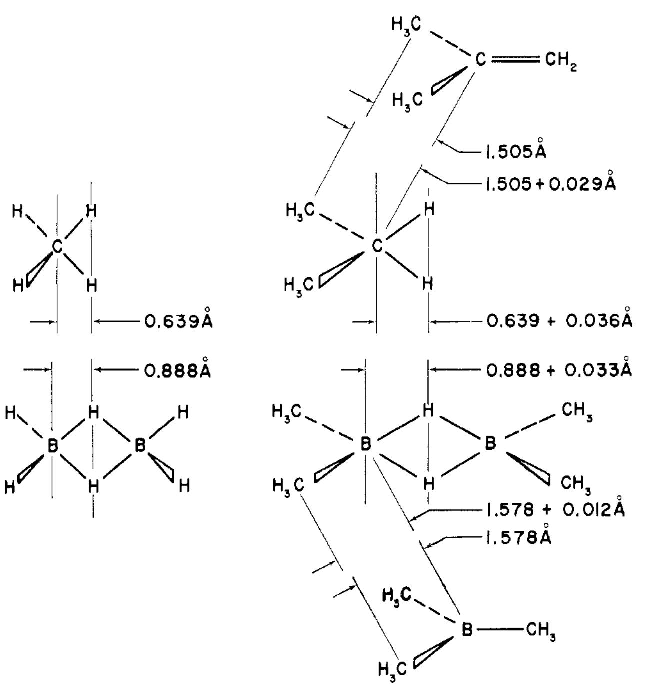
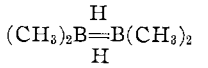


Figure 4.—Comparison of related structural parameters in boranes and hydrocarbons.

however, in excellent accord with calculations[16] based on a model force field in which it is assumed that all C–H bonds are identical except for steric environment (a fact which by no means proves that the effect is steric). Those who favor hybridization arguments could undoubtedly piece together a self-consistent picture notwithstanding the scant evidence provided by the borane bond angles.

Although it is fair to advance interpretations alternative to the popular hyperconjugative one, it is unwise to overstress the analogies depicted in Figure 4. This need for caution becomes evident on examination of the barriers to rotation where TMDB rather than $B(CH_3)_3$ is seen to be related to the model compound $(CH_3)_2C{=}CH_2$. Clearly, hyperconjugation is not involved in threefold barriers, for $B(CH_3)_3$ has nearly free rotation of its methyl groups[4] consistent with the symmetry-imposed exclusion of a threefold potential energy component. In TMDB the symmetry is broken and a threefold contribution is allowed for methyl rotations. It is probably significant that the barrier turns out to be approximately the same as in $(CH_3)_2C{=}O$, for it takes little reflection to recognize the similarity between the electron density distributions in



$$(CH_3)_2B\overset{H}{\underset{H}{=}}B(CH_3)_2$$

and $(CH_3)_2C{=}O$. For the sake of argument we have applied Hoffmann's extended Hückel MO treatment[17] to TMDB and acetone. In both cases the stable conformations were those observed experimentally. Moreover, the magnitude of the barrier calculated for acetone was correct. By contrast, the TMDB barrier was almost an order of magnitude higher than that inferred from the electron diffraction analysis, partly, perhaps, because of the excessive repulsions between hydrogens which seem characteristic of the Hoffmann program.

In summary, the results of the present study are not inconsistent with long-held views of bonding in small molecules. Unfortunately, however, the same impasses which are encountered in interpreting details of hydrocarbon structures are also encountered here. These serve to remind us of the superficiality of our present qualitative interpretational schemes.

Acknowledgments.—We wish to express our graritude to Dr. C. W. Heitsch for donating the sample of tetramethyldiborane. We are also indebted to Lockheed Electronics Co. and their technical publications staff for assistance in preparing the final document.

[16] E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, in press.

[17] R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963).

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The Reactions of 1-Isopropenylcarborane with Dinitrogen Tetroxide, Tetrafluorohydrazine, and Bromine

By W. E. Hill

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The preparation of several new compounds by reaction of 1-isopropenylcarborane with N_2O_4, N_2F_4, and Br_2 is reported. Derivatives of some of these compounds have been made. The susceptibility of the alkenyl group to radical attack is discussed as well as its inert nature with respect to ionic additions. Some physical properties of the new compounds are reported.

