5.23 (s, 1 H), 3.97-4.35 (m, 1 H), 2.77 (d, J = 7.2 Hz, 2 H), 1.86 (s, 3 H), 1.21-1.77 (m, 2 H), 0.91 (t, J = 7.2 Hz, 3 H); IR (thin film) 3275, 1660, 1620, 720 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.45; H, 8.71, N, 6.53.

***N*-(1-Benzylpropyl)-2-[(tributylstannyl)methyl]propenamide ((+)-65).** By the procedure described for the preparation of the amide (*S*)-(-)-**12**, 3.82 g (33 mmol) of *t*-BuOK, 3.26 g (15 mmol) of (-)-**64**, 31.7 mmol of *n*-butyllithium, and 5.27 g (16.2 mmol) of chlorotributyltin in 60 mL of THF afforded, after column chromatography (20:1 hexane/ethyl acetate), 5.15 g (69%) of (+)-**65** as a colorless oil; $[\alpha]^{23}_D$ +7.3° (*c* 3.76, $CHCl_3$); ^{1}H NMR δ 7.12 (s, 5 H), 5.38-5.66 (m, 1 H), 4.95 (s, 1 H), 4.88 (s, 1 H), 3.98-4.28 (m, 1 H), 2.73 (d, J = 7.2 Hz, 2 H), 1.84 (s, 2 H), 0.72-2.16 (m, 32 H). Anal. Calcd for $C_{26}H_{45}NO$: C, 61.68; H, 8.96; N, 2.77. Found: C, 61.89; H, 8.86; N, 2.95.

Reaction of (+)-65 with Isovaleraldehyde. By the procedure described for the preparation of the alcohol **29**, 0.47 g (5.5 mmol) of isovaleraldehyde, 3.79 (20 mmol) of $TiCl_4$, and 2.53 g (5 mmol) of (+)-**65** in 50 mL of CH_2Cl_2 afforded, after column chromatography (1:1 hexane/ethyl acetate), 1.60 g (100%) of the alcohol **67** as a colorless oil: $[\alpha]^{23}_D$ -23.6° (*c* 1.14, EtOH); ^{1}H NMR δ 7.11 (s, 5 H), 6.78-7.02 (m, 1 H), 5.50 (s, 1 H), 5.18 (s, 1 H), 3.58-4.66 (m, 3 H), 2.74 (d, J = 7.2 Hz, 2 H), 2.10-2.55 (m, 2 H), 0.80-1.92 (m, 14 H); IR (thin film) 3260, 1650, 1610, 765, 720 cm^{-1}.

By the procedure described for the preparation of the lactone **7h**, 1.35 g (4.44 mol) of this alcohol (**67**) and 10 mL of 5% HCl in 15 mL of dioxane afforded after column chromatography (5:1 hexane/ethyl acetate) 0.58 g (85%) of the lactone, $[\alpha]^{22}_D$ -42.8° (*c* 1.59, EtOH).

***N*-Methyl-*N*-[(*S*)-α-(methoxymethyl)phenethyl]-2-[(tributylstannyl)methyl]propenamide ((*S*)-(-)-68).** $[\alpha]^{26}_D$ -38.8° (*c* 3.71, $CHCl_3$); ^{1}H NMR δ 7.17 (m, 5 H), 4.10-5.00 (m, 3 H), 3.20-3.70 (m, 2 H), 3.26 (s, 3 H), 2.82 (s, 3 H), 2.50-3.00 (m, 2 H), 0.40-2.00 (m, 29 H); IR (thin film) 2850, 1750, 1425, 1060 cm^{-1}. Anal. Calcd for $C_{27}H_{47}NO_2Sn$: C, 60.42; H, 8.64; N, 2.81. Found: C, 60.46; H, 8.83; N, 2.61.

Novel Symmetrical and Mixed Carbamoyl and Amino Polysulfanes by Reactions of (Alkoxydichloromethyl)polysulfanyl Substrates with *N*-Methylaniline[1]

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Reactions of (alkoxydichloromethyl)polysulfanes with *N*-methylaniline can be rationalized by a "*carbamoyl*" route where the alkoxydichloromethyl group behaves via loss of alkyl chloride as a "masked" acid chloride or by a "*sulfenyl*" route which reflects fragmentation of the (alkoxydichloromethyl)polysulfanyl functionality into the corresponding alkoxy(thiocarbonyl) and sulfenyl components (cf. Scheme I). Application of this and related chemistry to bifunctional substrates arising from partial or complete chlorination of $[RO(C{=}S)]_2S_m$, R = Me, Et, *i*-Pr, and m = 1-4, has led to $Ph(Me)N(C{=}O)S_n(C{=}O)N(Me)Ph$, n = 2-12; $Ph(Me)N(C{=}O)S_nN(Me)Ph$, n = 1-6; $Ph(Me)NS_nN(Me)Ph$, n = 1-10; $RO(C{=}S)S_n(C{=}O)N(Me)Ph$, n = 2, 3; and $RO(C{=}S)S_nN(Me)Ph$, n = 1-5. These families allowed a test of reversed-phase high-pressure liquid chromatography for evaluating homologies in polysulfane series. Treatment of bis[2-propoxy(thiocarbonyl)] sulfide (**27c**) with sulfuryl chloride in the presence of calcium carbonate conveniently gave distillable bis(chlorocarbonyl)trisulfane (**14**), whereas the same procedure with SO_2Cl_2 alone gave directly (chlorocarbonyl)disulfanyl chloride (**12**) (see Scheme VII). Higher $Cl(C{=}O)S_mCl$, m = 3-5, were indicated but could not be isolated in the course of studies generalizing results on **14** to the preparation of higher $Cl(C{=}O)S_n(C{=}O)Cl$, n = 4-6. The new bis(carbamoyl) monosulfide **61** was obtained by the relatively slow triphenylphosphine or cyanide promoted desulfurization of bis(methylphenylcarbamoyl)disulfane (**4**) (eq 1 and 4); cyanide treatment of the higher polysulfanes $Ph(Me)N(C{=}O)S_n(C{=}O)N(Me)Ph$ for $n \geq 3$ rapidly gave disulfane **4** directly (eq 5).

Previous accounts from this laboratory[3-6] have described a number of examples of compounds containing primary (alkoxydichloromethyl)polysulfanyl moieties, $ROCCl_2S_n$ (R = methyl, ethyl). Since *N*-methylaniline rapidly and quantitatively converts substrates with one or two acid chloride and/or sulfenyl chloride functionalities to the corresponding stable carbamoyl and/or sulfenyl derivatives,[3] it was of interest to extend the *N*-methylaniline reactions to the title substrates. The present report defines two major pathways for these reactions and describes applications of this and related chemistry to generate several novel symmetrical and mixed families of *N*-methylaniline derivatives containing ten or more linearly connected sulfurs. The newly accessed compounds were used to fully test the scope and limitations of a reversed-phase high-pressure liquid chromatography (HPLC) method[5-7] for evaluating homologies in polysulfane series.

Results and Discussion

Reactions of *N*-Methylaniline with (Alkoxydichloromethyl)(chlorocarbonyl)polysulfanes. When title substrates 1[3] were treated with excess *N*-methylaniline followed by aqueous workup, as many as four products were obtained (Scheme I; Table I, lines 1-5). All of these products were recognized and quantitated on the basis of

(1) Preliminary reports of portions of this work have been presented: (a) Schroll, A. L.; Barany, G. Abstracts of the 17th Great Lakes Regional Meeting of the American Chemical Society, St. Paul, MN, June 1-3, 1983. (b) Larka, E. A.; Schroll, A. L.; Barany, G. In "Proceedings of the Thirty-First Annual Conference on Mass Spectrometry and Allied Topics, Boston, MA"; 1983; pp 577-578.

(2) (a) Taken in part from the Ph.D. Thesis of A. L. Schroll, University of Minnesota, 1986. (b) Present address: Department of Chemistry, St. Michael's College, Winooski, VT 05404. (c) Searle Scholar, 1982; National Institutes of Health Research Career Development Award, 1982-1987.

(3) Barany, G.; Schroll, A. L.; Mott, A. W.; Halsrud, D. A. *J. Org. Chem.* **1983**, *48*, 4750-4761, and references cited therein.

(4) Barany, G. *Tetrahedron Lett.* **1983**, *24*, 5683-5686.

(5) Barany, G.; Mott, A. W. *J. Org. Chem.* **1984**, *49*, 1043-1051.

(6) Mott, A. W.; Barany, G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2615-2621.

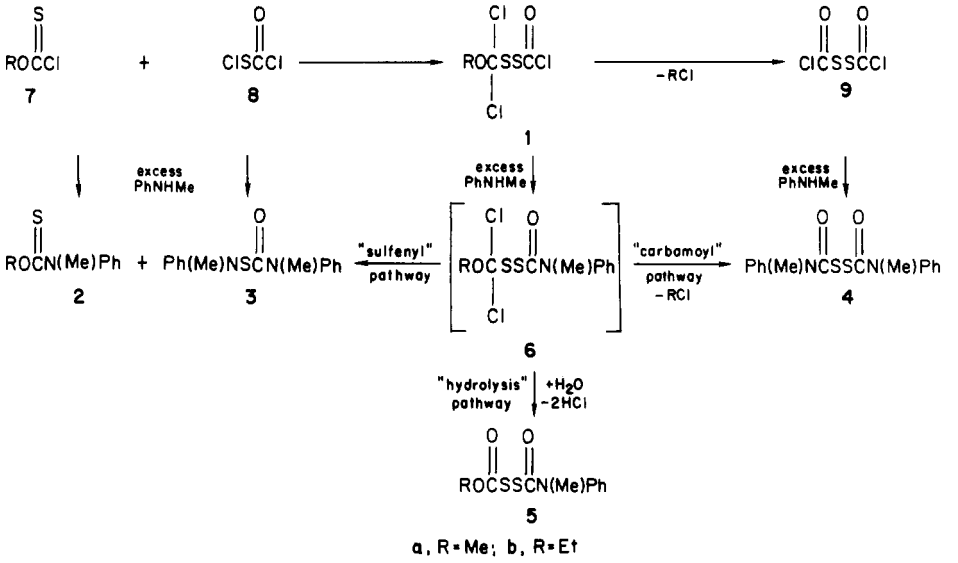
0022-3263/86/1951-1866$01.50/0

Table I. Reactions of (Alkoxydichloromethyl)(chlorocarbonyl)polysulfanes with *N*-Methylaniline[a]

substrate	conditions[a] solvent	equiv	time	overall yield, %	individual product yields, % sulfenyl	carbam	hydrol
1a	$CHCl_3$	5	1 h[b]	98[b]	**2a**, 50 and **3**, 50	**4**, 46	**5a**, 2
1a	$CHCl_3$	8	1 h	102	**2a**, 92 and **3**, 92	**4**, 10	
1b	$CHCl_3$	5	5 min	94	**2b**, 69 and **3**, 59	**4**, 23	**5b**, 3
1b	wet ether	5	5 min	84[c]	**2b**, 49 and **3**, 43	**4**, 18	**5b**, 20
1a	ether	8	10 h	72[d]	**2a**, 68 and **3**, 68	**4**, 2	**5a**, 2
10a	$CHCl_3$	8	1 h	82	**2a**, 79 and **11**, 77	**13**, 3	**15a**, 1
10b	$CHCl_3$	8	1 h	80	**2b**, 76 and **11**, 66	**13**, 4[e]	
10b	wet ether	5	5 min	78[f]	**2b**, – and **11**, –	13, 16	**15b**, 37[g]

[a] The appropriate substrate (1 M in specified solvent, see ref 3 and 5 for sources of **1** and **10**, R = Me and Et, respectively, in series **a** and **b**) was added at <5 °C to a solution of *N*-methylaniline (2 M) in a volume giving the indicated number of equivalents of amine. After the indicated time, ether solutions were filtered, and the ether filtrates or the chloroform homogeneous solutions were washed with aqueous HCl (1 N), further worked up and analyzed in the standard ways (ref 3 and General Methods of Experimental Section, this paper). "Sulfenyl", "carbamoyl", and "hydrolysis" pathways are defined in Schemes I and II. To calculate the overall yield, isolated yields of the two products from the sulfenyl pathway were averaged and added to the isolated yields of remaining products. The (methylthio)carbonyl isomer [MeS-(C=O)N(Me)Ph, see ref 3] was generally found at 2–4% of the level of **2a**. [b] The overall yield and product distribution was the same when the reaction time was 2 min. [c] When the corresponding experiment was carried out with substrate **1a**, *no* **2a** or **3** formed; instead a 2:1:1 ratio of **6a**, **4**, and **5a** formed (see Scheme III) in an overall yield of 75%. Also, when substrate **1b** was reacted with 5 equiv of *N*-methylaniline for 5 min in *dry* ether, *no* **2b** or **3** formed and **6b** was observed along with **4** and **5b** in a 4:3:2 ratio and 86% overall yield. [d] After filtration of the reaction mixture in ether, there was collected *N*-methylaniline hydrochloride, mp 125 °C (lit. mp 122–123 °C, see ref 3), corresponding to 104% yield for conversion of all three chlorines of starting **1a**. [e] Also, 5% of the product mixture was disulfane **4**. [f] Includes ~25% of **16b** (according to Schemes II and III; compare to note c of this table); as discussed in ref 14, quantitation of **16b** was complicated by its partial equilibration with **7b** and **19**. [g] Also, a further 2% was disulfane **5b**.

Scheme I



^{1}H NMR and HPLC parameters of authentic standards prepared by alternate routes in our earlier work.[3] Thiocarbamates **2** and carbamothioamide **3** formed in amounts *equal* to each other and at relatively greater levels when the excess of *N*-methylaniline was larger. In addition, bis(methylphenylcarbamoyl)disulfane (**4**) formed, and (alkoxycarbonyl)(methylphenylcarbamoyl)disulfanes (**5**) were observed in appreciable amounts in those cases when aqueous workup was carried out *shortly* after reactants were combined. These results are conveniently explained (Scheme I) by postulating **6** as the initial intermediates that form by reaction of *N*-methylaniline with substrate **1** at the acid chloride functionality.[8] Whereas carbamoyldisulfanes **5** are formally the "*hydrolysis*" products of intermediates **6** (see Scheme III, discussed below, for further details), the remaining products are explained by defining two pathways and applying them to **6**. The "*sulfenyl*" pathway mirrors with appropriate *N*-methylaniline derivatives (respectively, **2** and **3**) the two synthons, alkoxy(thiocarbonyl) chlorides (**7**)[3] and chlorocarbonylsulfenyl chloride (**8**),[3,9] which combine to form the original substrate (**1**). The "*carbamoyl*" pathway involves loss of alkyl halide from **6** and thus mirrors the novel synthetic route[3] to bis(chlorocarbonyl)disulfane (**9**) (Scheme I, top line). Extension of this chemistry to the trisulfane substrates **10**[5] (Table I, lines 6–8) gave principally products (Scheme II) that could be explained by a "sulfenyl" pathway, particularly *N*-methylanilide **11**[5] which is reflecting (chlorocarbonyl)disulfanyl chloride (**12**).[5,10] However, when aqueous workups of the reactions of **10** were carried out quickly, there were formed again appre-

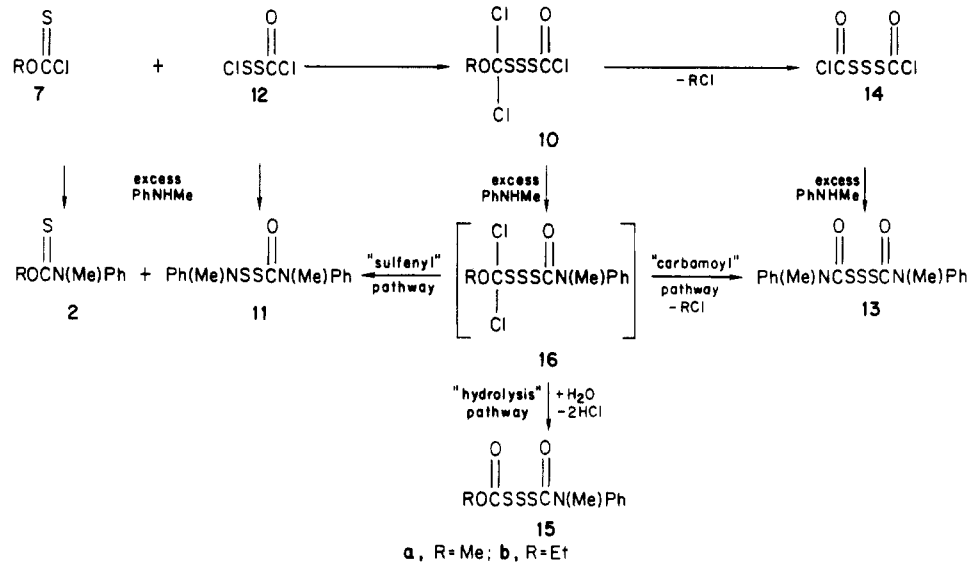
(7) (a) Honeyman, R. T.; Schrieke, R. R. *Anal. Chim. Acta* **1980**, *116*, 345–351. (b) Hiller, K. O.; Masloch, B.; Möckel, H. J. *Z. Anal. Chem.* **1976**, *280*, 293–297. (c) Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971–4972.

