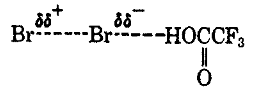
in the electrophilic nature of the halogenation reagent (II) thus modifying the structure of the intermediate


$$\overset{\delta\delta +}{Br}\text{------}\overset{\delta\delta -}{Br}\text{-----}HO\underset{\underset{O}{\|}}{C}CF_3$$

II

complex[9b] formed during the reaction with respect to those formed in acetic acid.

It has not been possible to obtain evidence uniquely in favor of either of these proposed effects but work is being carried in this direction.

When log k is plotted against $\Sigma\sigma^+$ (Figure 1) it is seen that the slopes of the correlation lines in the three solvents (water, trifluoroacetic acid, and acetic acid) are essentially the same even though the domains of absolute reactivity are quite different. It can be stated that the bromination of benzene and methylbenzenes is *isosensitive* to these solvents, the same structural correlations being obtained independent of thenat ure of the solvent.

Experimental Section

Preparation of Solvents and Reagents.—Commercial acetic acid (Prolabo) was distilled with a trace of bromine in the dark. Blank experiments showed that the acid obtained does not react with bromine in a noticeable quantity during the course of an experiment.

Commercial trifluoroacetic acid (Synthèse et Recherches) was distilled over phosphoric anhydride; lithium bromide (Prolabo R.P.) was dried at 180° for several days. Water could not be directly determined by the classical Karl Fischer method in this solvent because of the esterification of the methanol in the Karl Fischer reagent. Nevertheless by allowing the acid to react with an excess of dried pyridine (1 ml of acid with 10 ml of pyridine containing less than 100 mg/kg of water), water could be determined in the resultant salt solution. All acid fractions were then checked for dielectric constant and fractions outside the range 8.40–8.50 at 25° were not used, the water content being always less than 500 mg/kg.

Commercial substituted benzenes (K & K) and benzene (Prolabo Spectrograde) were purified by zone melting (solid products) or by preparative vapor phase chromatography (vpc). The purity of the liquid products was checked by vpc.

Measurement Methods and Experimental Results.—The rate constants were obtained by following the bromine concentration; two methods were used to cover the entire range of reactivity: (1) for highly reactive substrates, the couloamperometric method;[10] and (2) for the less reactive substrates a modification of the classical method of bromine determination by arsenic trioxide was used.

The reaction was shown to be first order with respect to each reagent. The reaction conditions were such that dibromination was insignificant, this being verified by vpc analysis of the reaction mixtures. The analytical samples were obtained by carbon tetrachloride extraction of the neutralized reaction mixtures.

For the case of toluene and m-xylene the two predominating monobromo products were identified by the comparison of the retention times with those of known products.

Registry No.—Benzene, 71-43-2; acetic acid, 64-19-7; trifluoroacetic acid, 76-05-1; methylbenzene, 108-88-3; 1,3-dimethylbenzene, 108-38-3; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4,5-tetramethylbenzene, 95-93-2; 1,2,3,4-tetramethylbenzene, 488-23-3; 1,2,3,5-tetramethylbenzene, 527-53-7; pentamethylbenzene, 700-12-9.

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[10] J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964).

The Reaction of Isocyanic Acid with Trifluoroacetic Anhydride. Preparation of Trifluoroacetyl Isocyanate and 2,2,2,2′,2′,2′-Hexafluorodiacetamide

WILLIAM C. FIRTH, JR.

American Cyanamid Company, Stamford Research Laboratories, Stamford, Connecticut

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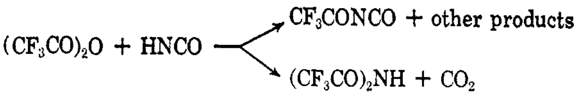
The reaction of isocyanic acid with trifluoroacetic anhydride (eq 1) has been found to be a useful method for the preparation of trifluoroacetyl isocyanate and 2,2,2,2′,2′,2′-hexafluorodiacetamide (perfluorodiacetamide). The relative yields of trifluoroacetyl isocyanate and perfluorodiacetamide are influenced by the reaction conditions. No successful reaction of isocyanic acid with a carboxylic acid anhydride appears to have been reported previously.[1–5]


$$(CF_3CO)_2O + HNCO \longrightarrow \begin{cases} CF_3CONCO + \text{other products} \\ (CF_3CO)_2NH + CO_2 \end{cases} \qquad (1)$$

Trifluoroacetyl isocyanate was prepared by the reaction of isocyanic acid and trifluoroacetic anhydride in a 2:1 mole ratio, respectively. The reaction was run on a small scale without solvent. The isocyanate was separated from carbon dioxide and other byproducts by fractionation in a vacuum line. When a 1:1 mole ratio of reactants was used the isocyanate was formed, but could not be separated from trifluoroacetic anhydride and trifluoroacetic acid, which were present according to an infrared spectrum.

Trifluoroacetyl isocyanate, bp 35°, was characterized by its molecular weight of 142 (calcd: 139) and fluorine nmr and infrared spectra. The infrared spectrum showed absorptions caused by the asymmetric isocyanate stretching vibration at 2275 and 2235 and the symmetric stretching vibration at 1444 cm^{-1}.[6] The carbonyl absorption was observed at 1787 cm^{-1}. The fluorine nmr spectrum contained a single peak at 77.4 ppm from trichlorofluoromethane (solvent and internal standard), in the CF_3 region.[7,8]

While an excess of isocyanic acid was used for the preparation of trifluoroacetyl isocyanate, an excess of trifluoroacetic anhydride was used for the preparation of perfluorodiacetamide.[9] The reaction time was also longer. Perfluorodiacetamide was isolated in about 90% yield (based on isocyanic acid) by fractionation in

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[1] Reactions of isocyanic acid with acid chlorides,[2,3] chlorides of phosphorus[2,3] and silicon,[2] trialkyltin oxides,[5] and trialkylantimony oxides[5] have been described elsewhere.

[2] P. R. Steyermark, *J. Org. Chem.*, **28**, 586 (1963).

[3] P. R. Steyermark, U. S. Patent 3,155,700 (1964).

[4] G. K. Weisse and R. M. Thomas, U. S. Patent 3,246,033 (1966).

[5] W. Stamm, *J. Org. Chem.*, **30**, 693 (1965).

[6] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956); H. Hoyer, *Ber.*, **89**, 2677 (1956).

[7] *Cf.* trifluoroacetic acid, which absorbs at 76.5 ppm under these conditions.[8]

[8] G. Filipovitch and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[9] Perfluorodiacetamide has been prepared by several other methods: (a) G. H. Smith, U. S. Patent 2,701,814 (1955); (b) J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Am. Chem. Soc.*, **84**, 2105 (1962); (c) W. S. Durrell, J. A. Young, and R. D. Dresdner, *J. Org. Chem.*, **28**, 831 (1963); (d) T. J. Mao, R. D. Dresdner, and J. A. Young, *J. Inorg. Nucl. Chem.*, **24**, 53 (1962).

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

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A previous report from this laboratory[1] has described a convenient method for the synthesis of a series of ω-bromoperfluoroalkanecarboxylic esters, $Br(CF_2CF_2)_n$-COOR, 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).