[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

Reactions of the Perfluoroalkylnitriles. III. Perfluoroalkylhydrazidines and Perfluoroalkyl-N-aminotriazoles[1]

BY HENRY C. BROWN AND DONALD PILIPOVICH

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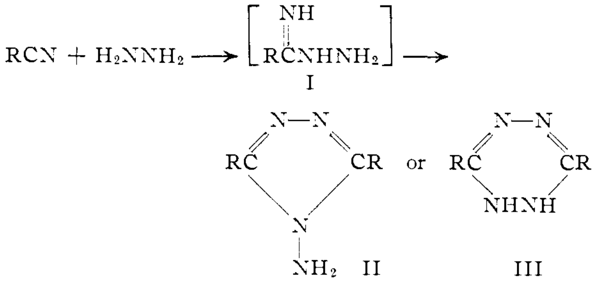
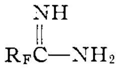
Perfluoroalkylnitriles, R_FCN, in which $R_F = C_3F_7$, C_4F_9, C_5F_{11}, or C_7F_{15} were treated with hydrazine under mild conditions to produce perfluoroalkylhydrazidines, $R_FC(NH_2){:}NNH_2$. These compounds are believed to be the first reported examples of free, unsubstituted hydrazidines. Perfluoroacetonitrile and perfluoropropionitrile with hydrazine yielded a secondary product believed to be the 1-N-amino-2,5-bis-(perfluoroalkyl)-triazole. *unsym*-Dimethylhydrazine with perfluoroalkylnitriles produced N-substituted hydrazines in all examples.

The reaction of organic nitriles with hydrazine has been known for many years.[2] The products isolated from these reactions, however, were always heterocyclic, although many investigators[3,4,5] proposed the intermediate formation of the hydrazidine structure I.


I II III

Apparently, in these early reactions, if this mechanism were operative, the hydrazidine underwent further reaction to yield the 1-N-amino-1,3,4-triazole II or the 1,2-dihydro-*sym*-tetrazine III.

Recently it has been shown that the perfluoroalkylnitriles react at low temperatures with ammonia to produce the stable amidine structure IV,[6,7] although the analogous reaction of the


IV

$R_FC(=NH)-NH_2$

hydrocarbon nitrile does not produce a stable product. The enhanced reactivity of the nitrile group attached to a perfluoroalkyl group and the stabilization of its addition compounds with nucleophilic reagents has been attributed to the strong inductive effect of the perfluoroalkyl group. Since this effect should apply also to the addition products obtained with the other nitrogen bases, the present study of the addition of hydrazine to the perfluoroalkyl nitriles was undertaken in the hope of isolating the previously unknown primary addition product.

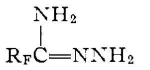
This paper describes the addition of hydrazine to a series of perfluoroalkyl nitriles beginning with trifluoroacetonitrile and including several of greater chain length. Briefly, the results obtained from the various nitriles were divided into two distinct categories: trifluoroacetonitrile and pentafluoropropionitrile produced compounds that appear to be the heterocyclic 1-N-amino-2,5-bis-(perfluoroalkyl)-triazoles upon reaction with hydrazine while perfluorobutyronitrile and the other perfluoroalkylnitriles of longer chain length produced the corresponding perfluoroalkylhydrazidine. *unsym*-Dimethylhydrazine reacted readily with each of the nitriles used to produce N,N-dimethylperfluoroalkylhydrazidines with no cyclic products being found.

The reaction of perfluorobutyronitrile with hydrazine hydrate is typical of the reactions in which the primary addition product could be isolated. This reaction proceeded easily at 0° to give a stable, white crystalline product in high yield; perfluoroalkylnitriles of longer chain length reacted more slowly at 0°, but the rate could be increased by raising the reaction temperature to approximately 30° or by adding a small quantity of 95% hydrazine.

