TABLE V
ANALYTICAL DATA FOR N-ALKYLHEPTASULFURIMIDES

Compound	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%S Calcd	%S Found	Mol wt Calcd	Mol wt Found
S_7NCH_3	4.74	4.70	1.19	1.39	5.52	5.60	88.54	90.0 ± 0.9	254	260
$S_7NC_2H_5$	8.98	9.74	1.88	1.97	5.24	5.02	83.90	83.6	268	272
$S_7NCH_2C_6H_5$	25.51	25.40	2.14	2.13	4.25	4.03	68.10	67.7	330	331
$S_7NCH_2CHCH_2$	12.89	12.76	1.80	1.83	5.04	5.19	80.30	80.35	280	271
$S_7NCH(CH_3)_2$	12.80	12.63	2.51	2.92	5.00	5.02	79.72	80.2	282	278

nitrogen), -5.29 (C_1 protons), -5.80 (C_2 proton); infrared spectrum (neat oil): 781 (s), 928 (s), 988 (s), 1039 (s), 1328 (m), 1418 (m), 1440 (sh) cm^{-1}.

N-Isopropylheptasulfurimide, a yellow oil, had R_f 0.42; nmr: τ -1.18 (doublet), -3.77 (septuplet) ($J = 7$ Hz); infrared spectrum (neat oil): 824 (s), 978 (s), 1116 (s), 1168 (m), 1335 (m), 1367 (m), 1383 (m), 1450 (m), 2920 (sh), 2960 (m) cm^{-1}.

Variation of Base.—Heptasulfurimide (5.00 g) was allowed to react with 1 equiv each of sodium, sodium hydride, sodium amide, lithium hydroxide, and ethyllithium at 0° as described above. In each case an intensely green or blue solution resulted. The color appeared to reach its maximum intensity almost immediately with ethyllithium and within 15 min with lithium hydroxide. Other bases were intermediate in rate, all being quite fast. The standard work-up procedure given above was followed. Results are summarized in Table I.

Variation of Temperature.—Heptasulfurimide (5.00 g) dissolved in 150 ml of tetrahydrofuran was allowed to react with 1.0 molar equiv of ethyllithium at 50, 21, 0, and $-28.5°$. After 5, 10, 15, and 45 min, respectively, the reaction mixtures were returned to 0° for 15 min whereupon 1.5 ml of methyl iodide was added. Work-up in the usual way (except that the water–ether extraction was dispensed with) led to the results shown in Table III. An additional reaction in which ethyllithium was added at $-28.5°$ and after 45 min the temperature was altered to 50° for 10 min before addition of methyl iodide was also carried out. Temperatures of 21 and 50° were maintained in a thermostated water bath while ice and nitromethane slush baths provided the 0 and $-28.5°$ temperature baths.

Decomposition of N-Benzylheptasulfurimide.—A crystalline sample of N-benzylheptasulfurimide was observed to decompose gradually at room temperature. After a few days thin layer chromatographic analysis showed a mixture of at least four components; however, after 3–4 weeks only sulfur and a new material with R_f 0.22[38] were prominent products. Chromatography of the decomposed mixture on silica gel followed by recrystallization from hot methanol gave a bright yellow solid of mp 102–103.5°. This material was identical in all respects with the compound previously identified as the thioamide of thiobenzoic acid[39] but subsequently characterized as benzylidinimine tetrasulfide.[40] A 1.00-g (3.1-mmol) sample of N-benzylheptasulfurimide was decomposed in an evacuated, sealed tube for 2 months prior to opening on the vacuum line. Investigation of the volatile materials demonstrated the presence of a readily condensable gas (0.77 mmol from PVT measurements). A sample of this gas gave a mass spectrum corresponding to that of ammonia. Absorption into a known excess of standard hydrochloric acid, followed by back-titration, showed 0.77 mequiv of base to be present.

(38) This R_f value is with carbon disulfide rather than hexane as eluent.
(39) R. Schenck, *Ann.*, **290**, 171 (1896).
(40) Y. Sasaki and F. P. Olsen, to be submitted for publication.

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Sulfurimide Anions.   III.   Alkylation of the Isomeric Hexasulfurdiimides[1,2]

BY EDITH M. TINGLE AND FREDRIC P. OLSEN

1,4- and 1,5-hexasulfurdiimides react with ethyllithium producing anions which effect nucleophilic substitution on methyl iodide to give N-methyl and N,N'-dimethyl derivatives of the respective 1,4- and 1,5-hexasulfurdiimide series. Under identical conditions 1,3-hexasulfurdiimide gives N-methylheptasulfurimide and dialkyl polysulfides. The latter reaction involves an anion of 1,3-hexasulfurdiimide as an intermediate.

