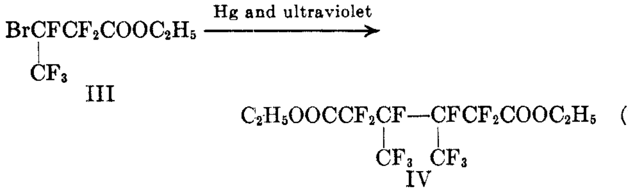
synthesis of very useful long-chain perfluoroalkanedicarboxylic esters.[2]

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.

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

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.



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

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 ($\delta = 0$ 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 $\delta = +69.8$ (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 $C_3F_7OC(\text{—}CF_3)FCF_2OC(\text{—}CF_3)FCF_2OC(\text{—}CF_3)FBr$ 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).

TABLE I

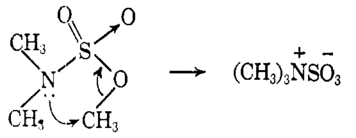
PROPERTIES OF ESTERS, $R_1R_2NSO_2OR$, AND BETAINES, $RR_1R_2\overset{+}{N}SO_3^-$

			Esters				Betaines								
									Calcd, %			Found,[a] %		
R_1	R_2	R	Bp (1 mm), °C	$n^{25}D$	Calcd, % N	Found,[a] % N	Prepn[b]	Mp, °C	C	H	N	C	H	N
CH_3	C_2H_5	CH_3	51–53	1.427	*c*		A	135[d]	31.3	7.2	...	30.9	7.2	...
$\overline{CH_2(CH_2)_3N}$		CH_3	*e*				B	122.5	...	...	8.3	...	...	8.2
$\overline{CH_2(CH_2)_3N}$		C_2H_5	~100	1.453	7.8	7.9	B	85			7.8			7.3
$\overline{CH_2(CH_2)_4N}$		CH_3	~85	1.463	7.8	7.8	B	104–105	40.2	7.3	...	39.6	7.3	...
$\overline{CH_2(CH_2)_4N}$		C_2H_5	~90	1.459	7.3	7.3	B	177–178	*f*					

[a] Analysis by Geller Laboratories. [b] See text for method. [c] *Anal.* Calcd: C, 31.3; H, 7.2. Found: C, 30.8; H, 6.8. [d] Reported previously as mp 133° by M. Delepine and R. Demars, *Bull. Sci. Pharmacol.*, **30**, 577 (1923); W. Traube, H. Zander, and H. Gaffron, *Ber.*, **57**, 1045 (1924). [e] Could not be distilled because of rapid rearrangement to the betaine. [f] Too little for analysis.

have occasionally been reported since, no mechanisms have been suggested.

A reasonable mechanism for the sulfamate rearrangement consists of an intramolecular four-centered process.



If such a process were operative and were two different esters mixed and heated together, no exchange of ester groups should occur, providing, of course, that the esters individually rearrange at approximately the same rate. The results we wish to report in this note indicate unequivocally, however, that exchange does occur and that the rearrangement, accordingly, cannot proceed exclusively, if at all, by an intramolecular process.

A series of nine sulfamic acid esters was prepared by the known[1] two-step procedure given in eq 1. Of

$$RR'NH + SO_2Cl_2 \longrightarrow RR'NSO_2Cl \xrightarrow{NaOR''} RR'NSO_2OR'' \quad (1)$$

these, the five previously unreported esters and their respective betaines are characterized in Table I.[2] The betaines were all obtained either (A) from the appropriate tertiary amine and pyridiniumsulfur trioxide by SO_3 exchange or (B) by thermal rearrangement of the corresponding ester.

Qualitative rearrangement rates were determined by heating the ester neat in a sealed tube under nitrogen, in a constant-temperature bath, usually at 130–131°, for an appropriate time interval. The tube was then cooled to 0°, and the contents were transferred to a separatory funnel and distributed between xylene and saturated salt water. The aqueous solution containing the betaine was heated at 70–80° for 2 hr to achieve hydrolysis and then the resulting solution was titrated with base (eq 2). The xylene solution of the ester was

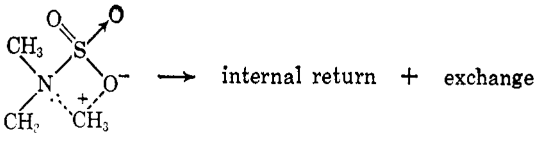
$$R_3\overset{+}{N}SO_3^- + H_2O \longrightarrow R\overset{+}{N}H_3 + HSO_4^- \xrightarrow{OH^-} SO_4^{2-} + H_2O \quad (2)$$

refluxed 3 hr with standard alkali. After cooling, the solution was back-titrated in order to determine the ester concentration.