Since the perfluoroalkylhydrazidines are a new type of compound, confirmation of the structure was sought by a variety of methods. Elemental analysis and the neutral equivalent of the hydrochloride confirmed the composition and molecular weight; the infrared spectra gave considerable information concerning structure, but could not differentiate between the two possible tautomers Va and Vb.


Va

$R_FC(=NH)NHNH_2$


Vb

$R_FC(NH_2)=NNH_2$

The principal absorption bands for the perfluoroalkylhydrazidines and the N,N-dimethylperfluoroalkylhydrazidines are shown in Table I.

For the unsubstituted hydrazidines, three bands were noted in the 3500–3100 cm.$^{-1}$ region. Each of the tautomers shown above would be expected to exhibit four bands in this region and a mixture of the tautomers to give a total of eight. The N—H stretching vibrations for the =NH, —NH_2 (*asym.*) and —NH– could not be definitely as-

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[1] Previous paper in this series, W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957). This paper represents a part of the dissertation presented by Donald Pilipovich to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was supported by the Chemistry Branch, Office of Naval Research under Contract Nonr 580(03); NR 356-333 with the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United Sates Government. Presented in part at the 136th National American Chemical Society Meeting, Atlantic City, N. J., September 16, 1959.

[2] V. Migridichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 73.

[3] A. Angeli, *Gazz. chim. ital.*, **23**(2), 101 (1893).

[4] E. Muller and L. Herrdegen, *J. prakt. Chem.*, [2] **102**, 113 (1921).

[5] A. Pinner, *Ber.*, **26**, 2126 (1893).

[6] D. Husted, U. S. Patent 2,676,985 (April 1954).

[7] W. L. Reilly and H. C. Brown, THIS JOURNAL, **78**, 6032 (1956).

TABLE I

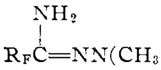
SPECTRAL CORRELATION IN THE 3500–1550 CM.$^{-1}$ REGION

Compound $R_FC(:NH)$-$NHNX_2$ R_F	X	Vibration NH$_2$(NH) stretch	C=N stretch	NH$_2$ deformation	NH deformation
C_3F_7	H	3430(m) 3295(m-s) 3140(s)	1690(s)	1655(s)	1590(w)
C_4F_9	H	3485(m) 3335(s) 3155(s)	1690(s)	1660(s)	1590(w)
C_5H_{11}	H	3480(s) 3360(s) 3175(s)	1690(s)	1655(s)	1587(w)
C_7F_{15}	H	3475(m) 3330(s) 3160(s)	1694(s)	1655(s)	1592(w)
CF_3	CH_3	3530(m-s) 3400(m)	1675(s)	1655(m-s)	
C_2F_5	CH_3	3505(m-s) 3380(m)	1670(s)	1655(m-s)	
C_3F_7	CH_3	3530(m-s) 3385(m)	1670(s)	1660(s)	

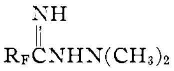
signed; it is probable, however, that the band at approximately 3150 cm.$^{-1}$ is due to symmetrical N–H stretching in the N–NH$_2$ group.

The correlation in the 1700–1600 cm.$^{-1}$ region is somewhat clearer. The two strong bands could be assigned to C=N stretching (1690 cm.$^{-1}$) and NH$_2$ deformation (1655 cm.$^{-1}$). The presence of only one band due to C=N stretching strongly suggests that only one tautomer is present since the C=N group in the non-equivalent structures should absorb at different wave lengths.

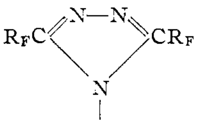
Unsymmetrical dimethylhydrazine was treated with trifluoroacetonitrile and pentafluoropropionitrile in order to obtain an hydrazidine from these compounds without cyclization to the N-aminotriazole configuration. The infrared spectra of these substituted hydrazidines, however, were also largely consistent with either of the tautomeric structures VIa and VIb.


