B. In Solution.—A deoxygenated solution of 2 ml of benzene and 8 ml of PFB was irradiated in a sealed quartz tube (15 × 180 mm) for 3 days. The solution turned slightly yellow. Unreacted PFB was removed by distillation and the residual benzene solution was analyzed by gc. A mixture of compounds similar to that obtained in the vapor phase was found, but, in different relative amounts and the conversion was low (~5%). Three products are predominant (73, 14, and 9%). The two minor ones (14 and 9%) have retention times identical with those of **9** and **14**. Evaporation of the solution gave a yellow crystalline residue. After one recrystallization from methanol, 150 mg of a white crystalline solid, **16**, mp 110–111°, was obtained.

Anal. Calcd for $C_{14}H_6F_{12}$: C, 41.81; H, 1.50; F, 56.69; mol wt, 402. Found: C, 42.10, 42.43, 42.50; H, 1.38, 1.88, 1.74; F, 55.49; mol wt, 402.

Hydrogenation of 9.—A sample of 0.1037 g of the cyclooctatetraene in ethanol was hydrogenated over palladium/charcoal. Rapid uptake of H_2 was observed, and the reaction was complete after 14 min; 0.0175 g H_2 was absorbed (2.08 mol equiv).

From a separate preparative hydrogenation run, a pure sample of the hydrogenated product, **3**, was obtained by gc separation (5-ft Carbowax column): ^{1}H nmr (CCl_4), a triplet centered at 6.67 (J = 8.0 Hz) (2 H) and complex multiplets between 0.9 and 2.6 ppm (8 H); ^{19}F nmr (CCl_4), a singlet at 3656 Hz; uv (methanol), no maxima above 220 mμ, 218 (ε 2.0 × 10^4), 225 (1.1 × 10^4).

Anal. Calcd for $C_{10}H_{10}F_6$: C, 49.18; H, 4.13; F, 46.69. Found: C, 49.42; H, 4.04; F, 47.57.

Photochemical Addition of *o*-Xylene to PFB.—A sealed quartz tube containing 8 ml of *o*-xylene and 1 g of PFB was irradiated with 2537-Å light for 5 days. Glpc analysis of the yellowish irradiation solution showed the formation of at least three new products in low yield. One major component isolated by glpc (silicone X-60 column) was a white solid, mp 72–73°, mol wt 430, thus in agreement with the formula $C_{16}H_{10}F_{12}$ (compound **18**).

Registry No.—PFB, 692-50-2; **1**, 781-13-5; **2**, 19640-15-4; **3**, 19640-16-5; **8**, 19640-17-6; **9**, 19640-18-7; **10**, 19640-19-8; **11**, 1580-25-2; **12**, 19640-21-2; **13**, 19640-22-3; **14**, 19640-23-4; **16**, 19640-24-5; **17**, 19640-25-6; **18**, 19640-26-7; **19**, 19669-17-1; **20**, 1554-49-0; **21**, 19640-28-9; **22**, 19640-29-0; **23**, 19640-30-3; **24**, 19640-31-4; 1,2,4,5-tetrakis(trifluoromethyl)benzene, 320-23-0; 2,3,6,7-tetrakis(trifluoromethyl)naphthalene, 2559-74-2.

Fluorinated Cyanates and Isocyanates. A New Type of Rearrangement

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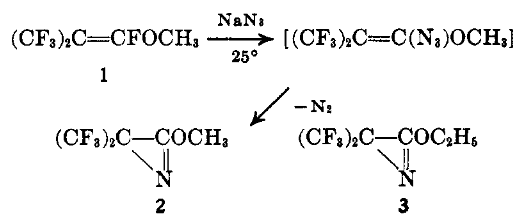
Three isomeric compounds, 2,2-bis(trifluoromethyl)-3-methoxy-2H-azirine (**2**), α-methylhexafluoroisopropyl cyanate (**12**), and α-methylhexafluoroisopropyl isocyanate (**7**), have been prepared. While the normal isomerization of cyanate **12** to isocyanate **7** did not occur, the novel rearrangement of azirine **2** to isocyanate **7** proceeded readily at 95°. α-Phenylhexafluoroisopropyl cyanate did rearrange, but with migration of the isocyanate group to the benzene ring.