(8) The experiments summarized in this section suggest that an acid chloride functionality is more reactive to *N*-methylaniline than an (alkoxydichloromethyl)disulfanyl group.

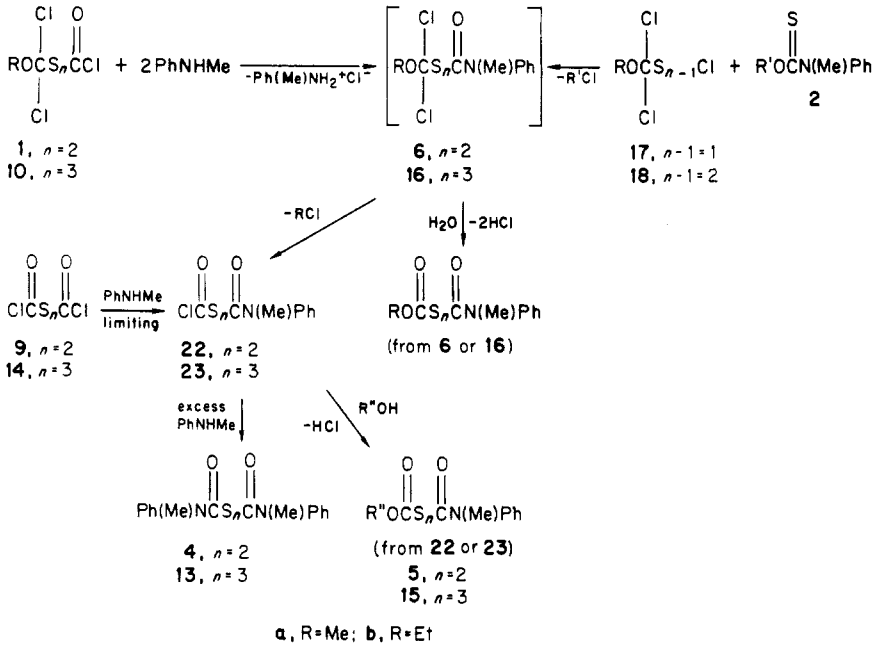
(9) (a) Freedman, B. French Patent 1 372 971, Sept. 18, 1964; *Chem. Abstr.* **1965**, *62*, 1363a. (b) Mott, A. W.; Eastep, S. J.; Słomczyńska, U.; Barany, G. *J. Labelled Compds. Radiopharm.* **1984**, *21*, 329–336.

(10) Böhme, H.; Brinkmann, M.; Steudel, H. P. *Liebigs Ann. Chem.* **1981**, 1244–1251.

Scheme II



Scheme III[14]



ciable amounts of the "carbamoyl" pathway product **13** [which mirrors bis(chlorocarbonyl)trisulfane (**14**)[5,11]], together with "hydrolysis" products **15**.

For additional insights into the mechanisms of the competing pathways just discussed, substrates **1** were treated with 2 equiv of *N*-methylaniline in ethyl ether, filtered quickly to remove the theoretical amount of *N*-methylaniline hydrochloride, and rapidly worked up. Under these conditions, the previously postulated disulfanes **6** were obtained as spectroscopically characterizable species which could then be subjected to a variety of further chemical transformations (Scheme III). Alternative syntheses of the intermediates **6**, involving Harris reactions[3,12] of sulfenyl chlorides **17**[3,13] with thiocarbamates **2**, were rapidly and efficiently carried out in chloroform-*d*. Both routes could be generalized starting respectively with substrates **10**[5] or disulfanyl chlorides **18**[5,10] to obtain the three sulfur-containing intermediates **16**.[14] Freshly generated **1** or **10** readily hydrolyzed to the corresponding carbamoyl polysulfanes (**5**, **15**), in accordance with expectation from experiments discussed earlier (Table I). When left to stand at 25 °C, **1** and **10** lost alkyl chloride within several hours to provide cleanly the unexpectedly stable chlorocarbonyl derivatives **22** and **23** (Scheme III), which were also found among the constituents from controlled reactions (inverse addition) of *N*-methylaniline with

(11) A superior synthesis of compound **14** is reported later in the present paper (see Scheme VII and accompanying text; Experimental Section).

(12) Harris, J. F., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 155–158.

(13) Douglass, I. B.; Osborne, C. E. *J. Am. Chem. Soc.* **1953**, *75*, 4582–4583.

(14) Compounds **16** also underwent the partial equilibrium $ROCCl_2SSS(C{=}O)N(Me)Ph$ (**16**) ⇌ RO(C=S)Cl (**7**) + ClSS(C=O)N(Me)Ph (**19**). The corresponding equilibrium based on **6**, namely $ROCCl_2SS(C{=}O)N(Me)Ph$ (**6**) $\stackrel{?}{\rightleftharpoons}$ RO(C=S)Cl (**7**) + ClS(C=O)N(Me)Ph (**20**) was *not* observed. However, authentic **20** was generated according to RO(C=S)N(Me)Ph (**2**) + SO_2Cl_2 → SO_2 + RCl + ClS(C=O)N(Me)Ph (**20**), and **20** was further characterized by trapping with *N*-methylaniline to give Ph(Me)NS(C=O)N(Me)Ph (**3**) or with thiols to give RSS(C=O)N(Me)Ph (**21**).

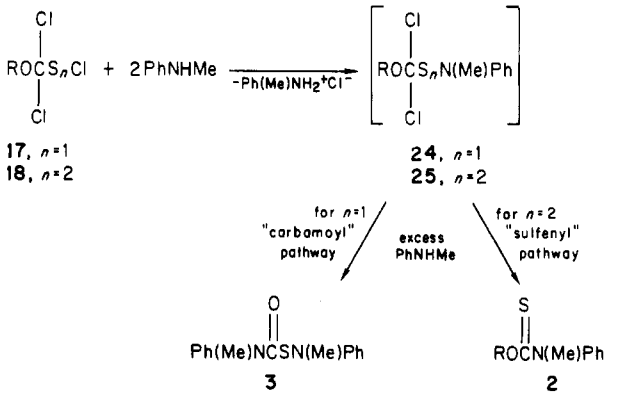
bis(chlorocarbonyl)disulfane (**9**)[3] and bis(chlorocarbonyl)trisulfane (**14**)[5,11] respectively. Intermediates **22** and **23** were readily characterized as they gave the expected products upon treatments with excess alcohol or excess *N*-methylaniline (Scheme III).

Reactions of *N*-Methylaniline with Further Substrates That Contain a Single (Alkoxydichloromethyl)polysulfanyl Moiety (Table II, Lines 1–11). The definitions of "carbamoyl" and "sulfenyl" pathways proved useful for understanding a large variety of results. The difference of a single sulfur atom in substrates **17** and **18** had strikingly different consequences in the *N*-methylaniline reaction (Table II, lines 1–4). We believe that in these cases, initial reactions (Scheme IV) are at the sulfenyl chloride functionality,[15] generating respectively intermediates **24** and **25**. In the former case, the "carbamoyl" pathway prevails to account for the major observed product which is carbamothioamide **3**, whereas in the latter case, thiocarbamates **2** form by a "sulfenyl" pathway.[16]

Regardless of which of three routes[1,3-6] was used to generate the other (alkoxydichloromethyl)polysulfanyl substrates considered in this section, the chemistry of their reactions with *N*-methylaniline was the same. The "sulfenyl" pathway leading in equal amounts to thiocarbamates **2** and the *N*-methylanilides of the sulfenyl component of the original substrate was always major. The "carbamoyl" pathway was minor; it provided the *N*-methylanilide reflecting an acid chloride functionality corresponding to loss of alkyl chloride from the alkoxydichloromethyl group.

Chlorination Products of Primary Bis[alkoxy(thiocarbonyl)] Sulfides and Polysulfanes, and Subsequent Reactions with *N*-Methylaniline. Experiments described in this section show how application of the previously developed understanding of the *N*-methylaniline reaction permits entry to a number of novel series of derivatives. Appropriate *bifunctional* substrates containing relatively stable (alkoxydichloromethyl)polysulfanyl functions were generated by partial or complete chlorination of $[RO(C{=}S)]_2S_n$, R = methyl, ethyl, n = 1–4 (**27–30**, series **a**, **b**; see Scheme V for present discussion and Scheme VI mentioned later for more complete analysis). Thus, it was known from our previous work[1,4,5] that treatment with excess sulfuryl chloride of **27–30** gives bis(alkoxydichloromethyl)polysulfanes (**31–34**) via rapid and specific intramolecular rearrangements of the initial chlorination adducts with the result that all of the sulfurs become linearly connected (Scheme V, top line). When trisulfanes **31** were treated with *N*-methylaniline (Table II, line 12), thiocarbamates **2** were formed in high yields, meaning that the "sulfenyl" pathway was expressed on the (alkoxydichloromethyl)sulfenyl groups on *both* sides of the central sulfur.[16] Extension (Table II, line 13) to the tetrasulfanes **32** gave as the principal process *dual* "sulfenyl" pathways whereby thiocarbamates **2** formed together with bis(methylphenylamino)disulfane (**36**), a compound which

Scheme IV



was made independently from *N*-methylaniline plus sulfur monochloride (S_2Cl_2). The bis(amino)trisulfane **37** was also found and presumably arises by disproportionations. Similarly, *N*-methylaniline with pentasulfanes **33** gave principally thiocarbamates **2** and bis(amino)trisulfane (**37**) as well as lesser amounts of bis(amino)tetrasulfane **38** and bis(amino)pentasulfane **39**.

The most interesting result in the reactions (Scheme V, bottom right; Table II, lines 13, 14) of *N*-methylaniline with bis(alkoxydichloromethyl)polysulfanes (**32**, **33**) was the observation of the *new* class of derivatives (**40**, **41**) which could be explained by invoking the more common "sulfenyl" pathway on one side and the less preferred "carbamoyl" pathway on the other side. Another way of accounting for products **40** or **41** was to assume that substrates **32** or **33** lose alkyl chloride (see top line of Scheme VI) to provide (alkoxydichloromethyl)(chlorocarbonyl)polysulfanes (**44**, **45**) as intermediates which react further with *N*-methylaniline in the fashion already defined (Schemes I and II). Lastly, there was no evidence for either a *dual* "carbamoyl" pathway to give bis(carbamoyl)polysulfanes (e.g., starting from **32**, no **62** was obtained; see next section for structure and *successful* means for preparation of derivative **62**), nor for any products of the form $RO(C{=}O)S_nN(Me)Ph$ or $RO(C{=}O)S_{n+1}(C{=}O)N(Me)Ph$ with $n > 2$ (these are known[3,5] for n = 1, 2) that might arise by a "sulfenyl" or "carbamoyl" pathway expressed on one side combined with a "hydrolysis" pathway (compare to Table I, lines 4 and 8) on the other side.

The *N*-methylaniline reaction was also used to probe *mixtures* resulting[17] from treatment of $[RO(C{=}S)]_2S_m$ with amounts of sulfuryl chloride that were insufficient to complete the chlorination/rearrangement of both thiocarbonyl groups. With appropriate conditions, the mixed species[18] **47–50** (center set of structures, Scheme VI) could be made to predominate, as monitored by ^1H and ^{13}C NMR which additionally revealed the unreacted **27–30** and the fully chlorinated **31–34**. Treatment at this stage with *N*-methylaniline gave rise by "sulfenyl" pathways to the family of [alkoxy(thiocarbonyl)](amino)polysulfanes (**51–55**); this set of results is analogous to several reported earlier (Table II, lines 7–11), and in each case the *major* component had the same number of sulfurs m as the parent $[RO(C{=}S)]_2S_m$. It was also found that in contrast to the result[17] with the corresponding disulfane, distillation of the mixture resulting from treatment of bis[methoxy-

(15) The experiments summarized in Scheme IV suggest that a sulfenyl chloride functionality is more reactive to *N*-methylaniline than an (alkoxydichloromethyl)disulfanyl group; compare to comment in ref 8.

(16) To balance the equations for reactions of *N*-methylaniline with either (alkoxydichloromethyl)disulfanyl chlorides (**18**) or bis(alkoxydichloromethyl)trisulfane (**31**) it is necessary to invoke bis(methylphenylamino) sulfide (**35**). We have synthesized authentic **35** and found that this compound does not survive the standard aqueous workup used in the *N*-methylaniline assay described in ref 3 and applied in this work. Compound **35** has been mentioned by the following: (a) Lambrech, J. A.; Hensley, W. H.; Kent, R. E.; Lynch, J. E. U.S. Patent 2 902 402, Sept. 1, 1959; *Chem. Abstr.* **1960**, *54*, 5716b. (b) Grabowski, T.; Wieczffinski, K. *Biul. Wojsk. Akad. Tech.* **1969**, *18*, 59–70, 71–83; *Chem. Abstr.* **1969**, *71*, 123805q, 123807s.

(17) As described more fully in ref 3, "cracking" distillation of the mixtures resulting from treatment of bis[alkoxy(thiocarbonyl)]disulfanes (**28**) with one equivalent of sulfuryl chloride provides alkoxy(thiocarbonyl) chlorides (**7**).

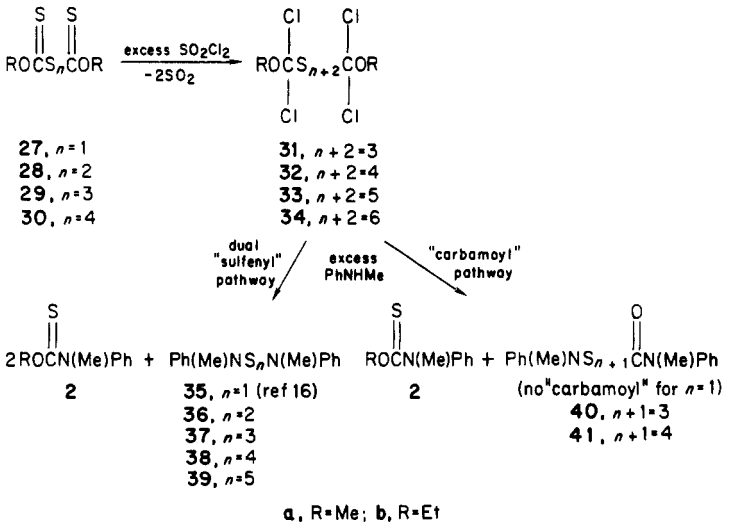
(18) Compounds **47** and **48** were also major products when potassium alkyl xanthates (**57**) were reacted respectively with (alkoxydichloromethyl)sulfenyl (**17**) or -disulfanyl (**18**) chlorides (Scheme VI).

Table II. Reactions of (Alkoxydichloromethyl)polysulfanyl Compounds with *N*-Methylaniline[a]