A previous paper[3] concerned the formation and reaction of the heptasulfurimide anion. This ion was shown to be formed by proton abstraction in competition with addition of the base to sulfur–sulfur and/or

(1) Presented at the Inorganic Chemistry Section of the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968; see Abstract No. O-52.
(2) Based on the M.S. thesis of E. M. T.
(3) B. A. Olsen and F. P. Olsen, *Inorg. Chem.* **8**, 1736 (1969).

sulfur–nitrogen bonds. The relative proportions of the two reactions depended on the base and the temperature used. Once formed the heptasulfurimide anion was relatively stable, persisting in solution—probably in equilibrium with a low concentration of some other species—for several days at room temperature. The ion was found to react with a variety of alkyl halides yielding N-alkyl derivatives of heptasulfurimide. This

paper concerns the possible extension of these reactions to the three isomeric hexasulfurdiimides.[4-8]

Results

1,4-Hexasulfurdiimide reacted with a 1:1 molar ratio of ethyllithium to give an intense blue-green solution analogous to that associated with the anion of heptasulfurimide.[8] Addition of methyl iodide discharged this color after a few minutes at 0° giving a pale orange solution. Thin layer chromatography showed the presence of five principal products which were separated by column chromatography. Three of these were readily identified as sulfur, unreacted starting material, and a dialkyl polysulfide mixture containing about equal molar ratios of methyl and ethyl groups. The fourth material, a low-melting solid, was identified as an N,N'-dimethylhexasulfurdiimide on the basis of the following properties. The infrared spectrum showed bands characteristic of N–S (798 cm^{-1}), C–N (1019–1094 cm^{-1}), and C–H (2850–2965 cm^{-1}) but no bands which could be attributed to an N–H group. The proton nmr spectrum consisted of a sharp singlet at -3.04 ppm. The mass spectrum showed an apparent molecular ion of composition $S_6N_2C_2H_6$ (calculated peak intensities at mass numbers 250–254: 100:7:27:2:4; found: 100: 8:26:1:3). An osmometric molecular weight of 250 ± 5 confirmed this grouping as the molecular ion. Other fragments observed in the mass spectrum corresponded to CH_3NS_x ($x = 1$–4), as well as NS, S_3, and S_2. The second new material, a higher melting solid, was identified as the N-methyl derivative of a hexasulfurdiimide from the following properties. It had a proton nmr spectrum consisting of a sharp singlet at -3.10 ppm and a broad peak at -3.76 ppm of relative areas 3:1. The infrared spectrum showed two peaks attributable to N–S stretching modes (803 and 745 cm^{-1}) as well as bands attributable to C–N (1062, 1122 cm^{-1}), C–H (2965–2855 cm^{-1}), and N–H (3305 cm^{-1}). The mass spectrum gave a molecular ion of composition $S_6N_2CH_4$ at mass 236. In addition to all fragments mentioned above for the dimethyl derivative, fragments corresponding to S_xNH ($x = 1$–4) were also observed.[9] Relative amounts of imides are summarized in Table I. Doubling the amount of the strong base, ethyllithium, increased the yield of the dimethyl derivative at the expense of the monomethyl- and unsubstituted diimides while the total recoverable imide in all forms remained unchanged. With the weaker base, lithium hydroxide, the total recoverable imide was higher but substantial amounts of mono- and unsubstituted diimides were also obtained.

When the 1,5 isomer of hexasulfurdiimide was treated with a 1:1 molar ratio of ethyllithium under identical conditions, an analogous series of compounds resulted. Sulfur, dialkyl polysulfides (with a methyl to

