[CONTRIBUTION FROM THE RESEARCH DIVISION, WYANDOTTE CHEMICALS CORP.]

Mechanism of Amine Crosslinking of Fluoroelastomers. II. Model Compound Syntheses and Studies[1,2]

K. L. PACIOREK, B. A. MERKL, AND C. T. LENK

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The preparation of two model compounds, 1,5,5-trihydro-4-iodoperfluorooctane and 4,4-dihydro-3-iodoperfluoroheptane, and their reactions with amines is described. Dehydroiodination was found to be the initial reaction. Primary amines added to 1,5-dihydroperfluorooctene-4 and 4-hydroperfluoroheptene-3. The latter afforded a mixture of tautomers, 3-(*n*-butylimino)-4,4-dihydroperfluoroheptane (IX) and 3-(*n*-butylamino)-4-hydroperfluoroheptene-3 (X), together with 3-(*n*-butylamino)-4-hydro-5-(*n*-butylimino)-perfluoroheptene-3 (XII), on treatment with butylamine. Secondary amines gave unidentified addition products. 4-Hydroperfluoroheptene-3 failed to dimerize on heating.

In continuation of earlier investigations of the mechanism of crosslinking of fluoroelastomers by amines, this paper reports the synthesis of certain model compounds and their reactions with selected amines. Previous work[3] conducted on the polymers indicated that at room temperature dehydrohalogenation is the primary reaction. This process proceeded more readily with the vinylidene fluoride–chlorotrifluoroethylene copolymer than with the vinylidene fluoride–perfluoropropene copolymer. With the view to defining more precisely the sequence of processes attendant upon the amine crosslinking of fluoroelastomers, two model compounds, 1,5,5-trihydro-4-iodoperfluorooctane (Va) and 4,4-dihydro-3-iodoperfluoroheptane (Vb), were synthesized.

$$\mathrm{RC_3F_6CH_2OH} \longrightarrow \mathrm{RC_3F_6CH_2OTs} \xrightarrow{\mathrm{KI/glycol}} \mathrm{RC_3F_6CH_2I} \xrightarrow{\mathrm{Zn/HOAc}}$$

Ia. R = HCF_2 IIa. R = HCF_2 IIIa. R = HCF_2
Ib. R = F IIb. R = F IIIb. R = F

$$\mathrm{RC_2F_4CF{=}CH_2} \xrightarrow{\mathrm{C_3F_7I}} \mathrm{RC_2F_4CFICH_2C_3F_7} + \mathrm{RC_2F_4CF{=}CHC_3F_7}$$

IVa. R = HCF_2 Va. R = HCF_2 VIa. R = HCF_2
IVb. R = F Vb. R = F VIb. R = F

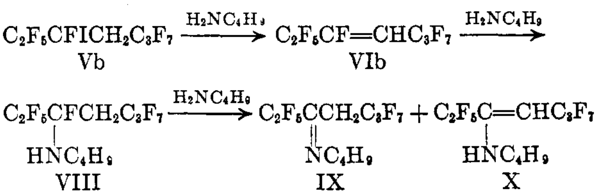
The olefins IVa and IVb[4] reacted with heptafluoropropyl iodide under the influence of ultraviolet radiation to afford Va and Vb, in addition to small quantities of the olefins VIa and VIb.

The structures of Va and Vb are thus reminiscent of the arrangement encountered in the vinylidene fluoride–chlorotrifluoroethylene copolymer (VII) [it is believed that the hydrogen in the position 1 in 1,5,5-trihydro-4-iodoperfluorooctane (Va) is relatively inert], but in neither of these iodides is there a possibility of formation of a conjugated system. However, it appeared advantageous to study initially some simple model compounds.

$$\mathrm{{-}CF_2{-}CFCl{-}CH_2{-}CF_2{-}CH_2{-}CF_2{-}}$$

VII

Treatment of Vb with equimolar quantities of butylamine, dibutylamine, and triethylamine in ether at room temperature afforded 80, 94, and 81% of the amine hydroiodides, respectively. The rates of the reaction were butylamine > dibutylamine >> triethylamine, as determined by the time it took for a given reaction mixture to attain a *p*H of *ca.* 6. Interestingly, reaction with butylamine afforded fluoride ion, whereas none was found in the dibutylamine and triethylamine reactions. Thus, it is believed that with the primary amine, dehydroiodination constituted the first step, followed by the addition of the amine to the resulting olefin, with concurrent or subsequent hydrogen fluoride elimination.



