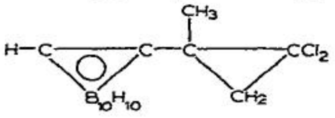
Reactions of phenyl(bromodichloromethyl)mercury with alkenylcarboranes

Previous studies in these Laboratories have been concerned with the preparation of gem-dihalocyclopropanes by the reaction of olefins with phenyl(trihalomethyl)-mercury compounds[1]. In this connection vinyl-, isopropenyl- and allylcarborane are of some interest as olefinic substrates, since the great steric bulk of the *o*-carboranyl substituent[2] and its $-I$ effect[3] should result in a greatly reduced reactivity of the C=C bonds (especially in the vinylic carboranes) toward the electrophilic dichlorocarbene intermediate. Since there is some evidence that steric effects can be important in CCl_2 addition to olefins[4,5], it was not certain if the dichlorocyclopropanation of vinyl- and isopropenylcarborane could be realized.

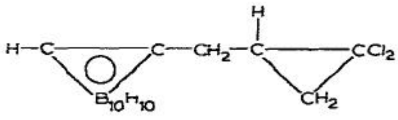
We report here the reactions of vinyl-, isopropenyl- and allylcarborane with $C_6H_5HgCCl_2Br$ in refluxing benzene, which gave the corresponding gem-dichlorocyclopropanes, (I), (II) and (III), in yields of 86%, 81% and 93%, respectively. While a quantitative assessment of the relative reactivities of these alkenylcarboranes toward this organomercury reagent was not attempted, the competition of equimolar quantities of each respective carborane and cyclohexene for a deficiency of phenyl(bromodichloromethyl)mercury resulted in formation of 7,7-dichloronorcarane in yields of 72–75%, while no cyclopropane products derived from the alkenylcarboranes were found. Thus, compared to cyclohexene, these *o*-carboranyl-substituted olefins indeed are quite unreactive. Purely qualitative observations suggested that, as might be expected on both steric and electronic grounds, the allylcarborane is more reactive toward CCl_2 than are the vinyl- and isopropenylcarboranes. As noted in the experimental section, greater excesses of mercurial reagent were required to consume completely the latter two than were required to consume completely the allylcarborane.



(I)



(II)



(III)

Experimental

General comments. All reactions were carried out under an atmosphere of dry argon. The alkenylcarboranes were products of the Olin Mathieson Chemical Corporation and phenyl(bromodichloromethyl)mercury was prepared as described previously[6]. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were recorded using a Perkin Elmer Model 237 infrared spectrophotometer. NMR spectra were obtained using a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm down field from tetramethylsilane and the spectra were recorded on samples in carbon tetrachloride solution.

1,1-*Dichloro-2-o-carboranylcyclopropane* (*I*). Vinylcarborane (4.0 g, 23.5 mmoles) was dissolved in 30 ml of benzene (distilled from calcium hydride) in a 100 ml three-necked flask equipped with reflux condenser topped with an argon inlet tube, magnetic stirring assembly and a dropping funnel. To this solution was added 20.75 g (47 mmoles) of phenyl(bromodichloromethyl)mercury in 30 ml of benzene and the resulting mixture was heated at reflux with stirring for 5 h. After this time, thin-layer chromatographic analysis showed that some vinylcarborane remained unconverted. A further 10 g of mercurial reagent was added and the reaction mixture was heated at reflux for another 3 h. This served to consume completely the starting carborane. The solution was filtered from 23.4 g of phenylmercuric bromide, m.p. 274–276°. Removal of solvent from the filtrate at 40°/20 mm left a viscous residue. Distillation at 0.01 mm (bath temperature 130–140°) gave 5.1 g (86%) of 1,1-dichloro-2-*o*-carboranylcyclopropane. The product was obtained as a viscous liquid which crystallized on standing to give material of m.p. 73–74°. (Found: C, 23.92; H, 5.24; B, 42.81; Cl, 28.27. $C_5H_{14}B_{10}Cl_2$ calcd.: C, 23.71; H, 5.53; B, 42.68; Cl, 28.06.)

Its infrared spectrum (pure liq.) showed bands at 3075 (s), 3050 (w), 2970 (s), 2945 (s), 2880 (m), 2870 (m), 2600 (vs), 1500 (m), 1475 (m), 1448 (w), 1424 (w), 1390 (w), 1315 (w), 1268 (w), 1216 (m), 1180 (w), 1127 (m), 1090 (m), 1071 (s), 1060 (m), 1040 (m), 1024 (s), 1008 (m), 972 (m), 950 (s), 860 (m), 830 (m), 815 (m), 760 (s), 728 (vs), 685 (vs), cm^{-1}. Its NMR spectrum (CCl_4) showed a broad singlet at 3.66 ppm and a complex multiplet from 2.6 to 0.5 ppm downfield from tetramethylsilane.

