

Results and ^1H 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. ^1H 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 precipitated 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; $\text{Cl}_2\text{C}(\text{S})$, 463-71-8; $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$, 918-52-5; $\text{F}_2\text{C}(\text{NO}_2)\text{CH}_2\text{OH}$, 3766-88-9; $\text{C}(\text{NO}_2)_3\text{CH}_2\text{OH}$, 918-54-7; $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OH}$, 17003-75-7; $\text{CF}_3\text{-CH}_2\text{OH}$, 75-89-8; $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$, 918-52-5; $(\text{O}_2\text{N})_2\text{C}(\text{CH}_2\text{OH})_2$, 2736-80-3.

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Synthesis and X-ray Photoelectron Spectra of Some Azines

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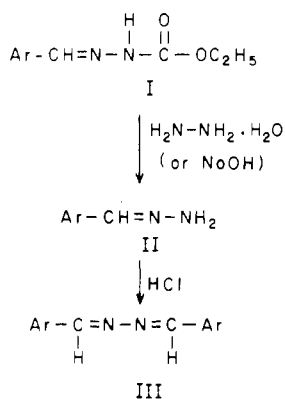
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Arylhydrazone-N-carboxylic esters (I) were treated with hydrazine hydrate, or sodium hydroxide, to give the hydrazones (II). Acidification of the latter produced the corresponding azines (III). The structures of compounds I–III were substantiated by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

The structure of hydrazone IIa was evident from its spectral data. Thus, its IR spectrum shows absorption bands at 1615 ($\text{C}=\text{N}$) 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

Scheme I



Compound I, II, III	Ar
a	$\text{C}_4\text{H}_3\text{S}$ (Thienyl)
b	$\text{C}_4\text{H}_3\text{O}$ (Furyl)
c	$\text{C}_4\text{H}_4\text{N}$ (Pyrrolyl)
d	$\text{C}_5\text{H}_5\text{S}$ (5-methyl thienyl)
e	$\text{C}_8\text{H}_6\text{N}$ (Indolyl)
f	$\text{C}_5\text{H}_6\text{N}$ (N-methyl pyrrolyl)
g	$\text{C}_5\text{H}_4\text{N}$ (pyridyl)

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, $-\text{C}(\text{H})=\text{C}$) (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 $\text{C}=\text{N}$ group. The high intensity of these bands is due to the immediate en-

Table I. Infrared, Electronic, and Nuclear Magnetic Resonance Spectral Data of Compounds IIa and IIIa-g

compd	yield, %	mp, °C	IR spectra ^a		electronic spectra ^b		NMR ^c					
			cm ⁻¹	ν	λ_{\max} , nm	ϵ	δ	assignments (no. of protons)				
IIa	82	62	1615 (s)	C=N	340	8 466	5.1 (br)	NH ₂ (2)				
			3200 (m)		305		9 844		6.9-7.2 (m)	Ar-H (3)		
			3380 (s)						7.85 (s)	-CH= (1)		
IIIa	95	150	1612 (s)	C=N	342	37 675	7.1-7.6 (m)	Ar-H (6)				
IIIb	90	117	1645 (s)	C=N	270	13 475	8.8 (s)	-CH= (2)				
					341		25 555		6.6-7.6 (m)	Ar-H (6)		
					336		37 190		8.6 (s)	-CH= (2)		
					333		37 090					
					327		35 150					
					237		2 655					
					255		4 820					
IIIc	93	150	1635 (s)	C=N	356	39 570	6.2-7.6 (m)	Ar-H (6)				
IIIc	93	150	3240 (s)	NH	255	4 820	8.5 (s)	-CH= (2)				
								10.8 (br)	NH (1)			
								2.5 (s)	-CH ₃ (6)			
IIIId	92	130	1610 (s)	C=N	352	47 460	6.8-7.3 (m)	Ar-H (4)				
IIIId	92	130	1610 (s)	C=N	270	12 870	8.8 (s)	-CH= (2)				
								7.0-8.6 (m)	Ar-H (10)			
								9.0 (s)	-CH (2)			
IIIe	91	305	1625 (s)	C=N			11.7 (Br)	NH (2)				
IIIe	91	305	3240 (s)	NH			4.0 (s)	N-CH ₃ (6)				
							6.3-7.4 (m)	Ar-H (6)				
							8.6 (s)	-CH= (2)				
IIIIf	93	110	1635 (s)	C=N	353	43 520	7.3-9.0 (m)	Ar-H } (10)				
IIIIf	93	110	1635 (s)	C=N	260	7 385		-CH= }				
IIIIf	93	110	1635 (s)	C=N	308	6 755						
					298		14 475					
					286			18 695				
					276				17 850			
					268					15 920		

^a KBr. ^b Ethanol. ^c Deuteriochloroform.