$$\underset{\mathrm{Vb}}{\mathrm{C_2F_5CFICH_2C_3F_7}} \xrightarrow{\mathrm{H_2NC_4H_9}} \underset{\mathrm{VIb}}{\mathrm{C_2F_5CF{=}CHC_3F_7}} \xrightarrow{\mathrm{H_2NC_4H_9}}$$

$$\underset{\mathrm{VIII}}{\mathrm{C_2F_5\underset{\substack{|\\ HNC_4H_9}}{C}FCH_2C_3F_7}} \xrightarrow{\mathrm{H_2NC_4H_9}} \underset{\mathrm{IX}}{\mathrm{C_2F_5\underset{\substack{\|\\ NC_4H_9}}{C}CH_2C_3F_7}} + \underset{\mathrm{X}}{\mathrm{C_2F_5\underset{\substack{|\\ HNC_4H_9}}{C}{=}CHC_3F_7}}$$

As 80% of an amine hydroiodide was obtained, it can be assumed that dehydroiodination under the selected conditions was the main process. The infrared spectrum of the olefin (see Fig. 1) exhibited strong absorption at 5.80μ and another band at 3.22 μ, indicating the presence of $R_fCF{=}CHR_f$ moiety. It is noteworthy that amine-treated vinylidene fluoride–chlorotrifluoroethylene copolymer exhibited bands in the same positions.

In support of the postulated steps VI → IX + X, the olefin VIb was treated with an equimolar quantity of butylamine. Butylamine hydrofluoride was precipitated, and distillation of the filtrates afforded a mixture of tautomers IX and X. The existence of the tautomers was indicated by absorption at 5.93 μ and 5.86 μ (see Fig. 2). The band at 5.93 μ is ascribed to carbon-to-carbon unsaturation,

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[1] This research was supported by the United States Air Force under Contracts AF 33(616)-5642 and AF 33 (616)-5544, monitored by the Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

[2] Presented in part at the 138th meeting of the American Chemical Society, New York, N. Y., September 1960.

[3] K. L. Paciorek, L. C. Mitchell, and C. T. Lenk, *J. Polymer Sci.*, **45**, 405 (1960), and references cited therein.

[4] E. T. McBee, D. H. Campbell, and C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 3149 (1955).

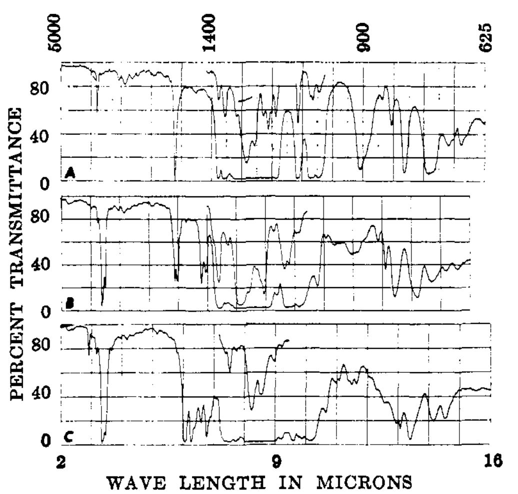
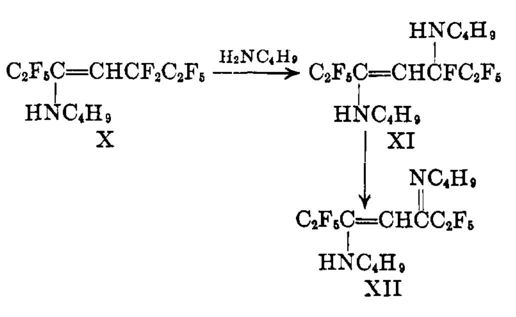


