a vacuum line. Identification was based upon melting point, analysis for nitrogen, fluorine nmr and infrared spectral data, and the mass spectrum. Carbon dioxide was isolated in about 90% yield. The reaction is a particularly facile route to perfluorodiacetamide, since a high yield was obtained at room temperature.

Reactions of anhydrides with potassium cyanate have been reported to give diacetamides indirectly.[10] Diacetamide was not obtained from isocyanic acid and acetic anhydride.[10a]

Experimental Section

The reactions were carried out using vacuum line techniques. Where necessary, compounds were handled in an atmosphere of dry nitrogen using a glove bag. The reaction tubes were constructed from Lab-Crest valves (Fisher and Porter Co.), which had polytetrafluoroethylene stems. Infrared spectra were obtained with a Perkin-Elmer Model 521 grating instrument. The fluorine nmr spectra were obtained with a Varian DP-60 high-resolution spectrometer at 56.4 Mc. The audio modulation system incorporated in the Varian V5321 integrator was used to record the spectrum, and side bands displaced at multiples of 2000 Kc were used for calibration. A Consolidated Electrodynamics Corp. Model 21-110B high-resolution instrument was used for the mass spectrum.

Isocyanic acid was made by a procedure similar to that described in the literature.[11,12] Treatment with silver oxide was unnecessary, because little, if any, hydrogen cyanide was present. Millimole quantities were volatilized into a vacuum line from a reservoir of the liquid acid and pumped on at −96° before use. Polymerization may occur at pressures greater than 140 mm.[13] An infrared spectrum of the gas compared well with the literature spectrum.[13] Trifluoroacetic anhydride (Eastman grade) was also introduced into the vacuum line from a reservoir of the liquid. An infrared spectrum of the gas was the same as the literature spectrum.[14]

Trifluoroacetyl Isocyanate.—Trifluoroacetic anhydride (2.3 mmoles) and isocyanic acid (4.5 mmoles) were condensed into a dry, 30-ml reactor at −196°. An exothermic reaction took place as the reaction mixture warmed to room temperature. After 1 hr of reaction, fractionation in a vacuum line gave three volatile fractions: carbon dioxide (2.4 mmoles) passed through a −132° trap; trifluoroacetyl isocyanate (0.85 mmole, 37% yield based on anhydride) passed through a −23° trap and was retained by a −132° trap; a solid, which was not identified, was retained at −23°. The reactor contained additional solid.

The trifluoroacetyl isocyanate was combined with additional material from other runs and refractionated using traps at −45 and −132°. The molecular weight (gas density) was 142 (calcd: 139); infrared absorptions of a 4.8-mm gas sample in a 100-mm cell were at 3293 (vw), 2457 (vw), 2367 (w), 2275 (vs), 2235 (s), 2173 (w), 2115 (vw), 1797 (ms, sh), 1787 (ms), 1780 (ms, sh), 1502 (vw), 1444 (m), 1407 (w, sh), 1306 (m), 1237 (ms), 1192 (ms), 1023 (s), 803 (w), 739 (mw), 734 (mw), 731 (mw, sh), and 678 cm^{-1} (vw); fluorine nmr (trichlorofluoromethane as solvent and internal standard) showed a peak at 77.4 ppm; mp −100°. The vapor pressure curve was measured in a grease-free system constructed from Lab-Crest valves (Fisher and Porter Co.).[15] The sample was first refractionated as described above and pumped on at −132°. At the end of the measurements the sample volatilized completely from the apparatus and the molecular weight was unchanged. Temperatures and pressures, °K (mm), were as follows: 298.6 (321.3); 273.2 (147.3); 249.4 (36.8); 244.9 (26.7); 241.4 (21.1); 231.4 (10.0). These data are described by the equation $\log P(\text{mm}) = -1725/T + 8.4666$; $\Delta H_v = 7.89$ kcal/mole; Trouton's constant 25.6; extrapolated bp 35 ± 1°.

