JOURNAL OF POLYMER SCIENCE: PART A VOL. 2, PP. 3803–3810 (1964)

Synthesis and Polymerization of 1-(Perfluoroacyl)aziridines

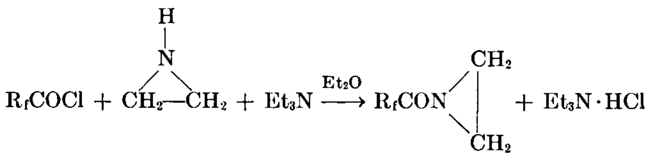
A. G. PITTMAN and R. E. LUNDIN, *Western Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, Albany, California*

Synopsis

The preparation and polymerization of representative 1-(perfluoroacyl)aziridines were examined. Polymerization of the aziridines was induced by heat, by certain inorganic nucleophiles such as cyanide, fluoride, and chloride, and by organic bases. Certain other inorganic nucleophilic reagents such as KI and KBr effected the rearrangement of the 1-(perfluoroacyl)aziridines to the isomeric 2-perfluoroalkyl-2-oxazolines. A possible reaction mechanism involving anionic polymerization in competition with oxazoline formation was discussed.

INTRODUCTION

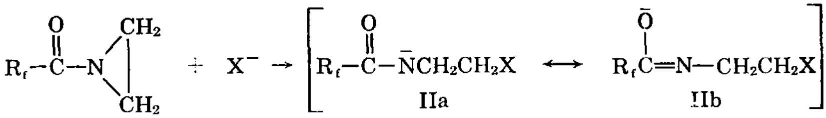
The 1-(perfluoroacyl)aziridines represent a versatile group of fluorine-containing compounds which has received little attention. Brace and McCormack[1] described a displacement reaction between ethylenimine and an α,α-dichloroperfluoroalkyl ester in which ring-opened products were obtained instead of the 1-(acyl)aziridines. We found that the 1-(perfluoroacyl)aziridines could be prepared in a straightforward manner by reaction of the corresponding perfluoro acid chlorides with ethylenimine, as shown in eq. (1).



(1)

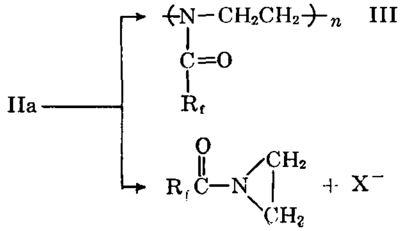
Removal of triethylamine hydrochloride and solvent from the crude reaction product left a heat-labile concentrate which could be stored at −78°C. for an indefinite period. At room temperature the concentrate normally polymerized exothermically within 2 hr. Instability of the crude product is apparently due to the presence of traces of the free bases Et_3N or ethylenimine. Purification of the aziridines was carried out by removing them from the concentrate under vacuum without application of external heat to the distillation pot. After purification, the aziridinyl derivatives exhibited increased stability, i.e., no sign of polymerization was noted with purified 1-(perfluorobutyryl)aziridine (I) until after 4 hr. at 24°C.

