The near ultraviolet absorption spectra were measured with a Beckman model DU spectrophotometer, using 1.000 cm. quartz cells and a hydrogen lamp source. The solvent used was absolute ethanol and readings were taken every 2 mμ in the regions of absorption maxima. The spectra are recorded in Figs. 2 and 3.

Analyses.[15]—Carbon, hydrogen and nitrogen were determined by combustion. Halogens with the exception of fluorine, were determined by the Carius tube method. Fluorine was determined by the method of Rickard, Ball and Harris.[16] The molecular weight determinations were made in absolute ethanol by the boiling point elevation method.

Conclusions

From the results of this investigation it would appear that the four-membered ring, which is remarkably stable in compounds of the polyfluoro type, is also stable in compounds which contain less than 20% fluorine. The compounds of the betaine structure produced in this work were very stable solids and decomposed only above their melting points, which in some cases were above 200°. However, the resonance which is postulated may increase the stability above that which would normally be expected. The stability is of chemical nature as well as thermal. This is especially true of those betaines containing a relatively large trialkylammonium grouping, as for example (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine.

A trialkylammonium group in the one position greatly enhances the reactivity of a fluorine atom attached to the two position of the cyclobutene ring. In previous work,[8] it had been found that 1-diethylamino-2,3,3,4,4-pentafluorocyclobutene was quite stable to reactions which would normally affect the fluorine, such as hydrolysis and alcoholysis. In this investigation it was found that in compounds of the type trialkyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride, especially in the case where the alkyl groups were small, hydrolysis and alcoholysis occurred readily. The difference between the electron donor character of the dialkylamino groups and the electron attracting character of the trialkylammonium groups makes a large difference in the electrophilic nature of the double-bonded carbon carrying the fluorine. This difference in electrophilic nature would account for the difference in reactivity with anionic reagents.

The reactivity of polyfluoroölefins with tertiary amines is associated in some manner with the presence of the cyclic structure. This is proved by the fact that octafluorobutene-2 failed to react with tertiary amines.

The reactivity of tertiary amines with hexafluorocyclobutene is greatly influenced by the size of the alkyl groups present in the amine. It was found that tri-*n*-butylamine reacted much slower than did trimethylamine. This phenomenon is assumed to be the result of steric hindrance.

OAK RIDGE, TENN. RECEIVED AUGUST 10, 1951

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[15] Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois; Galbraith Laboratories, Knoxville, Tennessee; and Frances Ball and R. R. Rickard of the Microchemical Group of the Analytical Research Section of this Laboratory.

[16] R. R. Rickard, F. L. Ball and W. W. Harris, *Anal. Chem.*, **23**, 919 (1951).

[JOINT CONTRIBUTION FROM THE UNIVERSITY OF TENNESSEE AND THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS COMPANY]

Reaction of Polyfluoro Olefins. VII.[1] Reactions of Pyridine and Derivatives with Hexafluorocyclobutene[2]

BY ROY L. PRUETT, CARL T. BAHNER AND HILTON A. SMITH

Pyridine and four of its derivatives have been found to react with hexafluorocyclobutene at room temperature. The time required for these reactions varied from several hours to a period of weeks. The betaine type compounds which were produced exclusively in the reaction of aliphatic tertiary amines with this butene followed by hydrolysis were produced only to a small extent when aromatic heterocyclic amines were used. The main product obtained in the latter case varied with the nature of the amine, but in each case where the product was isolable a trimer of hexafluorocyclobutene was produced to some degree. Usually this was the major product. The structural formula of this trimer has been proved and a mechanism is proposed which will account for it. An intermediate in the proposed mechanism has been isolated as the major product in one case.

Discussion

The reactions of aliphatic tertiary amines with hexafluorocyclobutene have been described.[1,3] The reactions of amines with this butene have been extended to include pyridine and four of its derivatives.