Alkoxyfluoroazirines.—Direct syntheses of fluoroazirines starting from fluoro olefins and azide salts were examined earlier with unpromising results.[1] Best results were obtained by isolating the intermediate α,β-unsaturated azide and decomposing it in a separate second step, both in our work with hexafluoropropylene and triethylammonium azide[1] and in other work with sodium azide.[2]

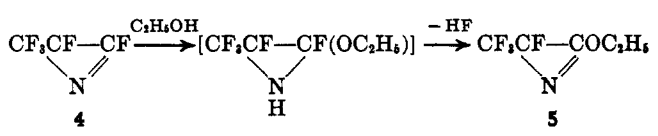
A successful one-step synthesis has now been accomplished starting with a fluoro olefin containing only one readily replaceable halogen and employing diglyme–water as solvent. Reaction of methyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propenyl ether (**1**) with sodium azide at 0–25° gave an 11% isolated yield of 2,2-bis(trifluoromethyl)-3-methoxy-2H-azirine (**2**). Azirine **2** is much less reactive than the related perfluoroazirines, particularly in its stability toward polymerization and addition of active hydrogen compounds. This lowered reactivity accounts for the ability of **2** to survive in part the reaction conditions. Azirine **2** does exhibit the expected[1] ir absorption for fluoroazirine C=N at short wavelength (5.48 μ).



$$(CF_3)_2C{=}CFOCH_3 \xrightarrow[25^\circ]{NaN_3} [(CF_3)_2C{=}C(N_3)OCH_3] \xrightarrow{-N_2} (CF_3)_2C\text{—}COCH_3 \;(\text{N bridge})\;\; \mathbf{2}$$

1 **2** **3**

The ethoxy compound **3** corresponding to **2** may have been the product obtained in unspecified yield by Knunyants and Bykhovskaya from sodium azide and octafluoroisobutylene in ethanol solution, although the ir band for C=N is indicated to be at 5.80 μ.[3] Azetene structures have been proposed by these workers for several such compounds, including **3** and **4**, structures which have not been confirmed in separate work.[1,2] Another product, derived by Knunyants and Bykhovskaya from the compound now known to be azirine **4**, can also be assigned one of two isomeric ethoxyazirine structures (probably **5**) rather than an azetene structure. Formation of **5** by addition of ethanol to the C=N bond and elimination of HF is in accord with known additions of other active hydrogen compounds to **4**.[1]



$$CF_3CF\text{—}CF{=}N \xrightarrow{C_2H_5OH} [CF_3CF\text{—}CF(OC_2H_5)\,NH] \xrightarrow{-HF} CF_3CF\text{—}COC_2H_5{=}N$$

4 **5**

A similar addition of water across the azirine C=N in **2** is indicated in the present work by the isolation of carbamate **6** as a by-product. The actual step of cleavage of the ring occurs at the carbon–carbon bond, and must be facilitated by the ability of the *gem*-trifluoromethyl groups to stabilize a negative charge. This mode of ring scission is abnormal for unfluorinated azirines and is also different from that postulated by

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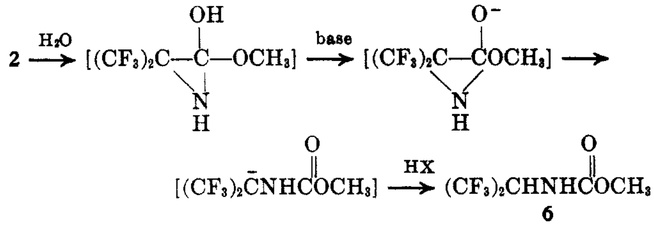
[1] C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 3716 (1965).

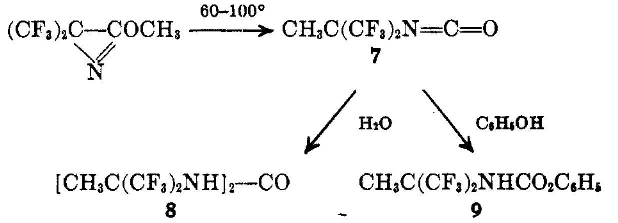
[2] R. E. Banks and G. J. Moore, *J. Chem. Soc.*, 2304 (1966).