The reactions of vinyl groups adjacent to a carborane nucleus have not been extensively studied. Cohen, *et al.*,[1] synthesized 1-isopropenylcarborane (I) and reported some of its reactions. These authors found that the alkenyl group could be hydrogenated and also that oxidation could be achieved though the product was not

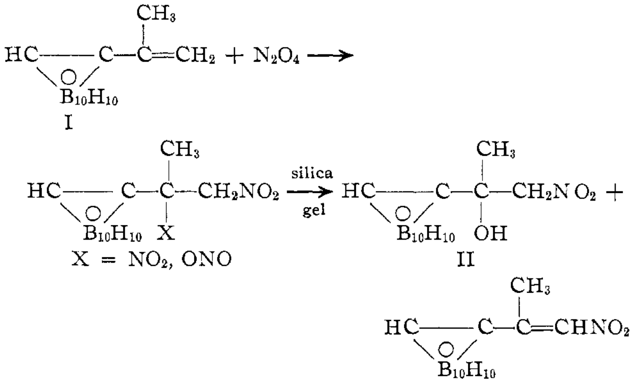
[1] M. M. Fein, J. Robinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 111 (1963).

identified. Oxidation with peroxytrifluoroacetic acid gave the epoxide, and attempts to add bromine and iodine monobromide under electrophilic conditions were reported as unsuccessful.[1] We now report some new compounds obtained from radical additions to the alkenyl group, and we confirm its unreactive nature toward ionic additions.

Results and Discussion

Radical additions to the alkenyl group in 1-isopropenylcarborane (I) proceed quite readily with addends such as dinitrogen tetroxide, tetrafluorohydrazine, and bromine when the last is irradiated with ultraviolet light.

Dinitrogen tetroxide reacts with (I) under conditions similar to those described by Stevens for hydrocarbon olefins and acetylenes.[2,3] The crude product was a mixture of the nitro nitrite and dinitro adduct, as identified by the infrared spectrum. Neither, however, survived chromatography over silica gel. The nitro nitrite was converted to nitro alcohol (II) and the dinitro adduct to nitro olefin (III) as given in eq 1. Evolution of an acidic gas (presumably HNO_2) on the column was observed.

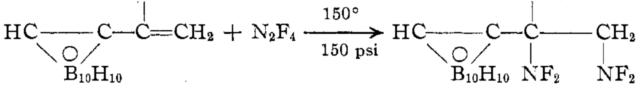

$$\underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2} + \mathrm{N_2O_4} \longrightarrow$$
I

$$\underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\underset{\mathrm{X}}{\mathrm{C}}}{-}\mathrm{CH_2NO_2} \xrightarrow[\text{gel}]{\text{silica}} \underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\underset{\mathrm{OH}}{\mathrm{C}}}{-}\mathrm{CH_2NO_2} +$$
X = NO_2, ONO II

$$\underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CHNO_2}$$
III (1)

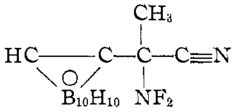
Attempts to dehydrate II by the usual method for converting nitro alcohols to nitro olefins were unsuccessful.[4] However, treatment of II with acetic anhydride yielded the corresponding acetate. Chromatography of the acetate over silica gel produced III.

Tetrafluorohydrazine reacts with I at high temperatures to give the bis-difluoramino derivative IV in good yield according to eq 2 and in accordance with the known reactions of hydrocarbon olefins.[5,6]


$$\underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2} + \mathrm{N_2F_4} \xrightarrow[150\ \text{psi}]{150^\circ} \underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\underset{\mathrm{NF_2}}{\mathrm{C}}}{-}\underset{\mathrm{NF_2}}{\mathrm{CH_2}}$$
I IV (2)

The reaction must be carried out in an all-metal reactor if a good yield of IV is to be obtained. When a glass reactor is used, extensive decomposition of the tetrafluorohydrazine into SiF_4 and NO results, and undesired side products are recovered. These products have not been identified.[7]