Pyridine derivatives might be expected to react differently from aliphatic tertiary amines due to either or both of two reasons: (a) the resonance possible because of the aromatic character of the amine, (b) the decreased basicity of the aromatic amine.

The first reaction investigated was that of pyridine with hexafluorocyclobutene. When allowed to stand together overnight, the two compounds did react. The initial product obtained was a black liquid mixture. This mixture was separated into the following components: recovered pyridine, a tar, and a mobile liquid of high density and low refractive index. This liquid analyzed for the molecular formula $(C_4F_6)_x$ and a molecular weight determination showed that the compound was a trimer of hexafluorocyclobutene.

This trimer was the only compound isolated, other than pyridine, when the ratio of pyridine to butene was comparatively high (approximately 1:1 molar). When only a small amount of pyridine was used, the product was a mixture of recovered pyridine, recovered butene, trimer and also a small

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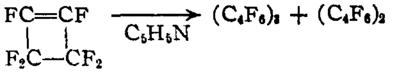
[1] The previous paper in this series is: R. L. Pruett, C. T. Bahner H. A. Smith, THIS JOURNAL, **74**, 1631 (1952).

[2] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company at Oak Ridge, Tennessee.

[3] K. E. Rapp, THIS JOURNAL, **73**, 5901 (1951).

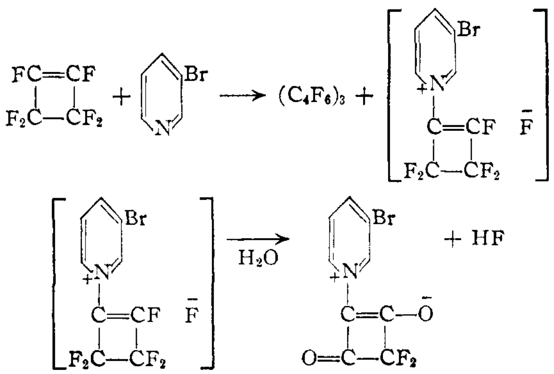
amount of a mixture of dimers. In all cases separation was difficult due to the formation of black tars.

The over-all reaction may be written as


I

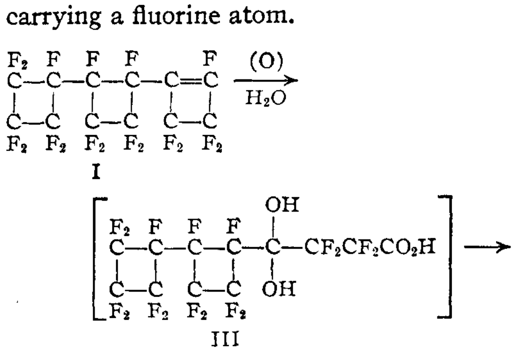
2-Chloropyridine failed to react with this butene when shaken with it on a mechanical shaker for ten days at room temperature. This may have been due either to the deactivating influence of the chlorine or to the steric hindrance of the chlorine in the 2-position. 2-Methylpyridine reacted vigorously with the butene but the tar formation was so great that no product was identified. 2,2′-Dipyridyl failed to react.

3-Bromopyridine also produced the trimer, but in this case the tar formation was not so great and another product was isolated. This product, a solid, was obtained after treatment with dilute hydrochloric acid and appeared to be a betaine. The probable reaction is

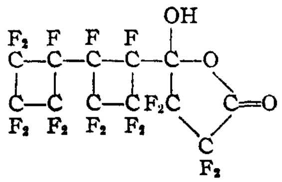

II

Ethyl nicotinate produced trimer, some dimers, and a solid product. Analysis of this solid gave the formula $C_{16}H_9NO_2F_{12}$, which is the formula obtained by the addition of ethyl nicotinate to the dimer of hexafluorocyclobutene. Ethyl isonicotinate gave a compound having this same empirical formula as the major product; only a small amount of the trimer was produced and no dimer.

