A General Strategy for Elaboration of the Dithiocarbonyl Functionality, -(C=O)SS-: Application to the Synthesis of Bis(chlorocarbonyl)disulfane and Related Derivatives of Thiocarbonic Acids

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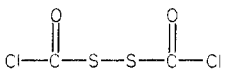
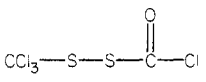
A variety of sulfenyl chlorides have been reacted with a variety of alkoxythiocarbonyl compounds to give adducts which then lose (spontaneously, or upon thermolysis, or in the presence of a Lewis acid catalyst) the alkyl chloride to provide an assortment of dithiocarbonyl compounds in good to excellent yields. The preparations of bis(chlorocarbonyl)disulfane (**1**), ((trichloromethyl)dithio)carbonyl chloride (**2**), ((alkoxycarbonyl)dithio)carbonyl chlorides (**3** and **4**), and (((alkylthio)carbonyl)dithio)carbonyl chlorides (**5** and **6**) by this methodology were optimized; some of the (alkoxydichloromethyl)disulfanyl adducts, e.g., $ROCCl_2SS(C{=}O)Cl$ (**10**) and $ROCCl_2SS(C{=}O)OR'$ (**54**), were reasonably stable and could be isolated. All new compounds were characterized by analytical data, ^1H and ^{13}C NMR, IR, UV, and mass spectrometry, and high-yield derivatizations with alcohols or *N*-methylaniline. The reaction with *N*-methylaniline was also adapted to a rapid, convenient, and precise analytical-scale assay of mixtures of compounds containing acid chloride and/or sulfenyl chloride functionalities. The kinetics, mechanism, and stereochemistry of the dithiocarbonyl synthesis are discussed.

As part of a program to develop amino protecting groups removable under mild reductive conditions,[1,2] we sought a convenient entry to a variety of dithiocarbonyl chlorides. These include bis(chlorocarbonyl)disulfane (**1**),[1,3] which might be expected[1] to react with primary amines to attach a dithiasuccinoyl function, and ((trichloromethyl)dithio)carbonyl chloride (**2**),[3] which is a synthetic precursor of carbamoyl disulfide derivatives of primary and secondary amines, as well as the novel compounds **3** to **6**.



1



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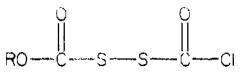
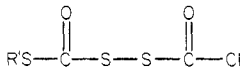
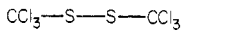


3, R = CH_3
4, R = C_2H_5



5, R' = CH_3
6, R' = C_2H_5



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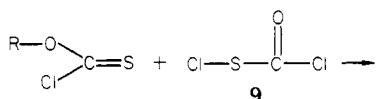
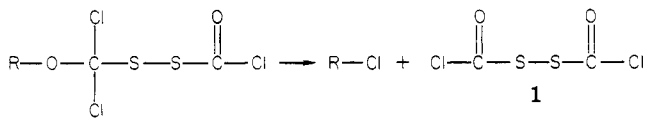
Both **1** and **2** are known, either by[3b] exchange (20-mmol scale) with BCl_3 on the relatively inaccessible acid fluorides[3b,4] or by partial hydrolysis[3a,5] of bis(trichloromethyl)disulfane (**7**).[6] Our optimal route (Scheme I) provided pure **1** in 75% yield (0.5-mol scale). The reaction of an alkoxythiocarbonyl chloride (**8**)[7] with chlorocarbonylsulfenyl chloride (**9**)[8] gave the isolable adduct **10**, which cleanly lost alkyl chloride with either heat or catalytic $FeCl_3$. Several side reactions were minimized: (1) facile rearrangement of **8**, especially when impure, to the more stable (alkylthio)carbonyl chloride isomers (**11**); (2) decomposition[7a,b] of **8** to alkyl chloride and COS; (3) formation of (alkyldithio)carbonyl chlorides (**12**)[2,9] as contaminants to certain preparations of **1**, **8**, and/or **10**; and (4) the decomposition of **1** into **9** plus COS.

Scheme I



8 **9**



10 **1**

a, R = CH_3; b, R = C_2H_5

Subsequently, the chemistry of Scheme I, which has only scattered precedents,[1,10] was generalized for the syntheses of **2** to **6** and related compounds by varying the thiocarbonyl or the sulfenyl chloride components. Preferred procedures for pure key starting materials and reference compounds which are inadequately described in the literature[11] were also worked out (see Table I for structural formulas and numbering schemes).

Results and Discussion

Preparation of Alkoxythiocarbonyl Chlorides (8). The obvious method, namely to react an alcohol or alk-

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(3) (a) Kobayashi, N.; Osawa, A.; Fujisawa, T. *Chem. Lett.* **1973**, 1315-1318. (b) Haas, A.; Helmbrecht, J.; Klug, W.; Koch, B.; Reinke, H.; Sommerhoff, J. *J. Fluorine Chem.* **1973/74**, *3*, 383-395.
(4) Haas, A.; Reinke, H. *Chem. Ber.* **1969**, *102*, 2718-2727.
(5) Our own efforts to reproduce the chemistry of ref 3a, which met only limited success, are sketched in the Experimental Section. We thank Dr. Kobayashi for helpful correspondence on this point.
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(8) (a) Friedman, B. French Patent 1 372 971, Sept. 18, 1964; *Chem. Abstr.* **1965**, *62*, 1363a. (b) Weiss, W. German Patent 1 224 720, Nov. 11, 1964; *Chem. Abstr.* **1966**, *65*, 12112h.
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(10) (a) Harris, J. F., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 155-158. (b) Douglass, I. B.; Evers, W. J. *J. Org. Chem.* **1964**, *29*, 419-420. (c) Maatschappi, N. V. British Patent 948 489, Feb. 5, 1964; *Chem. Abstr.* **1964**, *60*, 13147g. (d) Haas, A.; Klug, W. *Chem. Ber.* **1968**, *101*, 2617-2621. (e) Böhme, H.; Steudel, H. P. *Liebigs Ann. Chem.* **1969**, *730*, 121-132. (f) Zumach, G.; Kühle, E. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 54-63. (g) Kühle, E. "The Chemistry of Sulfenic Acids"; Thieme: Stuttgart, 1973; pp 68-70. (h) Böhme, H.; Brinkmann, M.; Steudel, H. P. *Liebigs Ann. Chem.* **1981**, 1244-1251.
(11) (a) Bögemann, M.; Peterson, S.; Schultz, O. E.; Söll, H. *Houben-Weyl Methoden der Org. Chem. 4th Ed.* **1955**, *9*, 772-915 especially 804-856. (b) Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing: New York, 1962; six volumes of which Vol. 3 and particularly Vol. 4 are relevant. (c) Duus, F. In "Barton-Ollis Comprehensive Organic Chemistry"; Neville Jones, D., ed.; Pergamon Press: Oxford, 1979; pp 373-487, especially pp 432-435. (d) Many of the techniques mentioned in these reviews date back 50 to 100 years and have proven to be unreliable when evaluated by modern spectroscopic and analytical methods.

0022-3263/83/1948-4750$01.50/0

Table I. Numbering Scheme and Proton Nuclear Magnetic Resonance Data of Synthesized Compounds[a] C_1-C_6

compd	structure	chemical shift, δ [b]	compd	structure	chemical shift, δ [b]
	MeCl	3.01	28b	MeO(C=O)SEt	3.81; 1.32, 2.87 (7.4)
	EtCl	1.48, 3.57 (7.2)	29a	EtO(C=O)SMe	1.30, 4.28 (7.1); 2.33
3	MeO(C=O)SS(C=O)Cl	3.96	29b	EtO(C=O)SEt	1.30, 4.27 (7.1); 1.31, 2.86 (7.3)
4	EtO(C=O)SS(C=O)Cl	1.36, 4.41 (7.1)			
5	MeS(C=O)SS(C=O)Cl	2.53	30a	MeS(C=S)SMe	2.76
6	EtS(C=O)SS(C=O)Cl	1.35, 3.10 (7.4)	30b	EtS(C=S)SEt	1.35, 3.37 (7.4)
8a	MeO(C=S)Cl	4.18	31a	MeS(C=S)Cl	2.68
8b	EtO(C=S)Cl	1.46, 4.61 (7.1)	31b	EtS(C=S)Cl	1.37, 3.21 (7.4)
10a	$MeOCCl_2SS(C=O)Cl$	3.76	33a	$MeOCCl_2SCl$	3.76
10b	$EtOCCl_2SS(C=O)Cl$	1.34, 4.11 (7.1)	33b	$EtOCCl_2SCl$	1.38, 4.09 (7.1)
11a	MeS(C=O)Cl	2.46	34a	$MeOCCl_3$	3.83
11b	EtS(C=O)Cl	1.36, 2.97 (7.4)	35a	MeO(C=O)SCl	3.97
12a	MeSS(C=O)Cl	2.58	35b	EtO(C=O)SCl	1.36, 4.44 (7.1)
12b	EtSS(C=O)Cl	1.36, 2.91 (7.3)	36a	MeO(C=O)SSMe	3.90; 2.49
14a	MeO(C=S)SS(C=S)OMe	4.24	36b	MeO(C=O)SSEt	3.89; 1.33, 2.81 (7.4)
14b	EtO(C=S)SS(C=S)OEt	1.43, 4.70 (7.1)	37a	EtO(C=O)SSMe	1.34, 4.36 (7.1); 2.49
15a	MeO(C=S)SMe	4.19; 2.57	37b	EtO(C=O)SSEt	1.33, 4.35, (7.2); 1.32, 2.80 (7.3)
15b	EtO(C=S)SMe	1.41, 4.65 (7.1); 2.55			
16a	MeO(C=S)SEt	4.17; 1.34, 3.14 (7.2)	38a	MeSCl	2.90
16b	EtO(C=S)SEt	1.34, 3.12 (7.4); 1.41, 4.65 (7.1)	38b	EtSCl	1.44, 3.15 (7.1)
			39a	MeSSCl	2.74
17a	MeS(C=O)SMe	2.44	39b	EtSSCl	1.45, 3.04 (7.3)
17b	EtS(C=O)SEt	1.30, 3.00 (7.4)	40a	MeSSMe	2.42
18	MeS(C=O)SEt	2.41; 1.29, 3.00 (7.2)	40b	EtSSEt	1.32, 2.71 (7.3)
19a	MeO(C=S)OMe	4.05	41a	MeSSSMe	2.56
19b	EtO(C=S)OEt	1.38, 4.50 (7.2)	41b	EtSSSEt	1.38, 2.89 (7.3)
20	MeO(C=S)OEt	4.04; 1.38, 4.51 (7.2)	42a	MeSSSSMe	2.64
21a	MeO(C=O)Cl	3.95	42b	EtSSSSEt	1.40, 2.97 (7.3)
21b	EtO(C=O)Cl	1.38, 4.38 (7.2)		MeSSSSSMe	2.67
22a	MeO(C=S)S(C=O)OMe	4.26; 3.87	43a	MeO(C=O)SS(C=O)OMe	3.92
22b	EtO(C=S)S(C=O)OMe	1.48, 4.72 (7.1); 3.86	43b	EtO(C=O)SS(C=O)OEt	1.34, 4.38 (7.1)
23a	MeO(C=S)S(C=O)OEt	4.25; 1.33, 4.34 (7.1)	54a	$MeO(C=O)SSCCl_2OMe$	3.93; 3.75
23b	EtO(C=S)S(C=O)OEt	1.48, 4.72 (7.1); 1.33, 4.33 (7.1)	54b	$EtO(C=O)SSCCl_2OMe$	1.35, 4.39 (7.1); 3.75
			55	$MeS(C=O)SSCCl_2OMe$	2.50; 3.76
24a	MeO(C=S)S(C=S)OMe	4.22	56	MeO(C=O)SS(C=O)OEt	3.92; 1.34, 4.38 (7.1)
24b	EtO(C=S)S(C=S)OEt	1.47, 4.67 (7.1)	61	MeS(C=O)SS(C=O)OMe	2.48; 3.93
25a	MeO(C=S)SSS(C=S)OMe	4.29	62a	$MeO(C=O)SSCCl_3$	3.97
25b	EtO(C=S)SSS(C=S)OEt	1.50, 4.75 (7.1)	62b	$EtO(C=O)SSCCl_3$	1.38, 4.42 (7.2)
26a	MeO(C=S)SSSS(C=S)OMe	4.25	63a	MeS(C=O)SSMe	2.43; 2.55
26b	EtO(C=S)SSSS(C=S)OEt	1.51, 4.67 (7.1)	63b	EtS(C=O)SSEt	1.31, 3.00 (7.4); 1.34, 2.86 (7.3)
27a	MeO(C=O)OMe	3.78			
27b	EtO(C=O)OEt	1.30, 4.19 (7.2)	64	MeSSEt	2.41; 1.34, 2.73 (7.3)
28a	MeO(C=O)SMe	3.82; 2.35	65a	MeO(C=O)S(C=O)OMe	3.89
			65b	EtO(C=O)S(C=O)OEt	1.34, 4.36 (7.1)

[a] The supplementary material contains Table V, which adds to this one ^{13}C NMR and IR data and in which the order of listing emphasizes homologies in structures and spectra. [b] In $CDCl_3$. Chemical shifts are listed in a way to match assignments with the structure as written. Two adjacent numbers followed by a parenthesized number, for example on line 2, 1.48, 3.57 (7.2), means in more detail δ 1.48, t, CH_3, and 3.57, q, CH_2 (J = 7.2 Hz), for that ethyl group.

oxide with thiophosgene,[7a-d,g,12] also generates *O,O'*-dialkyl thiocarbonates (**19**) which have physical properties similar to **8**. Therefore, the method of Sasse[7e,f] was adopted which involves chlorination of bis(alkoxy(thiocarbonyl))disulfanes (dialkyl dixanthogens) (**14**) followed by a "cracking" distillation. Critical variables were found[13] to include: (1) purity of starting **14**;[15,16] (2) reaction milieu (neat **14** or in hydrocarbon solvent); (3) chlorinating agent (Cl_2 gas or

(12) On the other hand, (alkylthio)(thiocarbonyl) chlorides (**31**) are best prepared from the alkanethiol and thiophosgene, and **31** separate readily from the *S,S'*-dialkyl trithiocarbonates (**30**) which are higher boiling. See: (a) Arndt, F.; Milde, E.; Eckert, G. *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 1976–1984. (b) Jensen, K. A. *J. Prakt. Chem.* **1937**, *148*, 101–106.