Fig. 1A. Infrared absorption spectra of 4-hydroperfluoroheptene-3, $C_2F_5CF{=}CHC_3F_7$ (0.03 mm. cell). B. Infrared absorption spectra of $C_2F_5\underset{\| \atop NC_4H_9}{C}CH_2C_3F_7$ and $C_2F_5\underset{| \atop HNC_4H_9}{C}{=}CHC_3F_7$ (0.03 mm. cell). C. Infrared absorption spectra of $C_2F_5\underset{| \atop HNC_4H_9}{C}{=}CH\overset{NC_4H_9 \atop \|}{C}C_2F_5$ (0.03 mm. cell)

whereas the imino group is probably responsible for the band at 5.86 μ. In addition to IX and X a small quantity of higher boiling material was also isolated. This material could be readily prepared by treating the mixture of IX and X with butylamine. This reaction was accompanied by precipitation of butylamine hydrofluoride. Structure XII was assigned to this compound, in agreement with its elemental analysis, infrared spectrum (see Fig. 3) and its mode of preparation. The parent mass as obtained by mass spectroscopy was found to be 419 which compares well with the value of 418.33 calculated for XII. Compound XII exhibited an absorption in the ultraviolet at 340 mμ (ε 11,000, cyclohexane), which indicates clearly the presence of a chromophore. While the wave length of this absorption seems abnormally high for the type of structure postulated, the available published data is too limited to confirm or eliminate structure XII.

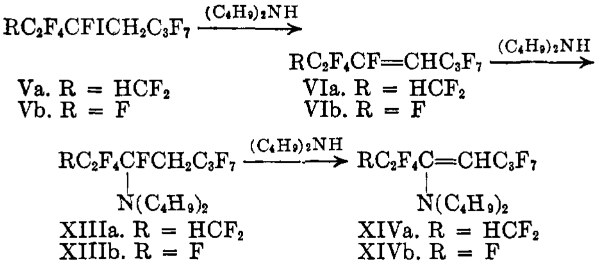
It could be assumed that the addition of butylamine to X proceeds in definite steps, *i.e.*,



$$\underset{\text{X}}{\underset{HNC_4H_9}{C_2F_5C{=}CHCF_2C_2F_5}} \xrightarrow{H_2NC_4H_9} \underset{\text{XI}}{C_2F_5\underset{HNC_4H_9}{C}{=}CH\overset{HNC_4H_9}{C}FC_2F_5} \longrightarrow \underset{\text{XII}}{C_2F_5\underset{HNC_4H_9}{C}{=}CH\overset{NC_4H_9}{\overset{\|}{C}}C_2F_5}$$

Surprisingly, the infrared absorption spectrum of XII in the 5–7 μ region resembled closely that of the amine crosslinked fluoroelastomers. Failure to isolate the intermediates VIII and XI was expected, as it has been shown by Pruett[5] that a structure containing the group $-NH-\overset{|}{C}F-$ readily eliminates hydrogen fluoride.

Inasmuch as in the Vb-dibutylamine reaction (in the absence of solvent) only a trace of fluoride ion was formed, it is apparent that under the conditions chosen very little addition took place. Further investigation revealed that dibutylamine added very slowly to the olefins VIa and VIb, accompanied by hydrogen fluoride elimination.



$$RC_2F_4CFICH_2C_3F_7 \xrightarrow{(C_4H_9)_2NH} RC_2F_4CF{=}CHC_3F_7 \xrightarrow{(C_4H_9)_2NH}$$

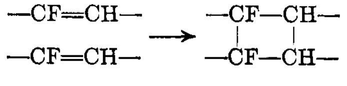
Va. R = HCF_2 VIa. R = HCF_2
Vb. R = F VIb. R = F

$$RC_2F_4\underset{N(C_4H_9)_2}{C}FCH_2C_3F_7 \xrightarrow{(C_4H_9)_2NH} RC_2F_4\underset{N(C_4H_9)_2}{C}{=}CHC_3F_7$$

XIIIa. R = HCF_2 XIVa. R = HCF_2
XIIIb. R = F XIVb. R = F

It is believed that dehydrofluorination of XIII to XIV proceeds more readily than the addition to VI. As observed, the rate of addition at room temperature was very low indeed; in sixty days a yield of only 55% was realized, based on the amine hydrofluoride precipitated. Heating at relatively low temperatures resulted in discolored solutions from which the pure monoamino derivative could not be isolated. The low addition rate of secondary amines to the original olefin presumably allows various side reactions to occur.