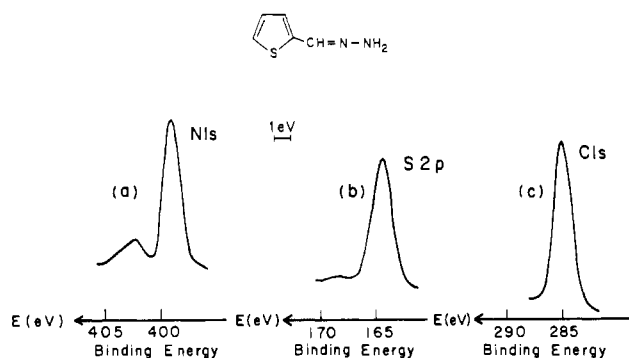


Figure 1. X-ray photoelectron spectrum of IIa: (a) N(1s) energy region, (b) S(2p) energy region, (c) C(1s) energy region.

environment of the C=N group (3). The NMR spectra agree well with the proposed structures and show signals characteristic for the protons of these azines, in their different environments (cf. Table I). The electronic spectra of these compounds show some resemblance to each other and show absorption maxima in the ranges 270-237 and 356-298 nm. These are $\pi \rightarrow \pi^*$ transition bands corresponding to 1L_b and 1L_a bands and are characteristic of the azine structure (2b).

The X-ray photoelectron spectra of some of these compounds are listed in Table II. The ionization of N(1s) electrons shows prominent shake-up lines (4, 5) in all of the compounds studied in this work (cf. Figures 1-4).

Experimental Section

General Information. Microanalyses were performed by Dr. A. Bernhardt, Microanalytisches Laboratorium, West Germany. The NMR spectra were run on a T-60 A spectrometer in CDCl₃, with Me₄Si as internal standard. The infrared and electronic spectra were measured on Unicam SP 1000 and Cary 17 spectrophotometers, respectively.

A McPherson ESCA-36 spectrometer with a Mg K α source (1253.6 eV) was used for measuring the X-ray photoelectron spectra; a cryogenic pump in the sample chamber maintained

Table II. Ionization Energies in Electron Volts

compd	C(1s)	N(1s)	S(2p)
IIa	285.2	399, 402.6 (s), 405 (s)	164.4, 168.1 (s)
IIIa	284.6, 288.4 (s)	398.8, 402.4 (s), 405.2 (s)	164.5, 168.2 (s)
IIIId	284.9, 288.5 (s)	399.05, 402.4 (s), 409 (s)	164.2, 167.8 (s)
IIIIf	285.2, 288.9 (s)	398.9, 400.3, 402.7 (s)	

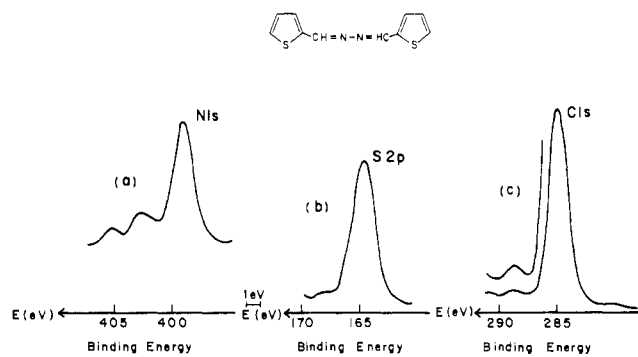


Figure 2. X-ray photoelectron spectrum of IIIa: (a) N(1s) energy region, (b) S(2p) energy region, (c) C(1s) energy region.

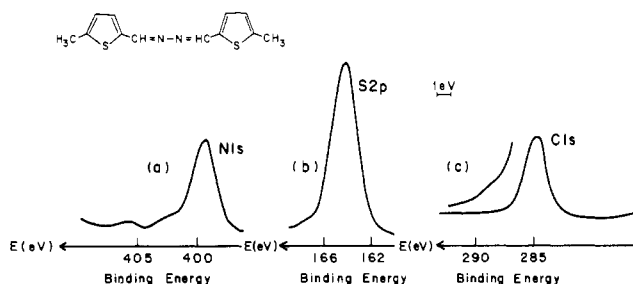


Figure 3. X-ray photoelectron spectrum of IIIId: (a) N(1s) energy region, (b) S(2p) energy region, (c) C(1s) energy region.

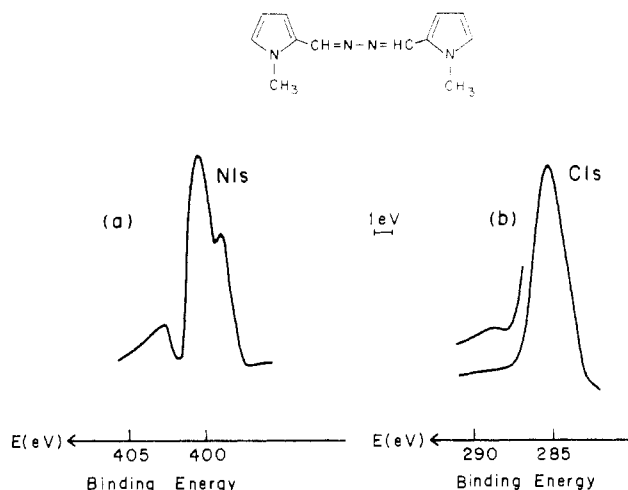


Figure 4. X-ray photoelectron spectrum of IIIf: (a) N(1s) energy region, (b) C(1s) energy region.

a pressure of less than 10^{-8} torr. Samples were mounted on aluminum mesh at room temperature.