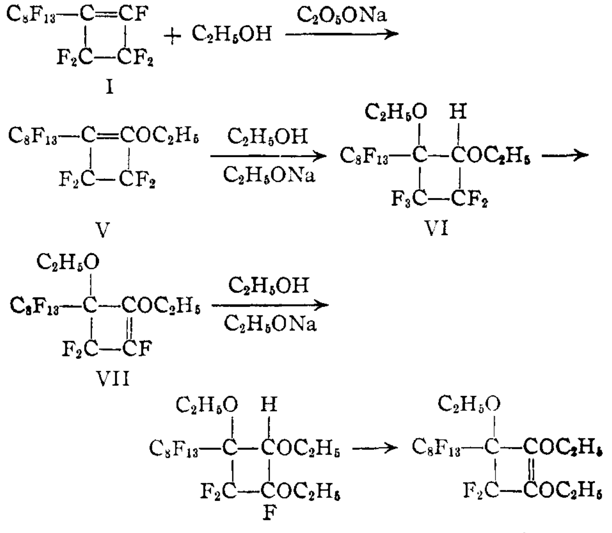
Oxidation of the trimer gave a liquid of composition $C_{12}F_{17}O_3H$. This liquid was soluble in cold sodium hydroxide solution, and slowly soluble in sodium bicarbonate solution. A compound having these properties could be produced if the double bond in the trimer were located on a carbon still carrying a fluorine atom.


I

III


IV

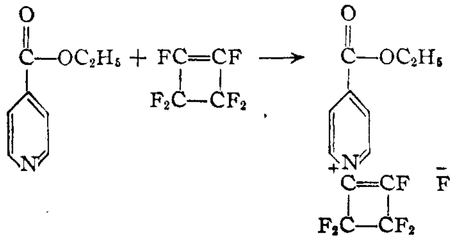
Additional evidence for this structure of the trimer has been found. When the trimer was treated with a boiling solution of sodium ethoxide in ethanol, a product of composition $C_{18}H_{15}O_3F_{15}$ resulted. This is consistent with the following reaction, which would be expected if the double bond were on a carbon still carrying a fluorine atom.


I V VI VII VIII IX

The addition mechanism, as has been proposed,[4,5,6] would account for this type of reaction.

A mechanism has been formulated which will account for all the products which have been obtained and for the structure of the dimer as given above. This mechanism consists of three steps which are outlined below, ethyl isonicotinate being used as the amine. When pyridine was used as the amine, a similar resonance structure for the compound produced in step 2 (XI) would place the negative charge on the number four carbon atom in the pyridine ring rather than on the oxygen.

STEP 1


X

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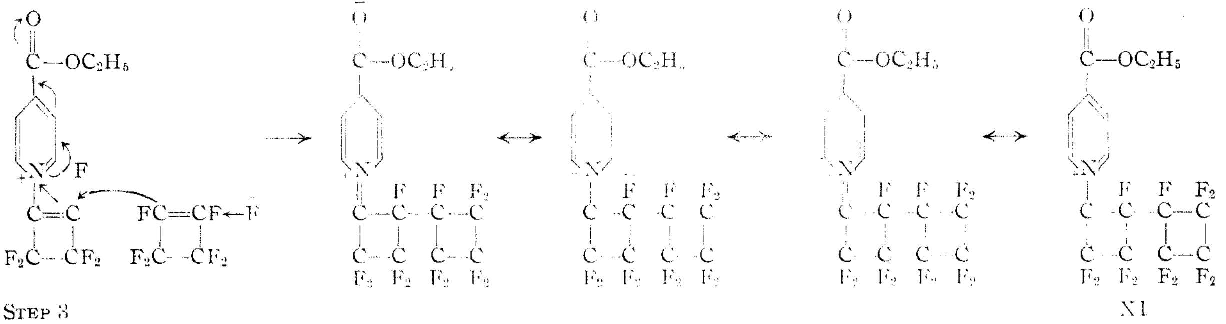
(4) K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., THIS JOURNAL, **72**, 3642 (1950).

