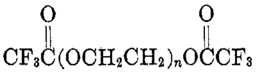
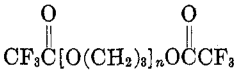
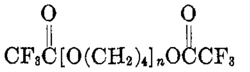
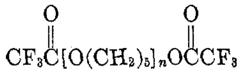
TABLE I

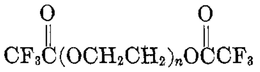
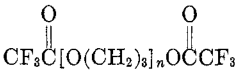
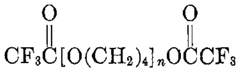
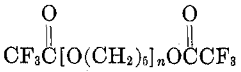
REACTION OF CYCLIC ETHERS WITH TRIFLUOROACETIC ANHYDRIDE (TFAA)

Ether	Amount, g (mol)	TFAA,[a] g (mol)	Conditions	Product	*n*	Yield		
						g	% based on ether	% based on TFAA[a]
Ethylene oxide	8.9 (0.20)	42 (0.20)	50 ml of CCl_3F solvent, 120°, 20 hr	 $CF_3\overset{O}{\overset{\Vert}{C}}(OCH_2CH_2)_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	11.6	22.8	22.8
					2	17.6	59	29.5
	44.5 (1.0)	42 (0.20)	120°, 20 hr		1	9.3	3.7	18.3
					2	23.2	15.6	40.0
					3	12.8	11.1	18.5
					(4)[b]	7.7	8.2	(10.0)
Trimethylene oxide	11.6 (0.20)	42 (0.20)	50 ml of CCl_3F solvent, 120°, 18 hr	 $CF_3\overset{O}{\overset{\Vert}{C}}[O(CH_2)_3]_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	14.0	25.6	25.6
					2	18.1	55.4	27.7
Tetrahydrofuran	14.4 (0.20)	42 (0.20)	120°, 18 hr	 $CF_3\overset{O}{\overset{\Vert}{C}}[O(CH_2)_4]_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	1.9	3.4	3.4
					2	0.3	0.9	0.5
	14.4 (0.20)	42 (0.20)	180°, 18 hr		1	41.7	73.9	73.9
					2	6.2	17.5	8.7
	72 (1.0)	42 (0.20)	120°, 18 hr		1	6.6	2.3	11.7
					2	5.0	2.8	7.0
	72 (1.0)	42 (0.20)	1.0 g of CF_3CO_2H, 120°, 18 hr		1	14.6	5.2	25.9
					2	26.5	15.0	37.4
Tetrahydropyran	17.2 (0.2)	42 (0.20)	200°, 18 hr	 $CF_3\overset{O}{\overset{\Vert}{C}}[O(CH_2)_5]_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	45.3	76.5	76.5
	17.2 (0.2)	42 (0.20)	120°, 18 hr			0	0	0

[a] TFAA = trifluoroacetic anhydride. [b] The fraction of bp 112° (0.225 mm) appeared to be primarily oligomer with $n = 4$.