Thus, while it seems evident that dehydrohalogenation constitutes the initial step in the amine crosslinking sequence, the succeeding process is less clear. The next step could be represented either as addition of an amine to the center of unsaturation, as discussed above, or by interaction of double bonds[6] to form a crosslink. An example of the latter is:



$$\begin{matrix}-CF{=}CH- \\ -CF{=}CH-\end{matrix} \longrightarrow \begin{matrix}-CF-CH- \\ | \quad\;\; | \\ -CF-CH-\end{matrix}$$

However, on heating 4-hydroperfluoroheptene-3 at 190–195° for sixty-seven hours only starting material was recovered. This result is in agreement with recent results of Park[7] on cyclobutane formation from various fluorinated ethylenes. He indicated that the presence of a hydrogen atom on one of the unsaturated carbons completely hinders the cyclization.

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(5) R. L. Pruett *et al.*, *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(6) J. F. Smith, *Rubber World*, **142**, 102 (1960).

(7) J. D. Park, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, **25**, 990 (1960).

EXPERIMENTAL[8]

p-Toluenesulfonate of 1,1,5-trihydroperfluoropentanol (IIa). 1,1,5-Trihydroperfluoropentanol (100 g., 0.431 mole), *p*-toluenesulfonyl chloride (87.5 g., 0.459 mole), and water (150 ml.) were placed in a 1-l., three-neck flask. The mixture was heated to 50° and sodium hydroxide (20 g.) in water (80 ml.) was added with stirring over a period of 0.5 hr. Heat was liberated during the addition, but the rate was controlled so that the temperature did not rise above 60°. Vigorous stirring was continued until the solution became neutral. The reaction mixture was cooled, extracted with ether, and the ether solution was washed repeatedly with concentrated aqueous ammonia and then water. After drying over anhydrous sodium sulfate and on evaporation of the ether an oil, 146 g. (88%), was obtained.

1,1,5-Trihydro-1-iodoperfluoropentane (IIIa). To a 1-l., three-neck flask equipped with a short column, thermometer, and a stirrer were introduced potassium iodide (136.1 g.), *p*-toluenesulfonate of 1,1,5-trihydroperfluoropentanol (211.2 g., 0.547 mole), and diethylene glycol (170 ml.). The resulting mixture was heated with stirring. 1,1,5-Trihydroperfluoro-1-iodopentane (IIIa) was not evolved until the temperature of the reaction mixture reached 190°. The product was washed several times with cold water and dried over magnesium sulfate. Fractionation afforded 153.5 g. (81%) of IIIa, b.p. 136–137°, n_D^{25} 1.3765.

Anal. Calcd. for $C_5H_3F_8I$: C, 17.54; F, 44.44; I, 37.13. Found: C, 17.61; F, 44.30; I, 37.38.

1,1,5-Trihydroperfluoropentene-1 (IVa). To a 500-ml., three-neck flask, equipped with a stirrer and an addition funnel, which was connected *via* a helices packed column to two vapor traps cooled in Dry Ice, were added zinc dust (34.4 g.) and acetic acid (227 ml.). The resulting mixture was heated in an oil bath to a moderate reflux. Over a period of 4 hr. IIIa (117.8 g., 0.344 mole) was added dropwise to the vigorously stirred mixture. The product (47.5 g.) was treated with solid sodium bicarbonate and dried over anhydrous sodium sulfate. Fractionation afforded 40.02 g. (60%) of IVa, b.p. 56–58°, n_D^2 1.3020.

Anal. Calcd. for $C_5H_3F_7$: C, 30.60; F, 67.83. Found: C, 30.46; F, 67.71.

1,5,5-Trihydro-4-iodoperfluorooctane (Va) *and 1,5-dihydroperfluorooctene-4* (VIa). Heptafluoropropyl iodide (16 g., 0.0541 mole), distilled (*in vacuo*) over anhydrous calcium chloride, was sealed *in vacuo* with similarly treated 1,1,5-trihydroperfluoropentene-1 (8.0 g., 0.0408 mole) in a Vycor tube. The tube was then placed 10 cm. from a Hanovia ultraviolet lamp with the liquid portion shielded with aluminum foil and was left under the ultraviolet radiation for 14 days. During this time some iodine was deposited on the walls of the tube. The tube was opened and the liquid was decanted from iodine. Fractionation at reduced pressure afforded 1.8 g. (12%) of VIa, b.p. 57–59° (100 mm.), n_D^2 1.3002.

