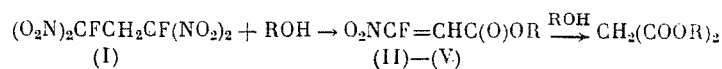


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The action of various nucleophilic reagents on 1,3-difluoro-1,1,3,3-tetranitropropane (I) leads to the elimination of nitro groups and hydrogen and fluorine atoms. The reaction may be stopped at an intermediate stage and ethyl 3-fluoro-3-nitroacrylate is isolated [1].

In the present work, we extended the study of the reaction of (I) with alkanols and discussed a possible pathway for the formation of esters of 3-fluoro-3-nitroacrylic and malonic acids.



R = CH₃ (II), C₂H₅ (III), *i*-C₃H₇ (IV), C₄H₉ (V).

The reaction proceeds at from -10 to +60°C. Depending on the reaction conditions, either alkyl esters of 3-fluoro-3-nitroacrylic acid (at from -10 to +30°C, 40-45% yields), or malonates (50-60°C, 25-30% yields) may be isolated.

Independently of the nature of the alkanol, gaseous NOF is liberated during the reaction as indicated by its IR spectrum (see Experimental).

In the case of the reaction of (I) with methanol, a PMR study was carried out on the entire course of the conversion of (I) to dimethyl malonate (X), which may be given by the following scheme:

The PMR spectral indices of the compounds studied are given in Table 1. The elimination of HNO₂ from the gem-fluorodinitroethyl radical has been described in our previous work [2]; (VI) was isolated from the reaction mixture and proved identical to the product of the reaction of (I) with sodium acetate [1].

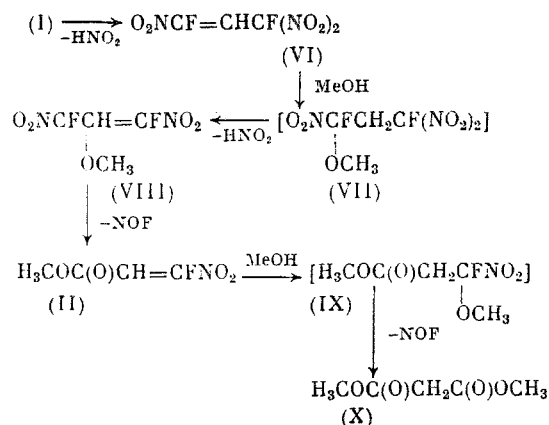
TABLE 1. PMR Chemical Shifts of Compounds Studied Relative to TMS (δ, ppm, J, Hz)

Compound	Proton type	δ	Signal structure	J _{HF}	J _{HH}
(O ₂ N) ₂ CFCH ₂ CF(NO ₂) ₂ (I)	1	4.97	t	14.3	
O ₂ NCF= ³ CHCOOCH ₃ (II)	1	3.90	s		
	2	6.78	d	22.0	
O ₂ NCF= ³ CHCOOCH ₂ ³ CH ₃ (III)	1	1.35	t		7.0
	2	4.33	q		7.0
	3	6.73	d	22.0	
O ₂ NCF= ¹ CHCF(NO ₂) ₂ (VI)	1	7.55	d.d	17.5	
				19.5	
O ₂ NCF= ² CHCF(NO ₂)OCH ₃ (VIII)	1	3.78	s		
	2	6.89	d.d	21.0	
				11.5	
H ₃ COC(O) ² CH ₂ C(O) ¹ OCH ₃ (X)	1	3.69	s		
	2	3.40	s		

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TABLE 2. Physical Constants and Analysis of Esters of 3-Fluoro-3-nitroacrylic Acid

Compound	Bp, °C (P, mm Hg)	n_D^{20}	Found, %				Calculated, %			
			C	H	N	F	C	H	N	F
$O_2NCF=CHCOOCH_3$ (II)	35-36(2)	1,4446	31,9	2,5	9,2	12,6	32,21	2,70	9,39	12,75
$O_2NCF=CHCOOC_2H_5$ (III)	43-44(2)	1,4468	36,6	4,0	8,4	11,5	36,82	3,71	8,59	11,65
$O_2NCF=CHCOOC_3H_7-t$ (IV)	52-53(2)	1,4458	40,4	4,6	8,1	10,8	40,68	4,55	7,91	10,73
$O_2NCF=CHCOOC_4H_9$ (V)	67-68(2)	1,4472	43,7	5,0	7,1	10,1	43,98	5,27	7,33	9,94



The reaction of (VI) with the alkanols studied gave esters (II)-(V). Intermediates (VII) and (IX) were not isolated from the reaction mixture. Product (VIII) was isolated and was found stable below 0°C but converts to (II) at a significant rate even at ~20°C; rapid conversion occurs upon heating (see Experimental).

EXPERIMENTAL

Preparation of Alkyl Esters of 3-Fluoro-3-nitroacrylic acid (II)-(V) (typical experiment). a. A mixture of 5.2 g (0.02 mmole) (I) and 5 ml methanol was stirred at 15-20°C for 5 h and evaporated in vacuum. Distillation of the residue gave 1.3 g (42%) (II). Products (III)-(V) were obtained by analogy in 40-45% yield. The physical constants of (II)-(V) and their elemental analysis data are given in Table 2.

b. A mixture of 4.3 g (0.02 mole) (VI) and 5 ml ethanol was stirred at 15-20°C for 5 h and evaporated in vacuum. Distillation gave 1.7 g (52%) (III). Products (II), (IV), and (V) were obtained by analogy in 50-55% yield.

1,3-Difluoro-1,3,3-trinitro-1-propene (VI). A mixture of 5.2 g (0.02 mole) (I) and 1.0 g (0.03 mole) methanol was maintained at 0-10°C for 48 h and then distilled in vacuum to give 2.7 g (62%) (VI), bp 57-58°C (1 mm), n_D^{20} 1.4612 [1].

1,3-Difluoro-1,3-dinitro-3-methoxy-1-propene (VIII). A mixture of 5.2 g (0.02 mole) (I) and 5 ml methanol was maintained at from -10 to -5°C for 5 h and poured into ice water; 2.1 g (52%) (VIII) was separated and maintained at 0°C. The structure of (VIII) was established by PMR spectroscopy (Table 1).

At 10-30°C, (VIII) liberated NOF, which was identified by IR spectroscopy (ν , cm⁻¹): 1035 s, 1510 m, 1840 m, 2388 m, 2610 w, 3340 m, 3640 w, 4442 m [4].

The liquid residue was distilled in vacuum to give 1.2 g (39%) (II), bp 35-36°C (2 mm), n_D^{20} 1.4447.

Dimethyl Malonate. A mixture of 5.2 g (0.02 mole) (I) and 10 ml methanol was gradually warmed to 60°C and maintained at this temperature for 3 h. Distillation gave 0.8 g (30%) dimethyl malonate, bp 91°C (20 mm), n_D^{20} 1.4190 [3].

CONCLUSIONS

The reaction of 1,3-difluoro-1,1,3,3-tetranitropropane with alkanols was used for the preparation of alkyl esters of 3-fluoro-3-nitroacrylic acid. 1,3-Difluoro-1,3,3-trinitro-1-propene and 1,3-difluoro-1,3-dinitro-2-alkoxy-1-propene were also isolated as intermediates.

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