$R_FC(NH_2)=NN(CH_3)_2$

VIa


$R_FC(=NH)NHN(CH_3)_2$

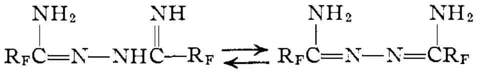
VIb



VII

The two bands in the 3500–3300 cm.$^{-1}$ could represent either the symmetric and asymmetric N–H stretching in the NH$_2$ group of VIa or the two stretching frequencies of the imino and secondary NH groups of VIb.

From the reaction of trifluoroacetonitrile and pentafluoropropionitrile with hydrazine, no primary addition product was isolated. A second reaction took place and, from analogy with the reaction of the hydrocarbon nitrile, presumably formed the 2,5-bis-perfluoroalkyl-1-N-amino-1,3,4-triazole (VII). The 1,2-dihydrotetrazine III formed in the reaction of hydrocarbon nitriles with hydrazine, is apparently not formed in this reaction since the infrared spectrum indicates the presence of an NH$_2$ group in the perfluoroalkyl-substituted product. Another structure, represented by the tautomeric forms VIIIa and VIIIb was considered for this secondary reaction product.


$R_FC(NH_2)=N-NHC(=NH)-R_F \rightleftarrows R_FC(NH_2)=N-N=C(NH_2)R_F$

VIIIa VIIIb

These structures could be formed simply by the addition of the nitrile to the original hydrazidine. The product obtained, however, was monobasic in the formation of a hydrochloride; there is at least a good possibility that VIII would be dibasic.

The basicities of the perfluoroalkylhydrazidines and the N,N-dimethylperfluoroalkylhydrazidines were determined and are shown in Table II.

TABLE II

IONIZATION CONSTANTS OF SOME PERFLUOROALKYLHYDRAZIDINES AND N,N-DIMETHYLPERFLUOROALKYLHYDRAZIDINES

Compound	K_b
$R_FC(NH_2):NN(CH_3)_2$	
CF_3–	9.34×10^{-11}
C_2F_5–	7.25×10^{-11}
C_3F_7–	6.76×10^{-11}
C_5F_{11}–	6.60×10^{-11}
$R_FC(:NH)NHNH_2$	
C_3F_7–	1.74×10^{-11}
C_5F_{11}–	1.48×10^{-11}

Although the ionization constants of the unsubstituted trifluoroacethydrazidine and the pentafluoropropionhydrazidine could not be determined, since these compounds were not isolated, it was felt that determination of the values for the other members of the series might show a progressive change and aid in understanding the reason for the secondary reaction of the lower members of this series.

The values obtained for the K_b in each series are of the same magnitude, and extrapolation would not show a value of K_b for trifluoroacethydrazidine or the pentafluoropropionhydrazidine sufficiently different to indicate a radical difference in reactivity between these two hydrazidines and the perfluorobutyrhydrazidine. The reason for the secondary reaction that occurs must, therefore, lie in the relative reactivities of the original perfluoroalkyl nitrile. This is borne out by the fact that trifluoroacetonitrile definitely reacts with perfluorobutyrhydrazidine, although no product was isolated in the preliminary experiment performed, while perfluorobutyronitrile does not react with the same hydrazidine.

The perfluoroalkylhydrazidines could not be converted to the silver or mercury salts when treated with silver oxide or mercuric oxide. Instead, they exhibited rather strong reducing action by reducing the cations to free silver and mercury. The oxidation products were not isolated. Perfluorobutyrhydrazidine formed perfluorobutyric acid when heated gently with 30% hydrogen peroxide; the acid was undoubtedly formed from an oxidized intermediate since a control reaction containing no peroxide showed no evidence of hydrolysis.