[3] I. L. Knunyants and E. G. Bykhovskaya, *Proc. Acad. Sci. USSR, Chem. Sect.*, **131**, 411 (1960).



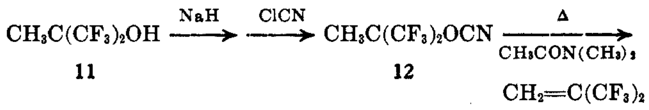
Banks and Moore to occur during hydrolysis of azirine **4**. In the latter case a carbon–nitrogen bond was said to be broken,[2] just as it is with unfluorinated azirines.

Isomerization of Azirine 2.—Synthesis of **2** under aprotic conditions, *i.e.*, in diglyme, to avoid hydrolysis reactions resulted in an increased yield of crude product. However, an attempt to purify this material by careful fractionation resulted in steady generation of a new, lower boiling product, **7**. Prolonged reflux resulted in 20% purified **7**, identified as the isocyanate by chemical and spectral methods. Reaction of **7** with water gave urea **8** and with phenol gave urethan **9**.



Fluorinated Cyanates.—A more conventional route to isocyanates such as **7** might be through the corresponding cyanates. Alkyl cyanates rearrange and trimerize readily and members of this class have only recently been isolated.[4] However, negative substituents on the alkyl moiety tend to stabilize cyanates, so that Grigat and Pütter[5] were able to prepare 2,2,2-trifluoroethyl cyanate (**10**) directly from 2,2,2-trifluoroethanol and cyanogen chloride in 80% yield. No details were given, but the stability of **10** to heat was apparently good. Alcohols containing two α-trifluoromethyl groups are readily obtained from hexafluoroacetone;[6] reactions of sodium salts of two of these fluoro alcohols with cyanogen chloride were carried out in attempts to prepare the corresponding cyanates.

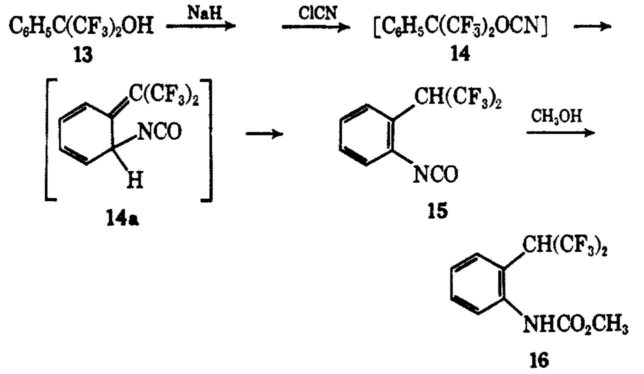
2-Methylhexafluoro-2-propanol (**11**) was converted into the sodium salt with sodium hydride and treated with cyanogen chloride to give α-methylhexafluoroisopropyl cyanate (**12**) in 80% yield. Cyanate **12** is unchanged after 6 hr at reflux (95°), confirming the stabilizing effect of α-trifluoromethyl groups in an alkyl cyanate.



$$\underset{\mathbf{11}}{CH_3C(CF_3)_2OH} \xrightarrow{NaH} \xrightarrow{ClCN} \underset{\mathbf{12}}{CH_3C(CF_3)_2OCN} \xrightarrow[CH_3CON(CH_3)_2]{\Delta} CH_2{=}C(CF_3)_2$$

Isomerization of cyanate to isocyanate is promoted by ionizing conditions;[7] so cyanate **12** was heated in dimethylacetamide. Ionization and recombination to isocyanate were not observed; instead, dissociation to 1,1-bis(trifluoromethyl)ethylene and a solid presumably derived from cyanic acid was promoted by the polar medium. Difficulty in generating from **12** a carbonium ion flanked by negative trifluoromethyl groups may favor the nearly exclusive occurrence of an elimination reaction by the less ionic E2 mechanism. A similar formation of olefin is reported to be the predominant reaction on thermolysis of even simple secondary alkyl cyanates.[8]

In order to forestall the elimination reaction and promote ionization, a benzylic alcohol was used. 2-Phenylhexafluoro-2-propanol (**13**) was converted into its toluene-soluble sodium salt and treated with cyanogen chloride. Although cyanate **14** may have been present as a higher boiling impurity, the major product (41%) obtained by distillation was *o*-(2H-perfluoroisopropyl)-phenyl isocyanate (**15**). The identity of **15** was established by its ir and nmr spectra, and by conversion into carbamate **16**.