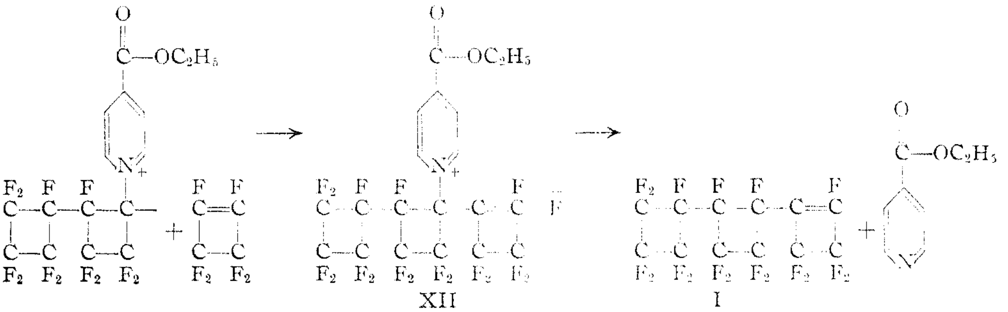
(5) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 3646 (1950).

(6) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950).

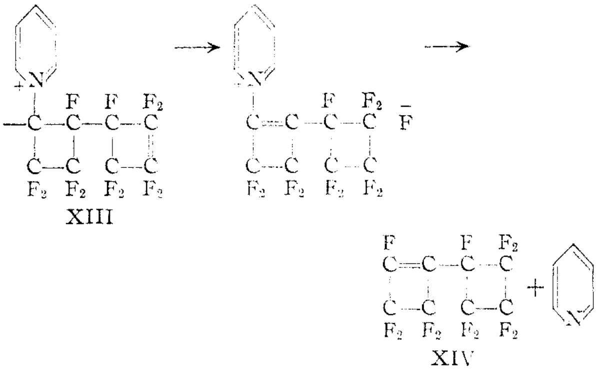
STEP 2



STEP 3



A side reaction involving the product of step 2 would account for the formation of dimer. For example, using pyridine rather than ethyl isonicotinate



Evidence has been obtained for each step in the above mechanism. (3,3-Difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium betaine (II), obtained from the reaction of 3-bromopyridine with hexafluorocyclobutene, must result from hydrolysis of the intermediate quaternary fluoride. The product of step 2 (XI) was isolated when the amine was either ethyl nicotinate or ethyl isonicotinate. The product of step 3, the trimer (I), was isolated in every case, except where no reaction at all occurred or where only a tar was formed.

Qualitative predictions concerning the relative resonance ability agree with the findings. Ethyl isonicotinate was the only amine from which the product of step 2 was isolated in good yields. This was also the only amine used which contained an electron-accepting group in the two or four position of the pyridine ring. It appears that resonance is necessary for both the formation and the stabilization of this type of compound.

The ultraviolet absorption spectra of each type of compound containing nitrogen was obtained in the region 220–400 mμ. (3,3-Difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium betaine gave a strong absorption band in the region of 230 mμ as did the aliphatic betaines.[1]

Experimental

Materials.—All the aromatic amines, with the exception of pyridine and ethyl isonicotinate, were obtained from Eastman Kodak Company. Pyridine was obtained from the Fisher Scientific Company. All these commercial amines were used without further purification. Ethyl isonicotinate was prepared by the method of Gilman and Broadbent.[7] The fraction used had a boiling point of 111° at 23 mm. Hexafluorocyclobutene was prepared by the method previously described.[4]

Reaction of Pyridine with Hexafluorocyclobutene.—Eighty milliliters of pyridine was placed in a stainless-steel reaction vessel and the vessel and contents were cooled in liquid nitrogen. After evacuation, 127 g. of hexafluorocyclobutene was added by gaseous transfer. The mixture was warmed to 0° and then allowed to stand at this temperature for 18 hours.