TABLE II

PHYSICAL AND ANALYTICAL DATA ON ETHER–TFAA ADDUCTS

Compd	*n*	Registry no.	Bp, °C (mm)	$n^{25}D$	Formula	C, %		H, %		F, %	
						Calcd	Found	Calcd	Found	Calcd	Found
 $CF_3\overset{O}{\overset{\Vert}{C}}(OCH_2CH_2)_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	2613-44-7	47 (6.5)	1.3275	$C_6H_4F_6O_4$[a]						
	2	31580-02-6	71 (1.5)	1.3516	$C_8H_8F_6O_5$	32.2	32.1	2.70	2.88	38.2	37.1
	3	31528-86-6	61 (0.02)	1.3696	$C_{10}H_{12}O_6F_6$	35.1	35.8	3.54	3.77	33.3	32.4
 $CF_3\overset{O}{\overset{\Vert}{C}}[O(CH_2)_3]_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	7647-95-2	95.5 (30)	1.3388	$C_7H_6O_4F_6$	31.4	31.2	2.26	2.24	42.5	42.3
	2	31528-88-8	134 (30)	1.3604	$C_{10}H_{12}F_6O_5$	36.8	37.1	3.71	3.76	35.0	34.9
 $CF_3\overset{O}{\overset{\Vert}{C}}[O(CH_2)_4]_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	31528-89-9	43–44 (0.1)	1.3459	$C_8H_8F_6O_4$	34.1	33.8	2.85	2.86	40.4	40.5
	2	31528-90-2	70–75 (0.1)	1.3709	$C_{12}H_{16}F_6O_5$	40.9	40.0	4.55	4.65	32.2	32.5
 $CF_3\overset{O}{\overset{\Vert}{C}}[O(CH_2)_5]_nO\overset{O}{\overset{\Vert}{C}}CF_3$	1	453-44-1	50 (0.25)	1.3538	$C_9H_{10}F_6O_4$	36.5	36.5	3.41	3.5	38.5	37.5

[a] Lit. bp 151–153°, $n^{25}D$ 1.3286 (at least 95% pure): S. D. Ross and M. Finkelstein, *J. Org. Chem.*, **22**, 847 (1957). Preparation was from a large excess of trifluoroacetic anhydride and ethylene glycol.

The reaction no doubt goes by ring-opening protonation of the ether since trifluoroacetic acid was shown to be a catalyst. To attempt to determine whether polymer was derivable under the reaction conditions using a larger THF–anhydride ratio, ratios of 10:1–100:1 (molar) were used. Under the latter conditions, conversion was low to give predominantly the adduct with two THF units.

Experimental Section

The typical procedure for reaction was to charge the reactants into a 240-ml stainless steel pressure vessel and heat at autogenous pressure, at temperature and time given in Table I. The reaction mixture was distilled.

No significant reaction occurred when THF and TFAA containing a catalytic amount of trifluoroacetic acid were refluxed for 24 hr at atmospheric pressure.

The physical and analytical data on all new compounds are in Table II. The ir and nmr (proton and ^{19}F) spectra were in agreement with the proposed structure. In the ir, the trifluoroacetate carbonyl had a strong absorption at 1740 cm^{-1}. The ^{19}F nmr for the CF_3 group was a sharp singlet in the range of 75.8–75.9 ppm relative to CCl_3F (internal standard and solvent, 5% concentration).

Registry No.—Trifluoroacetic anhydride, 407-25-0.

Reaction of Nitronium Fluoroborate with Olefins in Acetonitrile

MONTE L. SCHEINBAUM*[1] AND MARTIN DINES

Esso Research and Engineering Company, Linden, New Jersey 07036

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The Ritter reaction[2] is a convenient method of preparing amines or amides by reaction of olefins in acidic

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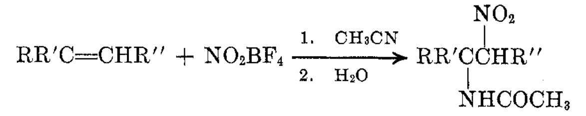
[1] To whom inquiries should be directed: Department of Chemistry, East Tennessee State University, Johnson City, Tenn. 37601.

[2] (a) J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, **70**, 4045 (1948); (b) T. Clark, J. Devine, and D. W. Dicker, *J. Amer. Oil Chem. Soc.*, **41**, 78 (1964).

media with hydrogen cyanide or nitriles. Treatment of olefins with halogens in nitrile solvents leads to α-halogenated amides;[3] other modifications of the Ritter reaction with *N,N*-dichlorosulfonamides or peracids in nitrile media have also been reported.[4]