TABLE I
REACTIONS OF HEXASULFURDIIMIDES

	% unreacted	% monomethyl	% dimethyl	% total recovered imides
1,4 Isomer				
1:1 C_2H_5Li	27	23	11	61
2:1 C_2H_5Li	6	6	50	62
2:1 LiOH	16	17	38	71
1,5 Isomer				
1:1 C_2H_5Li	31	27	15	73

ethyl ratio near 1:1), and unreacted 1,5-hexasulfurdiimide were present along with two new materials similar in R_f to those obtained in the previous reaction. A new, higher melting N,N'-dimethylhexasulfurdiimide was eluted after sulfur and identified as before by its proton nmr spectrum (a sharp singlet at -3.15 ppm) and by its infrared spectrum which consisted of C–H (2990–2783 cm^{-1}), N–C (1123–1035 cm^{-1}), and S–N (775 cm^{-1}) absorption but no N–H. The mass spectrum showed the same molecular ion pattern as before and a nearly indistinguishable set of fragments. A new N-methylhexasulfurdiimide resulted whose proton nmr spectrum consisted of a sharp singlet at -3.12 ppm and a broad peak at -4.02 ppm in the ratio of 3:1. The infrared spectrum showed N–H (3327 cm^{-1}), C–H (2990–2980 cm^{-1}), C–N (1123, 1060 cm^{-1}), and S–N (809, 766 cm^{-1}) absorption. The mass spectrum gave the molecular weight as 236 with fragmentation nearly indistinguishable from that of the previous N-methylhexasulfurdiimide. Yields are given in Table I. The N,N'-dimethyl derivative synthesized in this reaction was identical in all respects with a dimethylhexasulfurdiimide prepared by the reaction between trisulfur dichloride and methylamine as previously reported by Brasted and Pond.[10] Reaction of the 1,3 isomer of hexasulfurdiimide with a 1:1 molar ratio of ethyllithium gave the same intense intermediate color noted for the previous compounds. The crude reaction product obtained after addition of methyl iodide, however, contained only three major components, two of which were sulfur and dialkyl polysulfides. The third material was N-methylheptasulfurimide identical in all respects with an authentic sample. No materials corresponding to either di- or monomethylated derivatives of hexasulfurdiimide could be isolated. The alkyl polysulfide contained a substantial excess (2.2:1) of methyl over ethyl alkyl groups.

Discussion

The structure of the product from the alkylation of the 1,3 isomer bears little resemblance to the structure of the starting material. Nevertheless, the possibility of rearrangement in the 1,4- and 1,5-hexasulfurdiimides during reaction is considered unlikely. The major evidence against rearrangement comes from the finding of three unique sets of products from the reactions of the three imides. Rearrangement would be expected to occur only if one set of products were substantially more stable than another. If this were the case, at

(4) J. Weiss, *Angew. Chem.*, **71**, 246 (1959).
(5) H. G. Heal, *Nature*, **199**, 371 (1963).
(6) P. Tavs, H. J. Schulze-Steinen, and J. E. Colchester, *J. Chem. Soc.*, 2555 (1963).
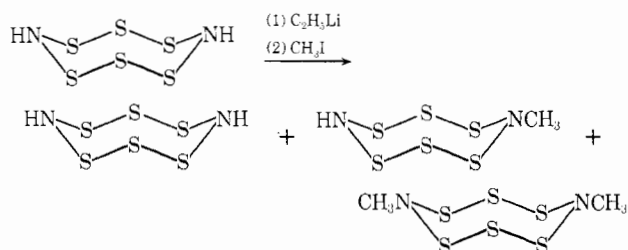(7) J. Weiss, *Z. Anorg. Allgem. Chem.*, **305**, 190 (1960).
(8) J. C. Van de Grampel and A. Vos, *Rec. Trav. Chim.*, **84**, 599 (1965).
(9) A very strong unassigned peak was also observed at mass 94.

(10) R. C. Brasted and J. S. Pond, *Inorg. Chem.*, **4**, 1163 (1965).

least two of the isomeric imides—if not all three—should have resulted in a common set of products. The recovery of part of the starting imide from both of these reactions uncontaminated by isomers provides additional support. We conclude, therefore, that the two series of mono- and dimethyldiimides obtained possess the same atomic arrangement of sulfur and nitrogen atoms as in the starting imides.[11] The alkylation reaction thus provides a link between the structures of the 1,4- and 1,5-hexasulfurdiimides and their corresponding mono- and dimethyl derivatives. There appears to be only one report[10] of the preparation of a dimethylated hexasulfurdiimide while monosubstituted hexasulfurdiimides do not appear to have been pre-


viously prepared.[12] The geometry of this known dimethyldiimide was not fully established, but 1,5 geometry was proposed[10] on the grounds that breaking and re-forming sulfur–sulfur bonds during the preparation from trisulfur dichloride and methylamine were more likely not to occur than to occur. The identity of the two materials provides mutual confirmation both for the structure proposed by Brasted and Pond for their product and for our assertion that there is no rearrangement during alkylation of the 1,4 and 1,5 isomers.

