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Sulfurimide Anions. II. Alkylation of Heptasulfurimide[1,2]

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The reaction of strong bases with heptasulfurimide in anhydrous tetrahydrofuran leads to proton abstraction in competition with addition of base to sulfur–sulfur and/or sulfur–nitrogen bonds. Proton abstraction, leading to the heptasulfurimide anion, is favored at low temperatures and by relatively weak bases such as lithium hydroxide. Once formed, the heptasulfurimide anion persists in solution, probably in equilibrium with a small quantity of another species, for days at room temperature and regenerates heptasulfurimide on acidification. The ion effects nucleophilic substitution on primary and secondary but not tertiary alkyl halides giving N-substituted alkyl derivatives of heptasulfurimide.

During the past decade heptasulfurimide,[3] three isomeric hexasulfurdiimides,[4–8] and two isomeric pentasulfurtriimides[9] have been isolated from the reaction of sulfur monochloride with ammonia in dimethylformamide. Of these materials, heptasulfurimide has been most widely studied. Reactions with formaldehyde,[10,11] carboxylic acids,[12] sulfur mono- and dichlorides,[13] benzoyl and acetyl chlorides,[10,13–15] cyclohexylcarbodiimide,[12] boron trihalides,[16,17] sulfur trioxide,[18] and $[(CH_3)_3Si]_2NH$[19] have been described. Acylation,[14] benzoylation,[14] and reactions with sulfur halides[20] have been reported for the hexasulfurdiimides while reactions of the pentasulfurtriimides have not been investigated. Tetrasulfurtetraimide[21] appears to behave similarly to heptasulfurimide; reactions with formaldehyde[21,22] and phenyl isocyanate[22] have been described.

Only two of the above reactions have employed basic conditions. Pyridine or potassium carbonate was used as an acid scavenger in acylation while dilute aqueous potassium hydroxide served as a catalyst in the condensation with formaldehyde. The remaining reactions employ neutral or acidic conditions. There has been a tendency to avoid subjecting the sulfurimides to strongly basic conditions where it has been supposed the eight-membered ring would not survive. Sodium and mercury salts of heptasulfurimide,[11,23,24] and of tetrasulfurtetraimide[23–25] have been reported, however, suggesting that such reactions might be successfully undertaken. While quite reasonable, the evidence presented for the formation of these ions was not compelling. Hydrolysis, for example, of the sodium salt of the presumed heptasulfurimide anion yielded ammonia, sulfur, and polysulfide ions while acidification gave sulfur dioxide, sulfur, and various sulfur acids. An attempted oxidation of the mercury salt of heptasulfurimide to bis(heptasulfurimidyl) by iodine gave only sulfur–nitrogen polymers.[26] In no case has a compound been isolated from any of these salts which contained the intact ring structure. We have consequently sought further evidence for the existence of the heptasulfurimide anion by exploring its possible use in nucleophilic substitution reactions with alkyl halides as a potential route to the previously unavailable N-substituted alkyl derivatives of heptasulfurimide.[27]

Results

In initial experiments evidence for the formation of a stable species identifiable as the heptasulfurimide anion was sought. Excess sodium hydride reacted with heptasulfurimide in anhydrous tetrahydrofuran at 0° liberating 1.00 mol of hydrogen gas for each mole of imide reacted. The resulting solution was intensely blue-green. When this solution was acidified by pouring onto ice-cold dilute hydrochloric acid, the color was immediately discharged and 48% of the starting imide could be recovered. When methyl iodide was added to the blue-green solution at 0°, a red oil containing several components was isolated. Hexane elution on a silica gel column gave a fairly good separation of these materials. Sulfur, the first component eluted from the column, was identified by its R_f value on thin layer chromatography and by its melting point. A second component was obtained as a pale yellow oil. At-

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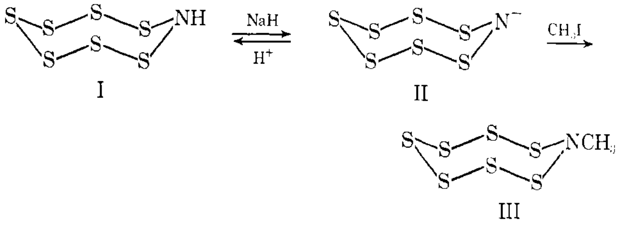
(27) H. G. Heal (private communication) has recently synthesized N-methylheptasulfurimide by treating methylamine with sulfur monochloride.

tempted crystallization from a variety of solvents failed to give a crystalline sample. The proton nmr spectrum showed a sharp singlet at −3.18 ppm consistent with an N–CH$_3$ group. The mass spectrum showed an apparent molecular ion of composition S_7NCH_3, plus fragments corresponding to S_x (x = 1–6), NS, and S_xNCH_3 (x = 1–5). The infrared spectra showed strong absorption at 1062 cm^{-1} attributable to a C–N stretching vibration and no absorption between 705 and 685 cm^{-1} (as might have been expected for an S–CH$_3$ group[28,29]). Absorption near 760 cm^{-1} was attributable to an N–S stretching mode. Coupled with an observed molecular weight (osmometric) of 260 ± 7 and a satisfactory elemental analysis, the composition and structure of the product were established as the N-methyl derivative of heptasulfurimide. The yield was 47%.[30] Solutions of the anion retained their characteristic color for at least 3 days at room temperature. Addition of methyl iodide during this period continued to produce N-methylheptasulfurimide with no observable decrease in yield.