The polymerization of the 1-(perfluoroacyl)aziridines evidently follows a different course from ethylenimine, which is not polymerized by bases[2,3] but undergoes acid-catalyzed polymerization involving positively charged nitrogen. Addition of small quantities (ca. 1%) of 50% acetic, trifluoroacetic, or 6*N* hydrochloric acid to I at room temperature did not effect polymerization. Attempts to polymerize I with BF_3 in ether or $AlCl_3$ in *n*-heptane were also unsuccessful. In both cases, monomer was recovered after 2 hr. at room temperature. On the other hand, addition of catalytic amounts of triethyl amine, pyridine, or ethylenimine to I at room temperature caused an instantaneous exothermic conversion to polymer. Polymerization was also effected by using other nucleophiles such as chloride, cyanide, or fluoride ion in diglyme. The relative stability of the 1-fluoroacylaziridines toward acidic substances and their susceptibility to nucleophilic attack is best explained on the basis of an electron deficiency in the aziridinyl ring caused by the strong electron-withdrawal properties of the perfluoroalkyl group. Heine and co-workers[4] have shown that nucleophilic reagents such as sodium iodide or sodium thiocyanate are effective catalysts for the rearrangement of certain 1-(aroyl)aziridines to the isomeric oxazoline derivatives and have postulated mechanisms involving initial attack of the nucleophile on the carbonyl and on the aziridine ring. Similar mechanisms can be invoked for the 1-(perfluoroacyl)aziridines in which the intermediates serve either as a polymerization catalyst or are converted to a 2-perfluoroalkyl-2-oxazoline. It was observed that, in a series of experiments with a catalytic quantity (2 mole-%) of potassium halide in diglyme, iodide ion gave virtually complete conversion of I to 2-perfluoropropyl-2-oxazoline, bromide gave an 80% conversion to polymer and 20% conversion to oxazoline, whereas chloride and fluoride gave polymer and no oxazoline. Considering an initial attack of halide on one of the carbons of the aziridine ring,



(2)

where X^- = halide anion



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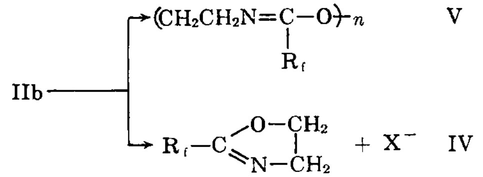

(4)

it can be seen that reformation of the aziridine could occur by intramolecular displacement of halide by nitrogen in a reversible reaction or that intramolecular displacement of halide by the oxy anion would yield an oxazoline (IV). Polymer formation is presumably a competing intermolecular reaction which occurs when the C—X bond is not easily broken by displacement. Polymer structures III and V appear feasible depending on whether initiation occurs through negatively charged nitrogen (IIa) or the oxy anion (IIb). The fact that the ease of oxazoline formation follows the order of ease of displacement of halides, $I^- > Br^- \gg Cl^-$, lends credence to the mechanism proposed. The NMR and infrared spectra of poly-1-(perfluorobutyryl)aziridine were similar to the spectra obtained from a sample of polyethylenimine which received a treatment with perfluorobutyryl chloride. On the basis of this spectral evidence, we favor structure III as being representative of the poly-1-(perfluoroacyl)aziridines.

EXPERIMENTAL

Boiling points and melting points are uncorrected. Melting points and polymer softening temperatures were obtained on a Fischer-Johns melting point block. Proton NMR spectra were taken on a Varian Associates 60 mcycle high resolution NMR spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. Infrared scans were run on the undiluted pure samples unless otherwise indicated.

Preparation of Monomers

Preparation of 1-(Perfluorobutyryl)aziridine (I). A three-necked 500 ml. flask equipped with a stirrer, nitrogen inlet, and rubber septum was dried and flushed with nitrogen. Then 200 cc. of anhydrous diethyl ether, 13.3 g. (0.13 mole) triethylamine and 5.6 g. (0.13 mole) ethylenimine were added to the flask, and the contents were placed under a nitrogen blanket and cooled in a Dry Ice–acetone bath to ca. −30°C. The mixture was stirred and 30 g. (0.13 mole) of perfluorobutyryl chloride was added slowly with stirring. The precipitated triethylamine hydrochloride was rapidly filtered from the cold ethereal solution; 17 g. of the hydrochloride was collected, indicating 94% conversion of the acid chloride. The ether was removed on a rotary evaporator, leaving 22 g. of a light brown liquid product. The crude material was distilled in a vacuum system (0.05–0.1 mm.) without applying external heat, and 20 g. (63%) of product was collected in a Dry Ice trap. The purified material was a clear liquid, b.p.

36°C./11 mm., n_D^{23} 1.3401. The infrared absorption spectra showed the C—H stretching at 3.25 and 3.35 μ and carbonyl absorption at 5.8 μ.