Anal. Calcd. for $C_8H_2F_{14}$: C, 26.39; F, 73.06. Found: C, 26.44; F, 73.09.

Reducing pressure further gave 7.6 g. (38%) of Va, b.p. 56–57° (10 mm.), n_D^2 1.3597.

Anal. Calcd. for $C_8H\ F_{14}I$: C, 19.53; F, 54.07; I, 25.80. Found: C, 19.58; F, 54.30; I, 25.76.

4,4-Dihydro-3-iodoperfluoroheptane (Vb). 1,1-Dihydroperfluorobutene-1 (8.9 g., 0.0543 mole), prepared by the procedure of McBee,[4] was treated with heptafluoropropyl iodide under the influence of ultraviolet radiation following the procedure described for the preparation of Va. Fractionation at reduced pressure afforded 9.98 g. (40%) of Vb, b.p. 40–42° (20 mm.), n_D^{15} 1.3419.

Anal. Calcd. for $C_7H_2F_{13}I$: C, 18.28; H, 0.43; F, 53.70; I, 27.59. Found: C, 18.41; H, 0.42; F, 53.85; I, 27.64.

Treatment of 1,5,5-trihydro-4-iodoperfluorooctane with butylamine. To 1,5,5-trihydro-4-iodoperfluorooctane (1.074 g., 0.00218 mole) cooled in ice was added butylamine (0.157 g., 0.00215 mole) in ether (5 ml.), followed by an additional 5 ml. of ether. The mixture was stirred in an ice bath for 1 hr. In 15 min. the solution turned cloudy and an oil was formed on the bottom which subsequently solidified. The mixture was gradually warmed to room temperature. In 2 days white crystals were observed and the *p*H dropped to 5. After an additional 8 days the crystals were filtered off under nitrogen pressure, washed with ether and dissolved in water. The amount of iodide ion liberated corresponded to 79.5% of dehydroiodination, whereas fluoride ion analysis showed 17.2% of dehydrofluorination.

The ether filtrate was distilled through a short column. When almost all the ether was removed the residue was distilled under reduced pressure, yielding material, 0.41 g., n_D^2 1.3060, which appeared (by infrared spectrum) to consist mainly of 1,5-dihydroperfluorooctene-4 admixed with some ethyl ether and some monoamino adduct.

Treatment of 1,5,5-trihydro-4-iodoperfluorooctane with dibutylamine. (a) *In Ether.* To 1,5,5-trihydro-4-iodoperfluorooctane (0.979 g., 0.00198 mole) was added dibutylamine (0.246 g., 0.00191 mole) in ether (5 ml.), followed by an additional 5 ml. of ether. The mixture was stirred in an ice bath for 1 hr. then left standing at room temperature. Within 10 min. of the addition white crystals appeared. During the next 4 days the *p*H dropped to 8. On standing for an additional 2 days, the *p*H dropped to 5. After 24 days (total time) the crystals were filtered under nitrogen pressure, washed with ether and dissolved in water. The aqueous solution was analyzed for fluoride and iodide ion. Fluoride ion was absent, whereas the amount of the iodide ion corresponded to 95% of dehydroiodination.

The ethereal filtrate was distilled through a short column. When almost all the ether was removed, the residue was distilled under reduced pressure and 0.41 g. of material, n_D^1 1.3181, was obtained, shown by infrared spectrum to consist of 1,5-dihydroperfluorooctene-4 and ether.

(b) *In the absence of solvent.* To ice-cooled, stirred 1,5,5-trihydro-4-iodoperfluorooctane (19.828 g., 0.0403 mole) was added dibutylamine (5.180 g., 0.0401 mole) over a period of 5 min. During that time the solution turned yellow from the original pink. After 0.5 hr. a mass of crystals was observed. The stopper was wired and the mixture was allowed to reach room temperature slowly. After 5 days ground citric acid was added to the yellowish mixture, it was covered with glass wool, and the product distilled *in vacuo* at room temperature. The yield was 94% based on iodide ion in the residue and 99% as determined from the weight of the distillate. The residue contained fluoride ion. The discrepancies in the values indicate the presence of some unchanged 1,5,5-trihydro-4-iodoperfluorooctane. The material, distilled under reduced pressure (115 mm.) from phosphorus pentoxide using an 8-cm. column packed with glass helices, afforded 10.9 g. of pure 1,5-dihydroperfluorooctene-4.