The reaction of 1,4-hexasulfurdiimide with a 1:1 molar ratio of base resulted, as expected, in a reasonable amount of the monomethyl derivative, but a significant amount of dimethylated diimide was also formed. The latter could arise either by an equilibrium disproportionation of the monoanion to dianion and neutral imide

$$2S_6N_2H^- \rightleftharpoons S_6N_2^{2-} + S_6N_2H_2 \qquad (1)$$
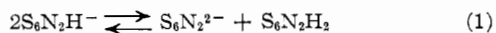
or by a proton transfer between the monoanion and the monomethyl derivative as it is formed in the second step, eq 2. Subsequent methylation would then give the dimethyl derivative without the necessity of having a dianion as an intermediate. As required by either of these schemes, there was a significant amount of un-

$$S_6N_2HCH_3 + S_6N_2H^- \rightleftharpoons S_6N_2CH_3^- + S_6N_2H_2 \qquad (2)$$
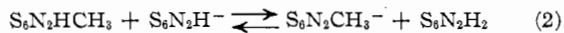
reacted hexasulfurdiimide remaining at the end of the reaction. Isolation of the polysulfide oils which were found to contain both the ethyl group of the ethyllithium and the methyl group of the methyl iodide

(11) The increased splitting of the N–S stretching mode as the two nitrogen atoms get closer together in the unsubstituted imides has been used as a criterion for assigning structures.[5] While the argument may or may not be theoretically sound, it nevertheless provided an assignment of structure which has subsequently been proven correct.[6] In the dimethyl derivative the compound obtained from the 1,5-diimide shows a single N–S absorption while that from the 1,4-diimide shows two.

(12) H. Heal (private communication) has also recently found all three of the dimethylhexasulfurdiimides to have been formed in a reaction between methylamine and sulfur monochloride.

showed the same competing addition reaction between the base and the hexasulfurdiimides as was found in the reaction with heptasulfurimide.[3] The competing reaction appears to be about equally important here as in the reaction with heptasulfurimide [60% total recoverable diimide vs. 52% (44% alkylimide plus 8% unreacted imide) for heptasulfurimide]. The amount of dimethyldiimide was substantially increased (from 11 to 50%) by the use of a 2:1 molar ratio of base; there was no significant increase in the amount of dialkyl polysulfides. The anion, once formed, appears to be less susceptible to nucleophilic attack by more base (relative to proton abstraction) than the neutral imide. Unreacted starting material, while in substantially reduced amount, was nevertheless present along with a small amount of the monomethyl derivative. The presence of these materials shows that more than 2 mol of base was consumed in the degradation of the diimide to polysulfide, consistent with the results found for heptasulfurimide. Since an average of more than one methyl group per mole of starting imide was incorporated into the products, the dianion must have been present in this reaction. This does not necessarily imply its presence in the 1:1 reaction but does at least show that the dianion is a stable chemical species and that it cannot be excluded from consideration in the 1:1 reaction. Even though proton abstraction by lithium hydroxide was fairly slow and resulted in a substantially less intensely colored solution than that from the stronger base, an appreciable amount of the dimethylated species was formed. The total yield of recoverable imides (71%) was higher than in either of the previous two cases while the yield of polysulfides was considerably reduced. As expected, less nucleophilic attack took place with the weaker, less nucleophilic base. From a synthetic point of view, however, the distribution of products is not as favorable for synthesis of either the mono- or dimethyldiimides as are the 1:1 and 2:1 ethyllithium reactions.

Since heptasulfurimide as well as the 1,4- and 1,5-hexasulfurdiimides could be successfully alkylated without rearrangement, the failure of the 1,3-diimide to survive under identical conditions was unexpected. The instability of the 1,3 isomer in the presence of base must arise from the proximity of the two N–H groups. Either the addition of base is favored over proton abstraction or, the ion, once formed, decomposes. The substantial excess of methyl over ethyl alkyl groups in the polysulfide fraction isolated from this reaction rules out the former possibility. Addition of base should have given an equimolar mixture of methyl and ethyl polysulfides.[3] Consequently, the primary function of the base is to abstract protons just as in the previous case, with the ion (either $^-$N–S–NH or $^-$N–S–N$^-$) being unstable. On the basis of the data currently available it is not possible to choose between these two ions.