The unusual rearrangement **14** → **15** may be another manifestation of the negativity of the trifluoromethyl groups, in that an essentially concerted and hence nonionic rearrangement to **14a** is favored over the normal ionization–recombination mechanism.

Mass Spectral Results.—The rearrangement **2** → **7** appears to be without precedent. Although 1,4 shifts with ring openings have been observed recently with aziridine derivatives,[9] these saturated rings cleaved at the carbon–nitrogen bond. In order to detect any correlation between thermally induced reactions and bond cleavage under electron bombardment, the mass spectra of azirine **2** and its isomers **7** and **12** were taken. At least a rough correlation is evident.

For azirine **2**, the mass spectrum showed major fragments resulting from cleavage of methyl and from loss of two difluoromethylene groups with the loss of methyl. The only major peak not necessarily involving loss of methyl is that for trifluoromethyl cation. The mass spectrum for isocyanate **7**, on the other hand, contained minor peaks for loss of methyl. The predominant fragmentations involved instead cleavage of trifluoromethyl and loss of difluoromethylene with the loss of trifluoromethyl. No peaks for direct loss of NCO were observed. Peaks involving cleavage of NCO dominate the mass spectrum of cyanate **12**, indicating the expected lower stability in the C–OCN bond in **12** compared with the C–NCO bond in **7**. However, loss of trifluoromethyl and to some extent of methyl occurs as well, so that several modes of fragmentation are available.

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(4) For a review of this chemistry, see E. Grigat and R. Pütter, *Angew. Chem. Intern. Ed. Engl.*, **6**, 206 (1967).

(5) E. Grigat and R. Pütter, *Chem. Ber.*, **97**, 3012 (1964).

(6) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1**, 145 (1967).

(7) J. C. Kauer and W. W. Henderson, *J. Amer. Chem. Soc.*, **86**, 4732 (1964).

(8) K. A. Jensen, M. Due, and A. Holm, *Acta Chem. Scand.*, **19**, 438 (1965).

(9) D. A. Tomalia and E. C. Britton, *Tetrahedron Lett.*, 2559 (1967).

Experimental Section[10]

2,2-Bis(trifluoromethyl)-3-methoxy-2H-azirine (**2**).—A mixture of 42.4 g (0.20 mol) of methyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propenyl ether (**1**)[11] and 100 ml of glyme was stirred magnetically in a 500-ml flask fitted with a side-arm dropping funnel and a condenser with wet-test meter attached. The mixture was held at −5 to 0° in an ice-water–acetone bath while a solution of 19.5 g (0.3 mol) of sodium azide in 75 ml of water was added dropwise over a 40-min period. The mixture was stirred another 1.5 hr at 0°, after which time 1.5 l. of gas had been evolved. Stirring was continued while the mixture was allowed to warm to 25°. After a total of 15 hr, 6.0 l. of gas had been evolved (without correction for expansion due to warming). The reaction mixture was diluted with 500 ml of water, and the lower layer was separated, washed with two 250-ml portions of water, dried, and distilled. A little ether was added to codistill with any hydrazoic acid which might have formed. Azirine **2** was obtained as 4.6 g (11%) of colorless liquid, bp 42–43° (80 mm). A sample was purified for analysis by glpc on a di(2-ethylhexyl) sebacate column at 75°: $n^{25}{}_D$ 1.3058; ir 3.29 and 3.36 (CH), 5.48 (ring C═N), and 6.85 and 6.95 μ (weak, small ring and/or CH_3 bond); nmr (neat), H′ at τ 5.72 (singlet, CH_3); ^{19}F (external reference) at 70.8 ppm (singlet, CF_3); mass spectrum (relative intensity), 207 (0.02), 192 (70), 188 (7), 173 (16), 154 (18), 142 (100), 110 (13), 92 (54), 76 (7), 69 (59), 50 (7), 43 (6), 31 (14), 29 (14), 15 (68).