Treatment of 1,5,5-trihydro-4-iodoperfluorooctane with triethylamine. To 1,5,5-trihydro-4-iodoperfluorooctane (0.969 g., 0.00197 mole) was added triethylamine (0.200 g., 0.00197 mole) in ether (5 ml.), followed by an additional 5 ml. of ether. The resulting solution was shaken in an ice bath for 1 hr., then slowly warmed to room temperature. After 2 days white needles were observed. After 28 days the *p*H was 7–8, and after an additional 4 days, it had dropped to 5. At that time the solution was red and some reddish material had deposited on the original white needles. The crystals were filtered under nitrogen pressure, washed with ether, and dissolved in water. The aqueous solution was analyzed for fluoride and iodide ion. The amount of iodide ion corre-

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(8) Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and by Spang Microanalytical Laboratory, Ann Arbor, Mich. The infrared spectra were taken on Baird Model B, double beam, infrared spectrophotometer by Mrs. Mildred Lewis of Wyandotte Chemicals Corp.

sponded to 82% of dehydroiodination, and fluoride ion was absent. The ethereal filtrate was distilled through a short column. When almost all the ether was removed, the residue was distilled under reduced pressure. The main fraction appeared to consist of 1,5-dihydroperfluorooctene-4 (by examination of infrared spectrum).

Treatment of 4,4-dihydro-3-iodoperfluoroheptane with dibutylamine. To ice-cooled 4,4-dihydro-3-iodoperfluoroheptane (13.231 g., 0.02876 mole) was added dibutylamine (3.716 g., 0.02876 mole) over a period of *ca.* 10 min. After standing for 10 days at room temperature, distillation *in vacuo* over citric acid afforded 8.61 g. of material. The yield was 99% as determined from the weight of the distillate and 95% as determined by analysis for iodide ion in the residue. Some fluoride ion was also present. The crude 4-hydroperfluoroheptene-3 was distilled from phosphorus pentoxide using a 16-cm. column packed with glass helices, b.p. 69–70°; n_D^5 1.2800 (estimated). The infrared spectrum supported the postulated structure.

Anal. Calcd. for C_7HF_{13}: C, 25.32; F, 74.38. Found: C, 25.18; F, 74.29.

Treatment of 4-hydroperfluoroheptene-3 with butylamine. To 4-hydroperfluoroheptene-3 (4.822 g., 0.0145 mole) in ether (10 ml.) at 0° butylamine (1.071 g., 0.0146 mole) was added slowly with stirring over a period of 15 min. Almost immediately a white precipitate was formed. Stirring at 0° was continued for an additional 8 hr.

The next day the material was filtered under nitrogen pressure. The precipitate, butylamine monohydrofluoride, was dissolved in water and analyzed for fluoride ion. The amount (0.0061 mole) corresponded to 87% yield.

Anal. Calcd. for $C_4H_{12}FN$: C, 51.57; H, 12.98; F, 20.40; N, 15.04. Found: C, 51.90; H, 12.95; F, 20.20; N, 15.24.

The filtrate was distilled at room temperature at reduced pressure and collected in a Dry Ice–cooled receiver. The material, 1.5 g. (53% yield), collected at 1 mm. consisted of the mixture of isomers IX and X. This was then redistilled, b.p. 49–51° (10 mm.) n_D^{25} 1.3342.

Anal. Calcd. for $C_{11}H_{11}F_{12}N$: C, 34.29; H, 2.88; F, 59.18; N, 3.63. Found: C, 34.26; H, 2.85; F, 58.89; N, 3.59.

The yellow residue left in the distillation flask was subsequently distilled under reduced pressure (using a short column) to yield a material, b.p. 47–49° (0.15 mm.), n_D^{25} 1.4060, identified as XII.