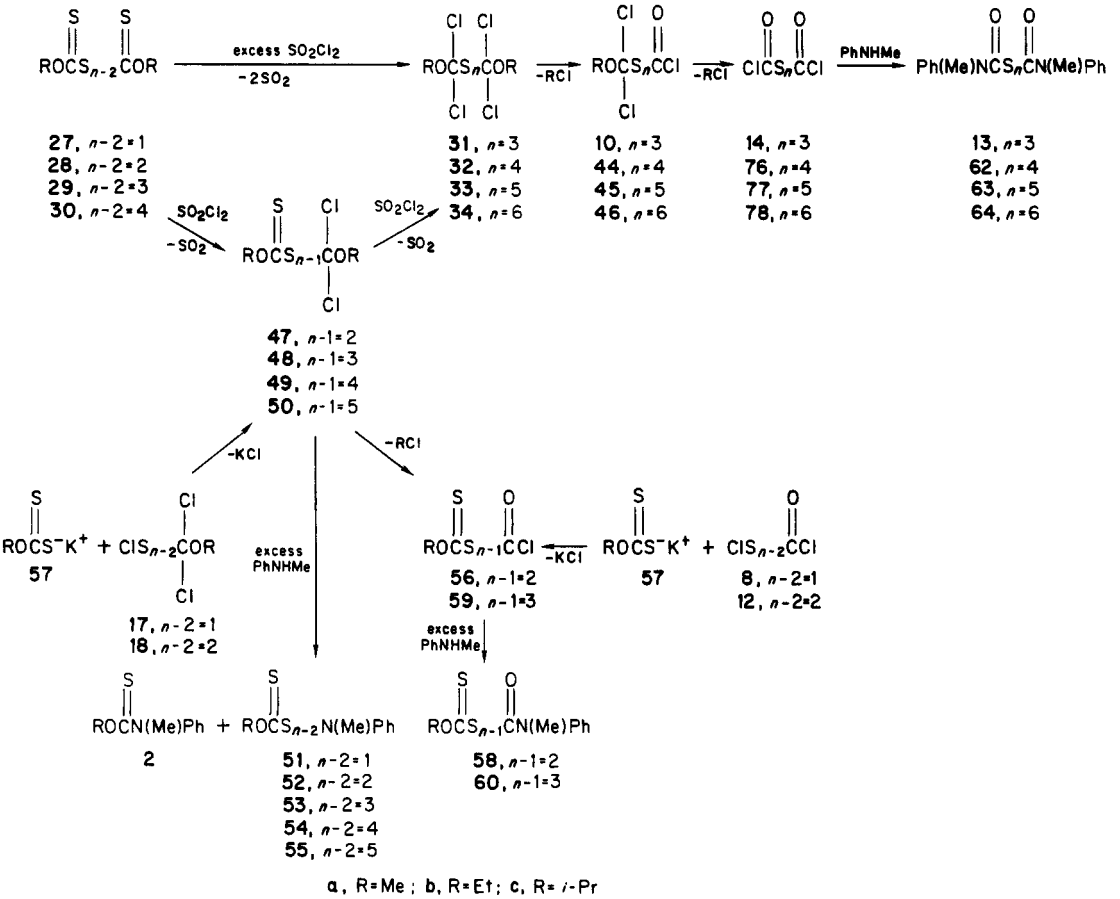
substrate	overall yield, %	individual product yields, %		
		sulfenyl pathway	carbamoyl pathway	other
$MeOCCl_2SCl$ (**17a**)[3,13]	92	**2a**, <2	Ph(Me)N(C=O)SN(Me)Ph (**3**),[3] 91	
$EtOCCl_2SCl$ (**17b**)[3,13]	90	**2b**, 2	Ph(Me)N(C=O)SN(Me)Ph (**3**),[3] 88	
$MeOCCl_2SSCl$ (**18a**)[5,10]	91[b,c]	**2a**, 91	Ph(Me)N(C=O)SSN(Me)Ph (**11**),[5] <1	
$MeOCCl_2SSMe$[4,6]	88[d]	**2a**, 73 and MeSN(Me)Ph,[3] 27	MeSS(C=O)N(Me)Ph (**21a**),[3] 13	MeSSMe, 50
$EtOCCl_2SSMe$[4,6]	86[d]	**2b**, 73 and MeSN(Me)Ph,[3] 19	MeSS(C=O)N(Me)Ph (**21a**),[3] 19	MeSSMe, 48
$MeOCCl_2SSEt$[4,6]	73[d]	**2a**, 63 and EtSN(Me)Ph,[3] 61	EtSS(C=O)N(Me)Ph (**21b**),[3] 11	
$MeOCCl_2SS(C{=}O)OMe$[3,5]	62	**2a**, 47 and MeO(C=O)SN(Me)Ph,[3] 57	MeO(C=O)SS(C=O)N(Me)Ph (**5a**),[3] 10	
$MeOCCl_2SS(C{=}O)OEt$[3,5]	74	**2a**, 62 and EtO(C=O)SN(Me)Ph,[3] 67	EtO(C=O)SS(C=O)N(Me)Ph (**5b**),[3] 7	
$MeOCCl_2SS(C{=}O)SMe$[3,6]	80	**2a**, 75 and MeS(C=O)SN(Me)Ph,[6] 75	MeS(C=O)SS(C=O)N(Me)Ph (**26a**),[3] 5	
$MeOCCl_2SSS(C{=}O)OMe$[5]	94	**2a**, 89 and MeO(C=O)SSN(Me)Ph,[5] 87	MeO(C=O)SSS(C=O)N(Me)Ph (**15a**),[5] 6	
$MeOCCl_2SSS(C{=}O)OEt$[5]	59	**2a**, 66 and EtO(C=O)SSN(Me)Ph, 48	EtO(C=O)SSS(C=O)N(Me)Ph (**15b**), <1	EtO(C=O)SN(Me)Ph,[3] 3
$MeOCCl_2SSSCCl_2OMe$ (**31a**)	81[b,c]	**2a**, 81	Ph(Me)N(C=O)SSN(Me)Ph (**11**),[5] <1	
$MeOCCl_2SSSSCCl_2OMe$ (**32a**)	85[b,e]	**2a**, 100[e] and Ph(Me)NSSN(Me)Ph (**36**), 58	Ph(Me)N(C=O)SSSN(Me)Ph (**40**), 5	**37**, 8; **38**, 4; **39**, 4; **53a**, 6
$MeOCCl_2SSSSSCCl_2OMe$ (**33a**)	78[b,e]	**2a**, 106[e] and Ph(Me)NS_3N(Me)Ph (**37**), 53	Ph(Me)N(C=O)S_4N(Me)Ph (**41**), 3; Ph(Me)N(C=O)SSSN(Me)Ph (**40**), 2	**36**, 6; **38**, 10; **39**, 3
$MeOCCl_2SSSSSSCCl_2OMe$ (**34a**)	88[b,e]	**2a**, 109[e] and Ph(Me)NS_4N(Me)Ph (**38**), 34	Ph(Me)N(C=O)SSSN(Me)Ph (**40**), 2; Ph(Me)N(C=O)S_4N(Me)Ph (**41**), 3[f]	**36**, 8; **37**, 25; **39**, 11

[a] Reactions were carried out and analyzed similarly to the way described in note *a* of Table I. The substrate (1 M in $CHCl_3$, see indicated references for sources of substrates) was added at 5 °C to the amount of *N*-methylaniline solution (2 M in $CHCl_3$) corresponding to 3 equiv of amine used per chlorine atom in the starting substrate, and reactions were worked up after 10 min at 25 °C. The "sulfenyl" and "carbamoyl" pathways are illustrated in Schemes IV and V and further discussed in the text; see also note *e* to this table. [b] When the identical experiment was carried out in the ethyl series **b**, yields and corresponding products agreed exactly, within experimental error. [c] No **35** was isolated, as explained in text ref 16. [d] The appropriate *O,S*-dialkyl dithiocarbonates were reacted with SO_2Cl_2 (both reagents 1 M in $CDCl_3$); toluene was included as an internal standard. After reaction with *N*-methylaniline, two washings were carried out with aqueous HCl (0.5 N rather than the usual 1 N) in an attempt to preserve the thioamide co-product. This was successful in the *S*-ethyl series whereas in the *S*-methyl series, dimethyl disulfide formed by partial hydrolysis of MeSN(Me)Ph. [e] Products under "sulfenyl" pathway reflect the *dual* process applied on both (alkoxydichloromethyl)sulfenyl groups of the substrate, whereas products under "carbamoyl" pathway reflect the carbamoyl process on one side and the sulfenyl on the other (Scheme V). Overall yield is calculated based on all products *excluding* thiocarbamates **2**; whereas the yield of **2** is calculated based on 2 equiv formed in the dual sulfenyl pathway and 1 equiv formed in the carbamoyl pathway. [f] Note that the anticipated carbamoyl product, pentasulfane **42**, did not form. The same experiment was carried out on a sample of **34a** that had been stored at −20 °C for 1.5 yr, and therefore, contained substantial levels of acid chloride **46a** by loss of MeCl from **34a** (see Scheme VI, middle of top line). In this case, both **42** and **43** were observed; ratios of carbamoyl products Ph(Me)N(C=O)S_nN(Me)Ph were 1.0:0.7:0.3:0.4:0.3:0.1 (n = 1–6, in given order). By comparison, ratios of Ph(Me)NS_nN(Me)Ph were 1.0:0.3:0.3:0.2:0.1 (n = 2–6, in given order).

Scheme V



Scheme VI



(thiocarbonyl)] sulfide (**27a**) with 1 equiv of sulfuryl chloride gave directly [methoxy(thiocarbonyl)](chlorocarbonyl)disulfane (**56a**) presumably by loss of methyl chloride from disulfane intermediate **47a**. Acid chloride **56a** was independently made from potassium methyl xanthate (**57a**) and chlorocarbonylsulfenyl chloride (**8**) (Scheme VI, bottom right), and **56a** with *N*-methylaniline gave the expected carbamoyl disulfane (**58a**).[19] The chemistry of the previous sentence was generalized to R = ethyl and 2-propyl (series **b**, **c**) and to trisulfane acid chlorides **59** and carbamoyltrisulfanes **60** (Scheme VI and Experimental Section).

Access to Bis(chlorocarbonyl)polysulfanes, the Corresponding *N*-Methylanilides, and Related Compounds. In our earlier work,[3] we described both bis(chlorocarbonyl)disulfane (**9**) and its *N*-methylanilide **4** (right side of Scheme I). For a number of reasons, we were

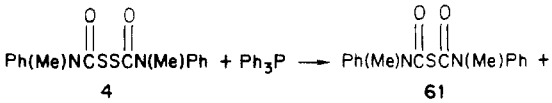
(19) Crystalline **58a** underwent a quantitative solid-state disproportionation upon storage for several months at 25 °C, yielding bis(methylphenylcarbamoyl)disulfane (**4**) admixed with elemental sulfur (details in Experimental Section). In contrast, crystals of two closely related compounds with similar melting points, namely **26a** (the isomer of **58a** with an oxygen and a sulfur switched; reported in ref 3, mp 80–81 °C) and **5a** (thiocarbonyl of **58a** replaced by a carbonyl; reported in ref 3, mp 84–85 °C) were entirely unchanged after 3 years of ambient storage.

Table III. Reactions Yielding Mixtures of Bis(carbamoyl)polysulfanes, Ph(Me)N(C=O)S_n(C=O)N(Me)Ph[a]

method	yield, (%)	product distribution, (%), n = 1	2	3	4	5	6	7	8	9	10	11	12
2 EtO(C=S)N(Me)Ph (**2b**) + SCl_2	100[b]	6	20	46	12	12	4						
2 *i*-PrO(C=S)N(Me)Ph (**2c**) + SCl_2	102[b]		2	91	5	2							
2 MeO(C=S)N(Me)Ph (**2a**) + S_2Cl_2	99[b,c]		0	1	97	*d*	2						
2 *i*-PrO(C=S)N(Me)Ph (**2c**) + S_2Cl_2	100[b]		0	<1	98	*d*	1						
2 MeO(C=S)N(Me)Ph (**2a**) + S_3Cl_2[e]	78[b,c]			3	13	61	12	4	3	3			
2 MeO(C=S)N(Me)Ph (**2a**) + S_nCl_2[f]	90[b,c,g]			<1	2	5	14	28	16	14	8	7	5
Ph(Me)N(C=O)SSS(C=O)N(Me)Ph (**13**) + 1 equiv of KCN	65[h,i]	5	90	5									
Ph(Me)N(C=O)SSS(C=O)N(Me)Ph (**13**) + 3 equiv of KCN	61[h,j,k]	94	5	2									
Ph(Me)N(C=O)SSSS(C=O)N(Me)Ph (**62**) + 1 equiv of KCN	83[h,l,m]	1	88	7	5								
Ph(Me)N(C=O)SSSS(C=O)N(Me)Ph (**62**) + 6 equiv of KCN	75[h,l]	95	2	2	1								

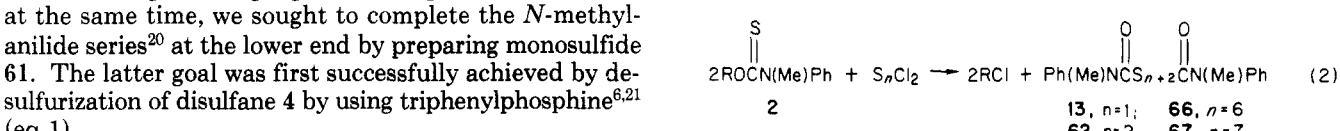
[a] Preparations of *pure* Ph(Me)N(C=O)S_n(C=O)N(Me)Ph, n = 1–6 [respectively **61**, **4** (ref 3), **13**, and **62**–**64**], are described in the Experimental Section. Assignments of higher polysulfanes, n = 7–12, are implicit from a number of compelling considerations (e.g., Figure 2 and accompanying discussion) presented throughout this paper. The Experimental Section further describes (hence information not repeated in this table) the in situ generations of bis(chlorocarbonyl)polysulfanes (**14**, **76**–**78**), which were characterized by reactions with *N*-methylaniline to yield distributions of bis(carbamoyl)polysulfanes which species with n = 2–8. [b] Procedure in Experimental Section, just before description of **62**, is entitled "Harris Reactions (eq 2) for Preparations of Bis(methylphenylcarbamoyl)polysulfanes". [c] Also observed was 10–15% of MeO(C=O)N(Me)Ph (ref 3), which formally differs from the starting material **2** of the reaction by substitution of a carbonyl group for a thiocarbonyl group. This *O*-alkyl carbamate byproduct arose during the reaction, as it was absent from starting **2a**. [d] Small amounts of bis(carbamoyl)pentasulfane **63** could not be quantitated in the presence of large amounts of tetrasulfane **62** because of the similarities in HPLC retention times (text Figure 2 and supplementary material Table V). [e] The S_3Cl_2 used was in fact a mixture of S_2Cl_2:S_3Cl_2:S_4Cl_2 = 0.2:1.0:0.1; details in last paragraph of General Methods in Experimental Section. [f] The S_nCl_2 used was the distillation residue in the S_3Cl_2 preparation; details with last paragraph of General Methods in Experimental Section. An empirical mol wt of 300 was assumed in setting up the reaction according to the indicated stoichiometry; when this weight was assumed to be 200, the distribution of polysulfanes was the same, but there was considerable unreacted **2a** remaining. The fact that the bis(carbamoyl)polysulfane distribution was centered about heptasulfane **65** is consistent with the results when the same S_nCl_2 was treated directly with excess *N*-methylaniline [see "Higher bis(methylphenylamino)polysulfanes" in Experimental Section]. [g] The polysulfane distribution was exactly the same when starting with the 2-propyl precursor **2c**, except that *no* *i*-PrO(C=O)N(Me)Ph (compared to note *b*) was formed. A further evaluation of these mixtures was achieved by treating with various numbers of equivalents of cyanide in the same way described for pure compounds **13** and **62** later in this table (lines 7–10). With a sufficient excess of cyanide, all HPLC peaks disappeared and were replaced by one due to monosulfide **61**; the amount of thiocyanate formed saturated at about 6 equiv indicating that the average polysulfane chain length was seven. Lesser amounts of cyanide were quantitatively converted to thiocyanate while the higher polysulfane peaks were rapidly degraded primarily to disulfane **4** (>85%), with a tailing distribution of higher polysulfanes. [h] The polysulfane substrates in $CDCl_3$ solution (0.15–0.2 M) were stirred together with heterogeneously suspended potassium cyanide until their endpoints (5 days, 25 °C); see notes *k* and *m* of this table for indication of intermediates and kinetics. Subsequently, the organic phase was washed twice with equal volumes of water and analyzed by HPLC and ^{1}H NMR. The combined aqueous washes were brought to a standard volume, and by modification of literature analytical methods (ref 31), a portion (5 mL) was treated in turn with concentrated H_2SO_4 (0.4 mL), 10% aqueous HNO_3 (10 mL), and 10% ferric alum indicator in 3% aqueous HNO_3 (10 mL). After dilution with water, the absorbance of red color was measured immediately at 480 nm and compared to freshly prepared KSCN standards (ϵ_{480} ~1 × 10^3). [i] Of the single equiv of cyanide used, 88% was recovered as thiocyanate. Further evidence that **4** was the major product came from the mp of the crystalline organic product, 240–243 °C (identical with literature value for pure **4**, ref 3). [j] Thiocyanate (1.7 equiv) formed in this experiment; with further equivalents of cyanide used, a full 2.0 equiv of thiocyanate was formed. The organic product had mp 87–90 °C, compared to 90–91 °C for pure **61** (this work). [k] The experiment was set up with toluene as an internal standard, and aliquots were quenched and evaluated by HPLC as a function of time. Disulfane **4** formed with $t_{1/2}$ ~2.5 min; the final yield was 82%. Interestingly, small amounts of tetrasulfane **62** and pentasulfane **63** formed as transient species under the reaction conditions even though they were absent from starting **13**. [l] Starting with 1 equiv of cyanide, quantitative conversion to thiocyanate; starting with 6 equiv of cyanide, 2.94 equiv of thiocyanate formed. The mp data on organic products from these two reactions were respectively 235–244 °C (compare to note *i*) and 82–88 °C (compare to note *j*). [m] The experiment carried out in analogous fashion to note *i* showed that disulfane **4** formed with $t_{1/2}$ ~3.5 min and final yield 97%. During the course of the reaction, up to 20% of trisulfane **13** formed, as well as small amounts of pentasulfane **63** and hexasulfane **64**.

interested in generating higher homologues of **9** and **4**, and at the same time, we sought to complete the *N*-methylanilide series[20] at the lower end by preparing monosulfide **61**. The latter goal was first successfully achieved by desulfurization of disulfane **4** by using triphenylphosphine[6,21] (eq 1).



4 61 (1)

Entries into the higher bis(carbamoyl)polysulfanes were first achieved by *dual* Harris reactions[3,12,22] of thiocarbamates (**2**) with dichloropolysulfanes (eq 2; Table III, lines 1–6). The expected products (**13**, **62**) were the major ones when freshly purified sulfur dichloride (n = 1) or sulfur monochloride (n = 2) was used, but considerable disproportionation occurred as evidenced by HPLC detection of linear polysulfanes with up to six sulfurs. Sulfur trichloride[23] (n = 3, 80% purity) led to primarily pentasulfane **63**, whereas a *residue* from the S_3Cl_2 preparation which contained a distribution of S_nCl_2 (n = 3–10) was



2 (2)

13, n=1; **66**, *n*=6
62, n=2; **67**, *n*=7
63, n=3; **68**, *n*=8
64, n=4; **69**, *n*=9
65, n=5; **70**, *n*=10

a, R=Me; b, R=Et; c, R=*i*-Pr

(20) A thorough literature search revealed that the only prior report of a bis(carbamoyl) monosulfide system was a brief mention as a minor component of the complex mixture of thermolysis products of carbamoyl sulfoxides: Gozzo, F.; Masoero, M.; Santi, R.; Galluzzi, G.; Barton, D. H. *Chem. Ind. (London)* **1975**, 221–226.

