[Contribution from the Lawrence Radiation Laboratory, University of California]

Fluorine-Containing Nitrogen Compounds. III. Some Alkyl Esters of Difluoronitroacetic Acid[1]

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Received June 30, 1961

The synthesis and some of the physical properties of the methyl, ethyl, trifluoroethyl, *n*-propyl, isopropyl, allyl, *n*-butyl, isobutyl, and *sec*-butyl esters of difluoronitroacetic acid are reported. Their infrared spectra are also briefly discussed.

The synthesis of difluoronitroacetic acid, by the hydrolysis of 2-nitro-tetrafluoroethyl nitrite, was first reported in 1957 by Knunyants and Fokin.[2] These authors also reported that esters of difluoronitroacetic acid could be prepared directly from the nitrite by alcoholysis, but described only the methyl ester. They obtained 2-nitrotetrafluoroethyl nitrite along with 1,2-dinitrotetrafluoroethane by the addition of dinitrogen tetroxide to tetrafluoroethylene.[3] The reaction proceeded explosively in the absence of a solvent but could be controlled by using chlorinated or fluorinated hydrocarbons as diluents. Addition of dinitrogen tetroxide to chlorotrifluoroethylene yielded a complex mixture of products including 1-chloro-2-nitrotrifluoroethyl nitrite, 1,2-dichloro-1-nitrosotrifluoroethane, 1,2-dichloro-1-nitrotrifluoroethane, 1,1,2-trichlorotrifluoroethane, and difluoronitroacetyl fluoride. Apparently no attempt was made to hydrolyze the 1-chloro-2-nitrofluoroethyl nitrite.

The addition of dinitrogen tetroxide to tetrafluoro, chlorotrifluoro-, and 1,2-dichlorodifluoroethylene has also been reported by Hass and Whitaker,[4] by Haszeldine,[5] and by Coffman,[6] but in these studies only the dinitrofluoroethane was isolated.

In the present study it was found that the addition of dinitrogen tetroxide to tetrafluoro- or chlorotrifluoroethylene could be carried out conveniently in the gas phase without the use of a diluent if the total pressure was kept below about one atmosphere. Tetrafluoroethylene produced 2-nitrotetrafluoroethyl nitrite and 1,2-dinitrotetrafluoroethane in the ratio of about 3 or 4:1, while chlorotrifluoroethylene produced 1-chloro-2-nitrotrifluoroethyl nitrite and 1-chloro-1,2-dinitrotrifluoroethane in about the same yield and ratio. With chlorotrifluoroethylene, under the conditions used in this study, no significant amounts of 2-chloro-2-nitrotrifluoroethyl nitrite or di- or trichloroethanes were found. Alcoholysis of the mixture of products from either olefin produced the corresponding ester in about the same yield. The esters prepared in this manner are listed in Table I. They were purified first by distillation through a 35-cm. vacuum-jacketed Vigreux column, then by careful fractionation on a 90-cm. spinning band column at a reflux ratio of 100:1, and finally by vapor phase chromatography on a 4-m. di-*n*-decyl phthalate partition column. The estimated purities listed in column three of Table I are for the distillate from the spinning band column[7]; those in column four are for material from the partition column. The esters thus purified were dried by passage in the vapor state through a small bed of 5A Molecular Sieve[8] prior to measurement of the physical properties listed in Tables I and II. The yields (Table I, column two) are of material from the spinning band column, corrected to compensate for the less than 100% purity of the material. The "molecular refractivity" for the CF_2NO_2 group (Table I, column eight) was calculated using values for the atomic refractivity of C, H, and O taken from Shriner and Fuson.[9]

Table II (columns two and three) lists the constants A and B for the vapor pressure equation, $\log P = A - B/T$ (P in mm. Hg and T in °K.), in the pressure range from about 300 to 800 mm. Hg. The normal boiling points (column four) were calculated from this equation. The critical constants listed in columns five, six, and seven were estimated by the method of Meissner and Redding[10] using the values of Mumford and Phillips[11] for atomic and structural parachors. The heats of vaporization (column eight) are at the normal

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission.

[2] I. L. Knunyants and A. V. Fokin, *Doklady Akad. Nauk S.S.S.R.*, **112**, 67 (1957).

[3] I. L. Knunyants and A. V. Fokin, *Doklady Akad. Nauk S.S.S.R.*, **111**, 1035 (1956).

[4] H. B. Hass and A. C. Whitaker, U. S. Patent **2,447,-504**, August 24, 1948.

[5] R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

[6] D. D. Coffman, M. S. Raasch, G. W. Rigby, P. L. Barrick, and W. E. Hanford, *J. Org. Chem.*, **14**, 747 (1949).

[7] The allyl and trifluoroethyl esters were not distilled ou the spinning band column. Purities listed for them are for material from the Vigreux column distillation.

