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

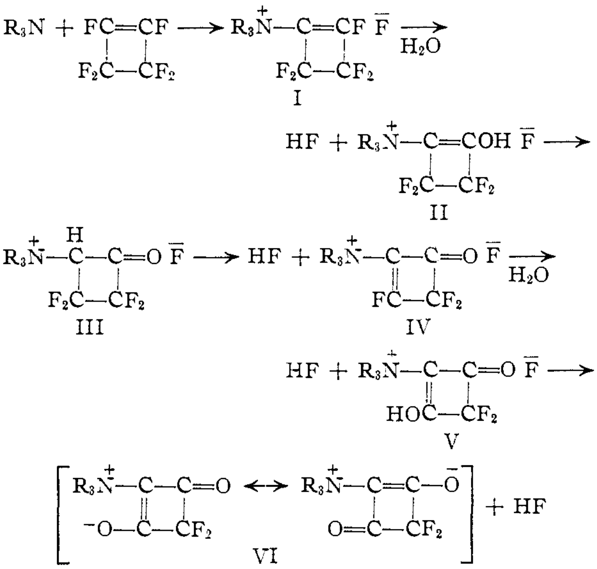
Reactions of Polyfluoro Olefins. VI.[1] Reactions of Aliphatic Tertiary Amines with Hexafluorocyclobutene[2,3]

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

Aliphatic tertiary amines have been found to react readily at room temperature with hexafluorocyclobutene. The initial quaternary salts obtained were very reactive toward water, alcohols and primary or secondary amines. Hydrolysis gave a series of stable compounds which, on the basis of chemical degradation, method of preparation and spectral data, are thought to be trialkyl-(3,3-difluoro-2,4-dioxocyclobutyl)-ammonium betaines.

Discussion

A previous article in this series[4] described the reaction of triethylamine with hexafluorocyclobutene, together with the subsequent hydrolysis. This reaction has been extended to include other aliphatic amines, and the hydrolytic products of these reactions have been investigated as to their chemical properties. The following series of reactions represents the probable course of the hydrolysis



Although the intermediates (II, III, IV and V) were so unstable and transitory that they could not be isolated, a derivative of II was prepared. This was accomplished by alcoholyzing the initial product of triethylamine with the butene in absolute ethanol, then adding a solution of picric acid in absolute ethanol. This produced (2-ethoxy-3,3,-4,4 - tetrafluorocyclobutenyl) - triethylammonium picrate.

Eight amines, ranging in carbon content from trimethylamine to tributylamine, were used to prepare compounds of type VI. Several trends were noted in this series of compounds. Although they were all insoluble in benzene, ether and other non-polar solvents, the lower alkyl members [for example: (3,3-difluoro-2,4-dioxocyclobutyl)-trimethylammonium betaine], were water soluble and only slightly soluble in alcohol while the higher members [for example: tri-*n*-butyl-(3,3-difluoro-2,4-dioxocyclobutyl)-ammonium betaine], were insoluble in water and soluble in alcohol. The melting point increased as the carbon content decreased. However, when the original amine contained three alkyl groups which were not the same, for example N-methyldiethylamine, the hydrolyzed product had a low melting point and high solubility in alcohol.

The rate of hydrolysis of the original quaternary salt varied with the size of the alkyl group. The lower members hydrolyzed instantaneously while in the case of tri-*n*-butyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride it was necessary to heat with a dilute basic solution. The rate of formation also varied inversely with the size of the alkyl group.

In at least one case, the quaternary salt was found to decompose to the original reactants. When tri-*n*-butyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride was dissolved in benzene–dibutyl ether solution and heated to 85–90°, hexafluorocyclobutene was evolved.

A synthesis in which triethylamine and 1-chloropentafluorocyclobutene were used showed that this type of reaction is not limited to hexafluorocyclobutene. Hydrolysis of the initial product gave the same betaine as that formed by hydrolysis of the quaternary salt of triethylamine and hexafluorocyclobutene.

The hydrolyzed products were found to be very stable and inert to the usual carbonyl reactions. They did not form a *p*-nitrophenylhydrazone, oxime or semicarbazone. This is not surprising in view of the conjugated nature of the carbonyl groups present in the proposed structure.