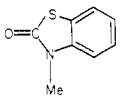
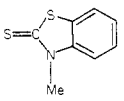
(13) NMR examination revealed that crude mixtures having incorporated one equiv of Cl_2 per mole of **14** contained several components of which the desired **8** never represented more than 70% and occasionally was entirely absent. Nonetheless, the correct product as judged by NMR (>85% purity) did distill upon "cracking" of the crude chlorination mixture. Our detailed studies, Barany, G., in preparation, account for the composition of the chlorination mixture and lead to the conclusion that in the overall procedure $RO(C{=}S)SS(C{=}S)OR + Cl_2 \rightarrow RO(C{=}S)Cl + 2\,S + COS + RCl$, and it is with this stoichiometry that the overall yield of **8** by optimal procedures was calculated to be 75–85%. Note that our understanding is different from the literature (ref 7e,f) stoichiometry, which predicts 2 $RO(C{=}S)Cl$ + 2 S, and which is also formally equivalent to the stoichiometry of the Ritter synthesis of dimethylthiocarbamoyl chloride (ref 14).

(14) Contrast to $R_2N(C{=}S)SS(C{=}S)NR_2 + Cl_2 \rightarrow 2\,R_2N(C{=}S)Cl + 2\,S$. See: (a) Ritter, E. J. U.S. Patent 2 466 276, April 5, 1949; *Chem. Abstr.* **1949**, *43*, 5038c. (b) Goshorn, R. H.; Levis, W. W.; Jaul, E.; Ritter, E. J.; Cairns, T. L.; Cupery, H. E. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 307–310. (c) Newman, M. S.; Hetzel, F. W. *J. Org. Chem.* **1969**, *34*, 3604–3606.

(15) Prepared by iodine oxidation of potassium alkyl xanthates. (a) Zeise, W. F. *J. Prakt. Chem.* **1845**, *36*, 352–362. (b) Rao, S. R. "Xanthates and Related Compounds"; M. Dekker: New York, 1971; pp 131–136. (c) Bulmer, G.; Mann, F. G. *J. Chem. Soc.* **1945**, 674–677. (d) Decomposition of **14** to *O,S*-dialkyl dithiocarbonates (dialkyl xanthates (**15**, **16**)) is known under the influence of heat (ref 15b) or vacuum distillation at 20 mm (ref 15c). (e) We found that preparations of **14a** were contaminated with 2–15% of **15a**; this caused concern because of the discovery (ref 17) that carrying out the Sasse synthesis on pure **15a** gave (methyldithio)carbonyl chloride (**12a**). Indeed, **12a** was separately identified (ref 18) as the principal proton-containing contaminant to **8a** when the "cracking" distillation was carried out at reduced pressure (ref 19). The problem of dixanthogen decomposition to xanthates was solved by washing the crude product of the xanthate oxidation (which was dissolved in ether) extensively with water (see also ref 16 and 20).

(16) In the ethyl series, diethyl xanthate (**16b**) did *not* contaminate diethyl dixanthogen (**14b**). Interestingly, oxidation with iodine of potassium ethyl xanthate (**13b**) in the presence of pure dimethyl dixanthogen (**14a**) led to some dimethyl xanthate (**15a**).

Table II. *N*-Methylaniline Derivatives[a]

compd	structure	mp, °C [bp, °C (mm)]	^{1}H NMR, δ[b] R	^{1}H NMR, δ[b] N-Me
46[c]	PhN(Me)(C=O)SS(C=O)N(Me)Ph	240-243		3.36
47[c]	PhN(Me)S(C=O)N(Me)Ph	71-72		3.27 (N—S) 3.38 (N—C)
48[c]		75-76 [115 (1)]		3.45
49[c]	$CCl_3SS(C=O)N(Me)Ph$	54-55		3.41
50	$CCl_3SN(Me)Ph$	*d*		3.71
51a[d,e]	MeO(C=S)N(Me)Ph	[81-89 (0.5)]	3.97	3.59
52	Cl(C=S)N(Me)Ph	34-35		3.74
53a[e]	MeS(C=O)N(Me)Ph	44-45	2.26	3.33
57a[c,e]	MeO(C=O)SS(C=O)N(Me)Ph	84-85	3.88	3.38
58a[d,e]	MeO(C=O)SN(Me)Ph	[60 (0.1)]	3.80	3.41
59a[e]	MeS(C=O)SS(C=O)N(Me)Ph	80-81	2.43	3.39
60a[e]	MeSS(C=O)N(Me)Ph	77	2.40	3.38
66a[e]	MeSN(Me)Ph	*d*	2.27	3.31
67a[e]	MeO(C=O)N(Me)Ph	40-42	3.70	3.30
68a[d,e]	MeS(C=S)N(Me)Ph	81-82	2.54	3.77
69[d]		88-90		3.86
70[d]	Cl(C=O)N(Me)Ph	87-89		3.39
71	PhN(Me)(C=O)N(Me)Ph	122		3.17

[a] Excerpted from Table IX in the supplementary material, which lists 29 compounds, literature melting points or boiling points or those that are known, elemental analyses, full NMR, and HPLC data. Unless specified otherwise, derivatives were obtained in nominally quantitative (98% ± 3%) isolated yields prior to distillation or recrystallization (products already usually pure by NMR and HPLC) by reaction at <5 °C of monofunctional acid chlorides or sulfenyl chlorides (1 M in $CHCl_3$) with slightly more than one volume of *N*-methylaniline (2 M in $CHCl_3$), as further detailed in supplementary material experimental section. [b] In $CDCl_3$. Shifts in aromatic region provided in Table IX. [c] Synthesis of this compound described in text Experimental Section. [d] Synthesis of this compound or further information of interest described in supplementary material experimental section or Table IX. [e] The corresponding ethyl compound (series b) was also made and is reported in Table IX.

SO_2Cl_2); (4) mode of solvent removal; and (5) temperature and pressure of distillation.[18b,19] Even after optimizing these variables, the crude **8** that was obtained (pure by NMR) could be shown by elemental analysis, density, and iodide titration data to be contaminated with 5–20% (w/w) of sulfur monochloride;[21] more formed later in the distillation. Also, within a day of standing even at −20 °C, new NMR peaks appeared which were tentatively assigned[13] to the tetrachloro tetrasulfur structure $ROCCl_2SSSSCCl_2OR$ arising from 1:2 addition of S_2Cl_2 to **8** (analogy to other chemistry reported later). Hence, to ensure *pure* **8**, it was necessary to quench the S_2Cl_2 prior to its possible reaction with **8**, which was successfully done in both the methyl and ethyl systems by adding a mixture of pentenes immediately to the product of the initial "cracking" distillation. An alternative approach for pure **8** was to specifically degrade S_2Cl_2 (and its 1:2 adduct with **8**) by iodide reduction.[22] For solubility reasons, the reduction was carried out with tetrabutylammonium iodide as a phase-transfer catalyst and with aqueous sodium thiosulfate for regeneration. Ethoxythiocarbonyl chloride (**8b**) was purified in 70% yield by this technique, but when the same chemistry was applied to the methyl system, transformations shown in Scheme II took place instead.

Synthesis and Chemistry of Bis(chlorocarbonyl)disulfane (1). Although the pure ((alkoxydichloromethyl)dithio)carbonyl chlorides (**10**) could be carried forward to **1**, it proved adequate to promote loss of alkyl chloride directly on reaction mixtures in which **10** had been generated in situ from **8a** or **8b** plus **9**. The adduct formed at 100 °C directly underwent further thermolysis (Scheme I) although some of **10** reverted to **9** plus **8**, which latter in turn either decomposed to alkyl chloride plus COS or rearranged to its isomer **11**. Therefore, isolated yields of **1** by the addition procedure were no better than ~45%. The *best* yields[23] of **1**, overall 75–80% after two vacuum

(17) Barany, G. *Tetrahedron Lett.* **1983**, in press.

(18) (a) Preparations of **8a** (methyl series) contained a 5–15% contaminant which was isolated by preparative GC (5% SE-30 on Chromosorb W, 58 °C) and fully characterized (IR, NMR, MS, *N*-methylaniline assay, alternate synthesis according to ref 2 and 9) to be **12a**. Preparations of **8b** (ethyl series) were generally obtained quite free of **12b**. (b) However, both in the methyl and ethyl series, the vacuum deteriorated toward the end of the "cracking" distillations, and the small after runs contained considerable **12**; conversely even for preparations using **14a** contaminated with **15a**, it was possible to collect the initial-boiling fractions which were quite free of **12a**. In summary, given pure starting **14** (ref 15 and 20) and terminating the "cracking" distillation at the proper point, it was possible to obtain crude **8** which was a single proton-containing component by NMR, and which was suitable for direct use in subsequent transformations.

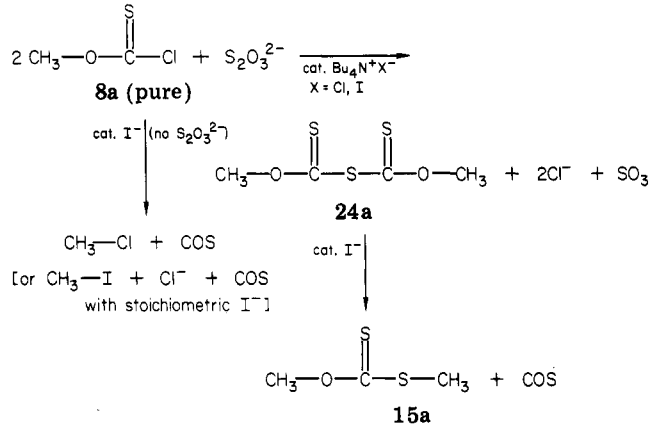
(19) Distillation at atmospheric pressure, as is done in ref 7e, was found to lead to 5–10% rearrangement of **8** to **11**.

(20) An illustration of the usefulness of this simple expedient in the *ethyl* series follows: A certain preparation of **14b** that was pure by NMR and gave elemental analyses completely in accord with theory was converted to **8b** by the standard procedures. Isolated **8b** from this "jinxed" **14b** was contaminated with diethyl carbonate (**27b**), identification of which is explained in the supplementary material. As judged by NMR, **27b** was already present in the crude chlorination mixture, and the amount isolated was reproducibly 12% (moles of **27b** formed per moles of starting **14b**). The same "jinxed" batch, when washed with water, no longer gave *any* **27b** to contaminate the **8b** formed in the next step.

(21) Review on S_2Cl_2 chemistry: Wiles, L. A.; Ariyan, Z. S. *Chem. Ind. (London)* **1962**, 2102–2105.

(22) Compare to an aqueous analytical method for iodide reduction of S_2Cl_2: Böhme, H.; Schneider, E. *Ber. Dtsch. Chem. Ges.* **1943**, *76*, 483–486.

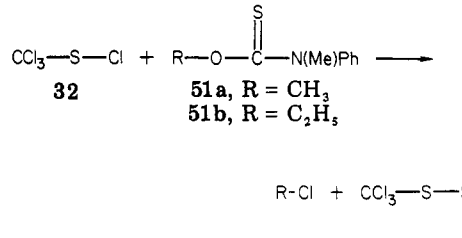
Scheme II



distillations, were obtained when crude **10** generated at 25 °C was cautiously treated with 0.2% (w/w) anhydrous $FeCl_3$.[24]

Alcohols reacted rapidly with **1** to give 90–95% yields of bis(alkoxycarbonyl)disulfanes (**43**), identical in all regards with material prepared by iodine oxidation of Bender's salts (**44**).[10e,25] Diisopropylamine with **1** gave bis(*N*,*N*-diisopropylcarbamoyl)disulfane (**45**), a new compound, and reaction[3a] of **1** with excess *N*-methylaniline gave a quantitative yield of bis(*N*-methyl-*N*-phenylcarbamoyl)disulfane (**46**). Under the same conditions, the quantitative product of *N*-methylaniline with **9** was *N*,*N*′-dimethyl-*N*,*N*′-diphenylcarbamoylsulfenamide (**47**), readily distinguishable from **46** by ^1H NMR and HPLC. The order of addition is critical, because *N*-methylaniline added to **9** gave primarily[10f] 3-methyl-2(3*H*)-benzothiazolone (**48**)[26] [see Table II for structures of *N*-methylanilides].