(21) (a) Schönberg, A. *Chem. Ber.* **1935**, *68*, 163–164. (b) Mukaiyama, T.; Takei, H. In "Topics in Phosphorus Chemistry"; Griffith, E. J., Grayson, M., Eds.; John Wiley: New York, 1976; Vol. 8, pp 587–645. (c) Harpp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1980**, *45*, 5155–5160 and references cited therein.

(22) Mühlstädt H.; Widera, R. *J. Prakt. Chem.* **1978**, *320*, 123–127.

(23) Fehér, F. In "Handbook of Preparative Inorganic Chemistry", 2nd Ed.; Brauer, G., Ed.; Academic Press: New York, 1963; Vol. 1, pp 373–375.

used to generate a mixture of *N*-methylanilides (**62–70**) with 4 to 12 sulfurs. At the same time, mixtures of bis(amino)polysulfanes (**36–39** and **71–75**) with 2 to 10 sulfurs were made by direct reaction of that residue with *N*-methylaniline (eq 3).

excess PhNHMe + S_nCl_2 ⟶ Ph(Me)NS_nN(Me)Ph (3)

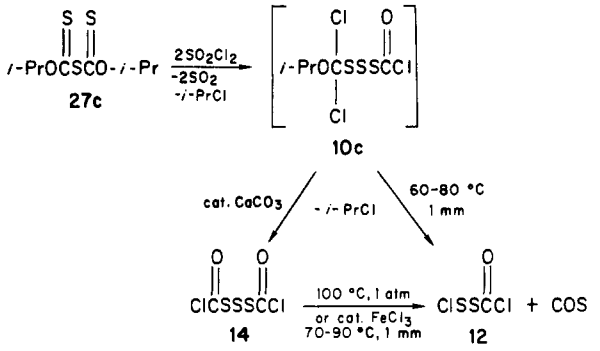
35, n=1 **71**, n=6
36, n=2 **72**, n=7
37, n=3 **73**, n=8
38, n=4 **74**, n=9
39, n=5 **75**, n=10

The best syntheses of analytically pure bis(carbamoyl)polysulfanes were by *N*-methylaniline treatments of the corresponding bis(chlorocarbonyl)polysulfanes (structures **14** and **76–78**, upper right of Scheme VI). The trisulfane **14** was first prepared[5] in situ by treatment of bis(methoxydichloromethyl)trisulfane (**31a**) with a catalytic amount of ferric chloride, but we now find[24] that chlorination in petroleum ether of bis[2-propoxy(thiocarbonyl)] sulfide (**27c**)[25] in the *presence* of catalytic calcium carbonate gives **14** directly (Scheme VII). The chlorination mixture was filtered and distilled at 0.2 mm to provide **14** for the first time as a relatively stable colorless liquid. In contrast, a standard chlorination (*no* calcium carbonate) was arrested at predominantly (2-propoxydichloromethyl)(chlorocarbonyl)trisulfane (**10c**),[26] which when subjected to distillation at 1–2 mm lost carbonyl sulfide and 2-chloropropane to give *directly* (chlorocarbonyl)disulfanyl chloride (**12**). This represents a practical and facile preparation of the useful reagent **12**,[5,10,27] which also arose from bis(chlorocarbonyl)trisulfane (**14**) when this compound was either thermolyzed at 100 °C or vacuum distilled from catalytic ferric chloride (see Scheme VII).

With some modifications in experimental details, it was also possible to extend the previous results and obtain bis(chlorocarbonyl)tetrasulfane (**76**) by chlorination of **28c** (Scheme VI, top line). Reagent **76**, although not vacuum distillable, was stable for months at 25 °C. However, on earlier occasions before the procedure was optimized, preparations of **76** were noted which decomposed to COS gas and S_2Cl_2. The importance of working in the 2-propoxy system (Scheme VI; series **c**) was emphasized by results when bis(methoxydichloromethyl)tetrasulfane (**32a**) was treated with $FeCl_3$: products included not only desired **76** but also bis(chlorocarbonyl)disulfane (**9**) and trisulfane (**14**) as well as S_2Cl_2 and MeS(C=O)Cl.

Pentasulfane **77** and hexasulfane **78** arose upon in situ chlorination[28] of **29c** and **30c**, respectively (Scheme VI, top line). In these cases, desulfurization and disproportionation were significant as reflected by the HPLC pattern of bis(carbamoyl)polysulfanes after derivatization with *N*-methylaniline. Even so, it was possible to isolate out of

Scheme VII



the mixtures the *pure* expected products (**63**, **64**) in modest yields.

Motivated by our isolation of a small amount of **40** upon *N*-methylaniline treatments of **32** (Scheme V), we wondered about the existence and possible properties of the corresponding (chlorocarbonyl)trisulfanyl chloride (**79**) and higher homologues of the known[3,5,9,10] **8** and **12**. The

ClC(S_n)Cl

8, n=1
12, n=2
79, n=3
80, n=4
81, n=5

Ph(Me)NC(S_n)N(Me)Ph

3, n=1
11, n=2
40, n=3
41, n=4
42, n=5
43, n=6

formation of **79–81** was concluded in certain experiments which were primarily directed at obtaining bis(chlorocarbonyl)polysulfanes (**76–78**). Thus, chlorinations of **28–30c** were carried out until the 2-propyl group was completely converted to 2-chloropropane, and the resultant mixtures were treated with *N*-methylaniline. The family of (carbamoyl)(amino)polysulfanes **40–43** were unambiguously noted, usually in small amounts, as components of the often complex product mixtures.

Related chemistry did, however, allow generation of *substantial* levels of derivatives **40–43**. This occurred when *N*-methylaniline was used to treat chlorination mixtures of **28–30c** at those stages when considerable levels of the 2-propoxydichloromethyl functionality (structures **44–46c**, middle of top line of Scheme VI) remained intact.[24] Now, by homology to results already described[8,26] (Schemes I and II, Table I; which describe series **a**, **b**), a "sulfenyl" pathway giving the *O*-2-propyl thiocarbamate **2c** as a coproduct, together with reaction of the acid chloride functionality on the other side in an apparent "carbamoyl" pathway, led to the required derivatives (**40–43**) as major components of the product mixtures.

Cyanide-Promoted Desulfurization of Bis(carbamoyl)polysulfanes. This paper has so far described sources for pure bis(carbamoyl)polysulfanes (**61**, **4**, **62–64**) with one to six sulfurs and for mixtures (**62–70**) of this family with 4 to 12 sulfurs (eq 2). We consider in this section the course of reactions of these compounds with heterogeneously suspended potassium cyanide. As a point of departure, we developed these conditions[29–31] for the

(24) An initial precedent for dithiocarbonyl formation by chlorination of *secondary* alkoxy(thiocarbonyl)sulfenyl compounds with subsequent facile loss of secondary alkyl chloride is reported in ref 9b; see also ref 6. We find in some of the systems studied in the present work that the (2-propoxydichloromethyl)polysulfanyl functionality can be quite stable as part of neat compounds; heating in vacuo (30–40 °C, 10–30 mm) for several h is required to completely drive off 2-chloropropane. On the other hand, solutions of these compounds in $CDCl_3$ at 25 °C lose 2-chloropropane quickly (10–30 min), limiting experiments that monitor their reactions by ^1H NMR.

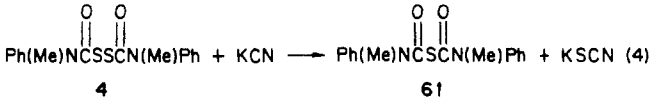
(25) Whitby, G. S.; Greenberg, H. *Trans. R. Soc. Canada Sect. 3* **1929**, *23*, 21–24; *Chem. Abstr.* **1930**, *24*, 593.

(26) As detailed in the Experimental Section description for **12** (method D), the chlorination mixture assigned to be primarily **10c** gave products in an *N*-methylaniline assay that were entirely analogous to the previously worked out chemistry of **10a** and **10b** (Scheme II; Table II, lines 6 and 7).

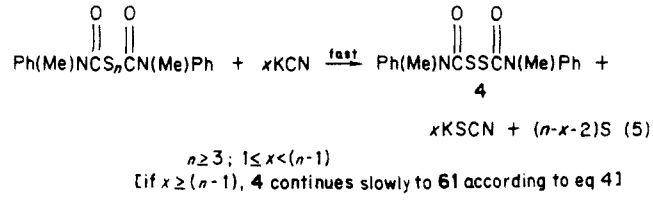
(27) Mott, A. W.; Barany, G. *Synthesis* **1984**, *8*, 657–660.

(28) In all experiments where chlorinations of **27–30c** (Scheme VI) were carried out under nominally identical conditions, the ease of the overall process (total conversion of 2-propyl groups to 2-chloropropane) was reproducibly found to be in the direction **28c** (easiest) < **30c** < **29c** < **27c**. These observations bear on the optimization of conditions for generating the corresponding bis(chlorocarbonyl)polysulfanes **76**, **78**, **77**, and **14** and on the competing pathways discussed in the following text paragraph which give the appropriate (chlorocarbonyl)polysulfanyl chlorides, respectively **79**, **81**, **80**, and **12**.

smooth and quantitative, although relatively sluggish, degradation of disulfane 4 to monosulfide 61 (eq 4).

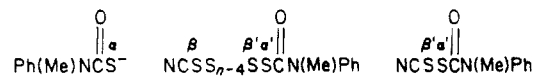


In contrast to the reaction (eq 4) of disulfane 4, rates and stoichiometries of cyanide treatments of higher bis(carbamoyl)polysulfanes showed a number of surprising features (Table III, lines 7–10; eq 5). Disulfane 4 was the



major product formed rapidly and directly (with minimal levels of polysulfanes of intermediate size) regardless of the number of sulfurs in the starting polysulfane. Furthermore, all of the cyanide introduced for the reaction was transformed to thiocyanate, and 1 equiv of cyanide was already sufficient to drive most of the starting polysulfane[32] directly to disulfane 4. Finally, the specificity of the desulfurization to carbamoyl polysulfanes was indicated by a control experiment which showed that *no* reaction ensued upon lengthy treatment (2 weeks) of dimethyl trisulfide under the standard reaction conditions.

The results just described are conveniently explained by postulating a particular affinity of the "β" sulfur of a polysulfane chain to attack by the cyanide nucleophile.[33] The driving force for scission of the bond between the "α" and "β" sulfurs is formation of thiocarbamate 82, with the



other product being polysulfanyl cyanate 83. For $n = 3$, 83 is identical with (thiocarbamoyl)cyanate 84, which by analogy to a disulfide synthesis due to Hiskey[34] should react with 82 to provide the observed product 4 plus thiocyanate. For $n \geq 4$, either 83 desulfurizes to 84, which again reacts with 82, or 82 directly attacks the "α'" sulfur to eject inorganic polysulfanyl cyanate. Attack of 82 on one of the other sulfurs of 83 is not a significant process, but may occur somewhat to account for transient levels of trisulfane 13 or higher species which are again attacked by cyanide at their "β" sulfurs. Finally, the appropriate inorganic chemistry of cyanide and elemental sulfur accounts for complete conversion of cyanide to thiocyanate.

Chromatographic and Spectral Characterization of Homologous Series of *N*-Methylanilides. In other recent work from this laboratory,[5,6] we have found good success in correlating reversed-phased HPLC retention times[35] with numbers of linearly connected sulfurs in a polysulfane chain. Data from the present work are summarized in Figures 1 and 2; details are in the supplementary material. Insertion of polar carbonyl functions into otherwise identical structures led to earlier elution, whereas substitution of a thiocarbonyl for a carbonyl or the change in alkyl group from methyl to ethyl to 2-propyl resulted in later elution (Figure 1). In three of four lengthy series first investigated in the present work (Figure 2), log k' was found to vary linearly with the number of sulfurs over the entire range of compounds. The sole exceptions are in the series Ph(Me)N(C=O)S_n(C=O)N(Me)Ph, where linearity begins with $n = 6$. In this series, trisulfane 13 elutes unexpectedly early, even before disulfane 4; furthermore, tetrasulfane 62 and pentasulfane 63 essentially coelute. Perhaps some conformational effects could account for these anomalies.

The polysulfane series were also characterized by UV, ^{1}H NMR, and mass spectrometry, as sketched in the Experimental Section and further documented in the supplementary material. UV allowed distinction between the generic chromophores XS_nX, $X(C{=}Y)S_nN$, and $X(C{=}Y)S_n(C{=}Y)X$, with X = O, S, or N and Y = O or S. The highly characteristic *N*-methyl singlet of the *N*-methylaniline derivatives facilitated unambiguous resolution of Ph(Me)N(C=O)S_n(C=O)N(Me)Ph for $n = 1$–6, Ph(Me)N(C=O)S_nN(Me)Ph for $n = 1$–4, Ph(Me)NS_nN(Me)Ph for $n = 1$–5, and MeO(C=S)S_nN(Me)Ph for $n = 1$–3; interestingly, the shifts did *not* vary monotonically with increasing number of sulfurs. Useful molecular ions (usually 2–10% of base intensity) upon electron impact were obtained with Ph(Me)N(C=O)S_n(C=O)N(Me)Ph for $n = 1$–4, Ph(Me)N(C=O)S_nN(Me)Ph for $n = 1$–3, Ph(Me)NS_nN(Me)Ph for $n = 2$–5, and MeO(C=S)S_nN(Me)Ph for $n = 1$–3. Isobutane chemical ionization provided additional evidence for assignments in the bis(carbamoyl)polysulfane series; quasi-molecular $(M + 1)^+$ ions were observed for $n = 1$–5 (intensities varying from 100% of base for $n = 1,2$ to 2–3% of base for $n = 3,4$ to 0.4% for $n = 5$; fragmentation patterns consistent for entire family, $n = 1$–6).

Experimental Section

General Methods. Most of the methods, instrumentation, and materials used have already been described.[3,5,36] Petroleum ether, in this text, refers to the solvent with bp 30–60 °C. The abbreviation "ρ" means density. Mixtures generated in the chlorination of 27–30 and related compounds were routinely evaluated by ^{1}H NMR at 80 MHz, and ^{13}C NMR spectra sup-

(29) Conversion of thiuram disulfides to thiuram monosulfides by use of alcoholic cyanide has long been known: von Braun, J.; Stechele, F. *Chem. Ber.* **1903**, *36*, 2275–2286. This work is the first to show that cyanide in heterogeneous suspension can effect desulfurization.

(30) Treatment of bis(methylphenylcarbamoyl)disulfane (4) with cyanide in methanol gave MeO(C=O)N(Me)Ph, which forms by methanolysis at the carbonyl group of 4 with co-products being COS, $^-$SCN, and PhNHMe (see Experimental Section for details, including a control reaction with authentic 61).

(31) As elaborated in Table III, note h, thiocyanate was determined by a modification of methods reported in the following: Ashworth, M. R. "The Determination of Sulfur-Containing Groups"; Academic Press: New York, 1972; Vol. 1, pp 79–81.

(32) This set of observations supported the identities of the higher members of the bis(carbamoyl)polysulfane series; see Table III, note g.

(33) (a) Parker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583–628. (b) Hiskey, R. G.; Harpp, D. N. *J. Am. Chem. Soc.* **1964**, *86*, 2014–2018. (c) Field, L. In "Organic Chemistry of Sulfur", Oae, S., Ed.; Plenum Press: New York, **1977**, pp 358–359 and references cited therein.

(34) Hiskey, R. G.; Carroll, F. I.; Babb, R. M.; Bledsoe, J. O.; Puckett, R. T.; Roberts, B. W. *J. Org. Chem.* **1961**, *26*, 1152–1155.

(35) $k' = (t_R - t_o)/t_o$; t_R = retention time; t_o = retention time (void) of mobile phase = 3.3 min. In practice, values of k' could be calculated with good experimental accuracy whenever 6 min $\leq t_R \leq$ 30 min. Separate experiments along lines suggested in ref 7b established that log k' decreases linearly with increasing percentage methanol in the methanol–water mobile phase (Figures 3 and 5 in supplementary material). Analysis of these graphs (Figure 4 and accompanying discussion in supplementary material) permitted the derivation of reliable formulas to predict t_R at any methanol–water ratio. Consequently, the comparisons of text Figures 1 and 2 are all normalized to a standard 4:1 ratio, even for compounds which were more appropriately chromatographed with other mobile phase compositions.