Gustafsson[5] has reported a somewhat similar compound, 1,1-dimethyl-3,5-dioxo-piperidinium betaine. This compound formed addition complexes with acids and inorganic salts. However he stated that the substitution of bromine for hydrogen in the 4-position decreased the tendency toward addition reactions. Therefore the relative inertness of the difluoro betaines should not be surprising. (3,3-Difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine showed no tendency to react with inorganic acids or salts. It did not decolorize solutions of bromine or potassium permanganate. However, (3,3-difluoro-2,4-dioxocyclobutyl)-trimethylammonium betaine formed

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[1] The previous paper in this series is: K. E. Rapp J. T. Barr, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., THIS JOURNAL, **73**, 749 (1952).

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

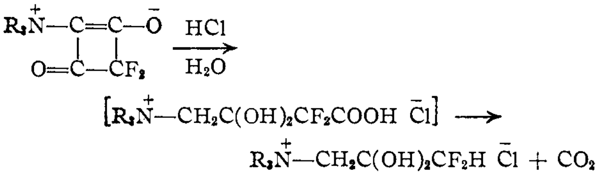
[3] Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September 10–13, 1951.

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

[5] C. Gustafsson, *Ber.*, **70B**, 1591 (1937).

an addition complex with NaI_3 in water which was quite stable and contained a molar ratio of three moles of betaine to one of inorganic salt. It also formed an unstable complex with sulfuric acid which reverted to the original components when recrystallization was attempted.

All the betaines containing small alkyl groups (those from N-methyldiethylamine, 4-methylmorpholine, N,N-dimethylethylamine and trimethylamine), reacted with boiling 3 *N* hydrochloric acid, splitting the ring and forming trialkyl-(3,3-difluoro-2-oxopropyl)-ammonium chloride monohydrates, together with carbon dioxide.



$$[R_3\overset{+}{N}\text{—}CH_2C(OH)_2CF_2COOH\ \overset{-}{Cl}] \longrightarrow R_3\overset{+}{N}\text{—}CH_2C(OH)_2CF_2H\ \overset{-}{Cl} + CO_2$$

The velocity of splitting was dependent on the size of the alkyl groups which were present. (3,3-Difluoro - 2,4 - dioxocyclobutyl) - triethylammonium betane failed to react with boiling 3 *N* hydrochloric acid, whereas with the dimethylethyl and trimethyl betaines the reaction was complete in four hours. The methyldiethyl betaine assumed an intermediate position. After refluxing with 3 *N* hydrochloric acid for four hours, the betaine was only partially converted to the ionic chloride; after 20 hours the reaction was essentially complete. The progress of the reaction was determined by testing for the evolution of carbon dioxide.

(3,3-Difluoro-2-oxopropyl)-trimethylammonium chloride monohydrate was found to undergo the usual reactions. In absolute ethanol it formed a picrate containing one mole of ethanol. The ethanol was removed by heating at 100° under reduced pressure for six hours.

(3,3-Difluoro-2-oxopropyl)-trimethylammonium chloride monohydrate reacted with *p*-nitrophenylhydrazine to form an anomalous hydrazone which contained two moles of ionic chloride to one of *p*-nitrophenylhydrazine. The chloride also reacted with sodium bisulfite to form a zwitterion. With hot concentrated potassium hydroxide it split to form trimethylamine. The latter is in line with the observation of Kroehnke,[6,7] who found that the action of alkali on 1-(2-oxoalkyl)-pyridinium salts produced 1-methylpyridinium hydroxide.

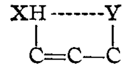
The fluorine atoms in the trialkyl-(3,3-difluoro-2,4-dioxocyclobutyl)-ammonium betaines were found to be susceptible toward Friedel-Crafts type reactions. (3,3-Difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine reacted easily with benzene in the presence of anhydrous aluminum chloride to produce (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine.

Whereas all the difluoro betaines had failed to react with acids, the diphenyl compound produced a hydrobromide easily and in good yields.