Synthesis and Chemistry of ((Trichloromethyl)dithio)carbonyl Chloride (2). Contrary to a result[3b] with the fluoro analogue, **2** could not be obtained from **9** plus thiophosgene (no reaction with heat (100 °C, 87 h) or light ($h\nu$ at 254 nm, 25 °C, 14 h)). The successful synthesis involved reaction of trichloromethanesulfenyl chloride (**32**) with **8** at 120 °C. The sluggishness of the initial reaction, 15–20 times slower than the reaction of **8** plus **9** to give **10** (Scheme I), explained why the trichloromethyl analogue of **10** would not accumulate in sufficient quantity for spectroscopic detection. Another consequence was that the decomposition (under all circumstances) or isomerization (particularly pronounced if **8** was contaminated with S_2Cl_2) of the starting material **8** represented a major competing pathway. Thus, although **8** was entirely consumed, the crude product mixture contained only about 30% of desired **2** as well as at least 50% of unreacted **32**. The physical properties of **2** and **32** were sufficiently similar that distillation failed to give desired product entirely free of starting material. Therefore, **32** was first reduced[27] with iodide to the much lower boiling thiophosgene. Subsequently, pure **2** was obtained in an overall yield of 21%; it gave quantitatively with *N*-methylaniline the expected trichloromethyl(*N*-methyl-*N*-phenylcarbamoyl)disulfane (**49**) free of *N*-methyl-*N*-phenyl-1,1,1-trichloromethanesulfenamide (**50**).[28] The carbamoyl disulfide **49** obtained this way was indistinguishable from material obtained by a Harris reaction[10a] (eq 1). The starting **51**, previously



described[29] from *N*-methyl-*N*-phenyl(thiocarbamoyl) chloride (**52**) and alcoholic alkoxide, was much better obtained from the quantitative reaction of *N*-methylaniline with **8**. Any **11** contaminating **8** was reflected by a corresponding amount of the isomeric *S*-alkyl *N*-methyl-*N*-phenylthiocarbamate (**53**) contaminating **51**. The isomer **53** also arose in low levels (0.5–4%), as quantitated by HPLC, upon various treatments of **51** including distillation and conversions via eq 1.

Synthesis of Additional Dithiocarbonyl Compounds. Other than **10**, the only reasonably stable (alkoxydichloromethyl)disulfanyl adducts encountered were the (alkoxycarbonyl)(methoxydichloromethyl)disulfanes (**54**), readily obtained from **8a** and alkoxycarbonylsulfenyl chlorides (**35**)[10f,30], or from methoxydichloromethanesulfenyl chloride (**33a**)[31a,d] and **19**, as well as ((methylthio)carbonyl)(methoxydichloromethyl)disulfane (**55**) from **33a** and **15a**.

The adducts **54** could be distilled at 0.07 mm, but at inferior vacuums partial loss of alkyl chloride to **3** or **4** occurred. Distillation at atmospheric pressure led to further decomposition: **54a** gave 65% of **3** and 29% of **35a** (loss of COS from **3**), while **54b** gave 82% of **35b**, 4% of **11a**, and a sizeable residue consisting primarily of **43b**. Treatment of **54** with $FeCl_3$ gave **3** and **4** in fair yields but the best preparations of **3** and **4** involved the smooth and rapid reaction of **9** with **19**. In this latter case, the presumed (dialkoxychloromethyl)(chlorocarbonyl)disulfane intermediate adduct could not be spectroscopically detected because of facile alkyl chloride loss.

The ((alkoxycarbonyl)dithio)carbonyl chlorides **3** and **4** reacted rapidly with the opposite alcohol to give the mixed compound (ethoxycarbonyl)(methoxycarbonyl)disulfane (**56**), pure by HPLC. This route to **56** was slightly superior to a synthesis involving **35a** plus **19b**, where the

(23) If all aspects of the chemistry to prepare **1** are taken into account, including ease and efficiency of preparation of starting materials **8** and (one step earlier) **14**, rates of addition of **9** to **8**, rates of loss of alkyl chloride from **10**, and physical properties of potential contaminating byproducts, one is led to conclude that so long as optimal protocols of this paper are used, the methyl (**a**) and ethyl (**b**) series provide equally good results.

(24) Treatment with 0.2% (w/w) $FeCl_3$ was overnight. It must be emphasized that whereas 2% (w/w) or even 0.5% (w/w) of $FeCl_3$ catalyzed a vigorous alkyl chloride release that was complete within minutes, the Lewis acid also facilitated breakdown of **1** to COS plus **9**. This phenomenon was manifested, more seriously on larger scales, by the inability to hold a vacuum better than 0.5 mm and by the identification of 50% or more of **9** in the distillate fraction supposedly (on basis of boiling range) containing only **1**.

(25) (a) Bender, C. *Liebigs Ann. Chem.* **1868**, *148*, 137–143. (b) Winter, G.; Woods, R. *Sep. Sci.* **1973**, *8*, 261–267; *Chem. Abstr.* **1973**, *78*, 140764n.

(26) (a) Besthorn, E. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1519–1526; (b) Mills, W. H.; Clark, L. M.; Aeschlimann, J. A. *J. Chem. Soc.* **1923**, *123*, 2353–2362; (c) Hunter, R. F. *Ibid.* **1930**, 125–147. (d) Kiprianov, A. I.; Pazenko, Z. N. *Zh. Obshch. Khim.* **1949**, *19*, 1523–1528; *Chem. Abstr.* **1950**, *44*, 3487g. (e) Fife, T. H.; Hutchins, J. E.; Wang, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 5878–5882.

(27) Perret, A.; Perrot, R. *Bull. Soc. Chim. Fr.* **1934**, [5], *1*, 1531–1548; *Chem. Abstr.* **1935**, *29*, 2505.

(28) (a) Argyle, C. S.; Dyson, G. M. *J. Chem. Soc.* **1937**, *2*, 1629–1634. (b) Horak, J.; Krajkarova, K. *Collect. Czech. Chem. Commun.* **1967**, *32*, 1619–1621; *Chem. Abstr.* **1967**, *67*, 10889u.

(29) Wheeler, H. L.; Dustin, G. K. *Am. Chem. J.* **1900**, *24*, 424–444.

(30) (a) Weiss, W.; Mühlbauer, E. German Patent 1 568 632, March 19, 1970. (b) Field, L.; Ravichandran, R. *J. Org. Chem.* **1979**, *44*, 2624–2629.

(31) (a) Douglass, I. B.; Osborne, C. E. *J. Am. Chem. Soc.* **1953**, *75*, 4582–4583. (b) Douglass, I. B.; Marascia, F. J. *Ibid.* **1955**, *77*, 1899–1900. (c) Douglass, I. B.; Warner, G. H. *Ibid.* **1956**, *78*, 6070–6071. (d) This work, from **8a** plus SO_2Cl_2.

expected **56** was contaminated with the symmetrical disproportionation products **43a** (2%) and **43b** (6%). Similar to the result in the trichloromethyl series, **3** and **4** gave carbamoyl disulfides (**57**) with *N*-methylaniline which were identical with the products of an alternate synthesis (cf. eq 1, ref 10e,f) and different from the *N*-methyl-*N*-phenylalkoxycarbonylsulfenamides (**58**) derived from **35**.

Reaction of **9** with **15** or **16** gave directly the (((alkylthio)carbonyl)dithio)carbonyl chlorides (**5**, **6**) without any intermediate adduct. A major difficulty was the ready tendency of **5** or **6** upon distillation to lose COS to give respectively **12a** or **12b**. However, the crude products (**5**, **6**) gave ((alkylthio)carbonyl)(*N*-methyl-*N*-phenylcarbamoyl)disulfanes (**59**) as the principal *N*-methylaniline derivatives, readily distinguishable from the alkyl(*N*-methyl-*N*-phenylcarbamoyl)disulfanes (**60**) derived quantitatively from **12**. The reaction of **5** with methanol gave (methoxycarbonyl)((methylthio)carbonyl)disulfane (**61**), also available[10f] from **15a** plus **35a**.

S-(trichloromethyl)sulfenyl *O*-alkyl thiocarbonates (**62**) were best prepared from **32** and **19** but were also accessible by reaction under vigorous conditions of thiophosgene with **35** or from the rapid reaction of **2** with the appropriate alcohol. Relatedly, *S*-alkylsulfenyl *O*-alkyl thiocarbonates (**36**, **37**), known[32] from reaction of thiols with **35**, were efficiently prepared from **12** plus alcohols or alkanesulfenyl chlorides (**38**)[33] plus **19**. Finally, *S*-alkyl *S*-alkylsulfenyl dithiocarbonates (**63**; note both R groups are identical) were obtained[10b,c] from **38a** or **38b** with **15** or **16**, respectively.

Spectral Characterization of Compounds. Supporting evidence for key structures, based on elemental analyses, mass spectra, and IR spectra, are recorded with the supplementary material. ^{13}C NMR data, entirely in accord with all proposed new structures, are summarized in Table III. Assignments of resonances were verified by comparisons of homologous compounds. Also, a novel way was developed to apply peak heights in the ^{13}C spectra for the semiquantitative analysis of a variety of mixtures (note *c* to Table III).

Quantitative Assay of Acid Chlorides and Sulfenyl Chlorides with *N*-Methylaniline. A wide assortment of compounds containing one or two acid chloride and/or sulfenyl chloride functionalities reacted smoothly with excess *N*-methylaniline to provide the appropriate derivatives in nominally quantitative yields (Table II). Many of these *N*-methylanilides were indefinitely stable compounds which were obtained analytically pure by crystallization or distillation. Their characterization by elemental analysis, ^1H NMR, mass spectrometry, IR, UV, and HPLC purity (supplementary material) was strong evidence for structures of the parent compounds.

It was often necessary in this work to determine the relative amounts of several components in reaction mixtures or in preparations of compounds with limited stabilities. A semiquantitative ^{13}C NMR technique was worked out (previous section), but more convenient, precise, and efficient was the analytical-scale reaction with excess *N*-methylaniline followed up by ^1H NMR and HPLC. Control experiments showed that this assay reconstructed the initial compositions of acid chlorides and sulfenyl chlorides in the mixture that was analyzed, and was linear over a two order of magnitude concentration range. Conversion to the *N*-methylanilides was quantitative (judged by internal standards) and rapid; only in two cases, conversion of **31** to **68** ($t_{1/2} \sim 8.9$ min) and **70** to **71** ($t_{1/2} \sim 17$ h), was the reaction not complete in 5 min. Further advantages were the *inertness* at 25 °C of the *N*-methylanilides, once formed, to further cleavage with excess *N*-methylaniline, as well as the *specificity* of this assay, in that the various isomers of carbonates, thiocarbonates, dithiocarbonates, *S*-sulfenyl thiocarbonates and dithiocarbonates, and bis(alkoxycarbonyl) and bis(alkoxythiocarbonyl) sulfides and disulfanes reacted with *N*-methylaniline either very slowly or usually not at all.

Kinetics, Mechanism, and Stereochemistry of the Methods for Dithiocarbonyl Functionality Elaboration. Some relevant rate data are presented in Table IV. The second-order rate constants for the addition of sulfenyl

Table III. Summary of Carbon-13 Nuclear Magnetic Resonance Data[a]

carbon (italic)	chemical shift,[b] ppm	Ψ-value[c] ± std dev	number compds
*C*H$_3$CH$_2$-	12-15	16.3 ± 2.7	49
*C*H$_3$S-		14.7 ± 3.5	24
MeS(C=O)-	12-16	13.7 ± 4.9	9
MeS(C=S)-	18-24	14.8 ± 1.9	4
MeSS-	22-24	16.5 ± 1.5	9
-*C*H$_2$S— of Et		17.1 ± 3.6	21
EtS(C=O)-	24-28	16.0 ± 2.5	7
EtS(C=S)-	30-35	18.6 ± 5.3	4
EtSS—	32-33	18.6 ± 2.6	8
*C*H$_3$O-		16.5 ± 4.9	33
MeO(C=O)S-	54-56	14.5 ± 3.3	15
MeO*C*Cl$_2$-	57	20.6 ± 8.5	6
MeO(C=S)-	59-63	17.0 ± 2.8	11
-*C*H$_2$O- of Et		19.4 ± 3.0	28
EtO(C=O)-	63-68	18.8 ± 3.0	15
EtO*C*Cl$_2$-	67.5	20.4 ± 4.6	2
EtO(C=S)-	69-74	20.0 ± 2.9	11
*C*Cl$_3$S-	98 ± 0.5	3.0 ± 0.6	5
*C*Cl$_3$O-	114	3.2	1
-O*C*Cl$_2$S-	115-117	3.6 ± 0.8	7
-O(*C*=O)Cl	150-151	5.0 ± 0.5	2
-O(*C*=O)O-	155-156	5.0 ± 0.5	2
-S(*C*=O)Cl	161-166	3.2 ± 0.5	13
-O(*C*=O)S-	162-173	4.4 ± 0.8	27
-S(*C*=O)S-	184-192	4.0 ± 0.7	9
-O(*C*=S)Cl	186-187	3.8 ± 0.2	2
-O(*C*=S)O-	195-197	4.9 ± 0.9	3
-S(*C*=S)Cl	197-198	4.1 ± 0.2	2
-O(*C*=S)S-	203-216	4.0 ± 0.5	16
-S(*C*=S)S-	224-225	4.8 ± 0.4	2

[a] Table XI in supplementary material contains all raw data. [b] Chemical shifts are normalized to $CDCl_3$ 77.0 ppm (J = 32 Hz); cf. MeCl = 25.8 ppm. [c] Two dimensionless quantities, Φ and Ψ, were defined as follows:

$$\Phi(\mathrm{Pk}) = [\mathrm{Ht(Pk)/Wt(compd)}]/[\mathrm{Ht(CDCl_3\ middle\ Pk)/Wt(CDCl_3)}]$$

$$\Psi(\mathrm{Pk}) = [\Phi(\mathrm{Pk})/\Delta][M_r(\mathrm{compd})/M_r(\mathrm{CDCl_3})]$$

where Δ is the degeneracy of the peak (Δ = 1 for most compounds, Δ = 2 if compound is symmetrical). Note that the spectra were recorded in $CDCl_3$ which effectively served as an internal standard, and that Ψ($CDCl_3$ at 77.0 ppm) = 1.0. Values of Ψ reproducibly reflect the nature of the carbon resonance and the formula: Wt%(compd in mix) = $100[\Phi(\mathrm{Pk})_{\mathrm{apparent}}/\Phi(\mathrm{Pk})_{\mathrm{pure}}]$ with $\Phi(\mathrm{Pk})_{\mathrm{apparent}}$ calculated as before with Wt(mix) substituted for Wt(compd), was used for semi-quantitative analysis of mixtures (estimated accuracy ±20%). Among the mixtures effectively analyzed by this technique were: (1) 1 contaminated with 9, 11, or 12; (2) alkoxydichloromethyl compounds (**10**, **33**, **54**) for correxponding carbonyl-containing compounds having lost alkyl chloride (1, 9, 3/4); (3) partial hydrolysates of 7 to 2 and 1.