Experimental[8]

Materials.—The perfluoroalkyl nitriles were prepared by: (1) the esterification of the perfluoroalkyl carboxylic acid with either ethyl or methyl alcohol, (2) ammonolysis of the ester to form the amide and (3) subsequent dehydration of the amide with phosphoric anhydride to yield the nitriles. The nitriles were used without further purification. All of the monobasic fluorocarbon acids were obtained from Minnesota Mining and Manufacturing Co. Perfluoroadiponitrile and perfluoroglutaronitrile were prepared by the method described by McBee.[9] Hydrazine, hydrazine hydrate and unsymmetrical dimethylhydrazine were obtained from Olin Matheson Co. and were used as received.

Perfluorobutyrhydrazidine. (**Method A**).—Into a 2-neck 200-ml. round-bottom flask equipped with a polytetrafluoroethylene-covered stirring bar, gas entry tube and Dry Ice cooled reflux condenser was placed 50 g. (1.00 mole) of hydrazine hydrate. The flask was then immersed in an ice-bath placed over a magnetic stirrer. Perfluorobutyronitrile (36 g., 0.18 mole) was bubbled slowly through the solution over a period of 2 hours while the liquid was stirred vigorously. After addition was complete, the ice-bath was removed and the flask was allowed to warm up to room temperature. To decrease the solubility of the solid product in the excess hydrazine, 25 ml. of cold water was added and the resulting slurry was filtered. The white solid obtained after thorough washing with ice-cold water to remove the excess hydrazine was recrystallized from water to yield 40 g. (97% yield) of pure perfluorobutyrhydrazidine, m.p. 69.5–70°.

Anal. Calcd. for $C_4F_7H_4N_3$: C, 21.1; H, 1.76; N, 18.5; F, 58.5. Found: C, 21.3; H, 1.96; N, 18.3; F, 58.6.

Method B.—Into a 50-ml. flask was placed a solution of 5.00 g. (0.024 mole) of perfluorobutyramidine in 25 ml. of ethyl ether. The flask was fitted with a water-cooled condenser and 0.8 g. (0.024 mole) of anhydrous hydrazine was added through the condenser. The mixture was stirred vigorously for 10 hours at room temperature and it was noted that the hydrazine (initially present as a separate liquid phase) was consumed. Ammonia was slowly evolved from the mixture. The ether was removed under reduced pressure and 0.5 ml. of anhydrous hydrazine was added to the solid to ensure complete reaction. Cold water was added to the slurry and the resulting mixture was filtered. The solid obtained was washed repeatedly with cold water to remove completely the excess hydrazine. Recrystallization of the white solid gave 4.5 g. (81% yield) of perfluorobutyrhydrazidine, m.p. 69–71°.

Perfluorovalerhydrazidine.—The same procedure described in method A was used to treat 2.0 g. (0.04 mole) of hydrazine hydrate with 3.0 g. (0.012 mole) of perfluorovaleronitrile. It was noted that the apparent rate of reaction was about the same as that observed in the reaction of hydrazine with perfluorobutyronitrile. The white solid formed was thoroughly washed with cold water and dried, yielding 1.5 g. (44% yield) of perfluorovalerhydrazidine, m.p. 88.5–90°.

Anal. Calcd. for $C_5F_9H_4N_3$: C, 21.7; H, 1.44; N, 15.2. Found: C, 21.8; H, 1.21; N, 14.8.

Perfluorocaprohydrazidine.—The apparatus described in the preparation of perfluorobutyrhydrazidine was modified to the extent that a pressure equalizing funnel was substituted for the gas entry tube. To 3.0 g. (0.08 mole) of hydrazine hydrate was added slowly 12.0 g. (0.041 mole) of perfluorocapronitrile. Reaction was quite slow at 0° but proceeded more rapidly when the mixture was raised to room temperature. The white solid formed was washed thoroughly with cold water. After drying in a desiccator the material was recrystallized from carbon tetrachloride to yield 12.0 g. (90% yield) of perfluorocaprohydrazidine, m.p. 102–104.5°.