We wish to report an extension of the Ritter reaction in which the electrophilic reagent is nitronium or nitryl fluoroborate, NO_2BF_4. This salt is known to nitrate and to initiate the polymerization of olefins.[5] These nitrative polymerizations are effected when NO_2BF_4 is contacted with neat olefins in the liquid state. We have found that olefins react with NO_2BF_4 in anhydrous acetonitrile at −15° to give products which on hydrolytic work-up afford vicinal nitroacetamido derivatives **1**. The products from primary, secondary, and tertiary olefins are acyclic, in contrast to the results with nitrosyl fluoroborate.[4b] Side products such as unsubstituted amides formed by simple Ritter reactions are easily separated by distillation at low pressure.



$$RR'C{=}CHR'' + NO_2BF_4 \xrightarrow[2.\ H_2O]{1.\ CH_3CN} RR'\underset{NHCOCH_3}{\overset{NO_2}{C}}CHR''$$

In this manner, propylene is converted to 1-nitro-2-acetamidopropane (**1a**, $R = CH_3$; $R' = R'' = H$)[6] (50%), isobutylene to 1-nitro-2-methyl-2-acetamidopropane (**1b**, $R = R' = CH_3$; $R'' = H$) (23%), and butene-2 to 2-nitro-3-acetamidobutane (**1c**, $R = R'' = CH_3$; $R' = H$) (13%). In the latter case, the identical product was obtained from either the cis or trans olefin. Although it was ascertained that no isomerization of the olefin occurred prior to reaction, other details of the work-up procedure during which isomerization of the nitroacetamide might occur preclude any definitive conclusions of the structure of the reaction intermediate.

Experimental Section

Melting points are uncorrected. Elemental analyses, nmr, and mass spectroscopy were performed by AID laboratory of Esso Research and Engineering Co. Acetonitrile was purified by distillation from P_2O_5. Nitryl fluoroborate was purchased from Alfa Inorganics.

A solution of 13.3 g (0.1 mol) of NO_2BF_4 in 200 ml of anhydrous acetonitrile was treated with 0.2 mol of olefin at −25° under nitrogen with stirring. Upon completion of the addition of olefin, 10 ml of water was introduced. The reaction was stirred for 0.5 hr and gradually warmed to ambient temperature under nitrogen. The mixture was diluted with 50 ml of benzene and the solvent was removed by evaporation at reduced pressure. The residue was extracted with methylene chloride and washed free of acid with aqueous sodium bicarbonate solution, then with brine, dried ($MgSO_4$), evaporated, and distilled under reduced pressure.

Propylene gave 7 g (50% yield) of 1-nitroacetamidopropane (**1a**): mp 103–104° (lit.[6] mp 104°); nmr (acetone-d_6) δ 1.25 (d, 3, CH_3CH, $J = 6.5$ Hz), 1.9 (s, 3, CH_3CO), 4.7 (m, 3, NCH_2CHN), and 7.5 ppm (broad, 1, NH). *Anal.* Calcd for $C_5H_{10}N_2O_3$: C, 41.08; H, 6.83; N, 19.29; mol wt, 146. Found: C, 41.04; H, 7.07; N, 18.92; mol wt, 146 (mass spectrum).

Isobutylene gave 3.7 g (23%) of 1-nitro-2-methyl-2-acetamidopropane (**1b**): mp 86° ($CHCl_3$–hexane); nmr ($CDCl_3$) δ 1.5 [s, 6, $(CH_3)_2C$], 2.0 (s, 3, CH_3CO), 4.9 (s, 2, CH_2), and 6.6 ppm (broad, 1, NH). *Anal.* Calcd for $C_6H_{12}N_2O_3$: C, 44.94; H, 7.55; N, 17.49. Found: C, 44.55; H, 17.52; N, 17.17.