(a) Reaction of Arylhydrazone-*N*-carboxylic Esters (I) and Hydrazine Hydrate. A mixture of the hydrazone ester (0.01 mol) and the hydrazine hydrate (0.01 mol) in 50 mL of ethanol was refluxed on a water bath for a period of 5 h. Evaporation of the solvent left a viscous oil, which proved to be the arylhydrazone (II). Crystallization of IIa from petroleum ether (60–80 °C) gave pale yellow crystals, mp 62 °C. The other hydrazones gave oily materials.

(b) Reaction of Arylhydrazones (IIa–g) and Hydrochloric Acid. A mixture of the arylhydrazone (0.01 mol) in ethanol (20 mL) and 6 N HCl (5 mL) was warmed on a water bath for 5 min. A heavy solid was precipitated, which was filtered off and crystallized from ethanol to give azines of thiophene-2-carboxaldehyde (IIIa), furan-2-carboxaldehyde (IIIb), pyrrole-2-carboxaldehyde (IIIc), 5-methylthiophene-2-carboxaldehyde

(IIIId), indole-3-carboxaldehyde (IIIe), *N*-methylpyrrole-2-carboxaldehyde (IIIIf), and pyridine-4-carboxaldehyde (IIIg).

Azine IIIa was also prepared by refluxing an alcoholic solution of the arylhydrazone-*N*-carboxylic ester Ia and aqueous sodium hydroxide (10%) for 1 h. The alcohol was evaporated, and the product was crystallized from petroleum ether (60–80 °C) to give a product, which proved to be identical with IIa. This product was treated with hydrochloric acid, as mentioned above, to yield azine IIIa.

(c) Preparation of Authentic Samples. (1) Hydrazone IIa was prepared by refluxing equimolar amounts of thiophene-2-carboxaldehyde and hydrazine hydrate in ethanol for a period of 5 h and then worked up as described previously. (2) Azines IIIa–g were prepared by refluxing the corresponding heterocyclic aldehyde (2 mol) and hydrazine hydrate (1 mol) in ethanol and then worked up. The products proved to be identical with those obtained from procedure b.

Elemental analyses were performed and submitted for review.

Registry No. Ia, 81291-64-7; Ib, 81291-65-8; Ic, 37526-50-4; Id, 83710-32-1; Ie, 15641-27-7; If, 83710-33-2; Ig, 83710-34-3; IIa, 31350-01-3; IIb, 31350-00-2; IIc, 83710-35-4; IId, 83719-44-2; IIe, 83710-36-5; IIIf, 83710-37-6; IIg, 51832-68-9; IIIa, 24523-46-4; IIIb, 5428-37-5; IIIc, 75841-29-1; IIIId, 83710-38-7; IIIe, 1233-49-4; IIIIf, 59618-86-9; IIIg, 6957-22-8.

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One-Step Synthesis of Esters of Aliphatic β -Chloro Sulfonic Acids. Their Sequential Conversion to Other Sulfonic Acid Derivatives

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A one-step synthesis of methyl 2-chlorohexane-1- and 2-chlorooctane-1-sulfonate by the novel free-radical addition of methyl chlorosulfonate to 1-hexene and 1-octene, respectively, is reported. These products were converted by standard techniques into the corresponding sodium and benzylthiuronium β -chlorosulfonic acid salts and sulfonyl chlorides. Dehydrochlorination of these latter products with triethylamine afforded regiospecific formation of trans- α,β -unsaturated sulfonyl chlorides, which were transformed by conventional methods into sodium and benzylthiuronium unsaturated and saturated sulfonic acid salts. Eleven new compositions of matter are reported.

Introduction

The halogen-sulfur bond of the halosulfonyl group is readily amenable to homolytic cleavage. Studied extensively has been the free-radical addition of aliphatic and aromatic sulfonyl halides to a variety of carbon-carbon unsaturated systems to yield β -halo sulfones (1–5). Also, *N*-chlorosulfonylphthalimide (6) and sulfonyl chloride fluoride (7) have been added to olefins under free-radical conditions to give *N*-(β -chloroalkyl)sulfonylphthalimides and 2-chloroalkanesulfonyl fluorides, respectively. Further, the free-radical addition of sulfonyl chloride to olefins has been reported to give β -chloroalkyl sulfones (6a). These results suggest the possibility that alkyl or aryl halosulfonates also could undergo free-radical addition to unsaturated hydrocarbons to provide a novel one-step synthesis of esters of