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

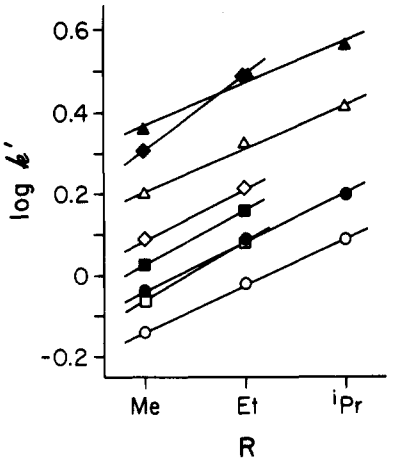


Figure 1. Relationship between HPLC retention (k', defined in ref 35) of various *N*-methylaniline derivatives and their structures. Elution was with methanol–water (4:1), and actual data are in supplementary material (Table V). Homologous series shown are the following: RS(C=O)N(Me)Ph (ref 3) (○), RSS(C=O)N(Me)Ph (**21a–c**) (●), RO(C=O)SS(C=O)N(Me)Ph (**5a, b**) (□), RO(C=O)SSS(C=O)N(Me)Ph (**15a, b**) (■), RO(C=S)SS(C=O)N(Me)Ph (**58a–c**) (△), RO(C=S)SSS(C=O)N(Me)Ph (**60a–c**) (▲), RO(C=O)SN(Me)Ph (ref 3) (◇), RO(C=O)SSN(Me)Ph (ref 5) (◆). Relevant but not shown are RO(C=S)N(Me)Ph (**2a–c**) which elute slightly later than the RS(C=O) isomers shown in graph; MeS(C=O)SS(C=O)N(Me)Ph (**26a**), log k' = 0.11 vs. log k' = 0.20 for isomer **58a** in graph; MeS(C=O)SN(Me)Ph (ref 6), log k' = 0.24 and its isomer MeO(C=S)SN(Me)Ph (**51a**), log k' = 0.32; and the remainder of the family MeO(C=S)S_nN(Me)Ph, n = 1–5 (**51–55a**) which are in Figure 2.

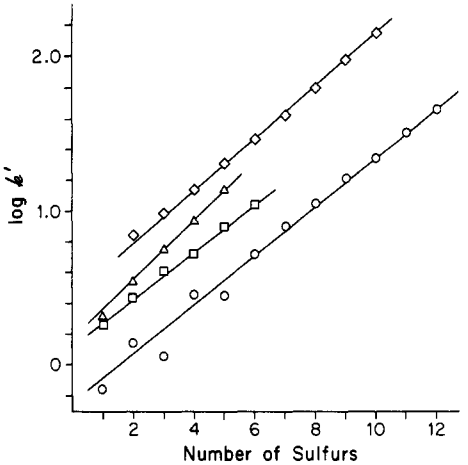


Figure 2. Relationship between HPLC retention (k', defined in ref 35) of various *N*-methylaniline derivatives and the number of sulfurs (n) in the polysulfane chain. Elution was with methanol–water (4:1), except those points of this graph for which log $k' > 1$ were calculated from retention times determined upon elution with methanol–water (9:1) according to formulas derived in the supplementary material, which also provides (Table V) all of the raw data. Homologous series shown are the following: Ph(Me)N(C=O)S_n(C=O)N(Me)Ph (**61, 4, 13, 62–70**) (○), slope 0.16; Ph(Me)N(C=O)S_nN(Me)Ph (**3, 11, 40–43**) (□), slope 0.15; MeO(C=S)S_nN(Me)Ph (**51–55a**) (△), slope 0.19; and Ph(Me)NS_nN(Me)Ph (**36–39, 71–75**) (◇), slope 0.16. For comparison, the supplementary material (Figure 6) presents graphs obtained under identical chromatographic conditions for six additional series: RO(C=O)S_n(C=O)OR′ with R and/or R′ = Me, Et, n = 2–6, all gave slopes of 0.20 (compare to ref 5, which shows that these series give parallel lines for n = 1–9); and RO(C=S)S_n(C=S)OR for R = Me, Et, *i*-Pr, n = 1–6, all gave slopes of 0.16 with in each of these three latter cases abnormally early elution by the disulfane (n = 2).

portive of the structural assignments were also recorded (details in supplementary material). Analytical HPLC was performed with a Beckman-Altex 334 system on Alltech Econosphere-ODS columns (4.6 mm × 25 cm), eluted with methanol–water (6:4–9:1, as appropriate) at 0.8–1.0 mL/min. Peak identifications were on the basis of retention times matching those of standards and, when necessary to identify higher homologues or to distinguish compounds with similar retentions, by rapid UV scanning employing the Beckman Model 165 detector. Although precise retention times varied with column batch, age, and chromatography conditions, the relative order of elution of compounds was always the same, and in particular the data[35] used to generate Figures 1 and 2 were all obtained with consecutive runs over a short time span. The same system was used for preparative HPLC on either a Zorbax-ODS or an Alltech G1810 column (10 mm × 25 cm) applied to fractionate the complex product mixtures arising from the title reactions of this paper. Sample mixtures (50–150 mg) were dissolved to near saturation in neat methanol, clarified by centrifugation, and loaded to fill a 2-mL injection loop. Elution was with the same solvents that for analytical HPLC gave retentions ranging from 15 to 45 min for the compounds of interest; preparative HPLC was carried out at 3.5 mL/min to result in somewhat longer retentions as well as peak widths of 5–15 min. Once fractions were verified by analytical HPLC to comprise a pure desired component, they were pooled, partially or completely concentrated by rotary evaporation, and sometimes extracted into CH_2Cl_2 followed by aqueous washes, drying ($MgSO_4$), and evaporation. This technique provided the initial samples of pure **36–39, 40,** and **51–53a** suitable for ^{1}H NMR and mass spectral measurements which suggested the structures. Yields of the preparative runs were difficult to establish with precision, but recoveries on pure standards were determined to vary from 80 to 95% for **3** and **62** to 25 to 40% for **36**. Those cases where the yield of HPLC isolation was lower seem to be correlated with chemical lability of compounds (e.g., containing multiple sulfurs or a S–N bond) together with their hydrophobicity as reflected by low solubility and lengthy HPLC retention.

Yields and product compositions of *N*-methylaniline reaction mixtures reported in this paper were determined in several ways giving self-consistent results. Reactions were carried out either on an analytical scale in the presence of toluene as an internal standard or on a suitable preparative scale (0.5–2.0 g), and the mole ratios of components were determined by ^{1}H NMR and HPLC (parameters tabulated in supplementary material). Additional confirmation of the quantitations of certain key components was achieved by taking a known weight of the product mixture, adding a known weight of a homologous pure compound (e.g., quantitation of **2a** in a mixture by adding pure **2b**), and then carrying out a second HPLC determination. Since homologous compounds with the same chromophore have identical integration constants, the information obtained could be used to calculate the weight percent of the compound measured relative to the total reaction mixture.

Dichloropolysulfanes,[23] as they were required for experiments reported in this section and in Table III, were generated in the following fashion: hydrogen sulfide (10 mL, ~0.35 mol) was condensed at −70 °C and then distilled over 30 min into neat sulfur dichloride (200 g, 1.9 mol) maintained at −70 °C. As the reaction was stirred, the volume visibly diminished and HCl evolved. After 2 h at −70 °C, excess SCl_2 was removed in vacuo at 25 °C, initially drawn from an aspirator (90 mm) and then an oil pump (1 mm). The resultant viscous orange liquid (35 g, ~60%) was a mixture of S_2Cl_2:S_3Cl_2:S_4Cl_2:S_5Cl_2:S_6Cl_2 = 1.0:0.7:0.4:0.4:0.1 by methanethiol assay.[3,5,37,38] A portion (6.2 g) was subjected to short-path distillation at 25 °C and ultra-high vacuum (3 × 10^{-5} mm), and a dichlorotrisulfane-enriched fraction (0.48 g) was collected in a chilled trap: S_2Cl_2:S_3Cl_2:S_4Cl_2 = 0.2:1.0:0.1 by methanethiol assay. The residue (3.5 g) comprised[38] S_3Cl_2:$S_{\geq 4}Cl_2$ = 0.2:1.0.

(37) For ^{1}H NMR data on methyl polysulfanes, see (a) ref 3. (b) Grant, D.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 3012–3017.

(38) The 80-MHz ^{1}H NMR used in this work could not resolve MeS_nMe for $n \geq 6$ (δ 2.69), but the family of MeS_nMe was clearly indicated for n = 2–10 by HPLC; compare to ref 3 and 7b. The HPLC method, which involved dilution of aliquots into methanol–water, was accompanied by some desulfurization which skewed the true distribution of MeS_nMe toward lower n and made it difficult to use the methanethiol assay to quantitate S_nCl_2 for $n \geq 3$.

***O*-Alkyl Methylphenylthiocarbamates 2.** This new method is more convenient than the conversion of alkoxy(thiocarbonyl) chlorides (**7**) described earlier.[3] Mixtures of the appropriate bis[alkoxy(thiocarbonyl)] sulfide (**27**) (11.5 g, 48 mmol) and *N*-methylaniline (0.2 mol) in $CHCl_3$ (200 mL) were stirred at 25 °C. After 70 h, the reaction mixtures were washed twice with equal volumes of 1 N aqueous HCl and once with water, dried ($MgSO_4$), and rotary evaporated to provide yellow oils. For **2a**, purification by distillation, bp 92–95 °C (0.2 mm) [lit.[3] bp 81–89 °C (0.5 mm)], gave product in 89% yield, Anal.; for **2b**, bp 94–98 °C (0.2 mm) [lit.[3] 83–86 °C (0.08 mm)], 84% distilled yield, Anal. For **2c**,[39] the initial oil (10.3 g, 102%) solidified upon standing at −20 °C for a few days. Pale yellow needles (7.6 g, 75%), mp 67–70 °C, were collected upon washing with cold petroleum ether, and the isolated **2c** was further characterized by Anal., MS, further details with supplementary material. It should be noted that **2c** prepared this way was free of its isomer *S*-(2-propyl) methylphenylthiocarbamate. An authentic sample (oil) of the latter compound was prepared from the corresponding commercially available (Alfa) acid chloride plus *N*-methylaniline by our general procedure,[3] NMR and MS of isomer also with supplementary material.

Generation of (Alkoxydichloromethyl)(methylphenylcarbamoyl)disulfanes 6 and -trisulfanes 16, and Some Subsequent Reactions (Scheme III). A. The appropriate (alkoxydichloromethyl)sulfenyl (**17**)[3,13] or -disulfanyl (**18**)[5,10] chloride (1 equiv) was added to an *O*-alkyl methylphenylthiocarbamate (**2**) (0.5 M) in $CDCl_3$. The alkyl group of **2** was completely converted to alkyl chloride within 1 min. The methyl derivative **6a** [NMR δ 7.1–7.5 (m), 3.74 (s), 3.39 (s)] then lost methyl chloride with $t_{1/2}$ ~18 min at 25 °C to yield (chlorocarbonyl)(carbamoyl)disulfane **22** [NMR δ 7.3–7.5 (m), 3.39 (s)] in turn characterized by the *clean* conversions with excess *N*-methylaniline in $CDCl_3$ to give bis(carbamoyl)disulfane **4** (80% isolated yield based on **2**) or with excess alcohol to give (alkoxycarbonyl)(carbamoyl)disulfanes **5** (~85% yield). Also, when **6a** was shaken for 1 min with 1 N aqueous HCl, 1 min after it was generated from **17a** plus **2a** or **2b**, the hydrolysis product **5a** formed (84%). The ethyl derivative **6b** [NMR δ 7.1–7.5 (m, 5 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.38 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H)] lost ethyl chloride with $t_{1/2}$ ~10 min at 25 °C, with subsequent reactions proceeding in the same way. Extending these findings to the trisulfane level, **16a** [NMR δ 7.1–7.5 (m), 3.70 (s), 3.39 (s)] formed rapidly from **18a** plus **2a**, but within 10 min was accompanied by ~20% each of methoxy(thiocarbonyl)chloride (**7a**) and a new peak assigned to (carbamoyl)disulfanyl chloride **19**[14] [NMR δ 3.44 (s)]. Later, methyl chloride was lost, with $t_{1/2}$ ~4 h, to yield (chlorocarbonyl)(carbamoyl)trisulfane **23** [NMR δ 3.40 (s)]; throughout this process, substantial **7a** (representing as much as 70% of the *O*-methyl groups) was present. Reaction at the endpoint (22 h) with excess *N*-methylaniline gave principally bis(carbamoyl)trisulfane **13** (60% based on starting materials for generating **16**) and **2a** (additional 12%, derived from **7a**). Also, **16b** [NMR δ 7.1–7.5 (m, 5 H), 4.05 (q, *J* = 7.1 Hz, 2 H), 3.39 (s, 3 H), 1.28 (t, *J* = 7.1 Hz, 3 H)] which within 1 min of generation contained ~30% of ethoxy(thiocarbonyl) chloride (**7b**) was then shaken with 1 N aqueous HCl to give a mixture of (ethoxycarbonyl)(carbamoyl)trisulfane **15b**, bis(carbamoyl)trisulfane **13**, (carbamoyl)disulfanyl chloride **19**, and unhydrolyzed **7b** in a 5:2:3:5 ratio. **B.** Over 5 min, *N*-methylaniline in ethyl ether (5.6 mL, 2 M, 11.2 mmol) was added at 5 °C to a solution of (methoxydichloromethyl)(chlorocarbonyl)disulfane (**1a**)[3] (1.4 g, 5.6 mmol) in ether (5.6 mL). After 5 min more at 5 °C, *N*-methylaniline hydrochloride (0.8 g, 100%) was removed by filtration, and evaporation of ether under a stream of nitrogen within 5 min gave **6a** (1.7 g, 97%), which lost methyl chloride (~10%) to give some **22** even as the ^1H NMR spectrum was rapidly recorded in $CDCl_3$ solution. With ether as solvent, generation of **6a** was clean as negligible starting **1a** remained unreacted, and negligible bis(carbamoyl)disulfane **4** formed. In contrast, for comparable experiments in $CDCl_3$, methyl chloride was completely lost within 2 h, but the *N*-methylaniline hydrochloride (which was soluble) continued to react with **22** so that when a workup was carried out after 48 h, **4** was shown to have formed in high yield (84% overall), contaminated with 12% of **5a**. In comparable experiments at the trisulfane level, **10a**[5] (0.7 g, 2.5 mmol) reacted according to the just described procedure with ether as solvent and gave a product (0.5 g, 60%) that comprised mainly **16a** with ~25% each of **7a** and **19**.[14] When this mixture was left standing at 25 °C, methyl chloride was lost to give **23**, and some hydrolysis of **16a** to **15a** occurred as well.

2-Propoxy(thiocarbonyl) Chloride (7c).[40] Sodium (5.0 g, 0.22 mol) was dissolved in 2-propanol (170 mL) by overnight reflux. After removal of unbound 2-propanol by rotary evaporation at 35 °C, the resultant salt was dissolved in ethyl ether (250 mL) and added dropwise to a solution of thiophosgene (25.0 g, 0.22 mol) in ethyl ether (100 mL) at −78 °C. The red color of $CSCl_2$ was quenched as the reaction warmed to −20 °C. Filtration and rotary evaporation at aspirator pressure gave a crude product (23.5 g) that was 35% (w/w) of **7c** (0.06 mol, 27%) with the remainder 2-propanol. Vacuum transfer in a short-path distillation apparatus at 25 °C and 1 mm gave a distillate (13 g) that was dissolved in pentane (150 mL), washed with water (2 × 125 mL), dried ($MgSO_4$), and concentrated to give **7c** (3.9 g, 13%), insufficiently stable to permit elemental analysis. The ^1H NMR revealed **7c** [δ 5.51 (m, *J* = 6.2 Hz, 1 H), 1.44 (d, *J* = 6.2 Hz, 6 H)] contaminated with ~8% of *O,O'*-bis(2-propyl)thiocarbonate [δ 4.86 (m, *J* = 6.2 Hz, 1 H), 1.29 (d, *J* = 6.2 Hz, 6 H)], but none of the isomer (2-propylthio)carbonyl chloride [δ 3.64 (m, *J* = 6.8 Hz, 1 H), 1.38 (d, *J* = 6.8 Hz, 6 H)]. The usual methods converted **7c** (0.2 g) to *N*-methylanilide **2c**[39] (0.23 g, 73%), pale brown needles, mp 70–72 °C, free of the *S*-2-propyl isomer (see end of description of **2** for properties of the isomer). Title compound **7c** decomposed to 2-chloropropane and COS after 1 day at 25 °C or after four months at −20 °C.

