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NEW COMPOUNDS

Synthesis of 2-Fluoro- and 2-Nitro-Substituted Thionocarbonates

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The syntheses and properties of seven new thionocarbonates containing 2-fluoro and 2-nitro substituents are described. These compounds are useful intermediates for the preparation of other energetic compounds.

A preliminary investigation (*1*) on the reactions of bis(2-fluoro-2,2-dinitroethyl) thionocarbonate (**1**) showed that it was susceptible to nucleophilic attack. The tetrahedral intermediates could be trapped and used to prepare a number of otherwise inaccessible compounds (*2*). Because of these interesting results, methods for the preparation of other thionocarbonates containing 2-fluoro and 2-nitro groups were examined. This paper presents the synthesis of seven new thionocarbonates with such substituents.

The first example of this class of compounds was prepared by the reaction of 2-fluoro-2,2-dinitroethanol with thiophosgene in the presence of strong base (eq 1). This method works well

$$2FC(NO_2)_2CH_2OH + Cl_2C{=}S \xrightarrow{OH^-} \underset{\mathbf{1}}{[FC(NO_2)_2CH_2O]_2C{=}S} \qquad (1)$$

with 2-fluoro alcohols, e.g., trifluoroethanol (see eq 2), but with

$$2F_3CCH_2OH + Cl_2C{=}S \xrightarrow{OH^-} \underset{\mathbf{2}}{(F_3CCH_2O)_2C{=}S} \qquad (2)$$

alcohols substituted only with 2-nitro groups deformylation of the alcohol occurs preferentially to thionocarbonate formation (eq 3). The method then is unsuitable for alcohols such as

$$RC(NO_2)_2CH_2OH \xrightarrow{OH^-} RC(NO_2)_2^- + CH_2{=}O + H_2O \qquad (3)$$

2,2-dinitropropanol and 2,2,2-trinitroethanol. It is also unsuitable for 2,2-difluoro-2-nitroethanol, but in this case it is due to extensive hydrolysis of the thionocarbonate to the carbonate during reaction.

Recently 1,1′-thiocarbonyldiimidazole and 1,1′-thiocarbonyldi-1,2,4-triazole (**3**) have been used as thiocarbonyl transfer reagents for the preparation of thionocarbonates and thioureas (*3–8*). For our purpose, 1,1′-thiocarbonyldiimidazole was ineffective due to side reactions involving the nitroalcohol and imidazole. Better results were obtained with **3**. An 88% yield of bis(2,2-dinitropropyl) thionocarbonate (**4**) was isolated from the reaction of 2,2-dinitropropanol with **3** under mild basic conditions (eq 4).

$$2CH_3C(NO_2)_2CH_2OH + \mathbf{3} \rightarrow \underset{\mathbf{4}}{[CH_3C(NO_2)_2CH_2O]_2C{=}S} \qquad (4)$$

Similarly, bis(2,2-difluoro-2-nitroethyl) thionocarbonate (**5**) was prepared in 71% yield (eq 5).

$$2F_2C(NO_2)CH_2OH + \mathbf{3} \rightarrow \underset{\mathbf{5}}{[F_2C(NO_2)CH_2O]_2C{=}S} \qquad (5)$$