Experiments showed that $(CH_3)_2NSO_2OC_2H_5$ and $CH_3(C_2H_5)NSO_2OCH_3$ rearranged at approximately the same (first order) rate during the first 40% conversion, the rate constant at 130° being approximately 2×10^{-5} sec^{-1}. Accordingly, a 1:1 mixture of the isomers was heated together. Fractional crystallization of the mixture led to the isolation of the pure crossed betaine, $(CH_3)_3N^+SO_3^-$, showing exchange had occurred. In separate experiments it was shown that heating a mixture of betaines under the conditions used for the rearrangement does not lead to disproportionation of the R groups and also that the rearrangement of ester to betaine is irreversible. In a second exchange reaction, $(CH_3)_2NSO_2OC_2H_5$ and methyl N-piperidinesulfonate, $\overline{CH_2(CH_2)_4N}SO_2OCH_3$, were heated together and the crossed betaines, $(CH_3)_3\overset{+}{N}SO_3^-$ and $\overline{CH_2(CH_2)_4N}^+$-$(C_2H_5)SO_3^-$, were definitely shown to be present by comparison of the infrared spectrum of the mixture with spectra of the authentic pure compounds. The other two betaines were also present.

Several important observations were made during the qualitative kinetic studies of the thermal rearrangement of $(CH_3)_2NSO_2OC_2H_5$. After about 40% conversion, the rate increased markedly indicating product catalysis, probably owing to the high polarity of the betaine which begins to function as a solvent. When the rate was measured starting with a 1:1 mixture of the ester and the betaine, only the faster rate was observed. Although both the first slower rate and the second faster rate appeared to be first order, the true order is probably mixed first and second. The kinetics were not studied in any further detail. The importance of solvent was demonstrated further by the fact that the ester did not rearrange in boiling xylene. However, a 1.96 *M* solution in trichlorobenzene at the temperature of boiling xylene gave a first-order rate constant of about 1×10^{-5} sec^{-1}.

Although the ester–betaine–solvent system is quite complicated, the crude kinetic data taken in conjunction with the evidence from the exchange experiments suggest that the rearrangement proceeds through some type of ion pair which permits sufficient dissociation to give intermolecular exchange as well as some internal rearrangement.



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[2] Detailed descriptions of all the compounds prepared, including infrared spectra, all taken as Nujol mulls, are given in the Ph.D. thesis of P. Z., University of Cincinnati, 1963.

Finally, some mention should be made of the properties of the betaines. These may be considered tertiary amine–sulfur trioxide addition compounds. The presence of three ethyl groups on nitrogen should lead to considerable B strain[3] in the complex and it is therefore not unexpected that the compound $\mathrm{CH_3(C_2H_5)_2\overset{+}{N}SO_3^-}$ could not be prepared. Although it is possible to prepare $\mathrm{(C_2H_5)_3\overset{+}{N}SO_3^-}$ from the tertiary amine and pyridiniumsulfur trioxide, it could not be prepared by rearrangement because side reactions predominate at the high temperature required. However, when the R groups are tied back as in the piperidine and pyrrolidine derivatives, the compounds are stable and the rearrangement of the corresponding sulfonates is observed. It appears that the groups on nitrogen in the ester play a greater role in determining the rate of rearrangement than does the nature of the migrating group on oxygen.

Experimental Section

In a typical ester preparation, methyl N-methyl-N-ethylsulfamate was prepared by treating ethylmethylamine[4] with sulfuryl chloride. The sulfamyl chloride was then stirred with a cyclohexane suspension of sodium methoxide. After filtering the NaCl, the solvent was evaporated and the ester distilled at 1 mm pressure. The corresponding betaine was prepared by method A. To 1.84 g of ethyldimethylamine in about 15 ml of H_2O, there was added 4 g of pyridiniumsulfur trioxide.[5] After about 10 min of shaking, the solid was separated and recrystallized from hot water, mp 135°. In a typical thermal rearrangment to betaine (method B), methyl N-piperidinesulfonate was heated under nitrogen at 130° for 20 min. After cooling, the crystals were washed with small quantities of ice water and, on drying, melted sharply at 104–105°. Attempted recrystallization from water or other solvents was unsuccessful.

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[3] H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, **75**, 16 (1953).

[4] J. Graymore, *J. Chem. Soc.*, 1490 (1931).