The 60 mcycle proton NMR spectrum of this material as a dilute solution in carbon tetrachloride showed a single sharp peak at 7.50 τ. To establish the shielding value of aziridine protons, 1-(3,5-dinitrobenzoyl)-aziridine was prepared by the method of Heine.[4] The four equivalent protons on the aziridine ring produced a sharp peak at 7.52 τ, confirming that I was an aziridine.

Because of the instability of the monomer, combustion analysis was carried out on the polymer as described subsequently.

A ring-opened derivative, *N*-(2-bromoethyl)perfluorobutyramide, was prepared as follows. A 0.5-g. (0.0021 mole) portion of I was added, with stirring, to 20 cc. of a cold (ca. 5°C.) 48% aqueous HBr solution. A white solid was formed immediately. It was filtered from the solution, washed several times with H_2O and dried; 0.61 g. (91% yield) of *N*-(2-bromoethyl)-perfluorobutyramide was obtained, m.p. 57–59°C. Sublimation of the solid at 0.7 mm. gave the pure product, m.p. 63–64°C.

ANAL. Calcd. for $C_6BrF_7H_4NO$: C, 22.50%; Br, 25.00%; F, 41.56%; H, 1.5%; MW, 320. Found: C, 22.30%; Br, 24.99%; F, 39.7%; H, 1.8%; MW, 343 (Rast).

Infrared spectra of the product in CCl_4 had the bands expected for a secondary amide: N—H at 2.95 μ, carbonyl at 5.78 μ, and N—H deformation at 6.5 μ.[5a]

The proton NMR spectrum of this compound in carbon tetrachloride showed a very broad band with its center at 3.10 τ arising from the amide proton, and a complex multiplet of the A_2B_2X type centered at 6.40 τ. Integration showed that the latter band represented 4.1 protons on the basis of the assignment of one proton to the broad peak. To confirm the assignment of the multiplet to the hydrogens of the methylene groups attached either to amide nitrogen or to bromine, the spectrum of *N*-(2-bromoethyl)octanoamide was obtained. The methylene protons of the bromoethyl moiety produced an incompletely resolved band centered at 6.46 τ.

1-(Perfluorooctanoyl)aziridine (VI). In a procedure analogous to that described for I, VI was prepared as a clear liquid, b.p. 44°C./0.1–0.2 mm., n_D^{23} 1.3330. Elemental analysis was carried out on the polymer obtained by allowing VI to stand overnight at 23°C.

ANAL. Calcd. for $C_{10}F_{15}H_4NO$: C, 27.33%; F, 64.92%; H, 0.9%. Found: C, 26.82%; F, 64.2%; H, 1.12%.

1,1′-(Perfluoroglutaryl)bisaziridine (VII). A procedure was used similar to that described by Heine for the preparation of 1-(aroyl)aziridines.[4] Into a Waring Blendor were placed 50 g. ice, 50 g. benzene, 4.0 g. (0.1 mole) NaOH, and 4.3 g. (0.1 mole) ethylenimine. After the mixture had been stirred for a few minutes to dissolve NaOH, 14 g. (0.05 mole) of perfluoroglutaryl chloride was added over a period of 10–15 min. The temperature was maintained at ca. 5°C. by addition of ice when needed. The benzene layer was separated and dried over $CaSO_4$. The water layer was extracted once with about 20 cc. of diethyl ether and the ether and benzene layers combined. The ether and benzene were removed on a rotary evaporator leaving 20 g. of a liquid product which contained residual benzene. The infrared spectrum of the residue confirmed the 1-(acyl)aziridine structure. Absorption was noted at 3.25 μ and 3.35 μ for the C—H stretching, 5.8 μ for the carbonyl, and in the 8–9 μ region for the C—F absorption. Several unsuccessful attempts at purification were made via high vacuum distillation. The higher boiling point of VII necessitated some heating during the distillation attempts which always resulted in a highly exothermic polymerization.