Anal. Calcd for $C_5H_3F_6NO$: C, 29.00; H, 1.46; F, 55.05; N, 6.77; mol wt, 207. Found: C, 29.60; H, 1.81; F, 55.29; N, 7.18; mol wt, 207 (mass spectrum).

The residue from distillation of **2** was sublimed at 70° (70 mm) and recrystallized from trichlorofluoromethane at −80° to give 2.2 g (5%) of methyl N-(hexafluoro-2H-isopropyl)carbamate (**6**), mp 85–88° (subl). An analytical sample, mp 88–90° (subl), was obtained by resublimation at 70° (100 mm): ir (KBr) 3.05 (NH), 3.23 and 3.36 (CH), 5.84 (C═O), and 6.39 μ (amide); nmr ($CFCl_3$), H′ at τ 4.3 (broad, 1, NH or CH), 5.0 (broad, 1, NH or CH), and 6.27 (singlet, 3, CH_3); ^{19}F at 74.7 ppm [doublet, $J_{FH} = 7$ Hz, $(CF_3)_2CH$]; mass spectrum (relative intensity), 225 (3), 206 (8), 205 (13), 194 (12), 186 (11), 174 (34), 166 (8), 156 (100), 154 (26), 124 (22), 113 (8), 112 (16), 92 (15), 74 (20), 69 (34), 59 (87), 51 (5), 50 (5), 44 (9), 42 (15), 32 (16), 31 (50), 29 (13), 28 (35), 15 (83).

Anal. Calcd for $C_5H_5F_6NO_2$: C, 26.68; H, 2.23; F, 50.64; N, 6.22; mol wt, 225. Found: C, 26.95; H, 2.22; F, 50.26; N, 6.13; mol wt, 225 (mass spectrum).

Similar results were obtained from the reaction of sodium azide with the propenyl ether when carried out at 30–50° in methanol–water medium.

α-Methylhexafluoroisopropyl Isocyanate (**7**).—A mixture of 14.3 g (0.22 mol) of sodium azide, 42.4 g (0.20 mol) of ether **1**, and 200 ml of diglyme was stirred at 25° while gas was slowly evolved. After 15 hr, 4.2 l. (89%) of gas (assumed to be nitrogen) had been evolved. Rough distillation of the reaction mixture up to 165° (1 atm) was used to separate the volatile products. Ir analysis of the crude distillate showed major bands at 5.45 (azirine **2**) and 5.9 and weak bands at 4.45 (isocyanate **7**) and 5.6 μ. Fractionation of the crude product in a spinning-band column, with very slow take-off since prolonged reflux was found to give rise to a low boiler, afforded 14.4 g of colorless liquid, bp 55–67° (a smaller amount of a mixture, bp 88–98°, was also obtained). Redistillation from P_2O_5 gave 8.4 g (20%) of isocyanate **7**: bp 61–62°; ir 3.30 and 3.39 (CH), 4.43 μ (NCO); nmr (neat), H′ (external reference) at τ 8.58 (septet, $J_{HF} = 1.1$ Hz, CH_3); ^{19}F (external reference) at 79.6 ppm (quadruplet, $J_{HF} = 1.1$ Hz, CF_3); mass spectrum (relative intensity), 207 (0.1), 192 (7), 188 (7), 142 (12), 138 (100), 118 (5), 95 (7), 92 (35), 88 (59), 74 (10), 69 (42), 31 (7), 15 (8).

Anal. Calcd for $C_5H_3F_6NO$: F, 55.05; N, 6.77, mol wt, 207. Found: F, 55.14; N, 6.72; mol wt, 207 (mass spectrum).

A sample of **7** slowly picked up water on standing to form crystalline urea **8**, which sublimed rapidly at ~200° without melting: ir (KBr) 3.00 (NH), 3.22 and 3.35 (CH), 5.94 μ (C═O), 6.35 (amide).

Anal. Calcd for $C_9H_8F_{12}N_2O$: F, 58.74; N, 7.22. Found: F, 58.68; N, 6.98.