The structure of the betaines which has been proposed is based on the following evidence: Elemental analysis and the negative test with potassium permanganate showed that, if the compound is monomolecular, a ring structure is necessary to fulfill the necessary valences. Molecular weight determinations proved that the compounds were monomolecular. This, together with the fact that a ring structure was present in one of the starting materials, was taken as sufficient evidence for the presence of a ring in the final product. The identification of trimethylamine as one of the splitting products when (3,3-difluoro-2-oxopropyl)-trimethylammonium chloride monohydrate was heated with alkali proved that there had been no migration of alkyl groups from the original trialkyl nitrogen grouping to the adjacent carbon. The solubility characteristics of the compounds also indicate a quaternary salt-type structure.

Thus it has been determined that a four-membered ring is present, and that a trialkylammonium group is attached to one of the ring carbons. The proven presence of a carbonyl group in the ionic chloride product obtained when the betaines were treated with dilute hydrochloric acid showed that at least one carbonyl group was present in the original betaine and the evolution of carbon dioxide was evidence of the second. These facts point to a structure of type VI, and this structure is produced by a mechanism which is entirely reasonable in light of the known tendency of the reaction products of hexafluorocyclobutene with amines and alcohols to split out hydrogen fluoride.[8]

The infrared and near ultraviolet spectra of these compounds also add support to this type of structure. The infrared spectra of (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, (3,3-difluoro - 2,4 - dioxocyclobutyl) - diethylmethylammonium betaine and (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine were obtained over the range of 2–15 μ, and they all showed strong absorption in the region 6.0–6.2 μ. Strongly conjugated carbonyl structures are known to cause absorption in this region.[9] Rasmussen, Tunnicliff and Brattain[10] examined the spectrum of acetylacetone and found a tremendously strong band at 6.1–6.3 μ which they attributed to the system



where XH and Y are participating as a hydrogen bond donor–acceptor system. This system is electronically similar to the one present in the betaines.

The ultraviolet absorption spectra of these three compounds were obtained over the range 220–440 mμ. (3,3-Difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine and (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine showed strong absorption maxima at 230 mμ, which

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[6] F. Kroehnke, *Ber.*, **68B**, 1177 (1935).

[7] F. Kroehnke and W. Heffe, *ibid.*, **70B**, 864 (1937).

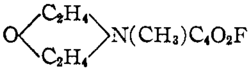
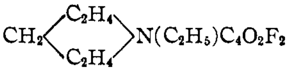
[8] K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., THIS JOURNAL, **72**, 3642 (1950); R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 3646 (1950); J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950).

[9] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structure," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[10] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

TABLE I

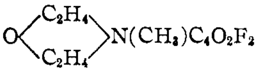
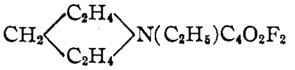
TRIALKYL-(3,3-DIFLUORO-2,4-DIOXOCYCLOBUTYL)-AMMONIUM BETAINES

Compound	Yield, %	M.p., °C.[a]	Recrystallization solvent	M.p., °C.[b]
$(CH_3)_3NC_4O_2F_2$	73	230–233	Methanol	233–234
$(CH_3)_2N(C_2H_5)C_4O_2F_2$	63	145–147	Ethyl acetate	153–154
$(C_2H_5)_2N(CH_3)C_4O_2F_2$	92	103–107	Ethyl acetate	126–127
	78	117–119		
$(C_2H_5)_3NC_4O_2F_2$[4]	92[c]	160–162	Methanol	166–167
$(C_4H_9)_2N(CH_3)C_4O_2F_2$	81	42–45	Methanol, −78°	68–70
$(C_4H_9)_3NC_4O_2F_2$	55[d]	106.5–107.5	Methanol–water	106.5–107.5
 $O{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}N(CH_3)C_4O_2F_2$	63		Methanol	215–215
 $CH_2{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}N(C_2H_5)C_4O_2F_2$			Methanol, −78°	174–175

[a] The melting points obtained during this work are uncorrected. They were obtained with a 360° thermometer with 76 mm. immersion in an insulated aluminum melting point block. The melting points listed in this column are those of the material from which the yields were calculated. [b] The melting points listed in this column are of the purified materials. [c] A 30% yield was obtained when 1 chloropentafluorocyclobutene was used instead of hexafluorocyclobutene. [d] The yield was 100% calculated from the reactive intermediate.