(32) (a) Brois, S. J.; Pilot, J. F.; Barnum, H. W. *J. Am. Chem. Soc.* **1970**, *92*, 7629–7631. (b) Smith, D. J.; Maggio, E. T.; Kenyon, G. L. *Biochemistry* **1975**, *14*, 766–771. (c) Bendall, M. R.; Lowe, G. *Eur. J. Biochem.* **1976**, *65*, 481–491.

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Table IV. Representative Rates of Reactions[a]

T, °C	sulfenyl chloride	thiocarbonyl	product	k, L mol^{-1} s^{-1}
		A. addition of -S-Cl to >C=S		
25	$CH_3O(C{=}O)SCl$	$CH_3O(C{=}S)OCH_3$	$CH_3O(C{=}O)SS(C{=}O)OCH_3$	0.2
25	$CH_3O(C{=}O)SCl$	$CH_3O(C{=}S)SCH_3$	$CH_3O(C{=}O)SS(C{=}O)SCH_3$	0.1
25	CH_3OCCl_2SCl	$CH_3O(C{=}S)SCH_3$	$CH_3OCCl_2SS(C{=}O)SCH_3$	2×10^{-2}
25	CH_3OCCl_2SCl	$CH_3O(C{=}S)OCH_3$	$CH_3OCCl_2SS(C{=}O)OCH_3$	8×10^{-3}
25	$Cl(C{=}O)SCl$	$CH_3O(C{=}S)OCH_3$	$Cl(C{=}O)SS(C{=}O)OCH_3$	1×10^{-2}
25	$Cl(C{=}O)SCl$	$CH_3O(C{=}S)SCH_3$	$Cl(C{=}O)SS(C{=}O)SCH_3$	2×10^{-3}
25	CCl_3SCl	$CH_3O(C{=}S)OCH_3$	$CCl_3SS(C{=}O)OCH_3$	2×10^{-3}
25	$CH_3O(C{=}O)SCl$	$CH_3O(C{=}S)Cl$	$CH_3O(C{=}O)SSCCl_2OCH_3$	3×10^{-4}
25	$Cl(C{=}O)SCl$	$CH_3O(C{=}S)Cl$	$Cl(C{=}O)SSCCl_2OCH_3$	2×10^{-6}
62	$Cl(C{=}O)SCl$	$CH_3O(C{=}S)Cl$	$Cl(C{=}O)SSCCl_2OCH_3$	3×10^{-5}
62	$Cl(C{=}O)SCl$	$C_2H_5O(C{=}S)Cl$	$Cl(C{=}O)SSCCl_2OC_2H_5$	6×10^{-5}
62	CCl_3SCl	$CH_3O(C{=}S)Cl$	$CCl_3SS(C{=}O)Cl$[b]	3×10^{-6}
62	CCl_3SCl	$C_2H_5O(C{=}S)Cl$	$CCl_3SS(C{=}O)Cl$[b]	1×10^{-5}
62	$CH_3O(C{=}O)SCl$	$Cl(C{=}S)Cl$	$CH_3O(C{=}O)SSCCl_3$	8×10^{-7}
62	$C_2H_5O(C{=}O)SCl$	$Cl(C{=}S)Cl$	$C_2H_5O(C{=}O)SSCCl_3$	6×10^{-7}

T, °C	substrate	product	k, s^{-1}
	B. loss of alkyl halide		
25	$CH_3OCCl_2SS(C{=}O)OCH_3$	$Cl(C{=}O)SS(C{=}O)OCH_3$[c]	6×10^{-6}
62	$CH_3OCCl_2SS(C{=}O)OCH_3$	$Cl(C{=}O)SS(C{=}O)OCH_3$[c]	2×10^{-4}
62	CH_3OCCl_2SCl	$Cl(C{=}O)SCl$[c]	3×10^{-5}
62	$C_2H_5OCCl_2SCl$	$Cl(C{=}O)SCl$[c]	8×10^{-5}
62	$CH_3OCCl_2SS(C{=}O)Cl$	$Cl(C{=}O)SS(C{=}O)Cl$[b]	5×10^{-6}
62	$C_2H_5OCCl_2SS(C{=}O)Cl$	$Cl(C{=}O)SS(C{=}O)Cl$[b]	2×10^{-5}
	C. loss of carbonyl sulfide		
62	$CH_3O(C{=}S)Cl$	CH_3Cl	6×10^{-7}
62	$C_2H_5O(C{=}S)Cl$	C_2H_5Cl	3×10^{-6}
62	$CH_3S(C{=}O)SS(C{=}O)Cl$	$CH_3SS(C{=}O)Cl$	2×10^{-7}
62	$CH_3O(C{=}O)SS(C{=}O)Cl$	$CH_3O(C{=}O)SCl$	6×10^{-9}
62	$Cl(C{=}O)SS(C{=}O)Cl$	$Cl(C{=}O)SCl$	no rxn[d]

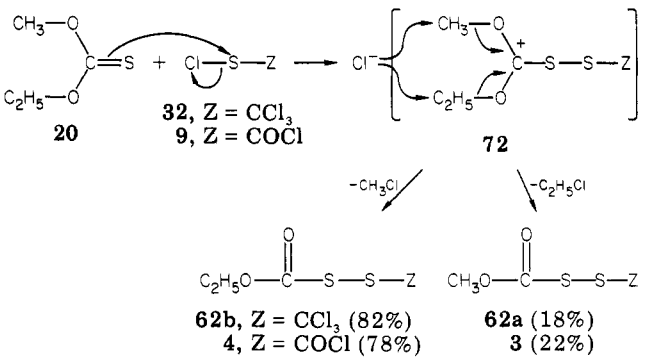
[a] Reactants were approximately 1.0 M in $CDCl_3$ with toluene (0.05–1.0 M) as an internal standard and were followed principally by ^1H NMR with end points and/or certain time points evaluated by the *N*-methylaniline assay. Reactions in category A were second order through several half-lives and were pseudo first order at the outset. Very fast rates were measured with reactants at 0.1 M or less. Reactions in category B were first order and followed to completion. The slower rates in category C were estimated based on relatively low conversion to product after one to three weeks. [b] Final yield 30–50% because of several side reactions more fully discussed in text. [c] Final yield 75–95% with indicated product essentially exclusively formed. [d] No (<0.2%) ClCOSCl formed after 207 h. All (100% ± 2%) starting material still present by *N*-methylaniline assay.

chlorides to thiocarbonyl compounds vary over seven orders of magnitude or more. Indeed, alkanesulfenyl chlorides RSCl (**38**) were so reactive that measurable rates could not be obtained and hence are omitted from the Table IV. Beyond that, the order of reactivity is RO(C=O)SCl (**35**) > $ROCCl_2SCl$ (**33**) > Cl(C=O)SCl (**9**) > CCl_3SCl (**32**). Regarding the thiocarbonyl component, the order of reactivity is $(RO)_2C{=}S$ (**19**) > RO(C=S)SR′ (**15**, **16**) ≫ RO(C=S)Cl (**8**) ≫ $Cl_2C{=}S$.

(Alkoxydichloromethyl)sulfenyl or disulfanyl derivatives lose alkyl chlorides to generate the corresponding carbonyl group containing compounds; lability is in the sequence $ROCCl_2SS(C{=}O)OR'$ > $ROCCl_2SCl$ > $ROCCl_2SS(C{=}O)Cl$. Under *thermolytic* conditions, ethyl chloride was lost three to four times faster than methyl chloride. *In contrast*, adducts such as **72** (Scheme III) were about four times more likely to lose methyl chloride than ethyl chloride. Similarly, iodomethane-catalyzed rearrangement of **20**, which also involves an addition–elimination mechanism in the addition of electrophiles across a thiocarbonyl, gave **29a** (loss of MeI) and **28a** (loss of EtI) in an 8:1 ratio.

Finally, the stereochemistry of the sequence for synthesis of the dithiocarbonyl functionality was examined (Scheme IV).[34] (*R*)-2-Octanol (86% optical purity) was converted

Scheme III

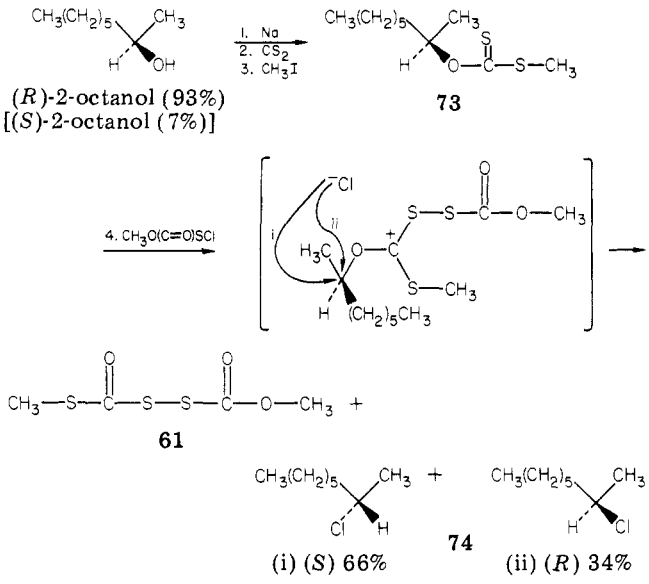


to (*R*)-*O*-2-octyl *S*-methyl dithiocarbonate (**73**), which reacted with **35a** to yield **61** plus 2-chlorooctane (**74**) with $[\alpha]^{25}_D$ +12.09°, corresponding to a mixture of (*S*)-2-chlorooctane and (*R*)-2-chlorooctane in a ratio of 66:34 (lit.[35] $[\alpha]^{20}_D$ (*S*)-2-chlorooctane +37.3°), indicating a 38% inversion of configuration (62% racemization). Therefore, it seems plausible to suggest a transition state for alkyl chloride formation that has some S_N2 character; also, the chlorine atom of the alkoxychloromethyl adduct must be sufficiently dissociated to allow considerable backside attack at the alkyl group.

(34) After our experiments on this topic were completed, we became aware of a closely related series of studies giving conclusions in accord with our own; see: Douglass, I. B.; Norton, R. V.; Cocanour, P. M.; Koop, D. A.; Kee, M. L. *J. Org. Chem.* **1970**, *35*, 2131–2136.

(35) Filippo, J. S.; Silbermann, J. *J. Am. Chem. Soc.* **1981**, *103*, 5588–5590.

Scheme IV



Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. IR spectra were obtained on 0.1 M solutions in $CDCl_3$ with a Perkin-Elmer 297 instrument, and NMR spectra were observed for $CDCl_3$ solutions with a Varian HFT80/CFT20 spectrometer at 80 MHz for protons and 20 MHz for ^{13}C. UV spectra were measured in 95% EtOH with a Beckman Model 35 recording spectrophotometer, and optical rotations were determined on neat samples in a Perkin-Elmer 241 spectropolarimeter. HPLC was carried out on a Beckman-Altex Model 334 system consisting of a 421 CRT controller, two 112 pumps, a 165 variable-wavelength detector, and an Ultrasphere-ODS column (4.6 mm × 25 cm) together with a Hewlett-Packard 3390A reporting integrator. Mass spectra were obtained on a Kratos/AEI MS-30, and elemental analyses were performed by MHW Laboratories, Phoenix, AZ.[36]

Materials. Unless indicated otherwise, solvents and chemicals were reagent grade and used without further purification. Suppliers were Aldrich, Eastman Kodak, Wateree Chemical (Camden, SC), and Fairfield Chemical (Blythewood, SC).