Table I. Data for 2-Fluoro- and 2-Nitro-Substituted Thionocarbonates

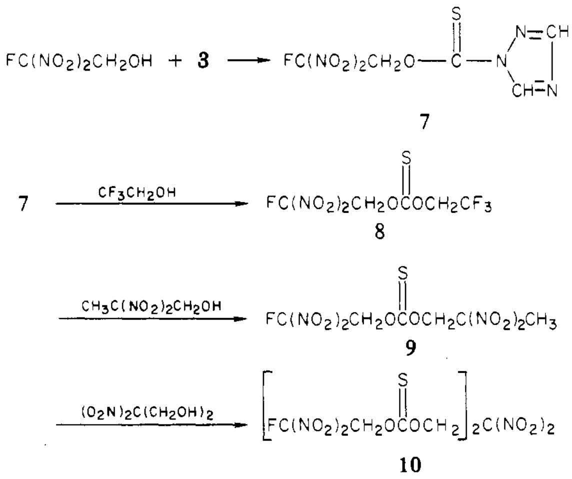
compd	yield,[a] %	mp or bp, °C	^{1}H NMR,[b] ppm
2	76	53 (60 torr)	4.79 q
4	88	87	5.21 s; 2 H 2.22 s; 3 H
5	71	63 (0.1 torr)	5.15 t
6	20	93	5.74 s
8	67	73 (1.2 torr)	5.55 d; 2 H 4.83 q; 2 H
9	57	63	5.53 d; 2 H 5.25 s; 2 H 2.26 s; 3 H
10	18	137	5.50 d; 4 H 5.34 s; 4 H

[a] Calculated on the basis of the alcohol. [b] The solvent was $CDCl_3$ with tetramethylsilane as an internal standard.

Under the same conditions with trinitroethanol, again side reactions predominated with copious gassing and destruction of the trinitroethanol. Bis(2,2,2-trinitroethyl) thionocarbonate (**6**) was finally obtained, albeit in low yield (20%), by the expedient of adding trifluoroacetic acid so the reaction could proceed under mild acidic conditions (eq 6). Attempts to synthesize 5,5-dinitro-2-thiocarbonyl-1,3-dioxane resulted in intractable gummy mixtures.

$$2C(NO_2)_3CH_2OH + 2CF_3CO_2H + \mathbf{3} \rightarrow \underset{\mathbf{6}}{[C(NO_2)_3CH_2O]_2C{=}S} \qquad (6)$$

Several unsymmetrical thionocarbonates were prepared by the consecutive addition of 1 equiv of 2-fluoro-2,2-dinitroethanol and then after a 24-h reaction period 1 equiv of a second substituted alcohol.



The yields of the unsymmetrical thionocarbonates ranged from good to poor. The two possible symmetrical thionocarbonates were also present in the crude reaction solutions.

Results and ^{1}H NMR data are summarized in Table I.

Experimental Section

***General Information*. Caution.** The polynitro compounds described in this paper are explosives and should be handled with due care. In particular, reactions should be run on a small scale behind adequate shielding. Personnel should be equipped with safety glasses and fire-retardant laboratory coats.

The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Satisfactory analyses were obtained for all compounds and were submitted for review. Analyses were performed for all elements except oxygen. Silica gel 40 (E. Merck) was used for chromatographic separations. The melting and boiling points are uncorrected. ^{1}H NMR data are in Table I.

***Bis(3,3,3-trifluoroethyl) Thionocarbonate* (2).** To a solution of 25.0 g (0.25 mol) of trifluoroethanol in 200 mL of water at 3 °C was added 25 mL of 10 N sodium hydroxide. Then, with vigorous stirring, a solution of 10 mL of thiophosgene in 15 mL of CH_2Cl_2 was added dropwise over 20 min at 4-6 °C. Stirring was continued for 1 h at ice-bath temperature. The CH_2Cl_2 phase was separated, dried ($MgSO_4$), and filtered and the solvent removed in vacuo. The residue was distilled to give 23.0 g (76%) of product.

***General Procedure*.** Pyridine (20 mL) was added dropwise to a stirred solution of the alcohol (0.91 mol) and **3** (0.42 mol) in 800 mL of CH_2Cl_2 at 3 °C. Stirring was discontinued and the solution placed in a refrigerator (4-5 °C) for 3-4 days. The precipatated 1,2,4-triazole was filtered and solvent removed from the filtrate under reduced pressure. The crude product was washed with water either by decantation or on a filter pad until the washes were colorless. The crude product was dried and purified by recrystallization or distillation.