Anal. Calcd. for $C_{15}H_{20}F_{10}N_2$: C, 43.06; H, 4.82; F, 45.41; N, 6.70. Found: C, 43.81; H, 4.70; F, 45.92; N, 6.83.

Treatment of the tautomeric mixture IX *and* X *with butylamine.* To the tautomeric mixture IX and X (1.60 g., 0.00415 mole) in ether (5 ml.), butylamine (0.585 g., 0.00800 mole) was added at 0° with stirring over a period of 10 min. Almost immediately a white precipitate was formed. Stirring at 0° was continued for an additional 6 hr. Subsequently the mixture was stirred at room temperature for an additional 24 hr. The material was filtered under nitrogen pressure and the precipitate was analyzed for fluoride ion. The amount (0.003 mole) corresponded to 40% yield, assuming two moles of fluoride ion for each mole of amine added. The filtrate was distilled at reduced pressure to yield 1.10 g. of XII.

Reaction of 1,5-dihydroperfluorooctene-4 (VIa) *with dibutylamine.* To ice-cooled 1,5-dihydroperfluorooctene-4 (0.547 g., 0.00149 mole) was added dibutylamine (0.190 g., 0.00147 mole). The resulting mixture was shaken and allowed to stand for 76 days in a desiccator. The resulting precipitate, dibutylamine monohydrofluoride, was filtered under nitrogen pressure and washed with hexane; yield 0.060 g., corresponding to 55% of compound XIVa, based on the original amount of amine.

Reaction of 4-hydroperfluoroheptene-3 with diethylamine. To 4-hydroperfluoroheptene-3 (4.934 g., 0.0149 mole) was added diethylamine (1.458 g., 0.0199 mole); the resulting solution was sealed in a glass tube and heated at 55° for 90 hr. The resulting solution was orange, and a brown precipitate was deposited on the sides of the tube. The tube was cooled, opened, and the orange liquid (4.31 g.) was decanted from the precipitate. This material was distilled at room temperature under reduced pressure. The fraction (3.5 g.) collected at 35 mm. consisted of diethylamine and 4-hydroperfluoroheptene-3. The fraction (0.4 g.) collected at 1 mm. appeared to be the desired material; however, its infrared spectrum pointed to a conjugated system inasmuch as bands at 6.08 and 6.35 μ were observed.

Anal. Calcd. for $C_{11}H_{11}F_{12}N$: C, 34.29; H, 2.88; F, 59.18; N, 3.63. Found: C, 34.27; H, 2.77; F, 55.13; N, 4.33.

Heat treatment of 4-hydroperfluoroheptene-3. 4-Hydroperfluoroheptene-3 (4.8 g.) purified by distillation over phosphorus pentoxide was heated in a sealed tube at 190–195° for 67 hr. Gas-phase chromatography and infrared spectroscopy of the product showed it to be pure starting material.

WYANDOTTE, MICH.

[CONTRIBUTION FROM THE MEDICINAL DIVISION, MALLINCKRODT CHEMICAL WORKS]

Reactions of Carbonium Ions with Dithiooxamides

RICHARD N. HURD, GEORGE DE LA MATER, AND JOHN P. McDERMOTT

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Xanthydrol reacts in glacial acetic acid with thioacetamide to form 9-thioacetamidoxanthene (I) and with dithiooxamide to form *N,N'*-bis(9-xanthenyl)dithiooxamide (II). Triphenylmethanol similarly forms *N,N'*-ditrityldithiooxamide (III). However, the reaction of benzhydrol and dithiooxamide in glacial acetic acid leads to dibenzhydryl dithioloxalate (IV). Possible mechanisms for these reactions are discussed.

In the course of preparation of a number of *N,N'*-disubstituted dithiooxamides, we have studied several possible synthetic routes to these compounds.[1] One of these involves the reactions of carbonium ions with thioamides under the conditions recommended some years ago for the use of xanthydrol as a reagent for the characterization of unsubstituted amides.[2]

Table I summarizes the results we obtained by

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[1] R. N. Hurd, G. De La Mater, G. C. McElheny R. J. Turner, and V. H. Wallingford, *J. Org. Chem.*, 26, 3980 (1961).

[2] R. F. Phillips and B. M. Pitt, *J. Am. Chem. Soc.*, 65, 1355 (1943).