[8] Linde Air Products Co., 30 East 42nd St., New York 17, N. Y.

[9] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, 1948, p. 45.

[10] G. W. Tomson, *Physical Methods of Organic Chemistry*, Vol. 1, Pt. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, 1959, p. 505.

[11] S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112 (1929).

TABLE I

PHYSICAL PROPERTIES AND YIELDS OF DIFLUORONITROACETATES

Ester	Yield, %	Est. Purity[a] (mole %) Dist.	V.P.C.	n_D^{25}	$d_{22.5}$	(M_D)[b]	(M_D)[c] for CF_2NO_2	Peak[d] Time (min.)
Methyl	25	98.0	99.96	1.35560	1.404	24.11	12.12	7.1
Ethyl	27	97.0	99.96	1.35642	1.302	28.41	11.80	10.6
Trifluoroethyl	33	85.3	99.1[e]	1.34893	1.604	29.84		6.0[f]
n-Propyl	27	94.9	99.4	1.36890	1.243	33.23	12.00	10.9
i-Propyl	27	97.4	99.7	1.36313	1.221	33.36	12.13	7.4
Allyl	32	83.1	99.7[e]	1.38272	1.281	32.96	12.20	10.3
n-Butyl	31	87.5	99.99[e]	1.37760	1.193	38.06	12.21	19.2
i-Butyl	10	95.1	99.99	1.37486	1.178	38.30	12.45	14.1
s-Butyl	24	95.5	99.9	1.37253	1.182	37.96 Av.	12.13	12.6

[a] Estimated by integration of the vapor phase chromatography peaks assuming all components to have the same relative response. [b] Molecular refractivity. [c] "Molecular refractivity" for the CF_2NO_2 group. [d] Peak time for chromatographing 50 λ on a 4-m.-long by 18-mm.-i.d. di-*n*-decyl phthalate on Firebrick (25 to 100) column at 146 ± 2° and an inlet pressure of 20 p.s.i.g., He carrier. [e] After two passes. [f] At 125°.

TABLE II

VAPOR PRESSURE AND RELATED CONSTANTS FOR DIFLUORONITROACETATES

Ester	A	B	nbp[a]	V_c (Ml./ Mole)	T_c (°K.)	P_c (Atm.)	ΔH_{vap} (Cal./ Mole)	Trouton's Ratio
Methyl	7.8314	1914.5	113.5	325.8	589.2	38.6	8350	21.6
Ethyl	7.6991	1934.4	128.3	386.9	610.1	33.5	8380	20.9
Trifluoroethyl	7.7242	1853.3	109.4	434.4	550.5	26.9	8000	20.9
n-Propyl	7.9821	2131.4	144.6	449.9	633.1	29.8	9170	21.9
i-Propyl	7.8314	2015.7	134.0	445.1	618.2	29.4	8660	21.3
Allyl	7.9810	2125.4	143.5	431.1	631.5	31.0	9160	22.0
n-Butyl	8.1419	2266.8	157.7	514.7	651.6	26.7	9680	22.5
i-Butyl	8.0005	2187.6	154.1	509.8	646.5	26.8	9340	21.9
s-Butyl	8.1688	2250.6	152.4	509.8	644.1	26.7	9610	22.6

[a] Normal boiling point.

boiling point and were calculated from the expression

$$\Delta H = \frac{4.57566BT^2(1 - P_r/T_r^3)^{1/2}}{(t + C)^2}$$

where the value 273.2 was used for C.[12] The Trouton ratios listed in column nine indicate only slight association of the liquids.

The melting point of the methyl ester was found to be about −71° while that of the isopropyl ester was about −77°. The other esters either melted below −80° or formed glasses at that temperature. It was found inadvertently that the methyl and isopropyl esters produced strong local anesthesia on contact with the skin. Presumably the others behave similarly.

The major infrared absorption bands for the nine esters prepared are listed in Table III together with tentative assignments. The carbonyl stretching frequency at about 1790 cm.$^{-1}$ is about the same as that found in trifluoroacetates.[13] While the asymmetric nitro stretching frequency at 1610–1600 cm.$^{-1}$ is shifted to higher frequency (compared with the normal alkyl nitro) by about the amount expected, the symmetrical nitro stretching frequency at about 1333–1319 cm.$^{-1}$ is shifted to lower frequency by an amount somewhat less than might be anticipated. Assignments of bands to modes associated with the alkyl groups are based on those of Katritzky, Lagowski, and Beard.[14] Two of the bands in isopropyl esters, at 1334–1328 cm.$^{-1}$ and 1184–1180 cm.$^{-1}$, are missing; they are probably obscured by the strong nitro and carbon fluorine bands in those regions. The skeletal band at about 1085–1080 cm.$^{-1}$ in isobutyl and *n*-butyl esters is likewise missing, and several bands listed as shoulders are not observed. The CCOO skeletal mode found in normal acetates[15] at about 1300 cm.$^{-1}$ is missing entirely, while that at 1266 to 1246 cm.$^{-1}$ is either missing or is obscured by the strong carbon fluorine band in that region.

