Reaction of Methoxycarbonylhydrazones with Hydrogen Sulfide: A New and Facile Synthesis of Tetrasulfides

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The interest concerning the chemistry of tetrasulfides is well documented[1-8]. In addition, tetrasulfides are efficient lubricant improving agents[9,10]. However, tetrasulfides are usually prepared starting from thiols or hydrodisulfides[11-15].

The object of the research which is outlined herein has been the development of a synthetic method for the conversion of carbonyl compounds to the corresponding tetrasulfides. Our method consists in the treatment of carbonyl compounds **1** with methoxycarbonylhydrazine[16] (**2**) to obtain the methoxycarbonylhydrazones **3** (Table 1) and subsequent reaction of these with hydrogen sulfide. Work-up of the mixture after three days at 90 °C provided the tetrasulfides **4** in fair to good yields (Table 2).

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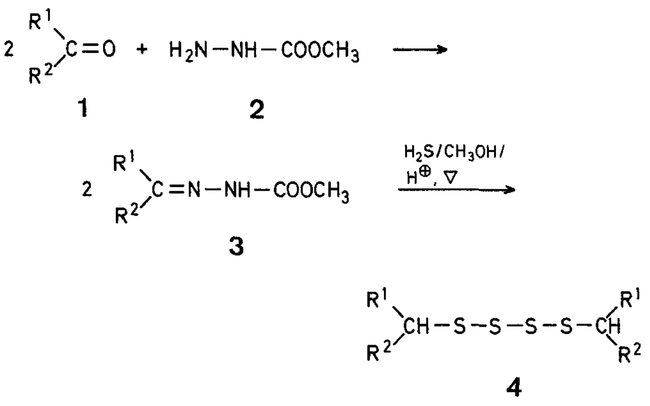
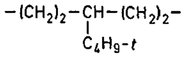
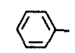


Alternatively, the methoxycarbonylhydrazones **3** can be isolated by evaporation of the reaction solution under reduced pressure at 50 °C (Table 1).

Tetrasulfides 4; General Procedure:

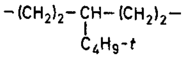
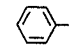
A methanolic solution (70 ml) of the methoxycarbonylhydrazone **3** (0.03 mol) is saturated with dry hydrogen sulfide, after that glacial acetic acid (5 ml) is added and then the obtained solution is placed in a glass tube at 90 °C for three days. The yellow solution is concentrated under reduced pressure at 45 °C, dichloromethane (80 ml) is added, the organic layer is washed with water (25 ml), and dried with sodium sulfate. The solvent is removed under reduced pressure and the crude, yellow product is purified by column chromatography (SiO_2 0.063-0.200 mm), hexane as eluent (Table 2).

Table 1. Methoxycarbonylhydrazones **3a-e**

Product No.	R^1	R^2	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. ν [cm^{-1}]		^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
						N—H	C=O	
3a	$-(CH_2)_5-$		97	oil	$C_8H_{14}N_2O_2$ (170.2)	3251	1718	1.4-1.9 (m, 6H); 2.2-2.6 (m, 4H); 3.78 (s, 3H)
3b	 $-(CH_2)_2-CH(C_4H_9\text{-}t)-(CH_2)_2-$		95	oil	$C_{12}H_{22}N_2O_2$ (226.3)	3257	1721	0.6-2.7 (m+s, 18H); 3.78 (s, 3H)
3c	n-C_6H_{13}	H	93	63-64°	$C_9H_{18}N_2O_2$ (186.3)	3280	1710	0.88 (t, 3H, J=6 Hz); 1.1-1.7 (m, 8H); 2.1-2.5 (m, 2H); 3.78 (s, 3H); 7.28 (t, 1H, J=6 Hz)
3d	n-C_3H_7	H	94	49-50°	$C_6H_{12}N_2O_2$ (144.2)	3259	1710	0.93 (t, 3H, J=7.5 Hz); 1.3-1.8 (m, 2H); 2.1-2.5 (m, 2H); 3.78 (s, 3H); 7.31 (t, 1H, J=6 Hz)
3e		H	90	140-142°	$C_9H_{10}N_2O_2$ (178.2)	3205	1700	3.78 (s, 3H); 7.3-7.5 (m, 3H); 7.6-7.8 (m, 2H); 7.90 (s, 1H)

[a] Satisfactory microanalyses obtained: C ±0.06, H ±0.04, N ±0.06, O ±0.03.