(Chlorocarbonyl)disulfanyl Chloride (12). A. In 80% yield from **17a** plus $FeCl_3$ (0.07% w/w), ρ = 1.64, as described in ref 5. **B.** Bis(chlorocarbonyl)trisulfane (**14**)[11] (22.3 g, 0.1 mol) was heated at 100 °C, and the progress of the thermolytic decomposition was followed by weight loss and *N*-methylaniline assay.[3] After 5 h, the molar ratio of **12**:**14**:S_2Cl_2 was 1.8:1.0:0.2, and heating was continued for an additional 3 h. The resultant mixture (16 g) was distilled through a short Vigreux column, the forerun containing S_2Cl_2 was discarded, and **12** was collected (8.0 g, 49%) at bp 48–53 °C (10 mm) [lit.[5] bp 49 °C (12 mm)], ρ = 1.65, Anal. **C.** Crude **14** (34 g), prepared as described below to just before the distillation step, was treated all at once at 25 °C with $FeCl_3$ (35 mg, 0.1% w/w). Vacuum was gradually applied, with care to minimize the spontaneous frothing, first from an aspirator at 50 mm for 30 min and then from an oil pump at 0.5 mm for 10 min. Although there was some weight loss (~10%), the product at this stage was still **14** by *N*-methylaniline assay. Short-path cracking distillation (bath 70–90 °C, bp 30–45 °C, 0.7 mm) followed over 1 h to give a product (12.4 g, ~50%) that was **12** contaminated with 15 mol % of S_2Cl_2 by *N*-methylaniline assay and that was further purified by distillation as described under method B. **D.** Bis[2-propoxy(thiocarbonyl)] sulfide (**27c**) (36 g, 0.15 mol) was dissolved with slight heating in petroleum ether (150 mL), and sulfuryl chloride (36 mL, 0.45 mol) was added as quickly as possible while maintaining the solution and controlling the spontaneous exotherm. The reaction mixture was then refluxed for 3 h and concentrated at aspirator vacuum on a rotary evaporator. The resultant oil (44.8 g, 99%) [NMR δ 4.71 (m, *J* = 6.2 Hz, 1 H), 1.40 (d, *J* = 6.2 Hz, 6 H)] was principally (chlorocarbonyl)(2-propoxydichloromethyl)trisulfane (**10c**), as verified by an *N*-methylaniline assay. In this assay, there was a quantitative observation (compare to Scheme II) of the products of a "sulfenyl" pathway (86% overall), namely *O*-2-propyl thiocarbamate **2c**, (carbamoyl)(amino)disulfane **11**, and carbamothioamide **3** in a ratio of 1.0:0.9:0.1, together with bis(carbamoyl)trisulfane **13**, the product of the "carbamoyl" pathway (14% overall). Short-path cracking distillation (bath 60–80 °C, bp 30–40 °C, 1–2 mm) over 4 h gave a product (24.4 g) that was **12**:**7c**:S_2Cl_2:2-chloropropane in a molar ratio of 1.0:0.2:0.1:0.4 and that was further purified by distillation as described under method

(39) An alternate but less convenient preparation of the new compound **2c** is described with **7c**.

(40) This compound has been reported in 35% yield from thiophosgene plus 2-propanol, bp 35 °C (4 mm) with satisfactory Anal., see McKinnon, D. M.; Queen, A. *Can. J. Chem.* **1972**, *50*, 1401–1406. Our experiences with **7c** described in this Experimental Section suggest that it is more labile than previously believed.

B to provide the title product (16.9 g, 67%), ρ = 1.64, Anal.

Bis(methylphenylcarbamoyl)trisulfane (13). A. A mixture of bis[methoxy(thiocarbonyl)] sulfide (**27a**)[3] (4.2 g, 23 mmol) and sulfuryl chloride (5.6 mL, 69 mmol) in petroleum ether (25 mL) was refluxed for 1 h, following which the solvent and excess SO_2Cl_2 were removed at aspirator vacuum through an 18-in. Vigreux column. The resultant yellow oil (7.4 g, 99%), which was[1,4,5] bis(methoxydichloromethyl)trisulfane (**31a**), was carefully treated with several portions of $FeCl_3$ (total ~50 mg), added at 15 °C over 2 h. When the weight reached 5.1 g (99% of theoretical weight loss of methyl chloride), the resultant crude bis(chlorocarbonyl)trisulfane (**14**) was filtered through glass wool directly into a solution of *N*-methylaniline in $CHCl_3$ (70 mL, 2 M, 140 mmol) at 5 °C. After 1 h at 25 °C, the reaction mixture was washed with 1 N aqueous HCl and water, dried ($MgSO_4$), and evaporated to give a brown oil (7.5 g, 89%) which contained mainly desired trisulfane **13** (68%), along with bis(carbamoyl)disulfane **4** (2%) as well as (carbamoyl)(amino)disulfane **11** (23%) and the corresponding sulfide **3** (7%). After a few days, crystals formed which were collected by washing with CCl_4 to provide analytically pure trisulfane **13** (3.4 g, 41%), mp 167–171 °C, which was recrystallized from CH_2Cl_2–CCl_4 [white cubes, mp 168–171 °C, Anal., MS, NMR δ 7.2–7.5 (m, 5 H), 3.34 (s, 3 H)], further data in supplementary material. **B.** Acid chloride **14**[11] (2.2 g, 9.8 mmol) was reacted with a solution of *N*-methylaniline in $CHCl_3$ (30 mL, 2 M, 60 mmol) by the usual procedure[3] to yield 3.4 g (94%) of a hard yellow solid, mp 151–161 °C, which was recrystallized from hot petroleum ether–CH_2Cl_2 (subsequently brought to −20 °C) to give in 74% recovery (two crops) colorless plates, mp 156–161 °C, >99% pure by HPLC, Anal.

Bis(chlorocarbonyl)trisulfane (14). A mixture of bis[2-propoxy(thiocarbonyl)] sulfide (**27c**) (36 g, 0.15 mol), sulfuryl chloride (36 mL, 0.45 mol), and calcium carbonate (1.5 g) in petroleum ether (150 mL) was refluxed for 5 h, then filtered, and concentrated on a rotary evaporator at aspirator vacuum. The resultant oil (34.8 g, 103%) comprised of **14** and **12** in a molar ratio of 8:1 by *N*-methylaniline assay (**7c** and **56c** were absent); furthermore, ^{1}H NMR signals attributable to starting **27c**, intermediate **10c** [δ 4.71 (m, J = 6.2 Hz, 1 H), 1.40 (d, J = 6.2 Hz, 6 H)], intermediate **56c**, and 2-chloropropane [δ 4.19 (m, J = 6.5 Hz, 1 H), 1.52 (d, J = 6.5 Hz, 6 H)] were all abolished. Distillation followed, with a small forerun of **12** and sometimes S_2Cl_2 being discarded, to provide the title product (26.9 g, 80%) as a colorless liquid at bp 73–79 °C (0.5 mm); redistilled in 88% recovery, bp 61 °C (0.3 mm); ρ = 1.64; Anal.; ^{13}C NMR δ 163.0. Good **14** was also amenable to successful redistillation at higher pressure, bp 110 °C (10 mm), and **14** was entirely stable, as judged by weight retention and the *N*-methylaniline assay, for 6 days at 25 °C. After 10 days, 18% of **14** had transformed to **12**; this value was 30% after 30 days.

Pure bis(chlorocarbonyl)trisulfane (**14**) (0.5 g, 2.2 mmol) was added at 5 °C to absolute methanol (50 mL); rotary evaporation gave directly crystalline bis(methoxycarbonyl)trisulfane[5] (0.47 g, 100%), mp 58–60 °C [lit.[5] mp 65 °C], HPLC purity >98%.

Evidence for (Methylphenylcarbamoyl)sulfenyl Chloride (20).[14] A solution of *O*-ethyl methylphenylthiocarbamate (**2b**) (0.23 g, 1.2 mmol) in $CDCl_3$ (1.2 mL) was treated at 5 °C with neat SO_2Cl_2 (95 μL, 1.2 mmol). ^{1}H NMR examination after 10 min revealed quantitative ethyl chloride and a singlet at δ 3.38 attributed to **20**. After 20 min, 2-propanethiol (110 μL, 1.2 mmol) was added to the cold reaction mixture; evaporation after 20 min more at 25 °C gave an oil (0.30 g) which comprised expected carbamoyldisulfane **21c** (0.38 mmol, 33%) together with the symmetric disulfanes **4** (0.33 mmol) and bis(2-propyl) disulfide (0.38 mmol). This distribution accounts for 96% of the 2-propyl groups and 86% of the methylphenylamino groups. In another experiment, **20** generated from **2b** (5 mmol) was reacted after 20 min with excess *N*-methylaniline to provide 0.9 g (62%) of a 4:1 mixture of expected carbamothioamide **3**[3] together with bis(carbamoyl)disulfane **4**.[3] Finally, when **20** in $CDCl_3$ was allowed to stand for 24 h at 25 °C, 3-methyl-2(3*H*)-benzothiazolone[3] cleanly formed (92% isolated yield), mp 66–72 °C [lit.[3] mp 75–76 °C].

(2-Propyl)(methylphenylcarbamoyl)disulfane (21c). First, (2-propyldithio)carbonyl chloride was prepared from 2-propanethiol (0.18 mol) plus chlorocarbonylsulfenyl chloride (**8**)[3] (0.2 mol) in dichloromethane (140 mL) by extension of our earlier procedure;[3] after distillation there was obtained 26 g (85%) of a clear yellow liquid, bp 81 °C (18 mm), ρ = 1.23, Anal.; ^{1}H NMR δ 3.24 (m, J = 6.8 Hz, 1 H), 1.35 (d, J = 6.8 Hz, 6 H); ^{13}C NMR δ 166.7, 42.6, 22.2. A portion of this acid chloride was then reacted with *N*-methylaniline according to the general procedure[3] to provide **21c** in quantitative crude yield. Recrystallization from pentane gave white needles (69% recovery), mp 54–55 °C, Anal., MS, further data with supplementary material.

Generation of (Chlorocarbonyl)(methylphenylcarbamoyl)disulfane (22) and -trisulfane (2: , and Some Subsequent Reactions (Scheme III). *N*-methylaniline (0.21 g, 2 mmol) in $CDCl_3$ (2 mL) was added at 5 °C to bis(chlorocarbonyl)disulfane (**9**)[3] (0.38 g, 2 mmol) in $CDCl_3$ (2 mL). A rapid workup (within 5 min) provided a mixture (0.36 g, 60% based on **9**) of approximately equimolar amounts of (chlorocarbonyl)(carbamoyl)disulfane **22** [NMR δ 7.3–7.5 (m), 3.39 (s)] and bis(carbamoyl)disulfane **4**. When the initial reaction mixture was rapidly quenched into excess ethanol prior to further workup, the product (0.39 g, 80% based on **9**) was comprised of **4** and (ethoxycarbonyl)(carbamoyl)disulfane **5b** derived from **22** and bis(ethoxycarbonyl)disulfane[5] derived from unreacted **9** in a ratio of 1.4:1.0:3.7. Results were similar when reactions were carried out for 18 h, indicating the relative stability of **22**. In entirely analogous fashion, equimolar bis(chlorocarbonyl)trisulfane (**14**)[11] (0.2 g, 0.9 mmol) and *N*-methylaniline (100 μL, 0.9 mmol) gave an approximately 1.0:0.6 mixture of (chlorocarbonyl)(carbamoyl)trisulfane **23** [NMR δ 7.1–7.6 (m), 3.40 (s)] and bis(carbamoyl)trisulfane **13**. Quenching into ethanol immediately after **14** and *N*-methylaniline were combined gave a product (0.3 g, quantitative based on **14**) comprised of **13**, (ethoxycarbonyl)(carbamoyl)trisulfane **15b** and bis(ethoxycarbonyl)trisulfane[5] in a ratio of 0.6:1.0:1.9, with *no* **5b**.

Bis[2-propoxy(thiocarbonyl)] Sulfide (27c). A solution of KOH (260 g, 85%, 3.9 mol) in 2-propanol (1.25 L) and water (100 mL) was chilled to 5 °C, and CS_2 (240 mL, 4.0 mol) was slowly added in small portions. Most, but by no means all, of the resulting xanthate crystals were dissolved with more water (500 mL), and ethyl chloroformate (180 mL, 1.9 mol) was added over 5 min at 25 °C. The oil which separated was extracted into ether (1.2 L), washed with water (2 × 1 L), dried ($MgSO_4$), and concentrated in vacuo to yield either directly, or after trituration with 2-propanol, 184 g (40%) of yellow needles, mp 47–52 °C, recrystallized in 93% recovery from hot 2-propanol (0.5 g/mL), to provide needles, mp 52–53 °C [lit.[25] mp 54 °C], Anal., NMR δ 5.74 (m, J = 6.2 Hz, 1 H), 1.45 (d, J = 6.2 Hz, 6 H). There was also obtained as an oil apart from the crystalline mass of desired **27c**, *S*-ethoxycarbonyl *O*-2-propyl dithiocarbonate [NMR δ 5.75 (m, J = 6.2 Hz, 1 H), 4.32 (q, J = 7.1 Hz, 2 H), 1.45 (d, J = 6.2 Hz, 6 H), 1.33 (t, J = 7.1 Hz, 3 H)]. The amount of this impurity was higher when levels of water used were more than those specified in the procedure just given.

Bis[2-propoxy(thiocarbonyl)]disulfane (28c). Solid potassium 2-propyl xanthate (**57c**) (110 g, 0.63 mol) in 2-propanol (0.2 L) and water (0.4 L) with I_2 (80 g, 0.31 mol) gave title product (68 g, 80%) as a hard yellow solid, mp 50–54 °C [lit.[25] mp 58 °C]. Colorless plates, mp 55 °C, were obtained in 86% recovery from hot 2-propanol (0.25 g/mL), Anal., NMR δ 5.69 (m, J = 6.2 Hz, 1 H), 1.40 (d, J = 6.2 Hz, 6 H).

Bis[2-propoxy(thiocarbonyl)]tri- and -tetrasulfanes (29c, 30c). Solid potassium 2-propyl xanthate (**57c**) (40 g, 0.23 mol) was suspended in ethyl ether (300 mL) at 5 °C, and freshly distilled SCl_2 (6.7 mL, 0.11 mol) or S_2Cl_2 (8.2 mL, 0.1 mol) in ether (25 mL) was added over 45 min. The reaction mixtures were then stirred for 1 h at 25 °C, filtered to remove the KCl that had formed and excess xanthate, and concentrated by rotary evaporation to yield the title products as yellow oils in crude yields of 90% and 69%, respectively. Oil **29c** solidified upon standing and was recrystallized from 2-propanol (0.4 g/mL) to yield pale yellow needles in 79% recovery, mp 45–48 °C, Anal.

Bis(methylphenylamino) Sulfide (35).[16] Freshly distilled sulfur dichloride (0.9 mL, 14 mmol) in petroleum ether (15 mL) was added to a solution of *N*-methylaniline (6.1 mL, 56 mmol) in petroleum ether (30 mL) that was chilled to −35 °C. Although there was an immediate precipitate, warming to 25 °C under good stirring was required to discharge the SCl_2 color. The yellow suspension was then immediately filtered to collect the *N*-methylaniline hydrochloride (3.6 g, 25 mmol, 89%), and the filtrate was concentrated under a stream of nitrogen to give the title

product (2.6 g, 76%), an orange oil [NMR δ 7.25 (s) and 7.19 (s) and 6.8–7.0 (m) [total 5 H], 3.29 (s, 3 H)]. Variations of this procedure with ethyl ether or $CHCl_3$ as solvents failed badly. Sulfide **35** stored at 25 °C in $CDCl_3$ solution or neat decomposed to *N*-methylaniline and elemental sulfur within a day, but the neat material was completely unchanged after 5 weeks at −20 °C. When dissolved in $CDCl_3$ (0.2 M solution) and washed for 15 sec with 1 N aqueous HCl, **35** was completely destroyed as the solution turned green; about 5–10% of the (methylphenylamino)sulfenyl groups were retained in the organic phase including some as disulfane **36**.

Bis(methylphenylamino)disulfane (36). Sulfur monochloride (1 mL, 12.5 mmol) in ethyl ether (5 mL) was added dropwise with vigorous shaking over 5 min at 5 °C to a solution of *N*-methylaniline (6 mL, 55 mmol) in ethyl ether (25 mL). *N*-Methylaniline hydrochloride (3.5 g, 24 mmol) precipitated almost immediately, but the reaction mixture was maintained at 25 °C for an additional hour. After filtration, the ether solution was washed twice with equal volumes of 1 N aqueous HCl and once with water. After drying ($MgSO_4$) and rotary evaporation, a yellow solid (2.8 g, 80%) was obtained, which was recrystallized from hot hexane as yellow cubes, mp 76–78 °C (lit.[16b] mp 78–80 °C) in 77% recovery. The title compound was stable for several weeks at 25 °C; IR ($CDCl_3$) 2800–3150 (w), 1600 (s), 1590 (w), 1490 (s), 1465 (w), 1445 (w), 1265 (m), 1080 (w), 1060 (w), 1025 (w), 845 (m) cm^{-1}; UV (95% EtOH) ϵ_{315} 9.6×10^3, ϵ_{298} 7.6×10^3, ϵ_{287} 8.8×10^3, ϵ_{268} 7.1×10^3, ϵ_{230} 1.2×10^4, ϵ_{200} 3.5×10^4; NMR δ 6.8–7.4 (m, 5 H), 2.99 (s, 3 H); Anal., MS, further data in supplementary material. When the same reaction was conducted in $CHCl_3$, the crude yield was comparable, but the product was obtained as an oil.

Bis(methylphenylamino)trisulfane (37). A sample that was primarily (~80%) S_3Cl_2 (0.31 g, 1.8 mmol) was reacted with *N*-methylaniline in $CHCl_3$ (5.5 mL, 2 M, 11 mol) in the usual manner to yield a yellow oil (0.52 g, 94%) that was shown by ^1H NMR and HPLC to be a mixture of **36**:**37**:**38** in a molar ratio of 1.0:1.0:0.9. The ratio of components found in the mixture reveal that disproportionation had occurred during the *N*-methylaniline reaction above and beyond the original ratio of dichloropolysulfanes. A portion of the cited mixture of *N*-methylanilides (96 mg) upon preparative HPLC gave pure **37** (8 mg) as crystals, mp 79–81 °C, formed at 4 °C from the methanol–water (17:3) eluent; Anal., MS, NMR δ 7.1–7.3 (m, 5 H), 3.31 (s, 3 H), further data in supplementary material.