TABLE II

ANALYSIS OF TRIALKYL-(3,3-DIFLUORO-2,4-DIOXOCYCLOBUTYL)-AMMONIUM BETAINES

Compound	Carbon, %		Hydrogen, %		Nitrogen, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3)_3NC_4O_2F_2$[a]	47.46	47.42	5.12	4.91	7.91	7.98
$(CH_3)_2N(C_2H_5)C_4O_2F_2$[b]	50.26	50.17	5.80	5.71	7.33	7.23
$(C_2H_5)_2N(CH_3)C_4O_2F_2$[c]	52.67	53.20	6.39	6.47	6.83	6.92
$(C_2H_5)_3NC_4O_2F_2$[d]	54.79	54.95	6.90	6.87	6.39	6.59
$(C_4H_9)_2N(CH_3)C_4O_2F_2$	59.75	59.65	8.10	8.04	5.36	5.63
$(C_4H_9)_3NC_4O_2F_2$	63.34	63.47	8.97	8.95	4.62	4.63
 $O{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}N(CH_3)C_4O_2F_2$	49.31	48.91	5.06	4.83	6.39	6.57
 $CH_2{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}N(C_2H_5)C_4O_2F_2$	57.13	56.85	6.54	6.40	6.07	6.05

[a] Calcd.: mol. wt., 177. Found: mol. wt., 174. [b] Calcd.: F, 19.88. Found: F, 19.10. [c] Calcd.: mol. wt., 205. Found: mol. wt., 202. [d] Calcd.: F, 17.33; mol. wt., 219. Found: F, 17.10; mol. wt., 226.

indicates conjugated unsaturation.[11] The substitution of phenyl groups for fluorine atoms caused the maximum to shift to 251 mμ, indicating that the phenyl groups change the characteristics of the resonating structure. It is possible that these groups undergo the type of resonance postulated by Kumler, Strait and Alpen for α-phenyl ketones.[12]

Experimental

Materials.—Trimethylamine, triethylamine, tributylamine and 1-ethylpiperidine were obtained from Eastman Kodak Company, and 4-methylmorpholine from Paragon Division of the Matheson Company, Inc. N,N-Dimethylethylamine, N-methyldiethylamine and N-methyldi-*n*-butylamine were prepared by the method of Clarke, Gillespie and Weisshaus.[13] Hexafluorocyclobutene was prepared by the dechlorination of 1,2-dichlorohexafluorocyclobutane, which had been prepared by the thermal dimerization of chlorotrifluoroethylene.[8] For the synthesis of 1-chloropentafluorocyclobutene, *unsym*-dichlorodifluoroethylene was heated with a slight molar excess of chlorotrifluoroethylene at 200° for 18 hours in a high pressure reactor,[14] producing the codimer, 1,2,2-trichloropentafluorocyclobutane, which distilled at 93.8–94.0° and melted at 32–33°. This intermediate was dechlorinated by the use of zinc and *n*-butyl alcohol. The 1-chloropentafluorocyclobutene thus obtained distilled at 32.2°, n^{25}_D 1.3201, d^{25}_{20} 1.505.

Initial Reaction between Tertiary Amines and Hexafluorocyclobutene.—Depending on the quantity of material desired, the initial reactions of the hexafluorocyclobutene with the tertiary amines were carried out either in a stainless steel reaction chamber,[8] or in sealed glass tubes. In all cases except one, complete reaction was obtained by allowing the two reactants to stand overnight in contact with each other at room temperature. For tri-*n*-butylamine, it was necessary to allow the mixture to stand at room temperature for five days to cause 55% reaction. As a rule, a slight molar excess of the hexafluorocyclobutene was employed.

Although the analysis of the reactive initial product from triethylamine and hexafluorocyclobutene gave indication of the molecular formula, the results were not sufficiently accurate to be conclusive. The less reactive tri-*n*-butyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride was found to be more easily purified. This was accomplished by two recrystallizations from dry benzene. The final product was a snow-white solid which decomposed above 82°.

Anal. Calcd. for $C_{16}H_{27}NF_6$: C, 55.31; H, 7.83; N, 4.03. Found: C, 55.08; H, 8.09; N, 4.06.