EXPERIMENTAL

Preparation of esters. Dinitrogen tetroxide from a supply cylinder was admitted to an evacuated 35-l. stainless steel

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[12] G. W. Thomson, *Physical Methods of Organic Chemistry*, Vol. I, Pt. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, 1959, p. 518.

[13] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1958, p. 183.

[14] A. R. Katritzky, J. M. Lagowski, and J. A. T. Beard, *Spectrochim. Acta*, **16**, 954 (1960).

[15] A. R. Katritzky, J. M. Lagowski, and J. A. T. Beard, *Spectrochim. Acta*, **16**, 964 (1960).

TABLE III

Infrared Absorption Bands of Difluoronitroacetates

Me	Et	CF_3CH_2	n-Pr	i-Pr	Allyl	n-Bu	i-Bu	s-Bu	
3640vw	3530vw	3640vw	3570vw	3570vw	3560vw	3570vw	3570vw	3570vw	C=O overtone
					3080vw				CH stretch
3000w	3000w	2960w	2990s	2990m		2950s	3010s	2980s	CH stretch
			2900sh	2940sh	2940sh	2870sh	2900sh	2890sh	
1800s	1790s	1820s	1790s	1790s	1790s	1790s	1790s	1790s	C=O stretch
1610s	1600s	1610s	1600s	1610s	1610s	1610s	1610s	1600s	Asym NO_2 stretch
				1471m					
				1456sh			1471s		CH_3 asym bend
	1464m	1453m	1464m		1450m	1464m		1460m	
						1425sh			CH_2 scissors
1450s									CH def sym Me
	1443m								CH_3 asym bend
		1418m			1425m				CH_2 sym bend
	1395s		1400m	1390sh		1393m	1403m		
				1380s			1389s	1385s	CH_3 sym bend
						1379w			
			1383m						
	1376s					1355s	1374m		CH_2 wag
			1359m						
1368s	1351s				1379s		1361m		
					1351s				
				1351s			1348m	1350s	CH wag
1333s	1319vs	1332s	1325s	1325s	1319s	1325s	1328s	1325s	Sym NO_2 stretch
		1248vs							
1242vs	1238vs	1250vs	1242vs	1238vs	1242vs	1239vs	1242vs	1239vs	CF
1206vs	1190vs	1190vs	1190vs	1190vs	1176vs	1183vs	1183vs	1190vs	
1172vs	1160vs	1163vs							
			1099vs	1149m		1122m		1126s	*
				1105s					
1111w					1081vw			1110s	
1095w									CH_3 rock
1053sh		1075m						1087s	
		1043m							
	1028s		1053s			1055m	1105vw	1031s	*
			1026s						
				1031s	1031s	1031s	1031s		
1029s									CH_3 ip rock
								998m	*
					995s				CH oop def
		979s							
943m									CH_3 ip rock
			943sh	943vw		962w	966m	966m	
			930sh	909s		926m	943m		*
		915m			943s		909m		
	855s		895m		895m	895vw			CH_2 rock
				864s		840m		877m	
								861s	*
			855w		855sh	853w	841vw		
848s		842m	844w	823s	844w	807s	833m	833s	
801s	815s	828s	803s	807m	803s	778w	797s	803s	
781w	775w	794s	763w	775w	778w	741w	778w	763w	
704w	704w	687w	704w	702w	704w	704w	704w	704w	

*CH_3 rock and skeletal modes, coupled.

Abbreviations: ip, in plane; oop, out of plane; vw, very weak; w, weak; m, moderate; s, strong; vs, very strong; sh, shoulder.

tank, to a pressure of 35 to 38 cm. Hg. The tank was then filled to a total pressure of 74 to 76 cm. Hg with tetrafluoroethylene[16] or chlorotrifluoroethylene. After the pressure had fallen to 35 cm. Hg (in about 4 hr.), 100 ml. of the desired alcohol was placed in a 300-ml. stainless steel high-pressure cylinder,[17] which was attached to the bottom of the tank by means of a suitable valve and coupling in such a manner as to form a removable low-temperature trap. The cylinder was then immersed in a liquid nitrogen bath and evacuated. The valve between the cylinder and the tank was opened, and the contents of the tank were condensed into the cylinder. Noncondensables were pumped off through an outlet valve on the cylinder. The valves to the cylinder were then closed, and the liquid nitrogen bath was replaced with one of ice water. (The alcoholysis is very exothermic, and considerable pressures are built up during this operation. Hence, the apparatus should be suitably barricaded.) The bath was allowed to warm to room temperature over 18 to 20 hr., the cylinder was cautiously detached, and its contents were poured into 500 ml. of water. The lower organic layer was separated, and the aqueous phase was extracted with three 100-ml. portions of methylene chloride. The combined organic phases were washed with 50 ml. of saturated aqueous sodium carbonate, dried over anhydrous magnesium sulfate, filtered, and distilled through a 35-cm. vacuum-jacketed Vigreux column to yield a forerun of methylene chloride and a cut containing mainly the crude ester. This cut was carefully fractionated on a 90-cm. spinning band column at a reflux ratio of 100: 1. The esters prepared and their yields are listed in Table I.