Isolation of N-methylheptasulfurimide as a major product is difficult to rationalize. Obviously both ring cleavage (breaking of sulfur–nitrogen bonds) and chain

lengthening (formation *and* destruction of sulfur–sulfur bonds) must be occurring under the basic conditions employed (requiring at least three or four steps).[13] Since the conditions under which the 1,3 isomer of hexasulfurdiimide rearranges to heptasulfurimide (0°, imide anion, tetrahydrofuran as solvent) approximate those used in the preparation of the imides[4–6] (−5°, dimethylformamide as solvent, ammonia as base), similar facile making and breaking of bonds would appear quite apt to occur under both conditions. Intense, blue colors are noted in the preparation of the imides suggestive of sulfur–nitrogen anions, although the latter do not appear to have been seriously considered as intermediates in this reaction.[14,15] The absence of tetrasulfurtetraimide, the low yields of the pentasulfurtriimides, and the low yield of 1,3-hexasulfurdiimide in the preparation of heptasulfurimide can be explained if anions are, in fact, involved. These four materials all contain a 1,3-N–S–N linkage, and even if they were formed, they would be expected to rearrange (as anions) to the anion of heptasulfurimide. The latter (after acidification) is the major product isolated in these reactions.[4,5]

The synthesis used to prepare the methyl derivatives of the 1,4-and 1,5-hexasulfurdiimides appears suitable for the preparation of other organic derivatives and should provide a convenient route to unsymmetrically substituted dialkyl derivatives. It does not seem likely that the method will prove suitable for use with the pentasulfurtriimides or for synthesis of tetrasulfurtetraimide derivatives since these all contain the linkage

$$\begin{array}{cc} H & H \\ | & | \\ -N-S-N- \end{array}$$

In agreement with these considerations we were unsuccessful in attempting to alkylate tetrasulfurtetraimide under similar conditions.

Infrared spectra were recorded for all compounds between 4000 and 170 cm⁻¹. Above 600 cm⁻¹ the observable bands represent predominantly stretching frequencies which, while useful in assigning gross structures, do not change much from one isomer to another.[11] Absorption in this region has been reported previously for the three diimides[5,16] and all bands observed[17] were within the limits given in the former paper[5] when spectra were run in the same solvent. The values in the latter paper[16] are presumed to be taken from the former. As might be expected, the N–H stretching band was rather strongly solvent dependent shifting nearly 200 cm⁻¹ when carbon disulfide was replaced by tetrahydrofuran as solvent. Absorption in this region for the methyl derivatives are included in the Experimental Section. The region between 600 and 170 cm⁻¹ is considerably more characteristic for each compound and

provides a more reliable means for ascertaining the identity or lack of identity of two suspect materials although these bands are difficult to assign owing to the low symmetry of the molecules. Absorption between 600 and 170 cm⁻¹ for all derivatives prepared and also for the unsubstituted diimides is given in Table II. Heptasulfurimide and N-methylheptasulfurimide are also included for comparison.

Experimental Section

Infrared spectra were recorded in the 4000–600-cm⁻¹ region on a Perkin-Elmer 521 grating instrument. Between 670 and 170 cm⁻¹ spectra were obtained on a Perkin-Elmer Model 301 equipped with Globar and mercury sources. The instrument was calibrated using the peaks of the water vapor spectrum. Proton nmr spectra were obtained on a Varian Model A-60 using carbon disulfide as solvent and tetramethylsilane as internal reference. Samples for mass spectra were introduced at room temperature by direct inlet into a Perkin-Elmer Hitachi Model RMU-6A. An ionizing potential of 80 eV was used. R_f values from tlc are for carbon disulfide as eluent on 0.25-mm air-dried silica gel plates. Molecular weights, melting points, and chromatography were as previously reported.[3]

Materials.—The three isomeric hexasulfurdiimides were isolated from the reaction of sulfur monochloride and ammonia in dimethylformamide as described by Heal.[5] Chromatographic separation on silica gel provided a good sample of the 1,4 isomer but mixtures of the 1,5 and 1,3 isomers. The latter were sepa-

Table II[a]