Isocyanate **7** (1.50 g, 0.0072 mol) and phenol (0.75 g, 0.008 mol) remained immiscible on mixing at 25°. Addition of 5 ml of benzene gave a homogeneous solution, but no spontaneous warming to indicate reaction. Pyridine (3 drops) was added and the mixture was allowed to stand 2 days. Solvent was then evaporated, and the solid residue was recrystallized twice from petroleum ether (bp 30–60°) at 0° to give 1.3 g (60%) of carbamate **9**: mp 45–46°; ir (KBr) 3.03 (NH), 3.25 (CH), 5.75 (C═O), 6.45 (amide), 6.27 and 6.69 μ (aromatic ring).

Anal. Calcd for $C_{11}H_9F_6NO_2$: C, 43.86; H, 3.01; F, 37.85; N, 4.65. Found: C, 44.20; H, 3.07; F, 37.87; N, 5.08.

α-Methylhexafluoroisopropyl Cyanate (**12**).—2-Methylhexafluoro-2-propanol (**11**) was prepared from an ether solution of 22 g (1.0 mol) of methyllithium (5.2% by weight) stirred at 0° in a flask fitted with a −80° condenser while 166 g (1.0 mol) of hexafluoroacetone was distilled in over 3 hr. Solvent was then distilled off and the residue was evacuated at 100 mm. Sulfuric acid (200 ml) was added dropwise and the product distilled. Redistillation afforded 165 g (91%) of **11**, bp 61–62°.[12]

A slurry was prepared under dry N_2 from 9.9 g (0.22 mol) of 53% sodium hydride–mineral oil and 100 ml of *p*-xylene. A solution of 36.4 g (0.20 mol) of **11** in 50 ml of *p*-xylene was added dropwise to the stirred slurry over 1 hr. The mixture was heated and stirred at 90–100° for 30 min, after which time evolution of gas had ceased. The mixture was then cooled to 10° and stirred while 14 g (0.23 mol, 12 ml at 0°) of cyanogen chloride was distilled in. The ensuing exothermic reaction carried the temperature as high as 46° during 1 hr. The reaction mixture was allowed to stand overnight and then distilled to give a 45-g cut, bp 80–125°. Redistillation gave 33.1g (80%) of cyanate **12**, bp 93–95°. An analytical sample was prepared: bp 95°; $n^{25}{}_D$ 1.3118; ir 3.30 and 3.37 (CH), 4.42 with shoulder at 4.53 (OCN), 8.75 μ (COC or CF); nmr (neat), H′ at τ 7.99 (septet, $J_{HF} = 1.2$ Hz, CH_3); ^{19}F at 78.7 ppm (quadruplet, $J_{HF} = 1.2$ Hz, CF_3); mass spectrum (relative intensity), 207 (0.3), 165 (37), 145 (37), 138 (5), 113 (17), 95 (27), 92 (15), 77 (52), 75 (10), 69 (100), 65 (10), 56 (17), 51 (17), 43 (11), 42 (5), 33 (14), 31 (8), 27 (8), 15 (6).

Anal. Calcd for $C_5H_3F_6NO$: F, 55.05; N, 6.77; mol wt, 207. Found: F, 55.14; N, 6.89; mol wt, 207 (mass spectrum).

A sample of **12** was recovered unchanged after refluxing for 6 hr. When 10 g of **12** was heated in 75 ml of dimethylacetamide, orange color developed rapidly and a low boiler was given off. The gas evolved (6 g, 80%) was identified as pure 1,1-bis(trifluoromethyl)ethylene by comparison of its ir spectrum with that of an authentic sample.

o-**(2H-Hexafluoroisopropyl)phenyl Isocyanate** (**15**).—2-Phenylhexafluoro-2-propanol (**13**) was prepared by a procedure similar to that in the literature,[13] bp 160–161°.