Chromatography. The distilled esters were chromatographed in 1-ml. portions on an 18-mm.-i.d. by 4-m.-long column of di-*n*-decyl phthalate on 42-60 mesh C-22 firebrick (25/100) at temperatures from 115 to 148°. Helium at an inlet pressure of 20 p.s.i.g. was used as the carrier gas. The major impurities in material from the spinning band column were identified as methylene chloride, the parent alcohol, and chlorodinitrotrifluoroethane (when chlorotrifluoroethylene was used as the starting olefin). A dozen or so trace impurities that were also observed were not identified.

Vapor pressures. Vapor pressures were measured over the pressure range of 300 to 800 mm. Hg with an isotenoscope similar to that described by Thomson.[18] The sample was introduced into the evacuated and outgassed isotenoscope by means of liquid nitrogen and was outgassed to constant vapor pressure at 20° through a bypass which was later sealed off. Mercury was used in the U-tube. Pressures were obtained from a Wallace and Tiernan Type FA 145 precision dial manometer.[19] Temperatures were obtained by means of a rapidly stirred silicone oil bath contained in a clear-walled Dewar flask and were observed with an Anschutz melting point thermometer to ±0.1°.

Infrared spectra. Spectra were obtained in the liquid phase in 0.025-mm. fixed-thickness sodium chloride cells on a Perkin-Elmer Infracord spectrometer. Their accuracy is estimated to range from ±20 cm.$^{-1}$ at the high frequency end of the spectrum to ±2 cm.$^{-1}$ at the low end.

Acknowledgment. The author is indebted to Mr. Virgil Du Val for assistance in the preparation of the chromatography column.

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(16) Tetrafluoroethylene was prepared by the thermal depolymerization of polytetrafluoroethylene. Chlorotrifluoroethylene and dinitrogen tetroxide were purchased from The Matheson Chemical Co., East Rutherford, N. J.

(17) Hoke, Inc., 1 Tenakill Park, Cresskill, N. J.

(18) G. W. Thomson, Physical Methods of Organic Chemistry, Vol. I, Pt. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, 1959, pp. 173-175.

(19) Wallace and Tiernan, Inc., 25 Main St., Belleville 9, N. J.

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Sulfur Heterocycles. II. 3-Aryl- and 3-Alkyl-2-thiazolidinone 1,1-Dioxides: New Class of Cyclic Sulfone

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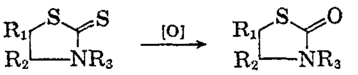
Received June 20, 1961

The oxidation of either 3-substituted-2-thiazolidinethiones or 3-substituted-2-thiazolidinones with hydrogen peroxide in hot acetic acid produces a new class of cyclic sulfone. The products have been assigned the structure of 3-substituted-2-thiazolidinone 1,1-dioxides.

The conversion of substituted 2-thiazolidinethiones to the corresponding 2-thiazolidinones (equation 1) generally has been effected either with alkaline hydrogen peroxide[2] or potassium permanganate[3] or mercuric oxide in acetic acid.[4] While these reagents are useful, the presence of certain substituents in the reactant would preclude their use. For example, a nitrile substituent in I would not survive treatment with alkaline hydrogen peroxide and has been shown to undergo hydrolysis in the mercuric oxide-acetic acid procedure.[5]



I II (1)

R_1, R_2, R_3 = H, Alkyl, Aryl

While investigating alternate methods of oxida-

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[1] Address correspondence to Department of Chemistry, John Carroll University, Cleveland 18, Ohio.

[2] A. H. Cook, J. A. Elvidge, and G. Shaw, *J. Chem. Soc.*, 2367 (1949).

[3] J. Takeda, *J. Pharm. Soc., Japan*, 422, 281 (1917); *Chem. Abstr.*, 11, 2456 (1917).

[4] Y. K. Yur'ev and S. V. Dyatlovitskaya, *Zhur. Obshchei Khim.*, 27, 3152 (1957).

[5] R. J. Gaul, W. J. Fremuth, and M. N. O'Connor, *J. Org. Chem.*, 26, 5106 (1961).