As expected, IV is easily dehydrofluorinated to the corresponding difluoraminonitrile V upon treatment with base.


$$\underset{\diagdown O \diagup\ \mathrm{B_{10}H_{10}}}{\mathrm{HC{-}C}}{-}\overset{\mathrm{CH_3}}{\underset{\mathrm{NF_2}}{\mathrm{C}}}{-}\mathrm{C{\equiv}N}$$
V

Unlike most alkenyl groups in hydrocarbon compounds to which bromine adds readily under ionic conditions, I was recovered unchanged from an ethanolic solution of 3 equiv of bromine stirred in the absence of light for 3 days. However, when I was dissolved in carbon tetrachloride containing 1 equiv of bromine and irradiated with ultraviolet light for 10 min, complete decolorization of the solution resulted, and the dibromo derivative of I was recovered.

Attempts to add HNF_2 in methylene chloride with sulfuric acid or Amberlyst 15 as catalysts were unsuccessful[8] as were attempts to add HCN across the double bond. These reactions, like that with bromine in ethanol, are essentially ionic in nature, and we believe they emphasize the low reactivity of the alkenyl group toward ionic additions.

To emphasize further the electronic effects of the carborane cage on the adjacent alkenyl group, we have found that bromine can be added to olefinic carboranes under ionic conditions when insulation between cage and the alkenyl group is provided.

The nmr spectra of these compounds contain some very interesting and unusual resonances. In addition to this, the coupling constants are frequently of unusual magnitude. For example, the resonance of the methyl group of 1,2-bis(difluoramino)-2-(1-carboranyl)propane appears as a triplet ($J_{H-F} = 2$ cps) of triplets ($J_{H-F} = 1$ cps). Decoupling experiments have shown that this results from the nonequivalence of the fluorine of both NF_2 groups. The spectra are reported in detail in the Experimental Section.

The position of the broad singlet assigned to the C–H resonance of the carboranyl cage appears to be dependent on steric factors as well as electronic effects. For example, 1,2-dibromo-2-carboranylpropane has an absorption at 4.37 ppm assigned to the carboranyl C–H while the bis-difluoramino compound has its C–H absorption at 4.03 ppm. This absorption as in 1-isopropenyl carborane occurs at 3.90 ppm.

Experimental Section

Starting Materials.—1-Isopropenylcarborane was prepared by the procedure reported in the literature.[1] It was recrystallized from *n*-heptane prior to use. Tetrafluorohydrazine was purified by vacuum-line distillation. The purity of the gas was determined by mass spectral analysis, and in all cases it was 99% pure.

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(2) T. E. Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959).

(3) T. E. Stevens and W. D. Emmons, *ibid.*, **80**, 338 (1958).

(4) H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 606 (1934).

(5) R. C. Petry and J. P. Freeman, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, Abstract S-46.

(6) R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 5912 (1961).

(7) These side products may be nitrosocarboranes or they may contain O←N=NF groups: T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

(8) W. H. Graham and J. P. Freeman, *J. Am. Chem. Soc.*, **89**, 716 (1967).

Dinitrogen tetroxide (Matheson Co.) was purified by air oxidation until there was no color on condensing at −196°.

Analyses.—Carbon, hydrogen, and nitrogen were determined by conventional combustion using MgO in the combustion tube. Fluoride was determined by titration with thorium nitrate[9] after hydrolysis with 10% sodium hydroxide in a 1:1 ethanol–water solvent and then adjusting the pH. Bromide was determined by titration with mercuric nitrate.

Melting Points were observed visually by placing the samples in 2-mm o.d. Pyrex tubes which were submerged in paraffin oil and heated to a rate of 1°/min. They are uncorrected.

Proton nmr spectra were obtained at 60 Mc on a Varian A-60 using tetramethylsilane as an internal standard. **Fluorine nmr spectra** were obtained at 40 Mc on a Varian HR-40 using CCl_3F as an internal standard. Fluorine spectra are reported in ppm from CCl_3F and designated ϕ.