Sodium hydride–mineral oil (11.3 g, 0.25 mol) was placed under nitrogen in a two-way sintered-glass filter funnel and rinsed with three 50-ml portions of dry ether. A 500-ml round-bottom flask was fitted to the top, the filter was inverted, and a solution of 48.8 g (0.20 mol) of **13** in 100 ml of ether was slowly introduced. The filter was rinsed with an additional 100 ml of ether and the mixture was stirred until nitrogen evolution ceased (15 min). The resulting solution was filtered and the solvent was evaporated, finishing at 0.5 mm for 1 hr on the solid residue. Dry toluene (100 ml) was added, the mixture was cooled at 0°, and 14 g (12 ml, 0.23 mol at 0°) of cyanogen chloride was distilled in over 30 min. The mixture was homogeneous after warming to room temperature, at which point a mildly exothermic reaction set in. After standing overnight, the salt was filtered off and rinsed with toluene. Distillation of the combined filtrate and washings gave 22.0 g (41%) of isocyanate **15**, bp 46.5–48.5° (2 mm), along with considerable high-boiling residue. An analytical sample purified by glpc had mp 28–29°; ir 3.25 and 3.35 (CH), 4.39 (NCO), 6.21 and 6.27 μ (aromatic C═C); nmr (neat), H′ (external reference) at τ 5.47 [septet, 1, J_{HF} = 8.5

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[10] Melting points and boiling points are uncorrected. Proton nmr spectra were obtained with a Varian A-60 spectrometer. Peak center positions for protons are reported as $\tau\ 10 - \delta_H$ ppm. Fluorine nmr spectra were obtained with a Varian A56/60 spectrometer using $CFCl_3$ as an internal standard, unless otherwise noted. Mass spectra were taken on a CEC 21-103C instrument at 70 eV; peaks of 5% or greater relative intensity are reported thus, *m/e* (relative intensity).

[11] R. J. Koshar, T. C. Simmons, and F. W. Hoffmann, *J. Amer. Chem. Soc.*, **79**, 1741 (1957).

[12] The nmr spectrum corresponded to that reported for this compound by E. G. Howard, P. B. Sargeant, and C. G. Krespan, *ibid.*, **89**, 1422 (1967), as obtained from a different synthesis.

[13] (a) D. C. England, French Patent 1,325,204 (1963); (b) B. S. Farah, E. E. Gilbert, and J. P. Sibilia, *J. Org. Chem.*, **30**, 998 (1965).

Hz, $CH(CF_3)_2$] and complex grouping at 2.5–3.5 for aryl H of approximate area 4; ^{19}F (external reference) at 84.3 ppm [doublet, J_{HF} = 8.5 Hz, $CH(CF_3)_2$].

Anal. Calcd for $C_{10}H_5F_6NO$: C, 44.62; H, 1.87; N, 5.21; F, 42.35. Found: C, 45.01; H, 2.12; N, 5.27; F, 42.31.

A sample of **15** was treated with excess methanol. After the exothermic reaction had subsided, excess methanol was evaporated and the residue of urethan **16** was recrystallized twice from petroleum ether: mp 74–75°; ir 3.08 (NH), 3.27, 3.32, and 3.36 (CH), 5.93 (C=O), 6.29 and 6.70 (aromatic C=C), 6.54 μ (urethan); nmr (saturated CCl_4) H′ at τ 6.38 (singlet, 3, OCH_3), 5.22 [septet, 1, J_{HF} = 8 Hz, $CH(CF_3)_2$] and complex multiplet at 2.1–2.9 for aryl H and NH (area 5). Addition of CF_3CO_2H moved NH (area 1) to τ 1.81, separate from unsymmetrical aryl H (area 4).

Anal. Calcd for $C_{11}H_9F_6NO_2$: C, 43.86; H, 3.01; N, 4.65; F, 37.85. Found: C, 44.28; H, 3.40; N, 4.76; F, 37.70.

Registry No.—**2**, 19755-54-5; **6**, 19755-55-6; **7**, 19755-56-7; **8**, 19755-57-8; **9**, 19779-34-1; **12**, 19755-58-9; **15**, 19779-35-2; **16**, 19755-59-0.

Structure Assignments in Polysubstituted Ethylenes by Nuclear Magnetic Resonance[1a]

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Received September 6, 1968

An nmr technique is described by which structures can be assigned to many di- and trisubstituted ethylenes simply from a knowledge of the vinyl proton resonance positions in the compound under study. The technique depends on the additivity of vinyl substituent shielding effects on the vinyl protons present. Tables of substituent shielding constants (σ values) for several common functional groups are presented, and various methods for obtaining σ values are outlined. Solutions to several structural assignment problems are presented, including cases in which steric and electronic interactions between substituents must be taken into account.