The polymer derived from the crude monomer had properties expected of a highly crosslinked structure in that it was extremely brittle, insoluble, and did not melt. Charring of the polymer commenced at 270–280°C.

Polymerizations

Uncatalyzed Polymerization of I. Purified I was placed in a 2-oz. screw-cap vial and allowed to stand at 23°C. A viscosity increase was noted after 4 hr. and complete solidification after 12 hr. A white, opaque solid polymer was obtained which softened at 190°C. and yielded a clear, somewhat brittle film on pressing at 175°C./1000 psi. The inherent viscosity of the polymer was 0.07 at 23°C. (1% solution in 1,3-bis(trifluoromethyl)benzene). The polymer was soluble in acetone, 1,3-bis(trifluoromethyl)benzene, and DMF and insoluble in CCl_4 and heptane.

Infrared analysis of the polymer revealed the disappearance of the carbonyl band at 5.8 μ and the presence of new bands at 5.98 μ (strong) and 3.02 μ (weak). The band at 5.98 μ is presumably due either to amide carbonyl or —N=C—O[6b] and the weak band at 3.05 μ to N—H stretching of secondary amide chain ends. The proton NMR spectrum of the polymer dissolved in trifluoromethylbenzene and run at 80°C. showed a single broad peak (line width approximately 9 cycles/sec.) centered at 6.15 τ which was not present in the spectrum of the solvent when run under the same conditions. This peak was somewhat asymmetric with the extra intensity on the high-field side. The position of the observed band is not unreasonable for the methylene protons in III and IV. The sensitivity was not sufficient to observe any terminal group resonances.

ANAL. Calcd. for $C_6F_7H_4NO$: C, 30.12%; F, 55.64%; H, 1.7%; N, 5.85%. Found: C, 29.90%; F, 54.35%; H, 1.9%; N, 5.93%. $\bar{M}_n$ = 3,728 (Mechrolab osmometer).

Modification of Polyethylenimine to a Structure III. An aqueous sample of polyethylenimine (MW 30,000–40,000) was dried by repeated azeotropic distillations with benzene and reacted with an excess of perfluorobutyryl chloride in acetone/chloroform with triethylamine as an acid acceptor.

The proton NMR spectrum of the modified polyethylenimine dissolved in trifluoromethylbenzene and run at 80°C. showed a single broad peak (line width at one-half height approximately 30 cycles/sec.) centered at 6.15 τ.

An infrared scan (KBr) showed absorption bands similar to those observed for poly-1-(perfluorobutyryl)aziridine.

Polymerization of a Crude Reaction Product of VI. Ether was stripped from a reaction mixture as described for the preparation of VI. After standing at room temperature for 45 min., the concentrate underwent a spontaneous exothermic polymerization, giving a clear, light-brown solid polymer with an inherent viscosity of 0.15 at 22°C. (1% solution in 1,3-bis(trifluoromethyl)benzene). The polymer melted at 142–145°C., yielded a clear brittle film on pressing at 135°C./1000 psi, and was soluble in benzotrifluoride and 1,3-bis(trifluoromethyl) benzene and insoluble in CCl_3, DMF, and hydrocarbon solvents.

ANAL. Calcd. for $C_{10}F_{15}H_4NO$: C, 27.33%; F, 64.92%; H, 0.9%; N, 3.2%. Found: C, 27.32%; F, 64.2%; H, 1.34%; N, 3.4%.

The carbonyl band at 5.8 μ had disappeared and new bands occurred at 5.98 μ (strong) and 3.05 μ (weak).