Heating the tri-*n*-butyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride to 85–90° caused decomposition to the original components. Seventy-five grams was dissolved in a mixture of 85 ml. of dibutyl ether and 400 ml. of benzene. The solution was heated to boiling and the gaseous product was collected in a cold trap surrounded by a Dry Ice–trichloroethylene-bath. The gas solidified in the trap and, after warming, boiled at 2°. The yield of hexafluorocyclobutene was 28 g. (59%).

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[11] E. A. Braude, *Ann. Repts. Progress Chem.*, **42**, 105 (1945).

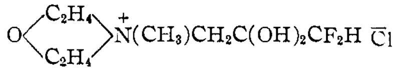
[12] W. D. Kumler, L. A. Strait and E. L. Alpen, THIS JOURNAL, **72**, 1463 (1950); E. L. Alpen, W. D. Kumler and L. A. Strait, *ibid.*, **72**, 4558 (1950).

[13] H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

[14] E. L. Kropa and J. J. Padbury, Canadian Patent 453,791 (1949); *C. A.*, **44**, 2019 (1950).

TABLE III

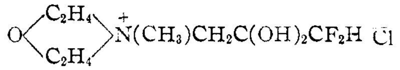
TRIALKYL-(3,3-DIFLUORO-2-OXOPROPYL)-AMMONIUM CHLORIDE MONOHYDRATES

Compound	Yield, %	M.p., °C.[a]	Recrystallization solvent	M.p., °C.[b]
$(CH_3)_3\overset{+}{N}CH_2C(OH)_2CF_2H\ \bar{Cl}$	97	135–137	Methanol–ethyl acetate	134.5–135.5
$(CH_3)_2\overset{+}{N}(C_2H_5)CH_2C(OH)_2CF_2H\ \bar{Cl}$	57	102–105	Ethanol–ether	102–103
$(C_2H_5)_2\overset{+}{N}(CH_3)CH_2C(OH)_2CF_2H\ \bar{Cl}$	35	90–95	Acetic acid–ethyl acetate	97–98
 $O(C_2H_4)_2\overset{+}{N}(CH_3)CH_2C(OH)_2CF_2H\ \bar{Cl}$	70	138–142	Methanol–ether	142–143.5

[a] The melting points listed in this column are those of the materials from which the yields were calculated. [b] The melting points listed in this column are of the purified materials.

TABLE IV

ANALYSIS OF TRIALKYL-(3,3-DIFLUORO-2-OXOPROPYL)-AMMONIUM CHLORIDE HYDRATES

Compound	Carbon, %		Hydrogen, %		Nitrogen, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3)_3\overset{+}{N}CH_2C(OH)_2CF_2H\ \bar{Cl}$[a]	35.04	34.79	6.86	6.77	6.81	6.81
$(CH_3)_2\overset{+}{N}(C_2H_5)CH_2C(OH)_2CF_2H\ \bar{Cl}$[b]	38.27	38.46	7.34	6.99	6.38	6.13
$(C_2H_5)_2\overset{+}{N}(CH_3)CH_2C(OH)_2CF_2H\ \bar{Cl}$[c]	41.11	41.15	7.76	7.82	5.99	5.49
 $O(C_2H_4)_2\overset{+}{N}(CH_3)CH_2C(OH)_2CF_2H\ \bar{Cl}$	38.79	39.15	6.51	6.51	5.66	5.75

[a] Calcd.: Cl, 17.24; F, 18.48. Found: Cl, 17.26; F, 18.60. [b] Calcd.: F, 17.38. Found: F, 16.73. [c] Calcd.: Cl, 15.17; F, 16.26. Found: Cl, 15.81; F, 17.03.

Due to the extreme reactivity, none of the other intermediate quaternary ammonium fluorides was purified.