The vessel was opened and the black liquid product was distilled at 40° and 1 mm. pressure until no more liquid distilled. For this operation, Dry Ice was used to cool the receiver and a liquid-nitrogen cold trap was placed in the vacuum line. A small amount of tarry residue remained after the distillation. The distillate separated into two layers and the lower layer was separated, washed once with dilute hydrochloric acid, twice with water, dried over anhydrous sodium carbonate and distilled. The pressure obtained with the use of a water aspirator was used for the distillation and a trap cooled in Dry Ice was placed in the line. The trimer, 1-[2-(heptafluorocyclobutyl)-hexafluorocyclobutyl]-2,3,3,4,4-pentafluorocyclobutene (I), distilled at 51–52° at 17 mm. pressure; the yield was 36%. No dimer was obtained in this reaction. The purified trimer had the following physical properties: $n^{25}{}_D$ 1.3246, $d^{25}{}_4$ 1.7767. From these physical data, the atomic refraction of fluorine was found to be 1.21.

Anal. Calcd. for $C_{12}F_{18}$: C, 29.65; mol. wt., 486. Found: C, 29.48; mol. wt. (vapor density method), 476.

Another reaction was carried out in which all the conditions were the same as above, except for the quantities of reactants. Ten milliliters of anhydrous pyridine and 137 g. of hexafluorocyclobutene were used. This gave 11% of recovered hexafluorocyclobutene, 50% of trimer and a liquid which collected in the cold trap. This liquid (dimer) dis-

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[7] H. Gilman and H. S. Broadbent, THIS JOURNAL, **70**, 2755 (1948).

tilled at 80–85.5° at atmospheric pressure and represented a 15% yield. The refractive index at 26° was 1.3045.

Anal. Calcd. for C_8F_{12}: C, 29.65. Found: C, 29.42.

Reaction of 3-Bromopyridine with Hexafluorocyclobutene.—Fifty-two grams of 3-bromopyridine was placed in a glass tube and the tube and contents were cooled in liquid nitrogen. Thirty-nine grams of hexafluorocyclobutene was added, the tube sealed, and then shaken on a mechanical shaker at room temperature for ten days.

The product was a black liquid mixture consisting of two layers. The lower layer was separated, washed with dilute hydrochloric acid and then washed with water. After drying over anhydrous sodium carbonate, it was distilled at reduced pressure. The yield was 12 g. (31%) of trimer.

The upper layer from the original reaction mixture was mixed with dilute hydrochloric acid. The liquid dissolved after which a brown solid began to separate. After cooling thoroughly, the mixture was filtered. The dried brown solid weighed 8.8 g. and melted at 195–205° dec. The yield of this crude (3,3-difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium betaine (II) was 13%.

The following purification procedure was used. The brown solid was dissolved in acetone and the solution was boiled with activated charcoal for a few minutes. The mixture was filtered to remove the bulk of the charcoal and the filtrate was centrifuged to remove the last traces of this contaminant. The acetone solution was then diluted with *n*-heptane and evaporated nearly to dryness. The resulting mixture was filtered to remove the white crystals. These were recrystallized twice by dissolving in acetone, adding an equal volume of absolute ethanol, and cooling to −78° in a Dry Ice–trichloroethylene-bath. The final product was snow-white and melted at 223–224°.

Anal. Calcd. for $C_9H_4NO_2F_2Br$: C, 39.16; H, 1.46; N, 5.09; Br, 28.95; F, 13.77. Found: C, 38.72; H, 1.66; N, 4.69; Br, 28.20; F, 13.77.

In another experiment 12 g. of 3-bromopyridine and 45 g. of the butene were shaken together for 12 days. This produced only a small amount of trimer and 3.0 g. of the crude betaine.

Reaction of Ethyl Nicotinate with Hexafluorocyclobutene.—Ten grams of ethyl nicotinate and 42 g. of hexafluorocyclobutene were shaken together in a sealed tube for ten days. The product was distilled at 60° and 1 mm. until no more liquid distilled. For this operation a Dry Ice-cooled receiver was used, together with a cold trap cooled by liquid nitrogen. The cold trap contained 7 g. (17%) of recovered hexafluorocyclobutene. Redistillation at 12 mm. gave 14.5 g. (35%) of trimer and less than 2% dimer.