Anal. Calcd. for $C_6F_{11}H_4N_3$: C, 22.0; H, 1.22; N, 12.4. Found: C, 22.3; H, 1.47; N, 13.0.

Perfluorocaprylhydrazidine.—To 3.75 g. (0.075 mole) of hydrazine in a 2-neck flask was added 29 g. (0.075 mole) of perfluorocaprylnitrile. The nitrile formed an insoluble layer that was difficult to disperse with mixing. The solid formed was filtered off and the filtrate was returned to the reaction flask. Through the water cooled condenser was added 1 ml. of 95$^+$ % hydrazine and a white solid immediately formed with the evolution of heat. The combined solids were filtered, washed with water, dried, and recrystallized from chloroform to yield 31.0 g. 97% yield of perfluorocaprylhydrazidine, m.p. 128–130°.

Anal. Calcd. for $C_8F_{15}H_4N_3$: C, 22.50; H, 0.92; N, 9.85; F, 66.83. Found: C, 22.6; H, 1.08; N, 10.1; F, 67.0.

Perfluoroglutarhydrazidine.—The apparatus used to prepare perfluorocaprohydrazidine was used to treat 6.0 g. (0.03 mole) of perfluoroglutaronitrile with 8.0 g. (0.16 mole) of hydrazine hydrate. The white solid formed was recrystallized from an alcohol–isopropyl ether solution to yield 7.0 g. (98% yield) of perfluoroglutarhydrazidine, m.p. 123° dec.

Anal. Calcd. for $C_5F_6H_8N_6$: C, 22.6; H, 3.01; N, 31.5; F, 42.9. Found: C, 22.4; H, 2.96; N, 31.4; F, 42.9.

Perfluoroadiphydrazidine.—From 10 g. (0.20 mole) of hydrazine hydrate and 6.0 g. (0.024 mole) of perfluoroadiponitrile, 7.5 g. (100% yield) of perfluoroadiphydrazidine was obtained. The white solid melted with decomposition at 131°.

Anal. Calcd. for $C_6F_8H_8N_6$: N, 25.8. Found: N, 25.4.

N,N-Dimethylperfluoroacethydrazidine.—Into a 2-neck 200-ml. flask containing a polytetrafluoroethylene covered stirring bar and equipped with a gas entry tube and a Dry Ice cooled condenser was placed 15.0 g. (0.25 mole) of unsymmetrical dimethylhydrazine. While the flask contents were cooled by an ice-bath and stirred by a magnetic stirrer, 19.0 g. (0.20 mole) of trifluoroacetonitrile was bubbled into the dimethylhydrazine. After addition of the nitrile the reaction mixture was allowed to warm to room temperature and unreacted starting materials removed under reduced pressure. The remaining solid was recrystallized several times from carbon tetrachloride to give 12.0 g. (39% yield) of N,N-dimethylperfluoroacethydrazidine, m.p. 91–93.5°. This procedure was used for the subsequent preparation of the other N,N-dimethylperfluoroalkylhydrazidines described below.

Anal. Calcd. for $C_4F_3H_8N_3$: C, 31.0; H, 5.15; N, 27.1. Found: C, 31.2; H, 5.28; N, 27.0.

N,N-Dimethylperfluoropropionhydrazidine.—From 10.0 g. (0.16 mole) of unsymmetrical dimethylhydrazine and 16 g. (0.13 mole) of pentafluoropropionitrile was obtained 22 g. (71% yield) of N,N-dimethylperfluoropropionhydrazidine, m.p. 82–83°.

Anal. Calcd. for $C_5H_8F_5N_3$: C, 29.3; H, 3.90; N, 20.5. Found: C, 29.2; H, 3.79; N, 19.9.

N,N-Dimethylperfluorobutyrhydrazidine.—The reaction of 15.0 g. (0.25 mole) of unsymmetrical dimethylhydrazidine with 37 g. (0.19 mole) of heptafluorobutyronitrile yielded 44 g. (88% yield) of N,N-dimethylperfluorobutyrhydrazidine, m.p. 80–81°.