Hydrolysis of Reactive Intermediates.—The reactive intermediates were hydrolyzed by adding the solid slowly, with stirring and cooling, to water. About 100 ml. of water was used for every 0.1 mole of reactant. All the intermediates reacted quickly and vigorously except tri-*n*-butyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride, which required heating with 5% potassium hydroxide to bring about the hydrolysis. After all the solid had been added, the solution was neutralized with concentrated potassium hydroxide. The temperature was maintained below 35° during this operation. The mixture was cooled thoroughly and filtered. The crystalline material retained was washed with a little cold water and dried. For the trimethyl intermediate, sodium hydroxide was used for the neutralization. The mixture of solids which initially precipitated was filtered, dried and extracted with hot acetone. Cooling the acetone extract produced crystals of (3,3-difluoro-2,4-dioxocyclobutyl)-trimethylammonium betaine. More crystals were obtained by evaporating the aqueous filtrate to dryness and extracting this residue with acetone. Yields, methods of purification and melting points for these compounds are presented in Table I; analytical data are presented in Table II.

Alcoholysis in Absolute Ethanol.—A portion of triethyl-(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride was added to absolute ethanol. The resulting solution was treated with a solution of picric acid in ethanol. Thorough cooling gave yellow crystals which after being filtered and dried, melted at 69–71°. Two recrystallizations from absolute ethanol resulted in a m.p. 78–79° with sintering at 76°.

Anal. Calcd. for $C_{18}H_{22}N_4O_8F_4$: C, 43.38; H, 4.45; N, 11.25; F, 15.25. Found: C, 43.90; H, 4.75; N, 11.66; F, 14.63.

Reactions of (3,3-Difluoro-2,4-dioxocyclobutyl)-trimethylammonium Betaine. 1. **Complex with Iodine–Sodium Iodide.**—A solution of 10 g. of iodine and 25 g. of sodium iodide in 100 ml. of water was added with stirring to a solution of 5 g. of (3,3-difluoro-2,4-dioxocyclobutyl)-trimethylammonium betaine in 20 ml. of water until the dark color of the iodine–sodium iodide solution failed to disappear. The mixture was allowed to stand for ten minutes, then the dark red-brown crystals were filtered and dried. The yield of crude material was 8.0 g. (91% calculated for three moles of betaine to one of iodine–sodium iodide). This material decomposed at 232–235° with the liberation of iodine vapors. Two recrystallizations from glacial acetic acid gave a final product of red-brown crystals which decomposed at 233–235°.

Anal. Calcd. for $C_{21}H_{27}N_3O_6F_6NaI_3$: C, 26.97; H, 2.91; N, 4.49; I, 40.71; Na (as sulfate), 7.60. Found: C, 27.12; H, 2.72; N, 4.24; I, 41.22; Na (as sulfate), 7.59.

2. **Complex with Sulfuric Acid.**—One and one-half grams of the betaine was dissolved by warming in 3 ml. of concentrated sulfuric acid. The solution was cooled and added with stirring to 50 ml. of absolute ether. Continued stirring gave a white solid, which was filtered under an atmosphere of nitrogen and dried. This extremely hygroscopic solid weighed 2.0 g. and melted at 103–108°. One recrystallization from methanol gave m.p. 207–210°. A second recrystallization gave 0.9 g. of white, non-hygroscopic solid melting at 231–233° which was identical with the starting material.

3. **Reaction with 3 *N* Hydrochloric Acid.**—(3,3-Difluoro-2,4-dioxocyclobutyl)-trimethylammonium betaine, and also the betaines produced from N-methyldiethylamine, N,N-dimethylethylamine and 4-methylmorpholine reacted with dilute hydrochloric acid. Ten grams of the betaine was refluxed with 20 ml. of concentrated hydrochloric acid and 60 ml. of water for four hours. This produced complete reaction in all cases except that of (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine, which had to be refluxed 20 hours to complete the reaction. The presence of carbon dioxide was confirmed by passing the exit gases through a saturated solution of calcium hydroxide.

(3,3-Difluoro-2-oxopropyl)-trimethylammonium chloride monohydrate and (3,3-difluoro-2-oxopropyl)-4-methylmorpholinium chloride monohydrate were isolated by evaporating the solution to dryness, adding acetone and filtering. Any additional salt was recovered by adding ether to the filtrate. (3,3-Difluoro-2-oxopropyl)-diethylmethylammonium chloride monohydrate and (3,3-difluoro-2-oxopropyl)-ethyldimethylammonium chloride monohydrate were isolated by evaporating the solution to a thick sirup under reduced pressure and then crystallizing by the addition of acetone. Data for these compounds are presented in Tables III and IV.