1,1-*Dichloro-2-o-carboranyl-2-methylcyclopropane* (*II*). A similar procedure was used in the reaction of 24.5 mmoles of isopropenylcarborane with a total of 63.2 mmoles of phenyl(bromodichloromethyl)mercury in benzene solution during 5 h at reflux. Filtration of phenylmercuric bromide and removal of volatiles left a viscous residue. This was distilled at 0.05 mm (bath temperature 110–123°) to give 5.3 g (81%) of 1,1-dichloro-2-*o*-carboranyl-2-methylcyclopropane. The initially liquid product crystallized on standing to give solid of m.p. 60–61° (sealed tube). An analytical sample was obtained by gas liquid partition chromatography (GLPC) using an MIT isothermal gas chromatograph with a 4 ft. × 12 mm glass column packed with 10% Apiezon L Grease on 80–100 mesh Chromosorb W with jacket at 180° and 15 psi helium. (Found: C, 26.98; H, 6.17; B, 40.34; Cl, 26.54. $C_6H_{16}B_{10}Cl_2$ calcd.: C, 26.96; H, 5.99; B, 40.45; Cl, 26.59.)

Its infrared spectrum (pure liq.) showed bands at 3100 (m), 3075 (m), 3000 (w), 2950 (w), 2940 (w), 2600 (vs), 1500 (w), 1460 (m), 1442 (s), 1400 (m), 1320 (w), 1260 (w), 1236 (m), 1175 (w), 1145 (sh), 1124 (s), 1095(sh), 1078 (s), 1060 (s), 1038 (m), 1021 (s), 1008 (m), 960 (w), 938 (m), 917 (w), 882 (w), 860 (w), 815 (sh), 785 (sh), 760 (vs), 730 (vs), 700 (m). The NMR spectrum consisted of a broad singlet at 3.61 ppm and a complex multiplet centered at 1.84 ppm.

1,1-*Dichloro-2-(o-carboranylmethyl)cyclopropane* (*III*). A mixture of 24.5 mmoles of allylcarborane and 49 mmoles of $C_6H_5HgCCl_2Br$ in 40 ml of benzene was heated at reflux under argon. Thin-layer chromatography showed that the starting carborane had been consumed after 2.5 h. Phenylmercuric bromide (17 g) was filtered. Solvent was removed from the filtrate at 10 mm to give a viscous liquid. Sublimation of the latter at 60°/0.01 mm gave 6.6 g of white solid. Extraction with pentane left another 0.4 g of phenylmercuric bromide. Evaporation of the pentane solution gave 6.2 g of white, crystalline solid, m.p. 58–59°. An analytical sample was isolated by GLPC. (Found: C, 27.00; H, 6.60; B, 40.08; Cl, 26.33. $C_6H_{16}B_{10}Cl_2$ calcd.: C, 26.96; H, 5.99; B, 40.45; Cl, 26.59.)

Its infrared spectrum (CCl_4 and Nujol mull) showed bands at 3070 (s), 3010 (w), 2965 (w), 2940 (w), 2860 (w), 2600 (vs), 1449 (s), 1401 (m), 1330 (w), 1269 (s), 1238 (m), 1220 (sh), 1145 (sh), 1129 (vs), 1118 (sh), 1070 (vs), 1069 (s), 1039 (vs), 1023 (vs), 1012 (sh), 976 (m), 940 (m), 921 (m), 910 (sh), 885 (m), 758 (s), 730 (vs), cm^{-1}. The NMR spectrum consisted of a broad singlet at 3.57 ppm, a doublet ($J = 6.5$ cps) at 2.40 ppm and a multiplet centered at 0.97 ppm.

Competition reactions. A mixture of 16.7 mmoles each of cyclohexene and vinylcarborane and 5.56 mmoles of phenyl(bromodichloromethyl)mercury in 20 ml of benzene was heated at reflux under argon with stirring for 5 h. Thin-layer chromatography established that the mercurial had been consumed completely. The solution was filtered from precipitated phenylmercuric bromide (94%). GLPC analysis of the filtrate (F & M Model 700 gas chromatograph, temperature program 40–240°, 48 psi, 20% General Electric Co. SE-30 Silicone Rubber Gum on Chromosorb W) showed that 7.7-dichloronorcarane had been formed in 74% yield. It was identified by comparison of its infrared spectrum and refractive index with those of an authentic sample.

In the case of isopropenylcarborane and allylcarborane the 7,7-dichloronorcarane yields were 75 and 72%, respectively. With all three alkenylcarboranes no CCl_2 addition products appeared to have been formed in these competition experiments.

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1 D. SEYFERTH, J. M. BURLITCH, R. J. MINASZ, J. Y.-P. MUI, H. D. SIMMONS, JR., A. J.-H. TREIBER AND S. R. DOWD, *J. Am. Chem. Soc.*, 87 (1965) 4259.
2 T. ONAK, *Advan. Organometal. Chem.*, 4 (1966) 263.
3 M. F. HAWTHORNE, T. E. BERRY AND P. A. WEGNER, *J. Am. Chem. Soc.*, 87 (1965) 4746.
4 L. H. KNOX, E. VELARDE, S. BERGER, D. CUADRIELLO, P. W. LANDIS AND A. D. CROSS, *J. Am. Chem. Soc.*, 85 (1963) 1851.
5 M. Z. NAZER, *J. Org. Chem.*, 30 (1965) 1737.
6 D. SEYFERTH AND J. M. BURLITCH, *J. Organometal. Chem.*, 4 (1965) 127.

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