Table 2. Dialkyl Tetrasulfides **4a-e**

Product No.	R^1	R^2	Yield [%]	m.p. [°C] b.p. [°C]/torr	n_D^{20}	Molecular formula[a] or Lit. data	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
4a	$-(CH_2)_5-$		89	125-127°/1.8	—	100°/0.1[15]	0.9-2.3 (m, 20H); 2.7-3.3 (m, 2H)
4b	 $-(CH_2)_2-CH(C_4H_9\text{-}t)-(CH_2)_2-$		83	—	1.5636	$C_{20}H_{36}S_4$ (404.5)	0.6-2.4 (s+m, 34H); 2.7-3.1 (m, 2H)
4c	n-C_6H_{13}	H	53	140-141°/1	—	$C_{14}H_{20}S_4$ (316.3)	0.89 (t, 6H, J=6 Hz); 1.0-2.0 (m, 20H); 2.88 (t, 4H, J=7.5 Hz)
4d	n-C_3H_7	H	56	90-92°/2	—	56°/0.1[15]	0.92 (t, 6H, J=7.4 Hz); 1.2-2.0 (m, 8H); 2.90 (t, 4H, J=7.3 Hz)
4e		H	29	51-52°	—	52-53°[11]	4.03 (s, 4H); 7.1-7.4 (m, 10H)

[a] Satisfactory microanalyses obtained: C ±0.05, H ±0.03, S ±0.03.

It is noteworthy that this procedure uses readily available reagents and provides a simple method for symmetrical tetrasulfides and is general for the preparation of primary and secondary dialkyl tetrasulfides.

The I.R. spectra were recorded with Perkin Elmer 297 Spectrophotometer. The ^{1}H-N.M.R. spectra were determined on a Varian EM 390 spectrometer. Samples were dissolved in $CDCl_3$ with tetramethylsilane as an internal standard. Microanalyses were performed using a Hewlett Packard Model 185 C,H,S analyzer. Melting points were obtained using a Büchi melting point apparatus and are uncorrected. Index of refraction were determined on a Galileo RG 701 refractometer.

Methoxycarbonylhydrazones 3; General Procedure:

A 50 ml flask is charged with methoxycarbonylhydrazine (**2**; 3.6 g, 0.04 mol), methanol (15 ml), acetic acid (2 drops), and the appropriate carbonyl compound **1** (0.04 mol). The resulting mixture is refluxed for 30 min, by the end of which time a solution has formed. This crude hydrazone **3** is used directly for the tetrasulfide synthesis.

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[1] L. Arizmendi, V. Martinez Vilche, *Corros. Sci.* **10**, 595 (1970); *C. A.* **74**, 6750 (1971).

[2] G. V. Leplianin, G. P. Gladyshev, *Kinet. Mech. Polyreactions, Int. Symp. Macromol. Chem. Prep.* **3**, 151 (1969); *C. A.* **75**, 49717 (1971).

[3] F. Feher, T. Gladden, D. Kurz, *Z. Naturforsch.* [b] **25**, 1215 (1970); *C. A.* **74**, 41640 (1971).

[4] C. G. Moore, M. Porter, *J. Chem. Soc.* **1965**, 6390.

[5] C. G. Moore, B. T. Trego, *Tetrahedron* **18**, 205 (1962).

[6] J. Llopis, J. M. Gamboa, C. Arizmendi, J. A. Gomez Minana, *Corros. Sci.* **4**, 27 (1964); *C. A.* **61**, 4997 (1964).

[7] M. B. Evans, G. M. C. Higgins, C. G. Moore, M. Porter, B. Saville, J. F. Smith, B. R. Trego, A. A. Watson, *Chem. Ind. (London)* **1960**, 897.

[8] C. G. Moore, R. W. Saville, *J. Chem. Soc.* **1954**, 2082.

[9] J. W. Allen, *U. S. Patent* 3267033 (1966); *C. A.* **65**, 16767 (1966).

[10] W. T. Mastin, *U. S. Patent* 3013969 (1961); *C. A.* **56**, 11910 (1962).

[11] S. Kawamura, Y. Abe, J. Tsurugi, *J. Org. Chem.* **34**, 3633 (1969).

[12] M. G. Voronkov, A. N. Pereferkorich, V. A. Pestunovich, V. Udre, *Zh. Org. Khim.* **3**, 2211 (1967); *C. A.* **68**, 6857 (1968).

[13] B. D. Vineyard, *J. Org. Chem.* **31**, 601 (1966).

[14] V. F. Birch, T. V. Cullum, R. A. Dean, *J. Inst. Petroleum* **39**, 206 (1953); *C. A.* **48**, 4428 (1954).

[15] G. F. Bloomfield, *J. Chem. Soc.* **1947**, 1547.

[16] This reagent is available from Aldrich Chemical Company, Inc., under the name methyl hydrazinocarboxylate.

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