4. **Reaction with Benzene in the Presence of Anhydrous Aluminum Chloride.**—A mixture of 10.0 g. (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, 200 ml. of benzene and 30.0 g. of anhydrous aluminum chloride was placed in a 3-necked flask fitted with a mechanical stirrer, reflux condenser and drying tube. The mixture was refluxed for one hour with vigorous stirring. During this time most of the solids dissolved, a considerable amount of

hydrogen chloride was evolved, and the solution turned black. The solution was then cooled and poured with vigorous stirring into a dilute hydrochloric acid–ice mixture. The black color disappeared and slightly yellow crystals began to separate. After standing for one hour, the solution was filtered and the solid was dried. This produced 10.5 g. (69%) of crude material, m.p. 122–132°. This solid was dissolved in 50 ml. of glacial acetic acid and the small amount of insoluble material was removed by centrifuging. The supernatant acetic acid solution was poured with stirring into 400 ml. of water and allowed to stand for 30 minutes, then filtered. The dried white solid weighed 7.0 g. (46%) and melted at 180–183°. Several recrystallizations from methyl acetate raised the m.p. to 188–189°.

Anal. Calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.49; H, 7.10; N, 4.21.

Reactions of (3,3-Difluoro-2-oxopropyl)-trimethylammonium Chloride Monohydrate. 1. Reaction with Picric Acid.—One gram of the chloride, dissolved in 10 ml. of absolute ethanol, was heated for 20 minutes with 20 ml. of a saturated solution of picric acid in ethanol. Thorough cooling of this solution produced slow crystallization of a slightly yellow solid which, after being filtered and dried, weighed 1.3 g. (68%) and melted at 133–135°. Two recrystallizations from absolute ethanol gave a final melting point of 137–138°.

Anal. Calcd. for $C_{14}H_{20}N_4O_9F_2$: C, 39.43; H, 4.73; N, 13.14; F, 9.54. Found: C, 39.39; H, 4.77; N, 13.23; F, 9.76.

This alcoholated picrate was heated in a drying pistol at 100° and 0.1 mm. for six hours, then reanalyzed.

Anal. Calcd. for $C_{12}H_{14}N_4O_8F_2$: C, 37.90; H, 3.71. Found: C, 38.24; H, 3.83.

2. **Reaction with *p*-Nitrophenylhydrazine.**—Two grams of the chloride was heated with 2.0 g. of *p*-nitrophenylhydrazine in 15 ml. of absolute ethanol. The solids dissolved and after about five minutes yellow crystals began to form. After 20 minutes the mixture was cooled and filtered. The solid produced by this method was purified by dissolving in methanol and reprecipitating with ether. The purified solid did not have a reproducible melting point; the melting points obtained ranged from 120–121° to 127–128°.

Anal. Calcd. for $C_{18}H_{31}N_5O_4F_4Cl_2$: C, 40.91; H, 5.91; N, 13.26; F, 14.38. Found: C, 40.78; H, 5.75; N, 13.58; F, 14.04.

3. **Reaction with Sodium Bisulfite.**—One gram of the chloride was dissolved in 2 ml. of water and treated with 5 ml. of saturated sodium bisulfite solution. A heavy precipitate was formed immediately. This weighed 1.8 g. after being filtered and dried but contained some inorganic material as indicated by the ash which remained after ignition. Recrystallization from water gave 0.9 g. (82%) of α-hydroxy-α-difluoromethyl-β-trimethylammonoethanesulfonate, dec. 190–192°. Another recrystallization from water gave glistening white crystals, dec. 190–191.5°.

Anal. Calcd. for $C_6H_{13}NO_4SF_2$: C, 30.90; H, 5.62; N, 6.01. Found: C, 30.98; H, 5.65; N, 5.99.

4. **Reaction with Concentrated Potassium Hydroxide.**—Two grams of (3,3-difluoro-2-oxopropyl)-trimethylammonium chloride monohydrate was heated with 6 ml. of 40% potassium hydroxide solution. The volatile amine was carried into a solution of picric acid in absolute ethanol. A precipitate began to form when the solution reached the boiling point. After ten minutes the refluxing was stopped and the picrate was filtered and dried, m.p. 214–217°. Recrystallization from absolute ethanol gave a m.p. of 219–220°. A mixed melting point with an authentic sample of trimethylamine picrate having a melting point of 220–221° gave a m.p. of 219–220°.