2,2,2,2′,2′,2′-Hexafluorodiacetamide.—As described above isocyanic acid (2.0 mmoles) and trifluoroacetic anhydride (4.0 mmoles) were condensed into a reactor at −196°. The reaction was allowed to proceed for 4 days at room temperature. The resulting mixture of solid and liquid was fractionated in a vacuum line using a −45° trap to retain the solid. A warm water bath was used to speed the transfer. A small amount of uncharacterized material remained in the reactor. The −45° condensate, after vacuum transfer to a tared bulb, weighed 0.3781 g (1.81 mmoles of the diacetamide, 90% yield based on isocyanic acid). Fractional vacuum sublimation gave a 46-mg forecut, which was discarded. A center cut of 83 mg was used for the analytical sample.

Anal. Calcd for $C_4HF_6NO_2$: N, 6.70. Found: N, 6.33, 6.50.

Additional properties were determined on the remaining product (0.249 g): mp[16] 86.4–87.0° (lit.[9b] mp 85°) and infrared absorptions (mineral oil) at 3300 (m), 3230 (ms), 3050 (m), 2640 (w), 1802 (s), 1748 (m), 1542 (ms), 1533 (ms, sh), 1330 (m), 1235 (s), 1212 (s), 1185 (s), 1123 (ms), 1093 (sh), 957 (w), 810 (w), 782 (m), 747 (w), 718 (w), 660 (ms), and 590 cm^{-1} (w). The spectrum is in good agreement with that expected for an acylic imide[17,18] if allowance is made for the expected shifts to higher frequencies due to fluorine. However, there are some variations from the literature values for perfluorodiacetamide; C═O absorptions were reported[9b,d] either at 5.64 and 5.74 μ or at 5.63 μ (calcd: 1773 and 1742, 1776 cm^{-1}) and NH absorptions were reported[9d] at 3.08 μ (calcd: 3247 cm^{-1}), none at *ca.* 1500 cm^{-1}. Major peaks in the mass spectrum follow (*m/e*, pattern, probable positive ion): 209, 0.074, $(CF_3CO)_2NH$; 140, 0.391, $CF_3CONHCO$; 112, 0.157, CF_3CONH; 97, 0.115, CF_3CO; 70, 0.130; 69, 1.000, CF_3; 51, 0.119; 45, 0.123; 44, 0.479; 43, 0.142; 20, 0.142; 18, 8.43, H_2O. ^{19}F nmr of a sample from another run showed a single peak at 76.0 ppm from trichlorofluoromethane (internal) in ethyl ether solution.[7]

Registry No.—Isocyanic acid, 75-13-8; trifluoroacetic anhydride, 407-25-0; trifluoroacetyl isocyanate, 14565-32-3; 2,2,2,2′,2′,2′-hexafluorodiacetamide, 407-24-9.

Acknowledgment.—Infrared data were obtained by Mr. N. Colthup, and the fluorine nmr spectra were determined by Mrs. M. Neglia and Dr. J. Lancaster. The mass spectral data were obtained by Mr. T. Mead.

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[10] (a) K. Brunner, *Ber.*, **47**, 2671 (1914); (b) W. Miller, *Monatsh.*, **36**, 929 (1915).

[11] G. Brauer, "Handbuch der Preparativen Anorganischen Chemie," Ferdinand Enke, Publishers, Stuttgart, Germany, 1960, p 352.

[12] Work done by Chemical Engineering Services of these laboratories.

[13] G. Herzberg and C. Reid, *Discussions Faraday Soc.*, **9**, 92 (1950).

[14] D. G. Weiblen in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, p 487.

[15] Pressures were measured with a 10-mm o.d. mercury manometer and a meter stick and are corrected to 0°. Temperatures were measured with a calibrated copper–constantan thermocouple made from Leeds and Northrup No. 24-55-1-A wire and a Leeds and Northrup temperature potentiometer, Catalog No. 8692.

[16] The melting point was obtained in a sealed capillary under an atmosphere of dry nitrogen and is corrected.

[17] J. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **34**, 545, 551 (1961).

[18] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, pp 266–267.

Coupling of Monobromoperfluoroalkanecarboxylic Esters

YUNG K. KIM AND OGDEN R. PIERCE

Fluorine Research Laboratories, Dow Corning Corporation,
Midland, Michigan 48640

Received July 11, 1967

A previous report from this laboratory[1] has described a convenient method for the synthesis of a series of ω-bromoperfluoroalkanecarboxylic esters, $Br(CF_2CF_2)_nCOOR$, and 3-bromoperfluorobutanoic ester. This investigation was undertaken to examine the possibility of coupling the monobromoperfluoroalkanecarboxylic esters *via* C–Br as the reactive center. The coupling would provide a new attractive method for the

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[1] Y. K. Kim, *J. Org. Chem.*, **32**, 3673 (1967).