[5] H. H. Sisler and L. F. Audrieth, *Inorg. Syn.*, **2**, 173 (1946).

The Base-Catalyzed Decomposition of Peroxypivalic Acid in Aqueous Solution

E. KOUBEK AND J. E. WELSCH

U. S. Naval Academy, Annapolis, Maryland 21402

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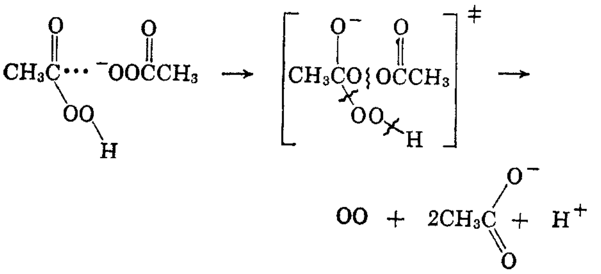
In an earlier paper,[1] it was suggested that the base-catalyzed decomposition of monosubstituted peroxyacids to parent acid and oxygen could proceed by at least two distinctly different mechanisms. For example, it appeared from kinetic and isotope-labeling experiments that both peroxyacetic and peroxychloroacetic acid[2] undergo decomposition *via* nucleophilic attack by the peroxy anion upon the carbonyl center of the peroxy acid leading to a transition state, as shown in eq 1.



(1)

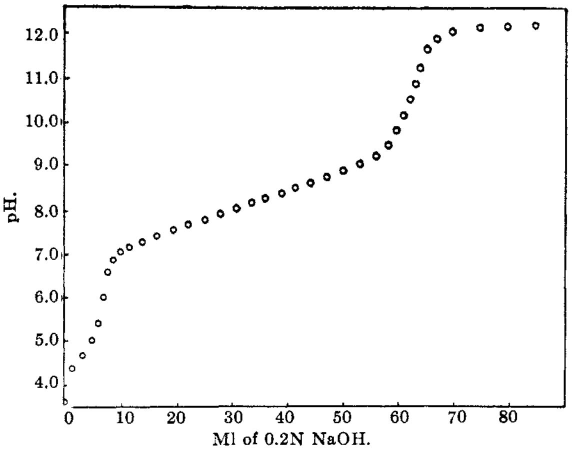
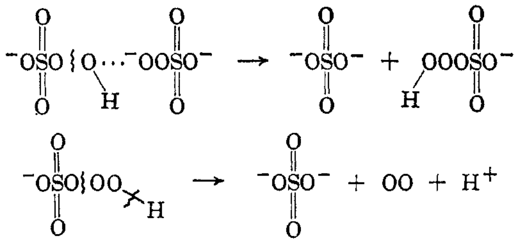


Figure 1.—Titration curve for peroxypivalic acid at 25°.

However, similar experiments upon peroxymonosulfuric acid[1] indicate that this compound undergoes decomposition mainly through nucleophilic attack by the peroxysulfate ion upon the outer peroxidic oxygen of the peroxybisulfate ion. This reaction is believed to lead to formation of the unstable intermediate (HSO_6^-), which rapidly decomposes to oxygen and bisulfate ion. (See eq 2.)



(2)

It was decided to further study this proposed duality of mechanisms by investigating the base-catalyzed decomposition of peroxypivalic acid. This particular compound was selected because of the well known steric effect of the *t*-butyl group upon reactions occurring at the carbonyl center.[3]

However, since the preparation of peroxypivalic acid could not be found in the literature, it was necessary to first develop a satisfactory synthesis. After several attempts we were successful in obtaining the desired compound in sufficient quantities to carry out our intended experiments. Figure 1 represents a typical titration curve of a sample of peroxypivalic acid. From this curve and several others, the pK_a of this new peroxy acid was determined to be 8.23 ± 0.03.

A study of the decomposition of this compound in carbonate buffer, containing appropriate amounts of EDTA, revealed that this peroxy acid also follows the generally observed decomposition pattern.[2,4,5] The rate of decomposition was found to be second order in total peroxide with a maximum at pH = pK_a = 8.23 ($k_{\mathrm{obsd}} = 3.4 \times 10^{-3}$ l./mole sec at 25°). A summary of

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[1] E. Koubek, G. Levey, and J. O. Edwards, *Inorg. Chem.*, **3**, 1331 (1964).

[2] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).

[3] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1960, p 318. We have also observed that peroxyacetic acid undergoes acid hydrolysis eight to nine times faster than peroxypivalic acid.

[4] D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

[5] J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).