INFRARED SPECTRA OF ALKYLIMIDES AND THEIR DERIVATIVES BETWEEN 600 AND 170 CM⁻¹

1,5-S₆N₂H₂		1,5-S₆N₂HCH₃		1,5-S₆N₂(CH₃)₂	
Nujol	Benzene	Nujol	Benzene	Nujol	Benzene
539 sh		509 m	520 s	575 m	579 w
520 sh		465 w	471 sh		476 w
495 m	500 m	456 w	460 m		458 w
	467 sh	428 w	435 m	432 w	432 w
423 m	432 m	384 m	393 m	384 m	393 m
	401 w	364 m	364 m		373 m
360 w	360 w	336 sh	288 sh	282 w	
294 sh			276 m	273 w	281 m
281 m	279 m	270 m	258 w		
	263 w (?)		195 w		
220 w		200 m			
	214 m	169 m			

1,4-S₆N₂H₂		1,4-S₆N₂HCH₃		1,4-S₆N₂(CH₃)₂	
Nujol	Benzene	Nujol	Benzene	Nujol	Benzene
469 br	468 s, br	492 m	502 m	572 w	570 w
330 br		460 w	467 m	467 w	465 w
355 m	360 m	419 br	364 m	383 m	381 m
273 br	273 m	368 br	291 w (?)	281 m	371 sh
226 s	218 s	276 br	275 m	198 w	358 sh
179 m	179 w	205 w	204 w		282 m
	166 w	200 w	200 w		198 w

S₇NH		S₇NCH₃	1,3-S₆N₂H₂	
Nujol	Benzene	Thin film	Nujol	Benzene
497 m	509 m	579 w	550 m	541 w
456 m	465 m	471 m	524 s	522 w
426 m		449 sh	498 s	489 w
352 m		365 s	469 s	467 m
272 m	274 br	284 s		456 sh
255 m	250 br	251 s	384 s	401 m
210 m	206 m	210 m	282 s	291 m, br
		190 m	264 m	261 s
			259 m	220 m
			228 m	172 w
			196 m	

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad.

(13) Free-radical processes, while not required, are not inconsistent with the requirement of these steps: G. P. Richter, Ph.D. Thesis, University of Minnesota, 1968.

(14) F. Feher, R. Kreutz, and R. Minz, *Z. Naturforsch.*, **20b**, 918 (1965).

(15) M. Goehring, H. Jenne, and E. Fluck, *Chem. Ber.*, **91**, 1947 (1958).

(16) H. Garcia-Fernandez and H. Heal, *Compt. Rend.*, **266**, 1449 (1968).

(17) One additional rather weak band was consistently observed at 775 cm⁻¹ for 1,5-hexasulfurdiimide.

TABLE III
REACTIONS OF HEXASULFURDIIMIDES

Amt of imide, mg	Amt of ethyllithium, ml	Amt of products, mg				
		Sulfur	Dimethyl-diimide	Poly-sulfides	Monomethyl-diimide	Starting material
		1,4 Isomer				
371	1.3 (1:1)	10	49	33	89	101
341	2.4 (2:1)	25	193	20	20	20
300	73 mg (LiOH) (2:1)	20	128	Trace	54	48
		1,5 Isomer				
273	1.0 (1:1)	6	46	21	77	84
		1,3 Isomer				
284	1.0 (1:1)	19	a	77	a	· · ·

a A 51-mg amount of N-methylheptasulfurimide isolated.

rated by preparative-scale thin layer chromatography on 1.0-mm silica gel plates. Approximately 40 mg could be separated on one 20 × 20 cm plate if the plate was activated at 120° for 6 hr prior to use. A final recrystallization from benzene gave the 1,5 isomer of R_f 0.23, lit.[5] 0.24; the 1,3 isomer of R_f 0.19, lit.[5] 0.22; and the 1,4 isomer of R_f 0.35, lit.[5] 0.34. These samples were shown to be free of isomer contamination by thin layer chromatography.[18,19]

Alkylation of 1,4-Hexasulfurdiimide.—A 100-ml flask containing a magnetic stirring bar, 60 ml of freshly distilled tetrahydrofuran, and 200–400 mg of hexasulfurdiimide was fitted with a rubber septum and cooled to 0° in an ice bath. A 1- (or 2-) molar equiv amount of 1.3 M ethyllithium was added by syringe to the stirred solution,[20] followed in 10 min by 0.5 ml of methyl iodide. The solution was then allowed to warm to room temperature. After standing overnight, the solvent was removed *in vacuo*, and the residual red oil was found by thin layer chromatography to contain five major materials. Chromatography on a 70-g silica gel column with hexane eluted first sulfur, identified by its R_f value and melting point, followed by N,N'-dimethylhexasulfurdiimide as a nearly colorless oil which soon crystallized to a solid of mp 24.5–25.5°, R_f 0.71; infrared spectrum (benzene): 2960 (m), 2923 (m), 2895 (w), 2880 (w), 2855 (m), 1452 (m), 1432 (m), 1250 (m), 1120 (m), 1059 (s), 846 (m), 820 (sh), 775 (s), 732 (w) cm^{-1}. Elution with 5% benzene gave a vile (characteristic) smelling yellowish oil whose nmr spectrum was identical with that of the mixed dialkyl polysulfides described previously in the methylation of heptasulfurimide with ethyllithium as base.[3] The ratio of methyl to ethyl groups was close to 1:1.