Preparation of 1-Nitro-2-(1-carboranyl)propene and 1-Nitro-2-hydroxy-2-(1-carboranyl)propane.—A 1-l. stainless steel Hoke bomb was charged with a solution of 1-isopropenylcarborane (0.217 mole) in 300 ml of diethyl ether. The bomb was cooled to −80°, evacuated, and charged with dinitrogen tetroxide (0.313 mole). The reaction was shaken at room temperature for 12 hr. Excess dinitrogen tetroxide was removed *in vacuo*. The reaction mixture was quenched in aqueous sodium bicarbonate. The organic layer was separated and dried over magnesium sulfate, and the solvent was then removed by distillation. The oily residue was chromatographed over silica gel to give 1-nitro-2-(1-carboranyl)propene, mp 73.5°, as a light green solid in 35% yield.

The proton nmr spectrum shows three absorptions centered at 2.25, 3.90, and 7.25 ppm, respectively. The absorption due to the methyl group at 2.25 ppm is split into a doublet (J = 2 cps) by the vinylic proton. The 3.90-ppm absorption due to the C–H on the carboranyl cage is a very broad singlet. The absorption due to the vinylic proton centered at 7.25 ppm is a quartet (J = 2 cps) due to interaction of the methyl protons. The infrared spectrum of the solid in Nujol shows an absorption at 1640 cm^{-1} due to the C=C stretching vibration and bands characteristic of a nitro group. *Anal.* Calcd for $B_{10}C_5H_{15}NO_2$: C, 26.20; H, 6.55; N, 6.11. Found: C, 26.20; H, 6.66; N, 6.19.

1-Nitro-2-(1-carboranyl)-2-hydroxypropane, a light yellow solid, mp 103°, was obtained in 65% yield. The proton nmr spectrum shows four absorptions centered at 1.35, 1.63, 3.95, and 4.67 ppm. The absorption at 1.35 ppm due to the hydroxyl proton is a solvent- and concentration-dependent singlet. All other absorptions are also singlets. The 1.63-ppm absorption is due to the methyl group and the 4.67-ppm absorption to the vinylic proton. The 3.95-ppm absorption is very broad and is assigned to the C–H on the carboranyl cage. The infrared spectrum confirms the presence of hydroxy and nitro groups. *Anal.* Calcd for $B_{10}C_5H_{17}NO_3$: C, 24.29; H, 6.48; N, 5.68. Found: C, 24.30; H, 6.88; N, 5.68.

Preparation of 1-Nitro-2-acetoxy-2-(1-carboranyl)propane.—A solution of 1-nitro-2-(1-carboranyl)-2-hydroxypropane (0.011 mole) in 10 ml of acetic anhydride and one drop of sulfuric acid was allowed to stir for 12 hr at room temperature. The solution was then poured into 200 ml of water and stirred for 2 hr. The solid that precipitated was filtered and recrystallized from *n*-hexane to give 1-nitro-2-acetoxy-2-(1-carboranyl)propane, as a light yellow solid, mp 83–85°, in 82% yield.

The proton nmr spectrum shows singlet absorptions at 2.10 and 1.80 ppm due to the isopropyl methyl and the acetoxy methyl groups, respectively. A broad singlet due to the C–H on the carboranyl cage is observed at 4.17 ppm. The methylene protons appear as an AB pattern with A at 5.17 ppm, B at 4.85 ppm, and J_{AB} = 13 cps. The infrared spectrum confirms the presence of acetoxy and nitro groups. *Anal.* Calcd for $B_{10}C_7H_{19}NO_4$: C, 29.10; H, 6.62; N, 4.84. Found: C, 29.60; H, 6.90; N, 4.80.

Preparation of 1,2-Bis(difluoramino)-2-(1-carboranyl)propane.—1-Isopropenylcarborane (0.011 mole) was washed into a 500-ml stainless steel Hoke bomb with 100 ml of carbon tetrachloride (Spectro grade). The bomb was cooled to −80°, evacuated, and charged with tetrafluorohydrazine (0.044 mole). The bomb was heated to 150° for 24 hr. Excess tetrafluorohydrazine and carbon tetrachloride were removed under vacuum and the remaining oil was washed into a round-bottom flask with fresh oil and distilled to give 1,2-bis(difluoramino)-2-(1-carboranyl)propane, bp 95° (∼3 mm), as a colorless liquid in 67% yield.