***Bis(3,3,3-trinitroethyl) Thionocarbonate* (6).** The general procedure was followed save that trifluoroacetic acid (0.42 mol) was added in place of the pyridine. The reaction solution was allowed to stand at ambient temperature for 14 days. The crude product was purified by elution from silica gel with CH_2Cl_2/hexane (1/1).

***Unsymmetrical Thionocarbonates* (8-10).** The general procedure was used with the following modifications. Equimolar amounts of 2-fluoro-2,2-dinitroethanol and **3** were allowed to react for 24 h (4-5 °C). Then 1 equiv of the second alcohol was added and the solution was placed in a refrigerator for 48 h. The products were purified by elution from silica gel with CH_2Cl_2/hexane.

Registry No. **2**, 83486-43-5; **3**, 63976-76-1; **4**, 80445-01-8; **5**, 80456-68-4; **6**, 80445-02-9; **8**, 83486-44-6; **9**, 83486-45-7; **10**, 83486-46-8; $Cl_2C(S)$, 463-71-8; $CH_3C(NO_2)_2CH_2OH$, 918-52-5; $F_2C(NO_2)CH_2OH$, 3766-88-9; $C(NO_2)_3CH_2OH$, 918-54-7; $FC(NO_2)_2CH_2OH$, 17003-75-7; CF_3-CH_2OH, 75-89-8; $CH_3C(NO_2)_2CH_2OH$, 918-52-5; $(O_2N)_2C(CH_2OH)_2$, 2736-80-3.

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Synthesis and X-ray Photoelectron Spectra of Some Azines

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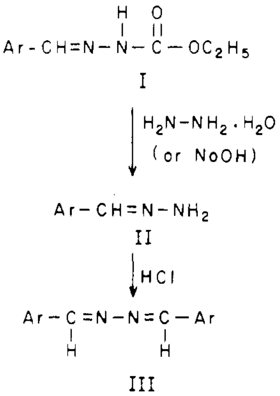
Arylhydrazone-*N*-carboxylic esters (I) were treated with hydrazine hydrate, or sodium hydroxide, to give the hydrazones (II). Acidification of the latter produced the corresponding azines (III). The structures of compounds I-III were substantiated by chemical and spectral analysis.

In a previous publication the synthesis and spectral properties of some arylhydrazone-*N*-carboxylic esters (I) were reported (*1*). The present work intends to describe the conversion of these esters (I) into the corresponding hydrazones (II) and azines (III). (Cf. Scheme I.) This study reports also the X-ray photoelectron spectra of hydrazone IIa as well as azines IIIa,d,f. Thus, when the arylhydrazone-*N*-carboxylic esters (I) were treated with hydrazine hydrate in ethanol, or with aqueous sodium hydroxide, the corresponding aryl hydrazones (II) were obtained. Treatment of the latter products with hydrochloric acid gave the corresponding azines (III).

Scheme I



Compound I, II, III	Ar
a	C_4H_3S *(Thienyl)*
b	C_4H_3O *(Furyl)*
c	C_4H_4N *(Pyrrolyl)*
d	C_5H_5S *(5-methyl thienyl)*
e	C_8H_6N *(Indolyl)*
f	C_5H_6N *(N-methyl pyrrolyl)*
g	C_5H_4N *(pyridyl)*

The structure of hydrazone IIa was evident from its spectral data. Thus, its IR spectrum shows absorption bands at 1615 (C═N) and 3380 (NH_2) cm^{-1}. The UV spectra agree well with the proposed structure (*2a*). The NMR spectrum lends further support to the structure and shows a broad signal at δ 5.1 (2 H, NH_2) which disappeared upon deuteration. It shows also signals in the range δ 6.8-7.2 (3 H, Ar—H) and a singlet at δ 7.85 (1 H, —C(H)═C) (cf. Table I). The spectral data of the azines (IIIa-g) are in agreement with their structures (cf. Table I). The IR spectra show very strong absorption in the region 1600-1645 cm^{-1}, which can be correlated to the C═N group. The high intensity of these bands is due to the immediate en-