Higher bis(methylphenylamino)polysulfanes arose by treating a portion (0.46 g) of the distillation residue described in the last paragraph of General Methods with *N*-methylaniline in $CHCl_3$ (6 mL, 2 M, 12 mmol) in the usual manner to provide a light brown oil (0.70 g). Assuming an average *n* in the starting S_nCl_2 of 5, this yield can be calculated to be 95% (100% if average *n* is 6; 90% if average *n* is 4). By HPLC, the product was shown to comprise **36**:**37**:**38**:**39**:**71**:**72**:**73**:**74**:**75** = 5:6:17:34:16:12:6:3:1 (centered about pentasulfane **39**). Note the agreement with the distribution of polysulfanes formed in Harris reactions (Table III, line 6) on the same starting S_nCl_2. Furthermore, tetrasulfane **38** [NMR δ 7.1–7.3 (m, 5 H), 3.34 (s, 3 H)] and pentasulfane **39** [NMR δ 7.1–7.3 (m, 5 H), 3.31 (s, 3 H)] were both isolated by preparative HPLC from appropriate reaction mixtures as described in Table II (lines 13–15) and gave satisfactory molecular ions upon MS as reported in the supplementary material.

All compounds in the title series had considerable end absorption upon rapid scan UV from 260 nm to 210 nm and then extended fine structure up to 330 nm at intensities approximately 0.25 of ϵ_{210}. Further absorption carried out to 380 nm.

Novel (methylphenylcarbamoyl)(methylphenylamino)polysulfanes (40–43), Ph(Me)N(C=O)S_nN(Me)Ph, arose in connection with studies summarized in Table II (lines 13–15 and note f), with the preparations of **76–78**, and in an attempt to prepare **79** from **7c** plus S_2Cl_2. These compounds homologate the known crystalline **3**[3] and **11**,[5] and HPLC evidence (Figure 2) is consistent with the structural assignments. Trisulfane **40** was isolated by preparative HPLC and characterized by MS (Table VII in supplementary material). Concerning the ^1H NMR of this family, the methylcarbamoyl singlet was constant at δ 3.38 whereas the methylsulfenyl singlet oscillated from 3.27 (*n* = 1) to 3.35 (*n* = 2) to 3.25 (*n* = 3) to 3.33 (*n* = 4). For $n \geq 2$, the family was characterized by rapid scan UV spectra that tailed gradually from the end absorption at 210 nm, reaching a broad plateau (or second maximum, for *n* = 2) at 280 nm with a ratio of ϵ_{280}:ϵ_{210} ~0.2–0.3. Low absorption continued out to wavelengths >350 nm, and the absorbances in this region were *more* intense than those of the appropriate representative of the family Ph(Me)N(C=O)-S_m(C=O)N(Me)Ph with similar HPLC retention.

Methoxy(thiocarbonyl) Methylphenylamino Sulfide (51a) via (Methoxydichloromethyl)[methoxy(thiocarbonyl)]disulfane (47a). A. A mixture of bis[methoxy(thiocarbonyl)] sulfide (**27a**)[3] (5.1 g, 28 mmol) and sulfuryl chloride (3.3 mL, 42 mmol) in petroleum ether (45 mL) was refluxed for 1 h. Concentration at aspirator vacuum gave a yellow oil (7.0 g, 101%) which comprised starting **27a**, disulfane **47a**,[41] and trisulfane **31a** in a molar ratio of 3:21:1 [singlets in ^1H NMR respectively at δ 4.22; 4.27 and 3.74; and 3.78]. The oil was taken up in $CHCl_3$ (50 mL) and added at 5 °C to *N*-methylaniline in $CHCl_3$ (75 mL, 2 M, 0.15 mol); after the usual workup a product (9.5 g) was obtained which consisted of **2a** (19 mmol), **51a** (14 mmol), **52a** (2 mmol), **58a** (5 mmol), **28a** (4 mmol), and **29a** (1.9 mmol). Medium-pressure liquid chromatography of 9.0 g was carried out on a Lobar Size B (2.5 × 31 cm) Lichroprep Si60 column developed with hexane–$CHCl_3$ (4:1) at ~2 mL/min, whereupon **51a** eluted well ahead of **2a** but was contaminated with bis[methoxy(thiocarbonyl)]di- (**28a**) and tri- (**29a**) sulfanes. The appropriate fractions were washed with water, dried ($MgSO_4$), concentrated, and placed under $CHCl_3$ (10 mL) at 4 °C overnight, whereupon yellow needles of pure title compound (0.9 g, 4.2 mmol, 17%) separated, mp 68–69 °C. Recrystallization was from hot methanol with water added to incipient turbidity, recovery 78% of pale yellow needles, >99% pure by HPLC, Anal., MS, NMR δ 7.1–7.3 (m, 5 H), 4.14 (s, 3 H), 3.45 (s, 3 H), best stored at −20 °C, further data in supplementary material. **B.** Methoxydichloromethanesulfenyl chloride (**17a**)[3,13] (2.0 mL, 17 mmol) was added to a suspension of potassium methyl xanthate (**57a**) (2.6 g, 18 mmol) in $CDCl_3$ (20 mL) at 5 °C. The reaction mixture was stirred for 15 min at 25 °C and then examined by ^1H NMR which showed primarily **47a**; the mixture was then filtered directly into *N*-methylaniline in $CHCl_3$ (50 mL, 2 M, 0.1 mol). The usual workup provided an oily product (4.3 g) which consisted of **51a**:**52a**:**2a**:**58a**:**29a**:MeO(C=S)SS(C=O)OMe[42] in a ratio of 1.0:0.2:0.8:0.4:0.2:0.6. Medium-pressure liquid chromatography on 3.0 g of this mixture, using conditions described above, gave title compound **51a** (1.0 g, 4.7 mmol, 39%), mp 67–70 °C, that was >99% pure by HPLC.

[Methoxy(thiocarbonyl)](methylphenylamino)polysulfanes (52a and 53a) via (Methoxydichloromethyl)[(methoxy(thiocarbonyl)]trisulfane (48a). Similar to method A for **51a**, three reactions were carried out in which bis[methoxy(thiocarbonyl)]disulfane (**28a**)[3] (2.1 g, 10 mmol) in petroleum ether (10 mL) was chlorinated with (i) 0.5, (ii) 1.0, and (iii) 1.5 equiv of SO_2Cl_2. After concentration, each reaction mixture was first analyzed by ^1H NMR and then added neat at 5 °C to the amount of a solution of *N*-methylaniline (2 M in $CHCl_3$) corresponding to 10 equiv of amine over the amount of SO_2Cl_2 used. Results: (i) with 93% incorporation of theoretical weight of Cl_2, there was obtained a mixture (2.5 g) of unreacted **28a** (6.2 mmol; δ 4.24), trisulfane **48a** (3.3 mmol; δ 4.29, 3.75), and tetrasulfane **32a** (0.4 mmol; δ 3.79), which converted to a mixture (2.8 g) of recovered **28a** (5.5 mmol) plus bis[methoxy(thiocarbonyl)]trisulfane (**29a**) (0.7 mmol; from disproportionation of **28a**) as well as thiocarbamate **2a** [4.5 mmol; δ 7.1–7.4 (m, 5 H), 3.97 (s, 3 H), 3.59 (s, 3 H)], disulfane **52a** [2.6 mmol; δ 7.1–7.3 (m, 5 H), 4.05 (s, 3 H), 3.31 (s, 3 H)], and trisulfane **53a** [0.6 mmol; δ 7.1–7.3 (m, 5 H), 3.97 (3 H), 3.39 (3 H)] with these products as quantitated by both ^1H NMR and HPLC accounting for 104% of the isolated weight; (ii) with 86% incorporation of theoretical weight of Cl_2, there was obtained a mixture (2.7 g) of **28a** (3.2 mmol), **48a** (5.1 mmol), and **32a** (1.7 mmol), which converted to a mixture (3.5 g) of **28a** (2.9 mmol), **29a** (0.4 mmol), **2a** (6.2 mmol), **52a** (4.1 mmol), **53a** (1.2 mmol), and **36** (0.5 mmol), with these products

(41) The mass spectrum of this mixture is in Table VII of the supplementary material; ions observed are supportive of the structure of the major component **47a**.

(42) A standard of this new compound was made in 50% distilled yield, bp 63–65 °C (0.2 mm), from potassium methyl xanthate and MeO(C=O)SCl in ethyl ether [NMR δ 4.25 (s, 3 H), 3.92 (s, 3 H)].

accounting for 95% of the isolated weight; (iii) with 86% incorporation of theoretical weight of Cl_2, there was obtained a mixture (3.1 g) of **28a** 71.2 mmol), **48a** (4.6 mmol), and **32a** (4.3 mmol), which converted to a mixture (4.6 g) of **28a** (1.1 mmol), **2a** (12.0 mmol), **52a** (2.9 mmol), **53a** (0.9 mmol), and **36** (3.3 mmol), with these products accounting for 92% of the isolated weight. A "carbamoyl" pathway on **48a** to form **60a** did not appear to take place (<0.2% formed) during any of these reactions.

Preparative HPLC on the *N*-methylanilide mixtures generated as indicated in the above paragraph, using methanol–water (3:1) as the eluent, gave each of **52a** and **53a** in acceptable purity for characterization by MS and ^1H NMR; see supplementary material.

[Methoxy(thiocarbonyl)](methylphenylamino)polysulfanes (54a and 55a) via (Methoxydichloromethyl)-[methoxy(thiocarbonyl)]polysulfanes (49 and 50). By analogy to the above procedure, bis[methoxy(thiocarbonyl)]trisulfane (**29a**)[3] (2.5 g, 10 mmol) in petroleum ether was chlorinated with 1.0 equiv of SO_2Cl_2 to yield 3.1 g (91% incorporation of the theoretical weight of Cl_2) of a mixture that was primarily **49a** [NMR δ 4.30, 3.80, contaminated with **28a** (<3%)]. Conversion with *N*-methylaniline gave a mixture (3.6 g) of **29a** (1.9 mmol), **2a** (7.1 mmol), **51a** (0.9 mmol), **52a** (0.6 mmol), **53a** (3.5 mmol), **54a** (0.8 mmol), **36** (0.2 mmol), **37** (0.6 mmol), and **38** (0.5 mmol), with these products accounting for 104% of the isolated weight. Also bis[methoxy(thiocarbonyl)]tetrasulfane (**30a**)[3] was chlorinated in the same manner (10 mmol scale) to yield a mixture (3.5 g, 97% incorporation of Cl_2) which was primarily the desired **50a** (>80%). Conversion with *N*-methylaniline gave a mixture (4.2 g) of **29a** (1.4 mmol), **2a** (8.9 mmol), **51a** (1.2 mmol), **52a** (1.3 mmol), **53a** (2.6 mmol), **54a** (0.7 mmol), **55a** (0.9 mmol), **36** (0.15 mmol), **37** (0.5 mmol), and **38** (0.7 mmol), accounting for 103% of the isolated weight.

[Methoxy(thiocarbonyl)](chlorocarbonyl)disulfane (56a). A. Sulfuryl chloride (21.5 mL, 0.27 mol) was added to a solution of bis[methoxy(thiocarbonyl)] sulfide (**27a**)[3] (49 g, 0.27 mol) in petroleum ether (270 mL). The reaction mixture was refluxed for 1 h, and the solvent was then removed at aspirator vacuum through a 18-in. Vigreux column to provide a crude chlorination mixture (66 g, 98% incorporation of Cl_2) which was subjected to a "cracking" distillation. The fraction (22.5 g) at bp 100–110 °C (2.5 mm) contained 75 mol% of desired **56a** (overall 35%) with most of the remainder methoxy(thiocarbonyl) chloride (**7a**). This fraction was redistilled through a 5-in. Vigreux column to provide 9.7 g (18%) of pure title product, bp 72 °C (0.4 mm), ρ = 1.48, Anal., pure by *N*-methylaniline assay more than 1 year after storage at −20 °C; ^1H NMR δ 4.27 (s); ^{13}C NMR of **56a** reported in Table IV in supplementary material. **B.** Chlorocarbonylsulfenyl chloride (**8**)[3] (15 mL, 0.18 mol) was added to a suspension of potassium methyl xanthate (**57a**) (28 g, 0.19 mol) in $CHCl_3$ (200 mL) at 5 °C. The reaction mixture was stirred for 30 min at 25 °C, then filtered, and concentrated to provide a mixture (29 g) of **56a** and bis[methoxy(thiocarbonyl)]disulfane (**28a**) in a molar ratio of 3.2:1.0. Short-path distillation provided pure title product (15 g, 41%), bp 87 °C (0.6 mm), ρ = 1.48, Anal.

[Ethoxy(thiocarbonyl)](chlorocarbonyl)disulfane (56b) was obtained exactly as in method B for **56a** but with potassium ethyl xanthate (**57b**). The crude product (37.4 g) contained **56b**, bis[ethoxy(thiocarbonyl)]disulfane (**28b**), and diethyl carbonate in a molar ratio of 2.8:1.0:0.6; short-path distillation gave **56b** (11.0 g, 28%), bp 65–67 °C (0.2 mm), ρ = 1.40, Anal.; see Table IV in supplementary material for NMR data.

[2-Propoxy(thiocarbonyl)](chlorocarbonyl)disulfane (56c) was obtained exactly as in method B for **56a** but with potassium 2-propyl xanthate (**57c**). The crude product (37.3 g, 90%, ρ = 1.35) was already in a high state of purity as judged by conversion of a portion to *N*-methylanilide **58c** (71% yield of a tan solid, mp 61–69 °C, that was >85% pure by ^1H NMR and HPLC). Short-path distillation was accompanied by decomposition, but the pure title product was obtained in 33% recovery at bp 76–80 °C (0.3 mm), ρ = 1.32, Anal.; see Table IV in supplementary material for NMR data.

[Methoxy(thiocarbonyl)](methylphenylcarbamoyl)disulfane (58a).[19] Acid chloride **56a** (2.9 g, 14 mmol) was reacted with *N*-methylaniline in $CHCl_3$ (44 mL, 2 M, 88 mmol) by the usual procedure[3] to yield 3.5 g (88%) of a yellow powder which was recrystallized in 76% recovery as white prisms from hot petroleum ether–CH_2Cl_2 (chilled to −20 °C); mp 92–94 °C, Anal., MS, NMR δ 7.3–7.5 (m, 5 H), 4.21 (s, 3 H), 3.38 (s, 3 H); further data in supplementary material. After several months storage at 25 °C, crystals of **58a** had undergone a quantitative solid-state disporportionation[19] to bis(methylphenylcarbamoyl)disulfane (**4**) admixed with elemental sulfur. This disproportionated material was an amorphous white powder, mp 240 °C [lit.[3] for pure **4**, mp 240–243 °C], characterized by NMR δ 7.41 (s, 5 H), 3.36 (s, 3 H), HPLC, Anal. Also, **58a** gradually heated over 10 min in a closed tube to a final temperature of 220 °C and then chilled gave quantitatively **4** plus *O,S*-dimethyl dithiocarbonate.[3]

[Alkoxy(thiocarbonyl)](methylphenylcarbamoyl)disulfanes (58b, 58c). The redistilled acid chlorides **56b** or **56c**, reacted as described for the preparation of **58a**, gave hard white solid *N*-methylanilides after 1 week under pentane at −20 °C for **58b** (77%), mp 53–55 °C, or directly after rotary evaporation at 25 °C for **58c** (83%), mp 83–85 °C. Recrystallizations were from hot petroleum ether–CH_2Cl_2; **58b**: 79% recovery, mp 55 °C, clear plates; **58c**: 76% recovery, mp 85 °C, clear cubes; Anal., MS, and further data on both **58b** and **58c** in supplementary material.

[Alkoxy(thiocarbonyl)](methylphenylcarbamoyl)trisulfanes (60) via [Alkoxy(thiocarbonyl)](chlorocarbonyl)-trisulfanes (59). Chlorocarbonyldisulfanyl chloride (**12**)[5,10] (1.0 g, 6.1 mmol) was added dropwise to a stirred suspension of the appropriate potassium alkyl xanthate (**57**) (1.05 equiv) in $CDCl_3$ (7 mL) at −7 °C. Reaction mixtures were stirred for a further 15 min at 25 °C, checked by ^1H NMR (Table IV, supplementary material; note that all the species including the byproducts reported in the ensuing discussion were clearly distinguished from one another) and then slowly poured directly into a $CHCl_3$ solution of *N*-methylaniline (10 mL, 2 M, 20 mmol) at 5 °C. The usual workup gave mixtures in which title products **60** were the major components as judged by ^1H NMR. The nominal overall yields based on weights of products isolated were 60–80%, although the HPLC dilution technique mentioned at the end of General Methods in this Experimental Section (using **58** with the same alkyl group as the reference) suggested that yields of **60** were on the order of 25%. The ratio of trisulfane **60** to disulfane **58** ranged from 8 in the methyl series **a** to 6 in the ethyl series **b** to 2 in the 2-propyl series **c**. In the methyl series **a**, **12** also served to oxidize **57a** so that **59a** (72 mol %) was contaminated with bis[methoxy(thiocarbonyl)]disulfane (**28a**) (8 mol %) and trisulfane (**29a**) (19 mol %); the corresponding *N*-methylanilide **60a** was contaminated with **28a** and **29a** in similar ratios. The oxidation side reaction was most serious in the methyl series (**a**) but was also noted in the ethyl series (**b**) at varying levels depending on precise conditions. In some experiments in the ethyl series (**b**) where amounts of **28–30b** were negligible, as much as 40% of ethyl chloride was observed possibly due to reaction[3] of ethoxy(thiocarbonyl) functions with excess disulfanyl chloride **12**. In the 2-propyl series (**c**), the chemistry was the cleanest with regard to lack of formation of polysulfanes **28–30c**, and at most 25% of 2-chloropropane was observed, although as already noted partial desulfurization of **59c** to **56c** was more pronounced than for methyl or ethyl (series **a**, **b**). Solutions of **59** in $CDCl_3$, upon standing for 1 day at 25 °C, showed evidence for **56** (~50%) and also the appropriate alkyl chloride (~20%), with the remainder still giving rise to **60** after reaction with *N*-methylaniline.