A number of the chloro compounds prepared, particularly if not pure, developed pressure after prolonged storage at 25 °C, so caution must be exercised when handling these. The following materials were best stored at −20 °C, where they were entirely stable for at least a year: **3**, **4**, **5**, **6**, **8**, **10**, **12**, **14a**, **33**, **35**, and **42**. The following had limited stability even at −20 °C: **25**, **26**, **38**, **54**, and **55**. Reported compounds not just listed were stable at 25 °C. All corrosive materials were kept in screw-cap tubes with Teflon-lined caps. Elemental sulfur residues, when formed, were readily dissolved in CS_2.

Iodide Titration. The organic sample (50 to 200 mg) was diluted with 1 mL of CH_2Cl_2, and then 1 mL of 0.5 M tetrabutylammonium iodide in CH_2Cl_2 was added. An aqueous solution of 1.0 N $Na_2S_2O_3$ was added 25 μL at a time with agitation until the iodine color was fully discharged, and the endpoint was checked by adding a few more drops of iodide solution. The wt % of S_2Cl_2 was calculated as follows: (mL of 1 N $Na_2S_2O_3/2$) × $M_{r(S_2Cl_2)}$ × 100/wt of sample in mg, or mL of $Na_2S_2O_3$ × 6,750/mg of sample. Controls established the linearity of this organic titration procedure, which appeared to be better suited than the literature[22] aqueous method for convenient examination of the types of samples encountered in this work.

Analytical *N*-Methylaniline Assay. A test mixture (approximately 0.5 N for functional groups) in $CDCl_3$ was quickly added at 0 °C with vigorous agitation to an equal volume of a 2 M solution of *N*-methylaniline in $CDCl_3$. After 5 min at 25 °C, reactions were first quenched and then washed twice with 1 N aqueous HCl; the organic phase was then taken for ^1H NMR and an aliquot was also diluted into MeCN for HPLC analysis. To demonstrate the speed of the method, several reaction mixtures were quenched 25 s after mixing at 0 °C. Compound numbers and the ratio of unreacted compound:*N*-methylaniline derivative follow: **3**, <0.01; **8a**, 0.8; **8b**, 2.3; **11a**, 0.11; **11b**, 1.25; **35a**, <0.01; **35b**, <0.01.

Bis(chlorocarbonyl)disulfane (1). Of four procedures to be described, A, B, and C show aspects of the chemistry, whereas D is preferred for preparative work.

A. A mixture of **9** (14 mL, 168 mmol), purified **8a** (5 mL, 58 mmol), and purified **8b** (10 mL, 95 mmol) with toluene (5 mL, 47 mmol, internal standard) was heated at 100 °C with monitoring of the reaction by ^1H NMR. Consumption of **8a** and **8b** was with $t_{1/2}$ of 16 min and 12 min, respectively, and disappearance of **10a** and **10b** was with $t_{1/2}$ of 230 min and 50 min. After 10 h, the *N*-methylaniline assay revealed 79 mmol of **1** (52%), 68 mmol of **9**, 1.2 mmol of **11a** (2% isomerization of **8a**), and 7.5 mmol of **11b** (8% isomerization of **8b**). In similar experiments with unpurified **8** (i.e., NMR pure but contaminated with S_2Cl_2), the amount of **1** formed was comparable but the amounts of isomers **11** were 10–30%. Distillation through an 8-in. Vigreux column at 40 mm gave 13.3 g (70 mmol, 46% overall) of **1** pure by the *N*-methylaniline assay. Pure **1** was recovered in 80–95% yield upon redistillation at 20 mm or below. A sample of **1** thus prepared[1] was unchanged after 7 years at 25 °C.

B. Pure **10a** *or* **10b** plus toluene (4:1, v/v) was heated at 100 °C. In the methyl case, loss of MeCl proceeded with $t_{1/2}$ = 11.5 h, or three times slower than when **10a** was generated in situ; also, up to 9% of **8a** was formed. Products after 65 h (*N*-methylaniline assay) were **1** (59%), **9** (11%), and **11a** (2%), while after 225 h, *no* **1** and only **9** (25%) and **11a** (4%) were present. Corresponding data in the ethyl case were: $t_{1/2}$ = 2.6 h, up to 12% **8b**; after 15 h, **1** (50%), **9** (12%), and **11b** (3%) were formed; after 114 h, **1** (2%), **9** (34%), and **11b** (4%) were formed. As a control, pure **1** plus toluene (1:5, v/v) was unchanged after 200 h at 100 °C.

C. Pure **10a** (6.9 g, 29 mmol) was treated with $FeCl_3$ (35 mg, 0.5% w/w). The temperature rose spontaneously to 40 °C as MeCl evolved vigorously. The crude product (5.0 g) was short-path distilled without fractionation to give 4.7 g (85%) of a mixture of **1** (93%) and **9** (7%) with no **8a** or **11a** (*N*-methylaniline assay).

D (Best). Crude **10a** *or* **10b** generated in situ at 25 °C on a 0.2–0.5-mol scale from **8** plus **9** (1.1 equiv) (5 days series **a**, 24 h series **b**) was chilled in ice, and $FeCl_3$ (total 0.2% w/w) was carefully added at less than 20 °C. With each few mg of $FeCl_3$, gas evolved, but the theoretical weight loss of alkyl chloride required overnight standing of the open flask at 25 °C. Most of the excess **9** was removed at aspirator pressure, and then short-path distillation (oil pump vacuum, dry ice cooling of receiving flask, bath 80 °C) gave **1** in 80% yield, bp 44–46 °C (0.2 mm),[24] 97% purity (*N*-methylaniline assay). Foreruns from this distillation, collected before heating the apparatus, contained **1** and **9**, and an amount of **11** corresponding to an overall yield of 2% (both series **a** and **b**). Redistillation through a 4-in. Vigreux column gave pure colorless **1**: bp 84 °C (20 mm) [lit.[3a] bp 82 °C (19 mm)]; ρ = 1.60; overall yield 76%. Anal. MS.

((Trichloromethyl)dithio)carbonyl Chloride (2). A mixture of **32** (50 mL, 0.45 mol), pure **8a** (43 mL, 0.5 mol), and toluene (8 mL, 75 mmol) was heated at 120 °C for 24 h. An *N*-methylaniline assay showed 20 mmol of **11a** (4% of **8a**) and 0.14 mol of **2** (32% based on **32**). The yield of **2** in the crude reaction product was similar when **8b** was used; when either **8a** or **8b** was contaminated with S_2Cl_2, the yields of **2** were comparable but the yields of the isomers **11a** or **11b** were 20–25%. Because in pilot studies desired **2** was contaminated with unreacted **32** even after two distillations, the crude reaction product was dissolved in CH_2Cl_2 (600 mL) and shaken briefly with aqueous KI (4 M, 225 mL, 0.9 mol). After washing with aqueous $Na_2S_2O_3$ (1 M, 900 mL, 0.9 mol) to remove I_2, the red (from $CSCl_2$) organic phase was dried ($MgSO_4$) and concentrated (60 g). Two distillations, bp 55 °C (0.6 mm) and bp 91 °C (10 mm) [lit.[3a] bp 92 °C (10 mm); lit.[3b] bp 40 °C (0.01 mm)], gave the very pale yellow **2** (23.4 g, 21%), ρ = 1.69. Anal. MS.

(36) MS or Anal. in text Experimental Section mean respectively that a fully interpreted mass spectrum or the elemental analysis data in accord with theory were obtained and are presented with the supplementary material.

((Alkoxycarbonyl)dithio)carbonyl Chlorides (3, 4). A. The appropriate thiocarbonate **19** (44 mmol) was cooled to −20 °C with dry ice, and **9** (4 mL, 48 mmol) was added. After 1 h at 25 °C, the mixture was distilled to provide colorless **3**, bp 39 °C (0.08 mm), ρ = 1.46, 74% yield, or **4**, bp 68 °C (0.3 mm), ρ = 1.39, 76% yield. Anal. and MS on both.

B. $FeCl_3$ (160 mg, 1% w/w) was added to **54a** (16.6 g, 70 mmol) at 0 °C for 1 h and then distilled twice, bp 54–55 °C (0.6 mm) and bp 86–87 °C (6 mm), to provide **3a** (8.1 g, 62%), ρ = 1.45. Anal. Similarly, **54b** (20 mmol), bp 64 °C (0.8 mm) and bp 139 °C (11 mm), provided **4** (52%), ρ = 1.37.

(((Alkylthio)carbonyl)dithio)carbonyl Chlorides (5, 6). The title compounds were synthesized via method A for **3**, but **15a** or **16b** were used, respectively, for 10 h at 0 °C. For **5**, crude product was obtained in 99% yield and was reasonably pure (80–95%) but contaminated with **11a** (~5%), **12a** (trace–15% depending on batch), **17a** (1–2%, the isomer of starting **15a**), and **28a** (~7%, absent in some batches). A successful short-path distillation, bp 68 °C (0.4 mm), gave desired **5** (51%) as a yellow liquid, ρ = 1.47, Anal., MS, contaminated only with 3% of **12a** (*N*-methylaniline assay). Distillation at inferior vacuums led to formation of an additional 20–30% of **12a**. For **6**, crude product (96%) was contaminated with **11b** (16%) and **12b** (7%). Short-path distillation, bp 76–78 °C (0.2 mm), gave **6** (46%), ρ = 1.33, Anal., contaminated with only 2% of **12b**. After 1 year at −20 °C, 8% of **12b** had formed from **6** which was otherwise intact.

Bis(trichloromethyl)disulfane (7). A quartz reaction vessel containing **32** (200 mL, 1.83 mol) and cyclohexane (800 mL, 7.35 mol) was irradiated under N_2 at 254 nm (Rayonet RPR-100 photoreactor). HCl evolution continued for two weeks, after which time rotary evaporation at 12 mm followed by fractional distillation through a Vigreux column provided *crude* **7** (bp 113 °C (0.7 mm)) as a yellow-orange liquid (160 g, 58%) that was ~90% pure by ^{13}C NMR but showed alkane-derived peaks in the ^{13}C NMR and IR spectra (2950, 2870, 1445 cm^{-1}) together with high C–H analysis. The impurities were removed neither by silica gel chromatography (ref 5) nor a second distillation. *Pure* **7**, a completely clear liquid, was obtained in about 50% weight recovery by treatment of the impure liquid at 25 °C for 2 h with 3 volumes of concentrated H_2SO_4, removal of the lighter organic layer from the charred lower phase by centrifugation, and fractional vacuum distillation through a 4-in. Vigreux column. **7**, bp 70 °C (0.25 mm) [lit.[6b] bp 87 °C (0.5 mm)], was pure by ^{13}C NMR; IR (NaCl plates) 775 (s), 725 (s) cm^{-1}, no C=O or C–H peaks; ρ = 1.77. Anal. MS.

Partial Hydrolysis of Bis(trichloromethyl)disulfane (7) (Reference 5). ^{13}C NMR revealed that the foreruns from the purification of *crude* **7** just described contained both **1** and **2** in amounts of 10–15% each based on **7**. Note that no water was added beyond that normally in H_2SO_4. Nonetheless, the results encouraged attempts to carry forward *pure* **7** to **1** and/or **2**. Reactions were followed by ^{13}C NMR, HPLC, and the *N*-methylaniline assay (**7** did not react, whereas **1** and **2** give **46** and **49**, respectively). Pure **7** (23 g, 77 mmol), water (4.2 mL, 230 mmol), and concentrated H_2SO_4 (22 mL) stirred vigorously for 10 h at 90 °C with no discernible hydrolysis, but after a further 16 h at 115 °C the mixture had turned black with much residue and was a single liquid phase. Pure **7** (1 mL, 5.9 mmol), water (0.3 mL, 16.5 mmol), and H_2SO_4 (1 mL) showed **1** (1%), **2** (13%), and **7** (86%) after 30 h at 110–115 °C and **1** (7%), **2** (16%), and **7** (77%) after a further 5 h at 115–120 °C. However, after 20 h at 120 °C, all disulfanes had hydrolyzed, and a yellow sulfur precipitate was noted in the suddenly brown reaction mixture. These data indicate that in our hands, partial hydrolysis is difficult to control and markedly a function of purity of **7**.