(18) Melting points are not a reliable criterion of purity or identity for the 1,3 and 1,5 isomers. The 1,4 isomer melts fairly reproducibly at 130–131° (lit.[3,5] mp 130, 133°) to a yellow liquid which soon undergoes decomposition. The 1,3 isomer, if heated slowly, undergoes decomposition at about 128–130° (lit.[3,5,19] mp 123, 130, 120°) concurrent with melting. The decomposition triggers the melting, however, and not *vice versa*. Thus, samples placed in a hot oil bath at 135 or 140° do not melt rapidly but decompose after 10–20 sec. The melting point in the absence of decomposition seems to be about 149°. At or above this temperature the material melts rapidly to a pale yellow liquid which soon turns red and effervesces. The 1,5 isomer behaves similarly usually decomposing between 150 and 155° on slow heating (lit.[3,5] mp 153, 155°) but survives for fairly long periods at higher temperatures. The "true" melting point appears to be near 197°.

(19) H. Garcia-Fernandez, *Compt. Rend.*, **261**, 745 (1965).

(20) Or 1 equiv of solid LiOH dried *in vacuo* at 100° over P$_2$O$_5$ was added, and the solution was stirred for 3.5 hr at 0° before addition of the methyl iodide.

Next off the column with the same solvent was the monomethylhexasulfurdiimide obtained as a solid of mp 51.5–53°, R_f 0.53; infrared spectrum (benzene): 3305 (s), 2965 (w), 2927 (w), 2890 (w), 2855 (w), 1432 (m), 1121 (w), 1062 (m), 1028 (m), 803 (s), 745 (m) cm^{-1}. A quantity of unreacted hexasulfurdiimide was slowly eluted by 20% benzene as the final fraction. This was identified as the 1,4 isomer by its infrared spectrum and R_f value. Quantities of all materials obtained are summarized in Table III.

Alkylation of 1,5-Hexasulfurdiimide.—This reaction was carried out exactly as above. Hexane first eluted sulfur followed by a new N,N'-dimethylhexasulfurdiimide obtained as a solid of mp 81.5–82°, R_f 0.68; infrared spectrum (benzene): 2962 (m), 2925 (m), 2885 (w), 2855 (w), 2785 (w), 1455 (m), 1432 (s), 1260 (m), 1122 (m), 1062 (s), 776 (s) cm^{-1}. Five per cent benzene eluted polysulfides consisting of a 1:1 molar ratio of methyl to ethyl groups followed by a new monomethylhexasulfurdiimide which crystallized as long white needles of mp 100.5–102°, R_f 0.57; infrared spectrum (benzene): 3305 (s), 2965 (w), 2925 (m), 2890 (w), 2855 (w), 2585 (w), 1518 (m), 1455 (w), 1435 (m), 1124 (m), 1062 (s), 810 (s), 768 (s) cm^{-1}. Quantities of all products are summarized in Table III. The dimethyldiimide from this reaction was indistinguishable by infrared, nmr, melting point, mixture melting point, and R_f data from a material obtained in the reaction between trisulfur dichloride and methylamine according to the directions of Brasted and Pond.[10]

Alkylation of 1,3-Hexasulfurdiimide.—Reaction conditions and chromatography were as above. The tlc of the crude reaction mixture showed only three major components. One was sulfur and a second was a dialkyl polysulfide mixture containing a methyl to ethyl group ratio of 2.2:1. The third component was eluted as an oil immediately after sulfur. It proved to be identical in all respects (infrared spectra, nmr spectra, R_f, mass spectra) with an authentic sample of N-methylheptasulfurimide prepared from heptasulfurimide.[3] Materials identifiable as mono- or dimethylated hexasulfurdiimide were sought but were not present. Quantities of all materials produced are given in Table III.