The proton nmr spectrum of the methyl group appears to be a triplet (average J_{H-F} = 2 cps) of triplets (average J_{H-F} = 1 cps) centered at 1.69 ppm. An absorption at 4.03 ppm due to the C–H on the carboranyl cage is also observed. The absorptions due to the methylene protons have the gross appearance of a triplet (J_{H-F} = 27 cps) centered at 4.10 ppm but the pattern is complicated by further coupling. The fluorine nmr spectrum shows two absorptions, a triplet (J_{H-F} = 27 cps) centered at ϕ −65.7 and a broad singlet at ϕ −36.7. The infrared spectrum confirms the absence of the double bond and contains bands characteristic of vicinal difluoramino groups. *Anal.* Calcd for $B_{10}C_5H_{16}N_2F_4$: C, 20.83; H, 5.55; N, 9.72; F, 26.38. Found: C, 21.82; H, 5.73; N, 9.85; F, 26.70.

Preparation of 2-(1-Carboranyl)-2-difluoraminopropionitrile.—1,2-Bis(difluoramino)-2-(1-carboranyl)propane (0.017 mole) was dissolved in 50 ml of methylene chloride. Fifty milliliters of absolute methanol was also added. The solution was cooled to 0° and sodium methoxide (0.044 mole) in 30 ml of methanol was added dropwise with stirring. After the addition was complete, the flask was allowed to warm to room temperature and stirred for 15 min. The reaction was quenched with water, the organic layer was separated, dried over magnesium sulfate, and filtered, and the solvent was removed *in vacuo*. The dirty white solid was then recrystallized from *n*-pentane to give 2-(1-carboranyl)-2-difluoraminopropionitrile, mp 58°, as a white solid in 87% yield.

The proton nmr spectrum of the methyl group appears as X_3 of an ABX_3 system. Only four of six lines are seen because of a very large J_{AB} (∼600 cps in similar systems). The absorption is centered at 1.75 ppm; the J_{AX} and J_{BX} couplings are small (1–2 cps) and not directly related to the observed splittings. A broad singlet at 3.95 ppm, due to the C–H on the carboranyl cage, is also observed. Owing to nonequivalence of the two fluorines, the F^{19} nmr spectrum appears as an AB system with A at ϕ −53.8, B at ϕ −44.2, and J_{AB} = 584 cps. The infrared spectrum shows a very weak absorption at 2280 cm^{-1} due to the cyano group and also has bands characteristic of a difluoramino group. *Anal.* Calcd for $B_{10}C_5H_{16}N_2F_2$: C, 24.19; H, 5.65; N, 11.29; F, 15.32. Found: C, 24.00; H, 5.73; N, 10.80; F, 15.50.

Preparation of 1,2-Dibromo-2-(1-carboranyl)propane.—1-Isopropenylcarborane (0.027 mole) was dissolved in 150 ml of carbon tetrachloride. Bromine (0.030 mole) was added and the solution was irradiated for 10 min with ultraviolet light. The solvent and excess bromine were removed *in vacuo* to give 1,2-dibromo-2-(1-carboranyl)propane, mp 53°, as a light gray solid. The yield was quantitative.

The compound shows a singlet absorption in its proton nmr spectrum due to the methyl protons at 2.13 ppm. The absorption due to the methylene protons appears as an AB system with A at ∼3.83 ppm, B at ∼3.95 ppm, and J_{AB} = 12 cps. There is also a broad singlet centered at 4.37 ppm due to the C–H on the carboranyl cage. No absorption corresponding to the double-bond stretching vibration is found in the infrared spectrum. *Anal.* Calcd for $B_{10}C_5H_{16}Br_2$: C, 17.45; H, 4.65; Br, 43.58. Found: C, 17.50; H, 4.81; Br, 43.70.

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