Both *cis*- and *trans*-butene-2 afforded the same product, but there was no isomerization of unreacted olefin observed during the course of reaction, as indicated by vpc. The brown oil obtained (7.3 g) was distilled to give a fraction, bp 70–75° (0.2 Torr), 1.5 g (12%), which was *N*-*sec*-butylacetamide: $n^{25}D$ 1.437 (lit.[7] $n^{25}D$ 1.436); ir ($CHCl_3$) 3260, 1650, 1545, and 870 cm^{-1}; nmr ($CDCl_3$) δ 0.90 (t, 3, CH_3CH_2), 1.10 (d, 3, CH_3CH), 1.45 (q, 2, CH_2), 1.98 (s, 3, $COCH_3$), 3.88 (q, 1, CH), and 7.0 ppm (broad, 1, NH). The second fraction, bp 105–106° (0.2 Torr), 2.1 g (13%), was 3-nitro-2-acetamidobutane (**1c**): mp 50–52° (ether, hexane), white crystals, mp 53.5° (sublimation, 30°, 0.2 Torr); ir ($CHCl_3$) 3260, 1650, 1545, 1385, and 1370 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (q, 3, CH_3CHNH, $J = 6.5$ and 1.5 Hz), 1.55 (d, 3, CH_3CHNO_2), 2.0 (s, 3, CH_3CO), and 4.7 ppm (m, 2, CHCH). *Anal.* Calcd for $C_6H_{12}N_2O_3$: C, 44.99; H, 7.55 N, 17.49; mol wt, 160. Found: C, 44.81; H, 7.57; N, 17.57; mol wt, 160 (mass spectrum).

Registry No.—**1a**, 31593-56-3; **1b**, 31662-22-3; **1c**, 31593-57-4; *N*-*sec*-butylacetamide, 1189-05-5; nitronium fluoroborate, 13826-86-3; propylene, 115-07-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7.

Acknowledgment.—The authors are indebted to Mr. R. Kelly, Miss M. A. Miciak, and Mr. J. J. Porcelli for experimental assistance.

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[4] (a) W. Theilacker, *Angew Chem.*, **79**, 63 (1967). (b) M. L. Scheinbaum and M. Dines, *Tetrahedron Lett.*, 2205 (1971); J. Beger, *J. Prakt. Chem.*, **311**, 746 (1969).

[5] G. A. Olah, H. W. Quinn, and S. J. Kuhn, *J. Amer. Chem. Soc.*, **82**, 426 (1960).

[6] C. A. Grob, C. Wagner, and P. Zoller, *Helv. Chim. Acta*, **67**, 1689 (1955).

[7] H. Windaus, *Ber.*, **40**, 81 (1907).

Formation of Sulfones in the Thermal Decomposition of Ylides Derived from *p*-Toluenesulfonylhydrazides

J. E. Baldwin*[1] and J. E. Brown

Chemistry Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Ylides of the type I were first prepared by Wawzonek and Meyer, who described the thermolysis at 185–195° of the example I (R = Me).[2] They obtained a large amount of a polymer of the *p*-toluenesulfonamide–formaldehyde type, along with *p*-toluenesulfonamide, ammonia, trimethylamine, and formaldehyde. Subsequently Robson and Speakman prepared *N*-trimethylammoniododecanesulfonamidate (II) and demonstrated by suitable trapping experiments that the two products observed on pyrolysis, a trapped nitrene (dimethyl sulfoxide or triphenylphosphine) and dodecanesulfonesulfonamide, were formed by cleavage of the N–N bond to yield a sulfonyl-nitrene intermediate III,[3] which would also account for the products observed in the former case (I, R = Me) (Chart I).

In the course of our investigations of the [2,3] sigmatropic rearrangements of nitrogen ylides,[4,5] we had occasion to prepare ammoniosulfonamidate (I, R = 3-methyl-2-butenyl; mp 138° dec) and have discovered that its thermolysis proceeds in a very different way to

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[1] A. P. Sloan Fellow, 1969–1971.

[2] S. Wawzonek and D. Meyer, *J. Amer. Chem. Soc.*, **76**, 2918 (1954).

[3] P. Robson and P. R. H. Speakman, *J. Chem. Soc. B*, 463 (1968).

[4] J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Commun.*, 31 (1970).

[5] J. E. Baldwin, J. E. Brown, and G. Hofle, *J. Amer. Chem. Soc.*, **93**, 788 (1971).