The dark residue from the original distillation was shaken with 1:1 hydrochloric acid solution. This gave a black lower layer which slowly solidified. This lower layer was shaken with dilute sodium hydroxide and then washed with water. The yield of crude product, which slowly melted above 50°, was 9.5 g. This was recrystallized by dissolving in acetone at room temperature and cooling to −78°. The product obtained by this method was slightly yellow and melted at 71–74°. Another recrystallization by the same method gave a melting point of 76–78°. The yellow solid was then sublimed at 70° and 0.06 mm., but the melting point was not changed.

Anal. Calcd. for $C_{16}H_9NO_2F_{12}$: C, 40.43; H, 1.91; N, 2.95. Found: C, 40.54; H, 2.06; N, 3.14.

Reaction of Ethyl Isonicotinate with Hexafluorocyclobutene.—Thirty-two grams of hexafluorocyclobutene and 21.5 g. of ethyl isonicotinate were shaken together for ten days. The product was distilled at 65° and 1 mm. until no more liquid distilled. The receiver was cooled in Dry Ice and a liquid nitrogen-cooled cold trap was used in the vacuum line. No hexafluorocyclobutene collected in the trap. A small amount of liquid collected in the receiver which, after redistillation, gave 2 g. (6%) of trimer and 2 g. (6%) of dimer.

The black residue from the original distillation was washed once with 1:1 hydrochloric acid solution and once with water, after which there remained 22 ml. of a very viscous liquid which weighed 32.7 g. Six milliliters of this black liquid was dissolved in about 20 ml. of dry ether. After decantation from the few black particles, the ether solution was cooled to −78°. After about two hours, a brown precipitate separated. The mixture was filtered; the dried solid weighed 5.0 g. and melted at 54–56°. This 5.0 g. of 1-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-4-carbethoxypyridinium carbeniate (XI) is equivalent to a 39% yield based on the hexafluorocyclobutene.

Further recrystallization from ether removed the color from the solid but did not change the melting point. This solid was distilled in a sublimation apparatus at 60° and 0.02 mm., after which the solid still melted at 64–66°.

Anal. Calcd. for $C_{16}H_9NO_2F_{12}$: C, 40.43; H, 1.91; N, 2.95. Found: C, 40.34; H, 1.88; N, 3.08.

Oxidation of Trimer.—Thirty-five and one-half grams of the trimer was dissolved in 300 ml. of acetone and the resulting solution was cooled to 5°. A solution of 18 g. of potassium permanganate in 100 ml. of hot water was added in small portions with stirring over a period of one hour. The temperature was maintained in the range 10–20° with the use of an ice-bath. After all the permanganate had been added, the mixture was stirred at 10° for one hour, then the ice-bath was removed and the mixture was stirred for an additional hour.

The mixture was filtered and the manganese dioxide was washed with acetone and with 50 ml. of water. The combined filtrates were concentrated to about 150 ml. and then acidified with concentrated hydrochloric acid. After adding sodium bisulfite to destroy the color, the concentrate was extracted with one 100-ml. portion, then two 50-ml. portions of ether. The combined ether extracts were distilled at 15 mm. until most of the ether had been removed. The residue was placed in a Hickman alembic molecular still. The product (IV, 14.5 g., 39%, $n^{22}D$ 1.3602) distilled at approximately 50° at 0.05–0.10 mm. Much degassing occurred during the distillation.

The distillate was redistilled in a similar manner, with only a trace of residue remaining. Distillation of the oxidized trimer in a 2-foot Vigreux column gave a constant boiling point of 45.5–46.5° at 0.5–0.7 mm., even though successive fractions had different refractive indices. For fraction 1, $n^{22}D$ 1.3332; for fraction 2, $n^{22}D$ 1.3418.