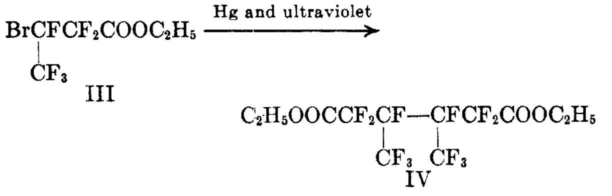
synthesis of very useful long-chain perfluoroalkanedicarboxylic esters.[2]

While intermolecular coupling of the varied monoiodoperfluoro compounds *via* C–I as the reactive center has been successfully effected by many investigators,[3] only two isolated examples of intermolecular coupling of monobromoperfluoro compounds involving C–Br as the reactive center have appeared in the literature.[4] To our knowledge no intermolecular coupling of compounds of the type $R(CF_2)_nCY_2Br$ ($n \geq 1$, R = any radical or functional group, Y = fluorine or perfluoroalkyl) to give rise to $R(CF_2)_nCY_2CY_2(CF_2)_nR$ has been described. Since it has been shown that the coupling of monobromoperfluoroalkanes does not occur by the use of zinc,[3c] the method involving the use of mercury and ultraviolet light was investigated and resulted in the successful coupling of the monobromoperfluoroalkanecarboxylic esters to yield the corresponding diesters.

Irradiation of a stirred mixture of the ester I and an excess of mercury at 25° yielded the expected known diester II[2a,b] in a moderate yield along with other unidentified by-products (reaction 1). In the substitution of mercury by silver nitrate or in the absence of mercury, the irradiation of Ia failed to yield an appreciable amount of IIa.

$$\underset{\substack{\text{Ia}, n = 1 \\ \text{b}, n = 2}}{Br(CF_2CF_2)_nCOOC_2H_5} \xrightarrow{\text{Hg and ultraviolet}} \underset{\substack{\text{IIa}, n = 1 \\ \text{b}, n = 2}}{C_2H_5OOC(CF_2CF_2)_{2n}COOC_2H_5} \quad (1)$$

Under reaction conditions similar to those mentioned above, ethyl 3-bromoperfluorobutanoate (III) gave the diester IV in a yield of *ca.* 42% based on the starting material consumed (reaction 2). Although it is likely that a mixture of stereoisomers (*meso* and *dl*) is formed from this coupling reaction, no attempt has been made to investigate the stereochemistry of the diester IV.



$$\underset{\text{III}}{BrCF(CF_3)CF_2COOC_2H_5} \xrightarrow{\text{Hg and ultraviolet}} \underset{\text{IV}}{C_2H_5OOCCF_2CF(CF_3){-}CF(CF_3)CF_2COOC_2H_5} \quad (2)$$

Experimental Section

All boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord. Gas chromatography was conducted on a F & M Model 720 using a 10 ft × 0.25 in. column containing 20% Dow Corning FS 1265 Fluod (10,000 centistokes) on Anakrom 90–100 mesh ABS. The ^{19}F resonance spectra were measured on a Varian high-resolution nmr spectrometer operating at 56.4 Mc. Chemical shifts are determined in parts per million using CCl_3F as an internal standard (δ = 0 ppm) with the positive direction on the high-field side.

All experiments were carried out under an atmosphere of dry nitrogen. No attempt was made to identify the products other than the coupled product.

Apparatus.—A 250-ml, three-necked, round-bottom quartz flask equipped with a stirrer, a condenser vented to a Dry Ice–acetone cooling trap, and a stream of dry nitrogen inlet is immersed in a water bath. A G.E. Model UA-2 ultraviolet lamp is rested in a quartz well which is immersed in the water bath about 2 in. away from the flask.

The Coupling of Ethyl Monobromoperfluoroalkanoates.—The coupling of ethyl 3-bromoperfluorobutanoate (III) is described as a typical example of the procedure.