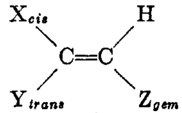
This paper describes a nuclear magnetic resonance technique by which geometric structures can be assigned to a wide variety of di- and trisubstituted ethylenes. The only data required on the compound under study are the resonance positions of its vinyl protons.

The principles underlying this technique were outlined several years ago by Goldstein and coworkers in a series of papers on the origin of nmr shielding effects.[2] The "differential shielding" method of Jackman and Wiley[3] which is also based on these principles provides only the relative vinyl proton chemical shifts in related *cis–trans* isomers. The procedure developed here will predict absolute vinyl proton resonance positions in all mono-, di-, and trisubstituted isomers, and complements existing methods for assigning configurations to *cis* and *trans* isomer pairs based on the magnitude of H–H coupling constants.[4]

The method is based on the independence and additivity of vinyl substituent shielding effects,[1] a concept simultaneously evolved by Pascual, Meier, and Simon.[5] However, the model compound technique described in the latter part of this paper greatly improves the ability of the method to differentiate between closely related polysubstituted ethylenes in which specific steric and electronic interactions between functional groups occur.

The structure assignment method applies in its simplest form to those ethylenes which can be pictured as being constructed from a relatively open, rigid >C=C< rack and a set of small, symmetrical substituents. The substituents must cause relatively little distortion of the molecular framework when attached to the ethylenic backbone, and be able to assume a geometry relative to the vinyl protons which is unaffected by the introduction of other functional groups. Such substituents will generally be smaller in size than Br, and have threefold (C_3) or greater symmetry with respect to rotation about the bond joining them to the ethylenic backbone.

Goldstein showed[2] that, in several simple ethylenes, introduction of such symmetrical substituents caused characteristic shifts in the nmr positions of nearby vinyl protons. It turns out that in a molecule bearing a number of symmetrical substituents the total shielding experienced by a vinyl proton is simply the sum of the shielding effects exerted by all the substituents present. The resonance position of the vinyl proton in such molecules (1) can be accurately calculated from eq 1.



1

$$\delta_{ppm} = -5.27 + \sigma_{cis\text{-}X} + \sigma_{trans\text{-}Y} + \sigma_{gem\text{-}Z} \qquad (1)$$

In this equation −5.27 ppm represents the resonance position of $CH_2{=}CH_2$[6,7] and $\sigma_{cis\text{-}X}$, $\sigma_{trans\text{-}Y}$, and $\sigma_{gem\text{-}Z}$

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[1] (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Division of Organic Chemistry, Abstracts of Papers, S24. Taken in part from Chapter VI of the Ph.D. Thesis of S. W. T., University of Wisconsin, Jan 1965. (b) National Institutes of Health Predoctoral Fellow, University of Wisconsin, 1961–1964.

[2] (a) E. B. Whipple, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **82**, 3010 (1960); (b) E. B. Whipple, J. H. Goldstein, and G. R. McClure, *ibid.*, **82**, 3811 (1960); (c) G. S. Reddy, J. H. Goldstein, and L. Mandell, *ibid.*, **83**, 1300 (1961); (d) G. S. Reddy and J. H. Goldstein, *ibid.*, **83**, 2045 (1961); (e) E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. H. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1963).

[3] (a) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 119–125; (b) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958); (c) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960); (d) ref 3a, pp 729–741.

[4] (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1966, pp 711–735; (b) P. Laszlo and P. von R. Schleyer, *Bull. Soc. Chim. Fr.*, 87 (1964); (c) J. Niwa, *Bull. Chem. Soc. Jap.*, **40**, 2192 (1967).

[5] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

[6] Vinyl proton resonances for simple ethylenes occur anywhere between −4.0 and −8.0 ppm (below) tetramethylsilane. A saturated 35° solution of $CH_2{=}CH_2$ in CCl_4 containing 5 vol. % TMS internal reference resonates at −5.323 ppm. Values obtained under different conditions are tabulated in ref 5.

[7] Ethylene is unique in that it bears no vinyl substituents. From an analysis of nmr data on a large number of substituted ethylenes, ethylene is predicted to resonate at −5.27 ± 0.10 ppm.