Anal. Calcd. for $C_{12}F_{17}O_3H$: C, 27.92; H, 0.20; F, 62.58. Found (fraction 1): C, 27.48; H, 0.54; F, 61.95; (fraction 2): C, 27.71; H, 0.77; F, 63.43.

Reaction of Trimer with Ethanol.—Twenty-one grams of trimer was added to a solution which resulted from the addition of 2 g. of sodium to 100 ml. of absolute ethanol. The trimer formed a lower layer. Shaking caused a sharp rise in temperature and the solution became cloudy. An additional 100 ml. of ethanol was added but the trimer still existed as a lower layer. The mixture was heated to reflux temperature, at which point the trimer dissolved. The mixture was refluxed for two hours. After cooling, two volumes of water were added, and the resulting lower layer was separated and washed three times with water. Distillation gave 3 g. (14%) of recovered trimer and a small fraction distilling at 39–42° at 0.4 mm. After this, the temperature rose sharply and the distillation was discontinued. Cooling the residue gave 11 g. of 3-[2-(heptafluorocyclobutyl)-hexafluorocyclobutyl]-1,2,3-triethoxy-4,4-difluorocyclobutene (IX) (67% based on sodium). This material was purified by recrystallization from methanol at −78°. Three recrystallizations by this procedure gave a final melting point of 51.5–52.5°.

Anal. Calcd. for $C_{18}H_{15}O_3F_{15}$: C, 38.31; H, 2.68; F, 50.50. Found: C, 38.64; H, 2.98; F, 50.38.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the compounds produced in this investigation were obtained by means of a Beckman model DU spectrophotometer. A quartz prism and a hydrogen discharge lamp were used. The quartz absorption cells were of 1.000 cm. length. The samples were dissolved in absolute ethanol and then diluted to the required concentrations. Readings were taken every 5 mμ, except in the regions of maximum absorption, in which case they were taken every 2 mμ. The spectra are recorded in Fig. 1.

Analysis.[8]—Carbon, hydrogen and nitrogen were determined by combustion. Halogens, with the exception of fluorine, were determined by the Carius tube method. Fluorine, in the presence of nitrogen, was determined by

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[8] Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois; Galbraith Laboratories, Knoxville, Tennessee; and Frances Ball and R. R. Rickard of the Microchemical Group of the Analytical Research Section of this Laboratory.

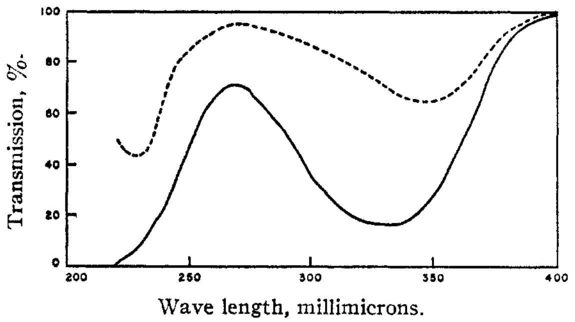

Fig. 1.—Ultraviolet absorption spectra of: —, 1-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-4-carbethoxypyridinium carbeniate, *c*, 4.61 × 10^{-4} mole/liter; · · · · (3,3-difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium betaine, *c*, 1.17 × 10^{-5} mole/liter.

the method of Rickard, Ball and Harris.[9] Fluorine, in the absence of nitrogen, was determined by the method of Clark.[10]

Conclusions

It may be seen that the nature of the products obtained from the reactions of tertiary amines with polyfluoroölefins varies greatly with the type of amine. There is little similarity between the products obtained from aliphatic tertiary amines and polyfluoroölefins and those obtained from aromatic heterocyclic tertiary amines with polyfluoroölefins.