Polymerization vs. Oxazoline Formation. A series of reactions with the use of 2 mole-% of the potassium halides KF, KCl, KBr, and KI in diglyme were carried out as follows. A 25-cc. round-bottomed flask was dried, flushed with nitrogen, and charged with the proper amount of halide and 5 cc. anhydrous diglyme. The solution was stirred and cooled to −30°C., and 1.6 g. I was added with a syringe. The cooling bath was removed and the solution was stirred overnight (12 hr.) at room temperature. After ca. $1^1/_2$ hr., solid polymer was noted on the walls of the flask when KBr, KCl, and KF were used. A clear homogeneous solution resulted when KI was employed. The liquid was then distilled into a Dry Ice trap *in vacuo* without applying external heat to the distillation pot. The solid polymer which remained in the distillation pot was then washed with H_2O, dried, and weighed. The distillate was diluted with 6 cc. H_2O and the upper H_2O–diglyme phase removed. The fluorocarbon layer was washed once with 2 cc. H_2O, dried, and examined by infrared spectroscopy and gas chromatography. The results of the experiments are summarized in Table I.

TABLE I
Effect of Halide

Halide	Polymer obtained, %	Liquid recovered, %	Composition of recovered liquid
KF	73	20	Monomer
KCl	80	20	Monomer
KBr	73	20	Oxazoline
KI	<1	>99	Oxazoline

Control experiments without added halide verified the catalytic action of the potassium halides. The polymers obtained were similar to the polymer obtained by the uncatalyzed polymerization of I. The oxazoline obtained from I is 2-perfluoropropyl-2-oxazoline, b.p. 135–136°C./760 mm., n_D^{23} 1.3345.

ANAL. Calcd. for $C_6F_7H_4NO$: C, 30.12%; F, 55.64%; H, 1.7%; N, 5.85%. Found: C, 30.98%; F, 55.8%; H, 2.1%; N, 5.82%.

The infrared spectrum of 2-perfluoropropyl-2-oxazoline revealed C—H stretching at 3.4–3.5 μ and —C=N— stretching (medium intensity) at 5.98 μ. This compound in carbon tetrachloride had a proton NMR spectrum that consisted of a single complex multiplet of the A_2B_2 type centered at 5.75 τ. The high-field half of this band showed an additional incompletely resolved triplet splitting ($J \approx 1.5$ cycle/sec.) presumably arising from spin-spin coupling between the two equivalent fluorines on the α carbon and the protons of the methylene group attached to the unsaturated nitrogen. To confirm the assignment of this band to the four oxazoline protons, the spectrum of 2-(3,5-dinitrophenyl)-2-oxazoline, prepared by the method of Heine[6] was obtained. The oxazoline hydrogens gave rise to a multiplet of identical appearance (except for the absence of the fluorine splitting) centered at 5.70 τ.

The oxazoline was also obtained when diglyme was used as a solvent with either a 1/50 or 1/1 mole ratio of NaI to 1-(perfluorobutyryl)aziridine. Polymer formation was not observed under any of the conditions in which NaI or KI were used.

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Résumé

La préparation et la polymérisation de représentants de la classe des 1-(perfluoroacyle)aziridines ont été examinées. La polymérisation des aziridines était initiée par la chaleur, par certaines substances nucléophiles inorganiques tels des cyanures, fluorures, chlorures et par des bases organiques. Certains autres réactifs nucléophiles tels que KI et KBr ont produit le réarrangement des 1-(perfluoroacyl)aziridines en isomères 2-perfluoroalcoyl-2-oxazolines. La possibilité d'un mécanisme de réaction impliquant une polymérisation anionique en compétition avec la formation d'oxazoline a été discutée.

Zusammenfassung

Die Herstellung und Polymerisation von repräsentativen 1-Perfluoracylaziridinen wurde untersucht. Die Polymerisation der Aziridine wurde durch Hitze, bestimmte anorganische Nucleophile wie Cyanid, Fluorid und Chlorid und organische Basen angeregt. Gewisse andere anorganische nucleophile Reagenzien wie KI und KBr bewirkten die Umlagerung der 1-Perfluoracylaziridine zu den isomeren 2-Perfluoralkyl-2-Oxazolinen. Ein möglicher Reaktionsmechanismus mit anionischer Polymerisation und gleichzeitiger Oxazolinbildung wird diskutiert.

Received December 6, 1963
Revised January 20, 1964