Anal. Calcd. for $C_6F_7H_8N_3$: C, 28.2; H, 3.14; N, 16.4. Found: C, 28.2; H, 3.28; N, 14.8.

N,N-Dimethylperfluorocaprohydrazidine.—From 4.0 g. (0.07 mole) of unsymmetrical dimethylhydrazine and 9.0 g. (0.031 mole) of perfluorocapronitrile was obtained 11 g. (100% yield) of N,N-dimethylperfluorocaprohydrazidine, m.p. 70–72.5°.

Anal. Calcd. for $C_8F_{11}H_8N_3$: C, 27.0; H, 2.25; N, 11.8. Found: C, 27.6; H, 2.40; N, 11.3.

2,5-Bis-(trifluoromethyl)-1-N-amino-1,3,4-triazole.—(1) The procedure used in this preparation was identical to that described under method A for the preparation of perfluorobutyrhydrazidine with the exception that the cooling bath was maintained below −30°. From 5.0 g. (0.10 mole) of hydrazine hydrate and 9.5 g. (0.10 mole) of trifluoroacetonitrile there was obtained 1.0 g. (10% yield) of pure, white 2,5-bis-(trifluoromethyl)-1-N-amino-1,3,4-triazole, m.p. 118–119.5°.

Anal. Calcd. for $C_4F_6H_2N_4$: N, 25.4; F, 51.8. Found: N, 24.8; F, 51.9.

(2) Into a heavy-wall Pyrex tube of approximately 150-ml. volume was placed 2.1 g. (0.07 mole) of anhydrous hydrazine. The tube was connected to a vacuum line and

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(8) Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(9) E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng., Chem.*, **39**, 415 (1947).

the air removed. The tube was then cooled in liquid air and 0.12 mole of trifluoroacetonitrile was condensed therein. The tube was sealed and allowed to warm up to room temperature where it was maintained for 10 hours. A pale yellow solid formed at the bottom of the tube. After the tube was cooled in liquid air and opened to the vacuum system, it was found that 0.045 mole of trifluoroacetonitrile was unreacted, indicating a 1:1 reaction of the nitrile with hydrazine. The solid was removed from the tube and recrystallized from water to yield 9.0 g. (100% yield) of 2,5-bis-(trifluoromethyl)-1-N-amino-1,3,4-triazole, m.p. 118.5–120°. A mixed melting point taken with the compound prepared in (1) showed no depression. The infrared spectra of the two preparations were identical.

2,5-Bis-(pentafluoroethyl)-1-N-amino-1,3,4-triazole.—Method 2 (above) was used to carry out a reaction of 9.5 g. (0.065 mole) of pentafluoropropionitrile and 1.85 g. (0.058 mole) of anhydrous hydrazine. The reaction was allowed to continue for 48 hours at room temperature. Eleven grams (100% yield) of a tan solid was removed from the tube but on exposure to the atmosphere it became red and gummy. A small portion recrystallized from water showed a long melting range. The remainder of this product was dissolved in dry benzene and treated with dry hydrogen chloride to form the hydrochloride. The final solid product was filtered and washed thoroughly with dry benzene and ethyl ether to give 2,5 bis-(pentafluoroethyl)-1-N-amino-1,3,4-triazole hydrochloride, m.p. 80–85° dec.

Anal. Calcd. for $C_6F_{10}H_3N_4Cl$: C, 20.1; N, 15.6; F, 53.0; Cl, 9.92; neut. equiv., 365.5. Found: C, 20.4; N, 15.4; F, 52.9; Cl, 10.2; neut. equiv., 361.7.