A stirred mixture of 140 g (0.462 mole) of III and 693 g of mercury was irradiated for 96 hr at 25°. The reaction mixture was taken into methylene chloride, and the excess mercury and salt were removed. Most of the methylene chloride was evaporated on the steam bath through a Vigreaux column. Gas chromatographic analysis of the resulting product showed 41.9% yield of IV (major product) based on the starting material consumed (31%). The crude product was distilled to yield gas chromatographically pure IV, bp 102–103° (3 mm), $n^{25}D$ 1.3570.

Anal. Calcd for $C_{12}H_{10}F_{12}O_4$: C, 32.30; H, 2.26. Found: C, 32.2; H, 2.39.

The infrared spectrum (CCl_4) showed a strong band at ~1770 cm^{-1} (C=O). The molecular weight by the vapor phase osmometry was found to be 460 (calcd 446). The ^{19}F resonance spectrum (CCl_4) showed signals centered at δ = +69.8 (CF_3), +109.1 (CF_2), and +174.0 ppm. (CF). The relative areas were 3, 2, and 1, respectively.

Compounds IIa (33.2% yield based on the starting material consumed, 36%)[5] and IIb (41% yield based on the unrecovered starting material, 45.9%)[5] were isolated and identified by comparison of the physical and spectral properties with those of known samples.

The Irradiation of Ethyl 3-Bromoperfluoropropionate (Ia) in the Absence of Mercury and in the Presence of Silver Nitrate.—About 110 g (0.435 mole) of Ia was irradiated for 67 hr while stirring at 60°. Gas chromatographic analysis of the reaction mixture indicated that little reaction occurred. Into the unreacted Ia was added 74 g (0.435 mole) of silver nitrate, and irradiation was continued for an additional 94 hr while stirring at 60°. The reaction mixture was taken into ether, and salt was removed. Gas chromatographic analysis of the resulting mixture after removal of ether showed the presence of starting material and the trace amount of several components having higher retention times.

Registry No.—IIa, 376-50-1; IIb, 423-91-6; IV, 14909-86-5.

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[2] (a) E. T. McBee, P. A. Wiseman, and G. B. Bachman [*Ind. Eng. Chem.*, **39**, 415 (1947)] report the synthesis of perfluoroadipic acid and derivatives by oxidation of 1,2-dichloroperfluorocyclohexene-1. (b) R. A. Guenthner [U. S. Patent 2,606,206 (1952)] describes the preparation of perfluorosebacic acid and derivatives by electrochemical fluorination of the corresponding acid of the hydrocarbon system, $(CH_2)_8(COOH)_2$. (c) A multistep synthesis of perfluoroalkanedicarboxylic acids has been reported by I. L. Knunyants, C.-Y. Li, and V. V. Shokina, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.*, 1462 (1961); *Chem. Abstr.*, **56**, 302*i* (1962).

[3] (a) A. L. Henne, *J. Am. Chem. Soc.*, **75**, 5750 (1953); (b) M. Hauptschein, M. Braid, and F. E. Lawlor, *ibid.*, **79**, 6248 (1957); (c) S. N. Tsoukalas, Ph.D. Thesis, University of Florida, 1966; *Dissertation Abstr.*, **27** (5), 1432B (1966); (d) W. T. Miller, E. Bergman, and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 4159 (1957); (e) R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 3606 (1953); (f) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *ibid.*, 1995 (1962).

[4] (a) A recent paper by G. A. Grindahl, W. X. Bajzer, and O. R. Pierce [*J. Org. Chem.*, **32**, 603 (1967)] report the coupling of α-bromodifluoromethyl-*s*-triazines in the presence of mercury at elevated temperature. (b) Tsoukalas[3c] reports the coupling of $C_3F_7OC(-CF_3)FCF_2OC(-CF_3)FCF_2OC(-CF_3)FBr$ in the presence of zinc.

[5] Gas chromatographic analysis.

The Mechanism of the Sulfamate Ester Rearrangement

PAUL F. ZIEGLER AND MILTON ORCHIN

Department of Chemistry, University of Cincinnati,
Cincinnati, Ohio 45221

Received July 17, 1967

More than 80 years ago, it was reported[1] that methyl N,N-dimethylsulfamate rearranged spontaneously at room temperature to the dipolar betaine, trimethylammoniosulfur trioxide. Although analogous reactions

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[1] R. Behrend, *Ann.*, **232**, 116 (1884).