From the results of this investigation, it may be concluded that a highly fluorinated group exerts a very strong attraction for electrons. It is known that in tris-(nonafluorobutyl)-amine the presence of the unshared electrons of the nitrogen atom cannot be detected by ordinary means, such as reaction with acids, methiodide formation, picrate formation, etc. Also the powerful electrophilic character of boron trifluoride is due to the electron pull of the fluorine atoms. In this investigation the stability of 1-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-4-ethoxypyridinium carbeniate and its analogs is due greatly to the ability of the fluorinated cyclobutyl rings to absorb the unshared electrons of the trivalent carbon atom. Since this type of compound did not form with aliphatic tertiary amines and is formed in greatest quantity when the attached amine also contains an electron-attracting group, it appears that both the fluorinated alkyl groups and the aromatic groups are necessary for complete stabilization.

Oak Ridge, Tenn.

Received August 10, 1951

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[9] R. R. Rickard, F. L. Ball and W. W. Harris, *Anal. Chem.*, **23**, 919 (1951).

[10] H. S. Clark, *ibid.*, **23**, 659 (1951).

[Joint Contribution from the University of Tennessee and the Research Laboratories, K-25 Plant, Carbide and Carbon Chemicals Company]

Reaction of Polyfluoro Olefins. VIII.[1] Reactions of Hexafluorocyclobutene with Isoquinoline and 3-Methylisoquinoline[2]

By Roy L. Pruett, Carl T. Bahner and Hilton A. Smith

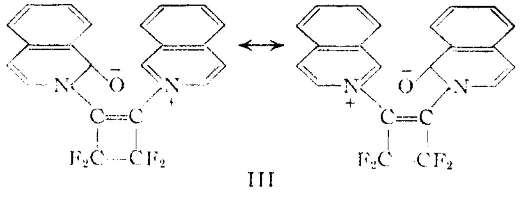
Isoquinoline reacted with hexafluorocyclobutene to give a compound sensitive to hydrolysis. The hydrolysis product was stable but could be degraded with acid to (3,3-difluoro-2,4-dioxocyclobutyl)-isoquinolinium betaine. 2-[2-Heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-isoquinolinium carbeniate was produced as a secondary product. 3-Methylisoquinoline with this butene gave, after hydrolysis, (3,3-difluoro-2,4-dioxocyclobutyl)-3-methylisoquinolinium betaine, together with an unidentified product. Quinoline did not react with hexafluorocyclobutene.

Discussion

In previous papers of this series, the reactions of hexafluorocyclobutene with aliphatic tertiary amines[3] and with pyridine and its derivatives[1] have been described. The reaction products of these two types of compounds with hexafluorocyclobutene were found to be only slightly similar in nature. Isoquinoline and 3-methylisoquinoline have been found to react in a manner analogous to each of these types, and also to produce a third type of reaction.

3-Methylisoquinoline reacted slowly with hexafluorocyclobutene in ether solution to give, in short periods of time, a compound which hydrolyzed to give a product having the betaine structure, (3,3-difluoro-2,4-dioxocyclobutyl)-3-methylisoquinolinium betaine (I). With longer periods of time this compound was also produced, but the major product was a solid which could not be purified.

Isoquinoline reacted easily with hexafluorocyclobutene in ether solution. Two products were isolated from the reaction mixture. One of these proved to be 2-[2-(heptafluorocyclobutyl)-2,3,3,-4,4-pentafluorocyclobutyl]-isoquinolinium carbeniate (II), an analog of the type of product which was isolated in the cases of ethyl nicotinate and ethyl isonicotinate with hexafluorocyclobutene.[1] The other, which was the major product, was isolated after hydrolysis, and analysis and molecular weight determinations indicated the formula $C_{22}H_{14}N_2OF_4$. Three of the possible structural formulas are



III

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[1] The previous paper in this series is: R. L. Pruett, C. T. Bahner and H. A. Smith, This Journal, **74**, 1638 (1952).

[2] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company at Oak Ridge, Tennessee.

[3] R. L. Pruett, C. T. Bahner and H. A. Smith, This Journal, **74**, 1633 (1952).