Preparation and Titration of Hydrochlorides of the Hydrazidines and Triazoles.—The same procedure was used for the preparation of the hydrochlorides of each of the various hydrazidines and triazoles: the compound was dissolved in an inert solvent such as hexane, benzene or ether, and dry hydrogen chloride was bubbled through the solution until it was no longer absorbed. In every instance the hydrochloride separated out and was removed from the solvent by filtration and purified by thorough washing with a solvent known to dissolve the free base. No recrystallizations were attempted. The neutral equivalents were determined by dissolving the salts in an ethyl alcohol–water solution and titrating to a phenolphthalein end-point.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. VI. A Convenient Synthesis of the Alkane and Cycloalkane Boronic and Borinic Esters and Acids

BY HERBERT C. BROWN, AKIRA TSUKAMOTO[1] AND D. B. BIGLEY[2]

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The addition of 1-pentene or cyclopentene to a solution of one-half the molar quantity of diborane in tetrahydrofuran solution at 0° results in the formation of 60 to 65% yields of di-*n*-pentylborane and dicyclopentylborane, readily converted to the corresponding borinic methyl esters by treatment with methanol. Equilibration of the initial reaction mixture with a deficiency of diborane (2 olefin/1 BH_3) leads to the preferred formation of di-*n*-pentylborane in the case of 1-pentene, but to the preferred formation of monocyclopentylborane (and tricyclopentylborane) in the case of the cyclic olefin, cyclopentene. Equilibration of the initial reaction mixtures at 25–50° with excess diborane leads to the formation of mono-*n*-pentylborane and monocyclopentylborane in yields of 65 and 73%, respectively. These boranes are readily converted to the methyl esters by treatment with methanol, and the esters are readily converted to the corresponding boronic acids by hydrolysis. Consequently, hydroboration of olefins provides a convenient synthetic route to the alkane and cycloalkane boronic and borinic acids and their derivatives.

The aliphatic boronic esters are generally synthesized by the reaction of the Grignard reagent with methyl borate at low temperatures.[3,4] The related borinic acids have been obtained from trialkylboranes by hydrolysis of the initial oxidation product[5] by the reaction with alcohols and aldehydes,[6] or by the hydrolysis of the dialkylboron chlorides[7] conveniently synthesized by the reaction of boron chloride with the trialkylboranes.[8] Diarylborinic acids have been synthesized by the reaction of the aryl Grignard reagent with alkyl borates in yields of 15–30%,[9] but this method does not appear to have been successfully utilized in the aliphatic series.

The observation that olefins rapidly undergo hydroboration to form the corresponding organoboranes in essentially quantitative yield[10] led to the investigation of this reaction as a possible route to the alkane and cycloalkane boronic and borinic acids. 1-Pentene and cyclopentene were selected as representative olefins for this study.

Results and Discussion

In the usual hydroboration procedure the diborane is either generated externally and introduced into a flask containing the olefin, or the diborane is generated *in situ*. In either case, the diborane is initially in the presence of an excess of olefin and the reaction generally proceeds to completion to the formation of the trialkylborane.[11] Accordingly, we examined the effect of introducing the olefin to a solution of diborane, in the hope that this procedure would permit the partial alkylation of the diborane.

In these studies the olefin was slowly added to a

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[1] American Cyanamid Co. Post-doctorate research assistant, 1958–1959.

[2] American Cyanamid Co. Post-doctorate research assistant, 1959–1960.

[3] H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).

[4] P. A. McCusker and L. J. Glunz, *ibid.*, **77**, 4253 (1955).

[5] J. R. Johnson and M. G. Van Campen, Jr., *ibid.*, **60**, 121 (1938).

[6] H. Meerwein, G. Hinz, H. Majert and H. Sonke, *J. prakt. Chem.*, **147**, 226 (1937).

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[11] In the case of a few highly substituted olefins, such as 2-methyl-2-butene, the reaction stops at the dialkylborane stage, whereas in more hindered cases, such as 2,3-dimethyl-2-butene, it stops at the monoalkylborane stage (ref. 10).