Methoxythiocarbonyl Chloride (Methyl Chlorothionoformate, 8a). The essence of this method is due to a patent by Sasse,[7e] but extensive improvements reported herein were required to obtain reliable results. Sulfuryl chloride (80 mL, 1 mol) was added quickly to a solution of **14a** (214 g, 1 mol) in 1 L of petroleum ether (bp 30–60 °C). The reaction mixture was refluxed (41 °C) for 1 h, and the solvent was then removed over 3 h at aspirator vacuum through a 16-in. Vigreux column. The crude chlorination mixture (274 g, 84% incorporation of Cl_2) was transferred to a smaller flask with a 3-in. Vigreux head and subjected to a careful "cracking" distillation at reduced pressure provided by an aspirator. All material (110 g) boiling from 28–65 °C at a bath temperature of 75–120 °C and a vacuum of 15–40 mm was collected in an ice-cooled receiver, and the time to stop the distillation was usually indicated by a pressure rise. The orange to black residue (78 g, 122% for 2 mol elemental sulfur) solidified overnight. The distillate, termed crude product, contained ~9% (w/w) of S_2Cl_2 as measured by iodide titration or by substituting the typically observed ρ of 1.31 into eq 2, which

$$\text{wt\% of } S_2Cl_2 = 100[1 - (\rho_{\text{pure 8}}/\rho_{\text{obsd}})]/[1 - (\rho_{\text{pure 8}}/\rho_{S_2Cl_2})] \quad (2)$$

is a linear interpolation of densities and gave results in excellent agreement with titration results. Crude product was *promptly* treated with a mixture of pentenes (bp 35–39 °C) (2.4 equiv over the estimated amount of S_2Cl_2, generally ~20 mL, 0.18 mol). The mixture was maintained overnight at −15 °C and then fractionated through a 7-in. Vigreux column into a receiver cooled in an ice–salt bath to provide the pale yellow liquid **8a**: bp 23–24 °C (12 mm); yield, 93 g (0.84 mol, 84%); ρ = 1.28. Anal. MS. The residue (15 g, 55 mmol based on M_r = 275) approximately corresponded to the expected amount of the 1:2 S_2Cl_2:pentenes addition product. Pure **8a** could be redistilled at atmospheric pressure, bp 95–96 °C [lit.[7b] bp 107–108 °C, lit.[7e] bp 85–100 °C, lit.[7f,g] bp 105–107 °C], but not without formation of some (2–16%, depending on short-path or Vigreux-column mode) of the isomer **11a**, as quantitated by IR, NMR, HPLC, and the *N*-methylaniline assay.

Ethoxythiocarbonyl Chloride (8b). A (Preferred). Following the same protocol as for **8a**, **14b** (242 g, 1 mol) with SO_2Cl_2 gave a crude chlorination mixture (304 g, 87% incorporation of Cl_2) which was cracked to provide crude product (117 g, ρ = 1.23 ± 0.02, ~10–15% (w/w) of S_2Cl_2 by iodide titration and eq 2) boiling from 45 to 85 °C, at bath 130–150 °C and vacuum 50–100 mm. A small forerun contained diethyl carbonate (**27b**) corresponding to 0.5% of **14b** (cf. ref 20), and a fraction collected after the main cut had been taken and the vacuum deteriorated contained **12b** amounting to up to 2% of **14b** (cf. ref 18b). Pentenes treatment of crude **8b** followed by vacuum distillation, bp 32–33 °C (14 mm) [lit.[7f] bp 52–55 °C (40 mm)], gave 94 g (75%) of pure **8b**, a pale yellow liquid, ρ = 1.19. Anal. MS. Redistillation data: bp 50–53 °C (26 mm) with 83% weight recovery; bp 125 °C [lit.[7e] bp 120–122 °C, lit.[7b,c] bp 127–128 °C, lit.[7a,d,g] bp 136 °C] with 82% (short path, no **11b**) or 60% (Vigreux column, 7% **11b** formed) weight recoveries.

B. On a 0.4-mol scale, 1 equiv of Cl_2 (monitor theoretical weight uptake) was added to neat **14b** at 25–30 °C (ice bath cooling necessary). Results from the cracking distillation were qualitatively in accord with Method A, but yields were erratic, crude product densities were often substantially higher, and the ^1H NMR spectrum taken immediately after completion of the distillation often showed the extra signals due to the presumed 1:2 S_2Cl_2:**8b** adduct.

Purification of Ethoxythiocarbonyl Chloride (8b) by Phase-Transfer Iodide Reduction. The crude material (50 g) from Method B above, characterized by a density (1.25–1.35) higher than that expected for pure **8b** (1.19) and also by additional NMR signals at δ 4.14 (q), 1.39 (t), J = 7.1 Hz, was mixed with CH_2Cl_2 (200 mL), and tetrabutylammonium iodide (1 g, 2.7 mmol) was dissolved. An equal volume of aqueous $Na_2S_2O_3$ (2 M) was added, and the mixture was stirred vigorously at 25 °C for 2 to 5 h. When reduction was complete as judged by NMR, the organic phase was dried ($MgSO_4$), filtered, and concentrated through a 16-in. Vigreux column at aspirator pressure. The resulting liquid was filtered to remove the iodide catalyst and redistilled, bp 44–46 °C (33 mm); overall recoveries of 55–70%, ρ = 1.19. Anal.

Reactions of Methoxythiocarbonyl Chloride (8a) under Conditions of Phase-Transfer Iodide Reduction (Scheme II). Reactions were set up, with *pure* **8a** and toluene (0.2 equiv, as internal standard) present at concentrations equivalent to those for the ethyl series (see previous paragraph), and followed by NMR and HPLC. Bis(methoxy(thiocarbonyl)) sulfide (**24a**) formed with $t_{1/2}$ = 140 min in a yield of 74% (recovery of methyl groups). After 1 to 4 days, **24a** was converted further to **15a**. With impure **8a**, the NMR signal at δ 3.79 assigned to the S_2Cl_2:**8** adduct was found to disappear with $t_{1/2}$ = 90 min. Further controls with pure **8a** revealed that (1) **24a** formed at the same rate when Bu_4NI was

replaced by Bu_4NCl; (2) when the reaction was carried out with **8a** plus **8b** (molar ratio 1.0:0.83), the products were **24a** (43%), **24b** (10%), and the mixed xanthic anhydride MeO-(C=S)S(C=S)OEt (47%); (3) when the aqueous $Na_2S_2O_3$ phase was replaced with aqueous NaI (2 M), no **24a** nor I_2 formed, but **8a** decomposed with $t_{1/2}$ = 430 min to MeI and COS; and (4) in the absence of any aqueous phase, Bu_4NI catalyzed the decomposition of **8a** to MeCl and COS.

Chlorocarbonylsulfenyl Chloride (9). Following Weiss,[8b] a 2-L flask with a thermometer, gas outlet tube, and large "football" magnetic stirring bar in a well ventilated hood was filled with trichloromethanesulfenyl chloride (**32**) (294 mL, 500 g, 2.7 mol) followed by a mixture of water (54 mL, 3.0 mol) in concentrated H_2SO_4 (620 mL). The heterogeneous mixture was vigorously stirred for 6 h at 45–50 °C as HCl evolved and then was stirred overnight at 25 °C to ensure complete reaction of **32** at the expense of a decreased yield of **9**, which can hydrolyze. The upper phase (280 g, 80%) was separated and distilled through a 3-in. Vigreux column, bp 97–101 °C (lit.[8b] bp 98 °C) to provide typically 230 g (65%) of the clear light yellow liquid title product, pure by *N*-methylaniline assay, ρ = 1.57. Anal. MS.

((Methoxydichloromethyl)dithio)carbonyl Chloride ((Chlorocarbonyl)(methoxydichloromethyl)disulfane, 10a). A mixture of **8a** (25 g, 0.23 mol) and **9** (21 mL, 0.25 mol) was maintained at 25 °C for 5 days (monitored by ^1H NMR, $t_{1/2} \sim$ 10 h, rate unaffected by hν at 254 nm). Vacuum distillation gave 10.5 g of a forerun which was mainly unreacted **9** but also contained **11a** (1% of starting **8a**) and **12a** (whatever amount originally contaminated **8a**). The title compound (42 g, 75%, pale yellow liquid) was obtained: bp 82–84 °C (0.4 mm) or bp 62 °C (0.08 mm); pure by ^{13}C NMR, ρ = 1.56. Anal. MS. Redistillation experiment: There was 65% recovery at bp 128–129 °C (19 mm) and the main fraction was pure by ^{13}C NMR.

((Ethoxydichloromethyl)dithio)carbonyl chloride (10b) was prepared from **8b** plus **9**. Reaction conditions: 25 °C; 24 h ($t_{1/2} \sim$2–3 h, some **1** formed). On a 0.1-mol scale, a 60% yield of colorless liquid title product was obtained: bp 77 °C (0.08 mm); ρ = 1.46. Anal. MS. After 2 months at 25 °C, ~40% of **10b** that was originally pure by ^{13}C NMR had been converted to **1**.

(Methylthio)carbonyl Chloride (11a). Pure **8a** (5 g) was treated at 0 °C with $FeCl_3$ (25 mg, 0.5% w/w) in a violent reaction accompanied by gas evolution. Two short-path distillations gave the title compound, pure by ^1H NMR and colorless: yield, 3.1 g (62%); bp 109–110 °C [lit.[12a] bp 110 °C]; ρ = 1.28.

(Alkyldithio)carbonyl Chlorides (12). A solution of alkanethiol (0.8 mol) in CH_2Cl_2 (200 mL) was added dropwise under N_2 with good stirring at −5 to +5 °C to a solution of **9** (74 mL, 0.89 mol) in CH_2Cl_2 (300 mL). Stirring was continued overnight at 25 °C to allow completion of the HCl evolution. Solvent was then removed under aspirator suction, and the residual liquid purified by distillation through a 3-in. Vigreux head. Products were clear yellow liquids obtained in 85–94% yields. **12a**: bp 47–49 °C (14 mm) [lit.[9] bp 55 °C (22 mm)]; ρ = 1.40. **12b**: bp 64–75 °C (11 mm), 78 °C (21 mm) [lit.[9] bp 59–60 °C (11 mm)]; ρ = 1.30. Anal. and MS on both. Deviations from this protocol resulted in preparations of **12** contaminated with the dialkyl disulfide (**40**). Compounds **12** were best stored at −20 °C; for example, **12a** after several weeks at 25 °C gave rise to a pressure buildup and substantial amounts of **38a**, **39a**, **40a**, **41a**, and **42a** (detected by NMR, compare to ref 37 where the identical compounds were identified in the decomposition of **38a**).

Bis(methoxy(thiocarbonyl))disulfane (Dimethyl Dixanthogen, 14a). KOH (350 g, 85%, 5.3 mol) was dissolved at 65 °C in MeOH (1 L), and the solution was chilled in an ice bath. CS_2 (350 mL, 5.8 mol) was added in 10 mL portions with vigorous manual agitation at a rate to keep the temperature below 15 °C. At the end of the addition, there was a yellow crystalline mass of potassium methyl xanthate and no separately discernible CS_2 layer. The minimal amount of water (800 mL) to dissolve the crystals was added and followed by iodine (670 g, 2.65 mol) in 10 g portions at under 10 °C until the persistence of a dark brown end point. A sufficient (small) amount of aqueous saturated $Na_2S_2O_3$ to quench the color was added, and the oily product (lower phase) was extracted into ether (1.5 L). The organic (upper) phase was washed three more times (this is *absolutely* essential; see ref 15 and 20) with water (600 mL each wash), dried over $MgSO_4$, filtered, and rotary evaporated (20 mm) to typically give 540 g of the yellow oily product (95%), best stored at −20 °C, MS.

Bis(ethoxy(thiocarbonyl))disulfane (14b). A procedure analogous to the procedure for the preparation of **14a** was used; potassium ethyl xanthate prepared in situ is better than commercially available material. Yields were excellent; **14b** was sometimes obtained as crystals, mp 25–27 °C [lit.[15c] mp 32.5 °C], but the oil was equally applicable for subsequent transformations. Anal. was satisfactory, but see ref 20. MS.

***O*-Methyl *S*-Methyl Dithiocarbonate (Dimethyl Xanthate, 15a). A.** Iodomethane (300 g, 2.1 mol) was added dropwise over 2 h to an ice-chilled solution of potassium methyl xanthate (310 g, 2.1 mol) in MeOH (1 L). An equal volume of water was added to dissolve salts, and after an additional water wash, the oily lower phase was dried over $MgSO_4$ to provide 222 g (87%) of an oil which contained 2–5% each of **28a** and **30a** in addition to the main product **15a**. Also, when the initial alkylation was conducted under reflux, the isomer **17a** contaminated **15a**. Distillation gave 154 g (60%) of **15a**: bp 69–71 °C (26 mm) [lit.[38a] bp 168 °C; lit.[38b] bp 65 °C (20 mm)]; 99.6% purity by HPLC; ρ = 1.18.

B. When the procedure of Bulmer and Mann[15c] was followed, **14a** (307 g, 1.43 mol) was destructively distilled, bp 63 °C (16 mm), to provide **15a** (108 g, 62%) contaminated with 8% of **17a**. This procedure was unwieldy on a larger scale because the gaseous byproducts led to pressure problems.

***O*-Ethyl *S*-Methyl Dithiocarbonate (15b).** The title compound was obtained by addition of iodomethane to potassium ethyl xanthate in EtOH (cf. method A for **15a**): yield, 66%; bp 62–64 °C (9 mm); ρ = 1.13; 97.5% purity by HPLC (the remainder was **17a**, but no **16b**, **18**, or **29a** were present).

***O*-Methyl *S*-Ethyl Dithiocarbonate (16a). A (Best Procedure).** Freshly made solid sodium ethanethiolate (46 g, 0.55 mol) was added over 2 h to a solution of **8a** (55 g, 0.5 mol) in ether (500 mL) at a rate to maintain a mild reflux (35 °C) by the spontaneous exotherm. The ether phase was washed with an equal volume of 1 N aqueous HCl, dried over $MgSO_4$, and concentrated to give a crude product (63 g, 93%) that was further purified by vacuum distillation (discard forerun): yield, 51 g (75%); bp 60–68 °C (13 mm); HPLC pure; ρ = 1.12.