Bis(methylphenylcarbamoyl) Sulfide (61). A. Triphenylphosphine (1.2 g, 4.5 mmol) and disulfane **4** (382 mg, 1.2 mmol) in $CDCl_3$ (12 mL) were refluxed for 4 days ($t_{1/2}$ ~25 h by ^1H NMR). The reaction mixture was concentrated and adsorbed onto a silica gel column (3 × 25 cm) which was washed with CH_2Cl_2–hexane (7:3) (750 mL) to remove excess triphenylphosphine and produced triphenylphosphine sulfide. Absolute methanol then eluted the title compound, which was obtained as a pale yellow oil (305 mg, 88%), >95% pure by ^1H NMR with the remainder *N,N'*-dimethyl-*N,N'*-diphenylurea.[3] Pure **61** was stable to reflux in methanol for 3 days, and reflux in $CHCl_3$ for 12 days. **B (Superior).** Potassium cyanide (230 mg, 3.5 mmol) was suspended in $CDCl_3$ (6 mL) containing dissolved bis(carbamoyl)disulfane **4**[3] (360 mg, 1.1 mmol), and the reaction mixture was stirred at 25 °C for 4 days ($t_{1/2}$ ~21 h by ^1H NMR, singlet at δ 3.36 converted to singlet at δ 3.29). The inorganic material (determined to include 1.3 mmol of thiocyanate) was removed by filtration, and the filtrate was concentrated to provide the title product (320 mg, 97%), pure by ^1H NMR. Recrystallization from CCl_4–hexane gave white plates in 77% recovery, mp 90–91 °C,

Anal., MS, further data in supplementary material.

Reaction of Bis(methylphenylcarbamoyl)disulfane (4) with Methanolic Potassium Cyanide.[30] Disulfane **4** (390 mg, 1.2 mmol) and potassium cyanide (93 mg, 1.4 mmol) were refluxed in methanol (10 mL). After 12 h, the mixture was evaporated, redissolved in $CHCl_3$ (3 mL), and washed twice with equal volumes of water, followed by two washes with 1 N HCl. The organic phase provided *O*-methyl methylphenylcarbamate[3] (120 mg, 61%), pure by ^1H NMR, whereas the aqueous phase contained thiocyanate (1.0 mmol, 83%). Intermediate timepoints showed that the reaction proceeded with $t_{1/2}$ ~0.2 h and that up to 10 mol % of monosulfide **61** formed. As a control, pure **61** (50 mg, 0.17 mmol) with potassium cyanide (13 mg, 0.2 mmol) in refluxing methanol (1.5 mL) for 14 h gave the same *O*-methyl carbamate (25 mg, 91%), $t_{1/2}$ ~1.2 h; negligible (<10%) thiocyanate formed.

Harris Reactions (eq 2) for Preparations of Bis(methylphenylcarbamoyl)polysulfanes. The appropriate sulfur dichloride (0.5 M) in benzene was added dropwise to an equal volume of an ice-chilled solution of an *O*-alkyl methylphenylthiocarbamate (**2**) (1 M) in benzene. After standing overnight at 25 °C, rotary evaporation gave oils or amorphous solids in nominally quantitative yields that proved by ^1H NMR and HPLC to be mixtures of bis(carbamoyl)polysulfanes; see Table III for compositions. Disproportionation appeared to be consistently less in the 2-propyl series **c**, by contrast to methyl or ethyl (series **a**, **b**). It should be noted that although in optimal cases, both **13** and **62** were obtained as ^1H NMR-pure solids after trituration with petroleum ether, analytical data on these materials deviated noticeably from theory (C, N low; S high) and mp determinations also suggested their inferiority to the crystals obtained as described elsewhere in this Experimental Section after *N*-methylaniline was reacted with the appropriate bis(chlorocarbonyl)polysulfanes (**14**, **76**).

Rapid scan UV spectra on the entire family of bis(carbamoyl)polysulfanes showed considerable tailing from the end absorption at 210 nm, with inflection points at 225 nm and 270 nm. Absorbance ratios were $\epsilon_{225}:\epsilon_{210}$ ~0.6–0.8 and $\epsilon_{270}:\epsilon_{210}$ ~0.05–0.2 with higher values for higher *n*. Cutoffs (wavelength for which absorption <2% of maximum) were 295 nm ($n = 1$), 300 nm ($n = 2$), 320 nm ($n = 3$), 340 nm ($n = 4$), 350 nm ($n = 5$), 360 nm ($n = 6$), and 370 nm ($n \geq 7$).

Bis(methylphenylcarbamoyl)tetrasulfane (62). A. Similar to method A for **13**, bis[methoxy(thiocarbonyl)]disulfane (**28a**)[3] (4.9 g, 23 mmol) was converted with SO_2Cl_2 to bis(methoxydichloromethyl)tetrasulfane (**32a**)[1,4,5] (7.8 g, 95%). After treatment with $FeCl_3$ (total ~150 mg) over 4 h (**32a** is appreciably less reactive than **31a**), the weight was 5.6 g (96% of theoretical weight loss of methyl chloride; ^1H NMR signal at δ 3.79 due to **32a** abolished). After reaction with *N*-methylaniline, the product oil (7.2 g, 91% based on **28a**) was comprised of bis(carbamoyl)disulfane **4** (1.7 mmol), trisulfane **13** (3.7 mmol), and tetrasulfane **62** (5.6 mmol) as well as bis(amino)disulfane **36** (6.0 mmol) and *S*-methyl methylphenylthiocarbamate[3] (7.5 mmol). **B (Best).** Acid chloride **76** (2.3 g, 8.9 mmol) was reacted with *N*-methylaniline in $CHCl_3$ (27 mL, 2 M, 54 mmol) by the usual procedure[3] to yield 3.4 g (96%) of a brown oil which solidified under petroleum ether at −20 °C. The off-white product (2.7 g, 76%), mp 110–117 °C, had 6% of **13** and 8% of **63** along with the remainder desired **62**. Recrystallization in 43% recovery from hot petroleum ether–CH_2Cl_2 (then cooled to −20 °C) gave **62** as clear plates, mp 118–123 °C, which were >99% pure by HPLC, Anal., MS, NMR δ 7.40 (m, 5 H), 3.39 (s, 3 H); further data in supplementary material. **C.** Bis[2-propoxy(thiocarbonyl)]disulfane (**28c**) (2.7 g, 10 mmol) and sulfuryl chloride (1.7 mL, 21 mmol) in ethyl ether (20 mL) were stirred at 25 °C for 18 h and then added at 5 °C to a solution of *N*-methylaniline in ether (30 mL, 2 M, 60 mmol). The precipitated *N*-methylaniline hydrochloride (2.7 g, 94%) was removed by filtration, and the ether layer was washed twice with 1 N aqueous HCl, dried ($MgSO_4$), and evaporated to provide a brown oil (3.9 g, 99%), that was principally **62** (71%), with some of the disproportionation products **13** and **63** (16% combined) and *O*-2-propyl thiocarbamate **2c** (13%). After standing for 3 days at −20 °C under petroleum ether, a solid (3.0 g, 76%), broad mp 60–100 °C, was collected that was a mixture of bis(carbamoyl)polysulfanes **4**, **13**, **62**, and **63** in a ratio of 1:2:15:2.

Higher bis(methylphenylcarbamoyl)polysulfanes arose by treatments of bis[2-propoxy(thiocarbonyl)]trisulfane (**29c**) and tetrasulfane (**30c**) as in method C described for **62**. Crude yields were essentially quantitative, and product distributions were similar to those reported later in this Experimental Section in connection with compounds **77** and **78**. The product mixture derived from **29c**, which had been freed of *N*-methylaniline hydrochloride by immediate filtration at 25 °C, gave rise to pure pentasulfane **63** as the one component which selectively came out of the ethyl ether solution upon further cooling and concentration (~25% yield, two crops). Recrystallization from hot ethanol–CH_2Cl_2 gave **63** in 70% recovery as clear needles, mp 143–146 °C, >99% pure by HPLC, Anal., MS, NMR δ 7.2–7.4 (m, 5 H), 3.34 (s, 3 H); further data in supplementary material. Pure hexasulfane **64** was obtained (~10% recovery) by taking the crude oil from the reaction of **30c**, dissolving in hot petroleum ether, filtering off **63**, chilling to −20 °C, and waiting 3 months, pale yellow cubes, mp 133–136 °C, >95% pure by HPLC, Anal., NMR δ 7.2–7.4 (m, 5 H), 3.38 (s, 3 H); further data in supplementary material. Other information on the title class of compounds is found with text Table III and with "Harris Reactions (eq 2)" in this Experimental Section following the description of **61**.

Bis(chlorocarbonyl)tetrasulfane (76). A mixture of bis[2-propoxy(thiocarbonyl)]disulfane (**28c**) (12.3 g, 45 mmol), sulfuryl chloride (10.8 mL, 135 mmol), and calcium carbonate (0.45 g) in petroleum ether (45 mL) was refluxed for 2 h. After filtration and rotary evaporation at aspirator pressure, 11.5 g (101%) of the title product was obtained [^{13}C NMR δ 163.6]. A portion (1.0 g) of this yellow oil, dissolved in $CHCl_3$ (5 mL), gave with *N*-methylaniline (12 mL, 2 M, 24 mmol) an oil (1.6 g, 106%) which comprised principally (~85%) a distribution of bis(carbamoyl) polysulfanes **4**:**13**:**62**:**63**:**64**:**65**:**66** = 4:3:74:13:5:2:1, together with ~5% each of *O*-2-propyl thiocarbamate **2c**, carbamothioamide **3**, and (carbamoyl)(amino)disulfane **11**. Isolation of pure **62** from this mixture of *N*-methylanilides has been described earlier (method B for **62**). Assay of **76** (82 mg, 0.32 mmol) with methanol (20 mL) at 5 °C to form the series of bis(methoxycarbonyl)-polysulfanes[5] occurred with evident significant scrambling: the product (73 mg, 0.30 mmol, 94%) was principally tetrasulfane (52%), but also contained tri- (16%), penta- (18%), and hexa- (14%) sulfanes.

Variations in reaction conditions were explored: **28c** (1.35 g, 5 mmol) and SO_2Cl_2 (1.2 mL, 15 mmol) in petroleum ether (5 mL) were refluxed for 3 h, in the *absence* of calcium carbonate, to give an oil (1.45 g, 87% for **44c**) which was reacted at 5 °C with *N*-methylaniline in $CHCl_3$ (25 mL, 2 M, 50 mmol). The usual workup yielded an oil (2.5 g, 98%) comprised of *O*-2-propyl thiocarbamate **2c** (1.7 mmol), (carbamoyl)(amino)trisulfane **40** (1.3 mmol), (carbamoyl)(amino)disulfane **11** (0.2 mmol), and carbamothioamide **3** (0.2 mmol) [total 34% of "sulfenyl" pathway; compare to Schemes I and II] as well as bis(carbamoyl)tetrasulfane **62** (3.2 mmol, 64% formed by "carbamoyl" pathway). Lengthy rotary evaporation of the initial oil brought the weight down to theoretical for **76**, but now *N*-methylaniline assay revealed substantial levels of trisulfane **13** and pentasulfane **63**. Ethyl ether was tested and gave somewhat better results, particularly with 1 equiv of SO_2Cl_2 per thiocarbonyl group of **28c**. The worst results were in $CDCl_3$: although 2-chloropropane formation was complete in 10 min at 25 °C, *N*-methylaniline assay revealed that ~50% of the overall products were the disproportioned ones (**13** and **63**); furthermore the original presence of S_2Cl_2 was indicated by its conversion to **36**.

The title compound when made in the *optimal* way was tested for stability at 25 °C (absolutely no change in pattern of *N*-methylaniline assay after 5 weeks) and 100 °C. In the latter case, after 1 day the *N*-methylaniline assay revealed a ratio of **62**:**40**:**11**:**36** = 1.0:0.2:0.2:0.4, suggesting the decomposition sequence (supported by other timepoints): **76** yields **79** plus COS; **79** yields **12** plus sulfur or S_2Cl_2 plus COS.

Bis(chlorocarbonyl)pentasulfane (77), with Putative (Chlorocarbonyl)tetrasulfanyl Chloride (80). Bis[2-propoxy(thiocarbonyl)]trisulfane (**29c**) (1.5 g, 5 mmol), sulfuryl chloride (1.2 mL, 15 mmol), and calcium carbonate (50 mg) in petroleum ether (5 mL) were refluxed for 2 h which time was sufficient to complete 2-chloropropane formation. After filtration and evaporation, the produced yellow oil (1.1 g, 80% assuming **77**) was dissolved in $CHCl_3$ (5 mL) and reacted with excess *N*-methylaniline (15 mL, 2 M, 30 mmol) at 5 °C. After workup, an oil (1.9 g, 105%) was obtained which comprised bis(carbamoyl)poly-

sulfanes with two to seven sulfurs, of which the major component (~85%) was the expected pentasulfane **63** (1.8 mmol, 36% based on **29c**), together with the series of (carbamoyl)(amino)polysulfanes of which the tetrasulfane **41** (1.3 mmol, 26%) was major and **3** (1.2 mmol, 24%), **11** (0.2 mmol), and **40** (0.4 mmol), **42** (0.3 mmol), and **43** (0.1 mmol) were also identified.

The same reactions in the *absence* of calcium carbonate led to an oil (1.6 g, 88% assuming **45c**, see Scheme VI), which was added neat to *N*-methylaniline (25 mL, 2 M, 50 mmol) at 5 °C. After workup, an oil (2.4 g) was obtained which comprised mainly *O*-2-propyl thiocarbamate **2c** (3.4 mmol, 68%), (carbamoyl)(amino)tetrasulfane **41** (2.3 mmol, 46%), and bis(amino)disulfane **36** (1.2 mmol, 24%), and smaller amounts (5–10% each) of *N*-methylanilides **3**, **11**, **37**, **38**, **40**, **62** and **63**.

Bis(chlorocarbonyl)hexasulfane (78). Bis[2-propoxy(thiocarbonyl)]tetrasulfane (**30c**) (1.7 g, 5 mmol), sulfuryl chloride (1.2 mL, 15 mmol), and calcium carbonate (50 mg) in petroleum ether (5 mL) were refluxed for 2.5 h, although 2-chloropropane release was complete after 1 h. After filtration and evaporation, the produced oil (1.3 g, 79%) was reacted with *N*-methylaniline (15 mL, 2 M, 30 mmol) in the usual manner to provide after workup an oil (2.1 g, 99%) of which the major component was the expected bis(carbamoyl)hexasulfane **64** (2.6 mmol, 52%). Also formed, by disproportionation, were bis(carbamoyl)polysulfanes **62** (0.3 mmol), **63** (0.9 mmol), **65** (0.4 mmol), and **66** (0.2 mmol); furthermore (carbamoyl)(amino)polysulfanes **3** (0.7 mmol), **11** (0.4 mmol), **40** (0.2 mmol), **42** (0.3 mmol), and **43** (0.2 mmol) were observed (note that any HPLC peak due to **41** would be obscured by the major one due to **64**).

Attempted Preparation of Putative (Chlorocarbonyl)trisulfanyl Chloride (79). Indirect evidence for small amounts of **79** has already been mentioned, from experiments on the thermolysis of bis(chlorocarbonyl)tetrasulfane (**76**), and on the preparations of penta- (**77**) and hexasulfanes (**78**). A solution of 2-propoxy(thiocarbonyl) chloride (**7c**) (0.26 g, 1.9 mmol) in $CDCl_3$ (0.5 mL) was chilled to −50 °C, and S_2Cl_2 (0.15 mL, 1.9 mmol) was added. Within 10 min of warming to 25 °C, ^1H NMR examination revealed complete conversion of the 2-propyl groups of **7c** to the alkyl chloride. Further conversion with *N*-methylaniline in the usual way gave an oil (0.15 g, quantitative) that comprised **62**:**13**:**40**:**41**:**36**:**37** = 14:1:2:2:8:1 by HPLC and ^1H NMR analysis. These results imply that **79** (as well as **80** by disproportionation) does form, but most of it reacts further with a second equivalent of **7c** to give **76**, while leaving the corresponding amount of S_2Cl_2 unreacted.

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Supplementary Material Available: Tabulations of all NMR, chromatographic, mass spectral, and analytical data as cross-referenced in the text, and additional figures and mathematical treatment dealing with the HPLC correlations described in this work (20 pages). Ordering information is given on any current masthead page.