Hydrobromide of (2,4-Dioxo-3,3-diphenylcyclobutyl)-triethylammonium Betaine.—One gram of this betaine was heated with 15 ml. of 48% hydrobromic acid for ten minutes. During this time a white precipitate formed. The mixture was cooled and the precipitate was filtered and dried. The yield was 1.3 g. (95%) of white solid, m.p. 168–170°. Two recrystallizations from glacial acetic acid gave a final melting point of 166–167°.

Anal. Calcd. for $C_{22}H_{26}NO_2Br$: C, 63.46; H, 6.29; N, 3.36. Found: C, 63.52; H, 6.40; N, 3.32.

When a sample of this bromide was heated for a few minutes with water and then filtered and dried, it was found to have reverted to the original (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine.

Absorption Spectra of (3,3-Difluoro-2,4-dioxocyclobutyl)-triethylammonium Betaine, (3,3-Difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium Betaine and (2,4-Dioxo-3,3-diphenylcyclobutyl)-triethylammonium Betaine.—The infrared absorption spectra were measured using a Perkin–Elmer model 21 double-beam spectrophotometer with a rock salt prism. The sample was prepared by evaporation of either a methanol or an acetone solution on rock salt plates. The spectra are recorded in Fig. 1.

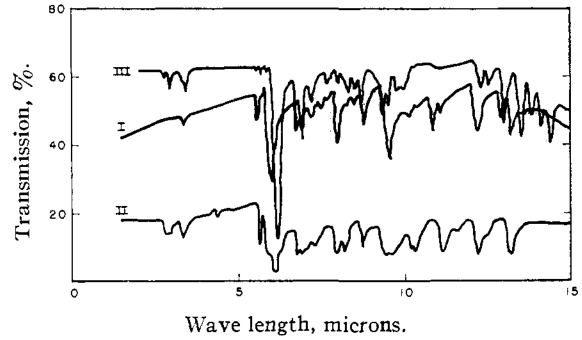


Fig. 1.—Infrared absorption spectra of: I, (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine; II, (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine; III, (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine; range, 2 to 15 microns; preparation, deposited from methanol or acetone.

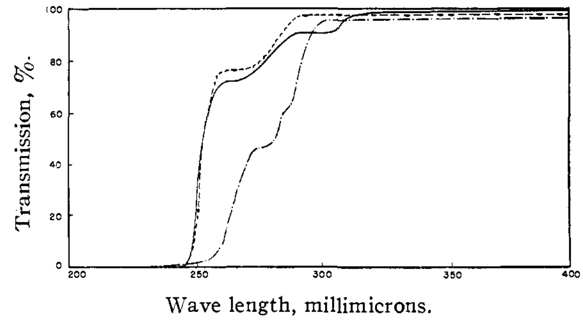


Fig. 2.—Ultraviolet absorption spectra of: —, (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, *c*, 1.69 × 10^{-3} mole/liter; ----, (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine, *c*, 1.98 × 10^{-3} mole/liter; —·—, (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine, *c*, 2.19 × 10^{-4} mole/liter.

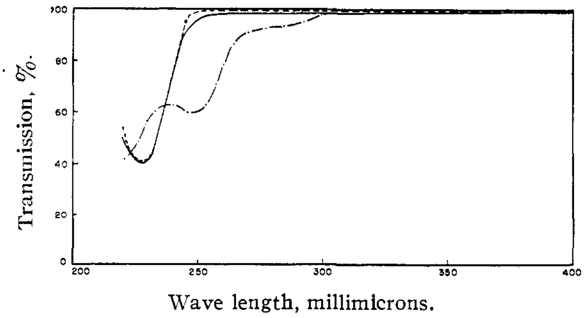


Fig. 3.—Ultraviolet absorption spectra of: —, (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, *c*, 1.69 × 10^{-5} mole/liter; ----, (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine, *c*, 1.98 × 10^{-5} mole/liter; —·—, (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine, *c*, 2.19 × 10^{-5} mole/liter.

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

[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

[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).