B. (Ethylthio)(thiocarbonyl) chloride (**31b**)[12b] (5 mL, 46 mmol) was stirred with MeOH (25 mL) for 2 h at 25 °C. Excess MeOH was evaporated and **16a** (3.1 g, 50%) was obtained: bp 65–66 °C (10 mm); HPLC pure.

C (Worst Procedure). When the literature method[38a] using potassium methyl xanthate and iodoethane was carried out, crude yields were 45–55%, substantial amounts of **28a** formed, and 5–15% of **15a** contaminated **16a** even through the distillation.

***O*-Ethyl *S*-Ethyl Dithiocarbonate (16b).** When the ratios and workup described for **15a** were used, iodoethane was added to a solution of potassium ethyl xanthate in EtOH over 2 h while maintaining a gentle reflux: yield, 55%; bp 72–73 °C (9 mm) [lit.[38b] bp 78 °C (18 mm)]; 98% pure by HPLC; ρ = 1.08.

***S*,*S*'-Dimethyl Dithiocarbonate (17a). A.** Solid sodium methanethiolate (1.8 g, 26 mmol) was added at 0 °C to a solution of **11a** (2 mL, 23 mmol) in ether (25 mL). After 1 h at 25 °C, salts were removed by filtration, ether was removed by rotary evaporation, and the crude product (2.3 g, 82%) was purified by distillation: yield, 1.7 g (61%); bp 46–47 °C (9 mm) [lit.[10b] bp 75–76 °C; lit.[39b] bp 70 °C (25 mm)]; ρ = 1.19.

B. On a 0.2-mol scale, **15a** and iodomethane (4:1, v/v) were heated at 75–110 °C for 60–140 h until no **15a** remained as judged by HPLC and NMR (MeI was replenished as necessary; $t_{1/2}$ = 8.5 h for this reaction when conducted on a small scale at 100 °C in a closed screw-cap tube). The title product was obtained in 57% yield, bp 167–168 °C [lit.[39a,c] bp 167–168 °C].

C. $FeCl_3$ (100 mg) was added in four batches 15 min apart to **15a** (5 g) at 100 °C. Each fresh addition of Lewis acid promoted

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more isomerization. A first short-path distillation gave an 85% mass recovery of a 3:7 mixture of **15a**:**17a**. This was further treated with more $FeCl_3$ (80 mg, 2% w/w) at 100 °C for 20 min and then distilled: yield, 3.6 g (72%); bp 53 °C (10 mm); 99% of **17a** by HPLC.

***S*-Ethyl *S'*-methyl dithiocarbonate (18)** was obtained from sodium methanethiolate and **11b** by the same technique as for **17a**, method A: yield, 75% (crude), 50% (distilled); bp 76–78 °C (13 mm) [lit.[39c] bp 83–85 °C (30 mm)]; 85% purity by HPLC with 11% of **17b**.

***O,O'*-Dimethyl Thiocarbonate (19a).** Sodium methoxide (12.3 g, 0.23 mol) was added slowly through the top of a condenser to an ice-chilled solution of **8a** (23.2 g, 0.21 mol) in dry ether (200 mL). A very vigorous reaction ensued causing the ether to reflux. After stirring for an additional 2 h at 25 °C, the reaction mixture was filtered, concentrated (16 g, yellow oil, 72%), and distilled (14.7 g, colorless, 66%): bp 119–120 °C [lit.[40] bp 119–120 °C]; ρ = 1.10.

***O,O'*-Diethyl thiocarbonate (19b)** was obtained from sodium ethoxide and **8b** by following the procedure for **19a**. Distilled yields were 40–46%, on up to a 0.5-mol scale: bp 59–60 °C (19 mm) [lit.[41a,b] 162 °C; lit.[41d] 53–55 °C (20 mm)]; ρ = 1.02.

***O*-Ethyl *O'*-Methyl Thiocarbonate (20).** The procedure given was adopted after preliminary experiments showed that reaction of **8a** plus ethoxide gave the isomer **29a** as well, and that reaction of **8b** with excess methoxide especially with spontaneous reflux gave considerable **19a** and **19b** through disproportionation or double addition. The title compound has been discussed once[39a] to be "of insufficient purity". Sodium methoxide (23.2 g, 0.43 mol) was added to **8b** (53.5 g, 0.43 mol) in ether (430 mL) at 20 °C. The reaction mixture was then washed with water, dried over $MgSO_4$, and rotary evaporated to give 43.6 g of an approximately 2:1 mixture of product **20** and unreacted starting material **8b**. The latter, which is difficult to remove entirely by fractional distillation, was removed by taking up the entire crude product in $CHCl_3$ (350 mL), treating with *N*-methylaniline (41.7 g, 0.39 mol) at 10 °C, washing twice with equal volumes of 1 *N* aqueous HCl, and drying over $MgSO_4$. Subsequent concentration, evaporation, and distillation left **51b** in the residue while the colorless liquid title product was obtained in 28% overall yield: bp 46 °C (30 mm); ρ = 1.06; pure by HPLC. Anal.

Treatment of *O*-Ethyl *O'*-Methyl Thiocarbonate (20) with Trichloromethanesulfenyl Chloride (32) (Scheme III). Thiocarbonate **20** (1 mL, 8.8 mmol) and **32** (1 mL, 9.1 mmol) in benzene (9 mL) were reacted overnight at 25 °C to give, after rotary evaporation, 1.95 g (87%) of a product mixture consisting of unreacted **20** (1%), *O,S*-dialkyl thiocarbonates **28b** and **29a** (1% total), **62a** (18%), and **62b** (81%) by HPLC analysis.

Treatment of *O*-Ethyl *O'*-Methyl Thiocarbonate (20) with Chlorocarbonylsulfenyl Chloride (9). Reaction conditions were identical to those of Method A for the syntheses of **3** and **4**. The ratio of **3** to **4** was determined by ^1H NMR and HPLC in several ways: (1) direct measurements on a crude reaction mixture; (2) analysis of **43a** and **56** after treatment with MeOH; (3) analysis of **56** and **43b** after treatment with EtOH; (4) analysis of **57a** and **57b** derived in the *N*-methylaniline assay. By all these criteria, the ratio of **4** (corresponding to **72** losing MeCl) to **3** (corresponding to **72** losing EtCl) was (3.5 ± 0.2):1.0 (Scheme III).

Iodomethane-Catalyzed Rearrangement of *O*-Ethyl *O'*-Methyl Thiocarbonate (20). A mixture of **20** (1 mL), iodomethane (0.3 mL), and toluene (0.2 mL, as internal standard) in a closed screw-cap tube was heated at 100 °C. Starting material disappeared with $t_{1/2}$ = 7.4 h (identical rate observed for rearrangement of **19a** to **28a**); the kinetics were pseudo-first-order for several half-times as monitored by HPLC and NMR. At *all* points of the reaction pathway, including the endpoint (3 days, reaction complete), the ratio of product *O*-alkyl *S*-methyl thiocarbonates **28a**:**29a** was 1.0:(8.1 ± 1.1).

***S*-Alkoxycarbonyl *O*-Alkyl Dithiocarbonates (22, 23).** On a 0.25-mol scale, the appropriate solid potassium alkyl xanthate (1 equiv) was added into an ice-chilled 2 M solution of the appropriate alkyl chloroformate (2 equiv) in ether. No spontaneous exotherm was noted, and the reaction was stirred for 4 h at 25 °C. The ether phase was then washed with water, dried over $MgSO_4$, concentrated (crude yields nearly quantitative with good NMR's), and distilled to give the title compounds, yellow liquids, in ~75% overall yields.

22a: bp 124–128 °C (33 mm); ρ = 1.28. Anal.

22b: bp 125–129 °C (28 mm); ρ = 1.22.

23a: bp 120–122 °C (15 mm); bp 132 °C (23 mm) [lit.[42b] bp 85–88 °C (3 mm)]; ρ = 1.22.

23b: bp 146–149 °C (27 mm) [lit.[42a] bp 133 °C (18 mm); lit.[42c] bp 69–75 °C (0.4 mm)]; ρ = 1.16.

Bis(methoxythiocarbonyl) Sulfide (24a). A. The method described earlier[42c] to give **24b** in 57% purified yield was, with some difficulty, adopted. Potassium methyl xanthate was generated in situ on a 2.65-mol scale and was completely in solution in MeOH–H_2O by following the initial details of the procedure for **14a**. Next, methyl chloroformate (92 mL, 1.2 mol) was added under ice cooling. The crystals which formed (215 g, mp 45–49 °C) were collected immediately on a Buchner funnel and recrystallized by dissolving in 1 L of MeOH at 55 °C, filtering, and adding 1 L of water. Considerable decomposition to **15a** occurred, which passed through as an oil. The crystalline product (pale yellow needles) was dried in a vacuum desiccator over KOH: yield, 77 g (35%); mp 52–54 °C [lit.[43] mp 55 °C]. Anal.

B. The only (scanty) literature reference[43] to the title compound was expanded upon: **14a** (22.9 g, 0.12 mol) in MeOH (140 mL) was added at <5 °C to KCN (7.9 g, 0.12 mol) in MeOH–H_2O (200 mL, 1:1 v/v). After 2 h at 25 °C, water (150 mL) was added and the ensuing crystals were collected: yield, 10.5 g (47%); less pure by elemental analysis than material prepared by Method A.

Methoxydichloromethanesulfenyl Chloride (33a). A. Chlorine gas was passed through a solution of **15a** (49 g, 0.4 mol) in pentane (250 mL) at −30 to −50 °C, with uptake monitored by occasional weighing and checking an exit bubbler. Actual uptake was 64–70 g (78% of theory for 3 equiv of Cl_2). The cold reaction mixture was then filtered through a glass-fritted Buchner funnel to remove the unstable white solid, methyl sulfur trichloride (62 g, 0.4 mol, 100%). The filtrate, and a cold pentane wash of the solid, were concentrated and vacuum distilled through a 3-in. Vigreux column: yield, 45 g (62%, yellow liquid); bp 60–61 °C (18 mm) [lit.[31a] bp 77 °C (35 mm)]; pure by ^{13}C NMR; ρ = 1.53. Anal. MS.

B. Methoxy(thiocarbonyl) chloride (**8a**) (17.3 mL, 0.2 mol) and SO_2Cl_2 (17.6 mL, 0.22 mol) were combined at 0 °C and allowed to stand for 3 h at 25 °C ($t_{1/2}$ of reaction ~10 min). A nominally quantitative yield of crude product was obtained which also contained 5% of methyl trichloromethyl ether (**34a**)[31b,c] readily removed in the subsequent fractional distillation: yield, 25.3 g (70%); bp 60 °C (13 mm); pure by ^{13}C NMR (free of **9**).

Ethoxydichloromethanesulfenyl Chloride (33b). Method A for **33a** was followed with **15b** on the same scale; there were obtained 89% of theoretical Cl_2 uptake, 92% of the theoretical amount of $MeSCl_3$, and a 90% distilled yield of the yellow title product: bp 55–56 °C (8 mm), bp 73–75 °C (26 mm) [lit.[31a] bp 88 °C (33 mm)]; pure by ^{13}C NMR; ρ = 1.40. Anal. MS.

Alkoxycarbonylsulfenyl Chlorides (35). The appropriate alcohol (0.74 mol) was added dropwise into a stirred solution of **9** (64 mL, 0.77 mol) in ether (275 mL), which was then refluxed for 16 h. After removal of solvent, the pale yellow title products were obtained by distillation through a 3-in. Vigreux column.

35a: 88% yield; bp 31–32 °C (12 mm), bp 67–69 °C (75 mm) [lit.[30a] bp 73–74 °C (100 mm); lit.[30b] bp 67–68 °C (74 mm)]; ρ = 1.39.

35b: 83% yield; bp 41–42 °C (14 mm), bp 59–60 °C (23 mm) [lit.[10e,30a] bp 45–47 °C (15–16 mm), lit.[3b] bp 77–79 °C (32 mm)]; ρ = 1.27; stored at −20 °C because a sample stored 6 months at

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25 °C had accumulated ~20% ethyl chloroformate (**21b**).

***S*-Methylsulfenyl *O*-Methyl Thiocarbonate ((Methoxycarbonyl)(methyl)disulfane, 36a).** At 0 °C, **12a** (10 g, 70 mmol) was added to MeOH (50 mL). Excess solvent was removed by rotary evaporation, and the crude product (7.3 g) was distilled: yield, 5.8 g (60%); bp 68–73 °C (12–13 mm) [lit.[32b] bp 30–33 °C (0.6 mm)]; ρ = 1.23; colorless liquid.

***S*-Ethylsulfenyl *O*-Methyl Thiocarbonate (36b). A.** On a 0.1-mol scale, a solution of ethanethiol (2 M) in CH_2Cl_2 was added at 10 °C to 1 equiv of **35a** (2 M) in CH_2Cl_2. After stirring 2 h at 25 °C, solvent was removed by rotary evaporation, and the title compound was obtained in 78% distilled yield: bp 71–73 °C (8 mm) [lit.[32a] bp 53–54 °C (1 mm); lit.[32c] bp 81.5–84 °C (2 mm)]; ρ = 1.18. Anal. MS.

B. Similar to Method A for **3**, ethanesulfenyl chloride (**38b**) (1.8 mL, 21 mmol) that had been freshly made by chlorination of diethyl disulfide[33] was added to cooled **19a** (2.0 mL, 19 mmol), and distillation provided a 77% yield of **36b**, bp 77 °C (10 mm).

***S*-Alkylsulfenyl *O*-ethyl thiocarbonates (37)** were obtained by reaction of **12** with EtOH as described for **36a**.

37a: yield, 79% (crude), 72% (distilled); bp 99 °C (28 mm); ρ = 1.17. Anal.

37b: yield, 89% (crude), 84% (distilled); bp 35–39 °C (0.08 mm) [lit.[10f] bp 94–98 °C (14–19 mm); lit.[32a] bp 74–75 °C (0.5 mm); lit.[32b] bp 45 °C (0.1 mm)]; ρ = 1.16. Anal.

Bis(methoxycarbonyl)disulfane (43a). A. KOH (16.5 g, 85%, 0.25 mol) was dissolved in MeOH (100 mL) and this solution was cooled in an ice bath. COS was bubbled through for 5 min and provided a weight increase of 14.4 g (96%). The Bender's salt (**44a**) was precipitated from the green solution by adding ether (300 mL) and cooling to 0 °C. A pale gray solid was collected by filtration, washed with ether, and dried in a vacuum desiccator over P_2O_5 and paraffin. Yield: 27.4 g (84%), mp 142–143 °C dec. A portion of **44a** (1.0 g, 7.9 mmol) was dissolved in water (5 mL), and a saturated (3.26 g per 100 mL) solution of iodine in $CHCl_3$ was added dropwise at 25 °C until the persistence of a brown color (40 mL added). The color was quenched with aqueous $Na_2S_2O_3$, and the organic layer was separated, dried ($MgSO_4$), and evaporated to give a solid product (0.57 g, 79%), mp 33 °C [lit.[31b,10e] mp 36 °C].

B. Bis(chlorocarbonyl)disulfane (**1**) (28 g, 0.15 mol) was added dropwise over 1 h to MeOH (100 mL) at 0 °C, as HCl rapidly evolved. After further stirring at 0 °C for 10 min, the reaction mixture was allowed to warm to 25 °C and the solvent was removed by rotary evaporation to furnish a white solid product identical with that from Method A: yield, 25.0 g (93%); mp 33–34 °C; pure by HPLC. The product was washed with petroleum ether: mp 35–36 °C, hard, transparent plates. Anal. MS.

Bis(ethoxycarbonyl)disulfane (43b). A. In similar fashion to the procedure for **43a**, the Bender's salt **44b** was obtained in 53% yield and oxidized with I_2 to give quantitatively **43b** as a colorless oil, pure by HPLC.

B. From **1** added over 30 min to 10 volumes of absolute EtOH at 5–10 °C, the title product was obtained in 90% yield; further purification was achieved with 83% weight recovery by bulb-to-bulb distillation: oven 40–80 °C (0.16 mm) [lit.[44] bp 98–101 °C (2.5 mm)]; colorless oil. Anal. MS.

Bis(*N*,*N*-diisopropylcarbamoyl)disulfane (45). A solution of **1** (2 mL, 17 mmol) in $CHCl_3$ (32 mL) was added over 20 min at <10 °C to a well-stirred solution of diisopropylamine (10 mL, 71 mmol) in $CHCl_3$ (35 mL). After 1 h at 25 °C, an equal volume of 1 N aqueous HCl was added which dissolved the diisopropylammonium hydrochloride precipitate. The organic layer was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation (chase several times with petroleum ether, bp 30–60 °C) until yellow crystals formed: yield, 5.1 g (94%); mp 103–106 °C; recrystallized (53%) from hexane–$CHCl_3$, mp 113–115 °C; white needles; NMR δ 3.9 (br m, 1 H), 1.33 (d, J = 6.6 Hz, 6 H); IR ($CDCl_3$) 2970 (m), 1675 (s), 1400 (m), 1270 (s), 1210 (m), 1030 (m), 805 (m) cm^{-1}. Anal. MS.

Bis(*N*-methyl-*N*-phenylcarbamoyl)disulfane (46). Neat **1** (2 mL, 17 mmol) was added slowly to a well-stirred, ice-salt bath-chilled 2 M solution of *N*-methylaniline in $CHCl_3$ (36 mL, 4.3 equiv of amine). After 1 h at 25 °C, 1 N aqueous HCl (40 mL) and additional $CHCl_3$ (60 mL) were added. The organic phase was washed twice with an equal volume of 1 N aqueous HCl, dried over $MgSO_4$, filtered, and evaporated to provide **46** (5.7 g, quantitative) as yellow crystals, mp 225–230 °C, recrystallized as transparent needles from hot CCl_4–$CHCl_3$ (3:2) in 60–85% recovery or from hot acetone in 75% recovery; further data are given in Table II and in the supplementary material.

***N*,*N*'-Dimethyl-*N*,*N*'-diphenylcarbamoylsulfenamide (47).** A solution of **9** (10 mL, 0.12 mol) in $CHCl_3$ (240 mL) was added to *N*-methylaniline (55 mL, 0.51 mol) in $CHCl_3$ (250 mL) at <5 °C. Workup in the standard way (cf. **46**) gave the title compound as an oil (32.0 g, 98%) which solidified after chasing on the rotary evaporator several times with petroleum ether, mp 65–67 °C. Attempted purification by high-vacuum distillation failed. Successful recrystallization (65–80% recovery) as white needles was from hot hexane (30 mL per 1 g; less volume led to oils and decomposition); further data are given in Table II and in the supplementary material.

3-Methyl-2(3*H*)-benzothiazolone (48). On a 0.1-mol scale, two volumes of a 1 M solution of *N*-methylaniline in $CHCl_3$ were added over 4 h at 0–10 °C to one volume of a 1 M solution of **9** in $CHCl_3$. After stirring 1 h at 25 °C, workup in the standard way (cf. **46**) gave a nominally quantitative yield of a solid material, mp 65–73 °C, consisting of the title compound admixed with 5 mol% of **46**. Recrystallization from hexane effectively removed **46** (less soluble) and provided desired **48** as transparent plates, pure by NMR and HPLC, in ~50% overall yield based on **9**; further data are given in Table II and the supplementary material. The ratio of *N*-methylaniline to **9** was critical; when this was 1:1 or 1.5:1, the nominal crude yields of essentially pure **48** were 50% and 70% respectively, and when the ratio was 3:1, the yield of **48** was 72% with a further 25% of **9** accounted for as **47**.

Harris Reactions for the Syntheses of Carbamoyl Disulfides 49 and 57 (Eq 1). The appropriate sulfenyl chloride, **32** or **35** (1.0 equiv), was added to a 1 M solution in benzene of **51**. After the solution was kept overnight at 25 °C, the solvent was rotary evaporated to provide products as oils in nominally quantitative yields, containing at most 1–2% of the isomeric thiocarbamates **53** above and beyond what was originally contaminating starting **51**. Recrystallization from hexane gave 65–75% recoveries of solids which had the identical melting points as, and no mp depression upon admixture with, the same carbamoyl disulfides prepared from *N*-methylaniline plus **2**, **3**, or **4** (Table II).

(Alkoxycarbonyl)(methoxydichloromethyl)disulfanes (54). The appropriate **35** (44 mmol) was added to **8a** (4.0 mL, 48 mmol) at 0 °C. After 10 h at 25 °C, the mixture was distilled to provide **54a**, bp 64 °C (0.07 mm), ρ = 1.45, 60% yield, or **54b**, bp 72–74 °C (0.07 mm), ρ = 1.37, 75% yield. Anal. and MS were satisfactory on both colorless liquids.

((Methylthio)carbonyl)(methoxydichloromethyl)disulfane (55). Equimolar amounts of **33a** and **15a**, both suitably diluted in $CDCl_3$, reacted smoothly at 0 °C to provide MeCl and the title compound in solution, pure by ^1H and ^{13}C NMR, free both of starting materials and of **5**.

(Ethoxycarbonyl)(methoxycarbonyl)disulfane (56). A. **19b** plus **35a**, 22-mmol scale, were reacted 1 h at 0 °C to yield the title compound: 94% (crude), 73% (distilled); bp 69 °C (0.07 mm); ρ = 1.28. Anal. MS.

B. When **3** was added at 0 °C to absolute EtOH, similar to Method B for **43b**, a 90% yield of **56** was obtained: colorless liquid; pure by HPLC (no **43a** or **43b**).

(Methoxycarbonyl)((methylthio)carbonyl)disulfane (61). The title compound was obtained by a method similar to method A for **56** but **19b** was replaced with **15a**: 70% yield; bp 72 °C (0.1 mm) [lit.[10f] 86–88 °C (0.2 mm)]; ρ = 1.34; pale yellow liquid. Anal. MS.

***S*-Trichloromethylsulfenyl *O*-Alkyl Thiocarbonates (62). A.** The title compounds were obtained via a similar method to Method A for **3** or **4**, but with **32** instead of **9**. **62a**: 69% yield (distilled); bp 61 °C (0.3 mm), bp 123 °C (10 mm); ρ = 1.57. **62b**: 68% yield; bp 70–72 °C (0.4 mm) with **8b**, **29b**, and **27b** as more volatile byproducts removed in the distillation; ρ = 1.48. Anal. and MS on both.

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B. The appropriate **35** (24 mmol) and thiophosgene (36 mmol) were heated at 100 °C in a sealed tube for the indicated time and then fractionally distilled. **62a**: 24 h; bp 55 °C (0.1 mm); ρ = 1.57. **62b**: 96 h; bp 53–56 °C (0.1 mm); ρ = 1.49, both colorless liquids.

Stereochemistry of Sequence for Dithiocarbonyl Group Synthesis (Scheme IV). A solution of (*R*)-2-octanol (4.9 g, 37.7 mmol) in toluene (20 mL) was refluxed with sodium (0.69 g, 30 mmol) until all of the sodium had dissolved. After cooling to 25 °C, CS_2 (2.3 g, 30 mmol) was added with stirring. After 10 min, a solution of MeI (4.3 g, 30 mmol) in ether (25 mL) was added and reacted for a further hour. The reaction mixture was washed with water (50 mL), dried ($MgSO_4$), evaporated, and distilled to give pure (*R*)-*O*-2-octyl *S*-methyl dithiocarbonate (**73**): yield, 3.98 g (60%); bp 70–74 °C (0.2 mm) [lit.[34] bp 102 °C (0.4 mm)]; $[\alpha]^{25}_D$ + 6.44 (lit.[34] for *S* isomer, –6.75); NMR δ 5.70 (m, J = 6.1 Hz, 1 H), 2.54 (s, 3 H), 1.0–1.9 (m, 13 H), 0.88 (skewed t, 3 H). The starting (*R*)-2-octanol used had $[\alpha]^{25}_D$ –8.5° (lit.[45] –9.9°).

The optically active xanthate **73** (3 g, 13.6 mmol) was reacted with **35a** (1.73 g, 13.6 mmol) which was slowly added at 0 °C. After additional standing at 25 °C for 2 h, the 2-chlorooctane was separated by distillation: yield, 0.80 g (40%); bp 50 °C (10 mm); $[\alpha]^{25}_D$ +12.09°; NMR δ 4.03 (m, J = 6.4 Hz, 1 H), 1.50 (d, J = 6.5 Hz, 3 H), overlapping 1.0–1.8 (m, 10 H), 0.88 (skewed t, 3 H).

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Supplementary Material Available: Additional experimental details, including all compounds not explicitly described in text, and tabulations of all spectral, analytical, and chromatographic data (28 pages). Ordering information is given on any current masthead page.

Notes

Structural Effects on the Electron-Donor Ability of Carbonyl Bases. A Quantitative Analysis

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Recent studies[1,2] on the charge-transfer (CT) equilibria between carbonyl bases and iodine in "inert"[3] solvents (reaction 1) have shown the nonadditivity of substituent effects on the free energies of complexation, $\Delta G°_1$, corresponding to the process shown.

$$R_1CO\ R_2 + I_2 \rightleftharpoons R_1CO\ R_2 \cdots I_2 \qquad (1)$$

The results given in Table I for ketones, disubstituted amides (R_1 = Me, R_2 = NMe_2, NEt_2), and tetrasubstituted ureas (R_1, R_2 = NMe_2, NEt_2) clearly illustrate this phenomenon.

It is also known that hydrogen-bonding complexes between carbonyl bases and proton donors are also subject to nonadditive substituent effects.[4] The attempts to rationalize these facts have considered *either* the steric hindrance to the planarity of the N–CO–N moiety[5] *or* the saturation of the electron-accepting power of the carbonyl group.[4] We feel that these two mechanisms are by no means mutually exclusive, and in this work, we have determined several free energies of association between iodine and carbonyl bases in order to achieve their quantitative dissection.

Discussion

The quantitative separation of steric and electronic saturation effects is based upon the following assumptions.

(i) The sum of the inductive and resonance contributions is the same for the methyl and *tert*-butyl groups. This contention is substantiated as follows: the experimental values for $(\Delta G°_1)_{MeCOMe}$ and $(\Delta G°_1)_{MeCO\text{-}t\text{-}Bu}$ are the same within experimental errors, as seen in Table I. We also

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