Effect of Base.—Table I shows the percentages of II obtained from the reaction of heptasulfurimide with sodium hydride, sodium amide, lithium hydroxide, and ethyllithium at 0°. In each case the heptasulfurimide ion formed was detected by conversion to III with methyl iodide. Also listed are the quantities of the two major identifiable by-products, sulfur and dialkyl polysulfides. The latter were eluted slowly as the third component from the column with hexane or more rapidly with hexane containing 10% benzene. They had distinctly characteristic unpleasant odors, contained less than 0.2% nitrogen, and were also formed when sulfur replaced heptasulfurimide as the starting material. Their proton nmr spectra showed absorption in the −2.3 to −2.7 ppm region comparable with data of Grant and Van Wazer[31] for the chemical shifts of dimethyl polysulfides. These (absolute) chemical shifts are reported to be strongly solvent dependent but the relative chemical shifts are solvent independent.[31] As seen from Table II both relative and absolute chemical shifts for our materials measured in carbon tetrachloride are in good agreement with those reported by Grand and Van Wazer. It was possible to identify methyl polysulfides with two through seven sulfur atoms in our product mixture. Although no evidence for dimethyl sulfide formation was observed, it cannot be claimed to be absent since it would have been lost when the tetrahydrofuran was removed *in vacuo* prior to preparation of the nmr samples. Integration showed a ratio of approximately 2.5:2:3:3:1 of materials with seven, six, four plus five (combined), three, and two sulfur atoms.

TABLE I

EFFECT OF BASE ON ANION FORMATION

Base	Yield, % S_7NCH_3	Yield, g S^a	Yield, g $R_2S_x{}^a$
Na	36	1.01	0.51
$NaNH_2$	41	0.95	*b*
C_2H_5Li	44	0.48	1.48[c,d]
NaH	47	0.56	0.89
LiOH	82	0.09	0.12

[a] From 5.00 g of heptasulfurimide. [b] This reaction did not give any of the "typical mixture" of alkyl polysulfides found in the other reactions. [c] This material consisted of both ethyl and methyl polysulfides. [d] Use of 1 mol of methyl-, *n*-butyl-, or phenyllithium per mole of imide at 0° in place of ethyllithium produced little variation in the yields of N-methylheptasulfurimide, the amount being 44 ± 3% in each case. The composition of the alkyl polysulfides was, of course, different and in each case contained both methyl groups and the alkyl group originating with the alkyllithium.

TABLE II

ANALYSIS OF $(CH_3)_2S_x$ FORMED IN ALKYLATION REACTIONS OF HEPTASULFURIMIDE

	Grant and Van Wazer		Exptl results	
x	Chem shift, ppm	Diff, ppm	Chem shift, ppm	Diff, ppm
1	−2.16			
		0.22		
2	−2.38		−2.39	
		0.14		0.15
3	−2.52		−2.54	
		0.10		0.10
4	−2.62			
		0.01	−2.64[a]	<0.01
5	−2.63			
		0.03		0.03
6	−2.66		−2.67	
		0.03		0.03
7	−2.69		−2.70	

[a] Splitting into separate peaks was usually not observed for these two materials.

The usual dialkyl polysulfides were not observed in the sodium amide reaction, while with ethyllithium the polysulfides formed differed from those of the other reactions in that ethyl as well as methyl alkyl groups were present. Integration of the proton nmr spectra of the polysulfide fraction showed one ethyl group to be present for each methyl group. Chromatography of these sulfides produced partial separation into a predominantly methyl fraction and a predominantly ethyl fraction (both of varying chain lengths.) There was no indication of the presence of an unsymmetrical methyl ethyl polysulfide fraction.

Effect of Temperature.—The reaction between heptasulfurimide and ethyllithium was carried out at four temperatures between 50 and −28.5°. In each case the temperature of the solution was adjusted to 0° for 15 min after the addition of ethyllithium and before the addition of methyl iodide, the latter being added at

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(28) J. E. Stewart, *J. Chem. Phys.*, **30**, 1259 (1959).

(29) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., London, 1962, p 354.

(30) Methyl iodide and heptasulfurimide in tetrahydrofuran for 100 hr at 35° gave no trace of the N-methyl derivative; unreacted heptasulfurimide was quantitatively recovered.

(31) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).

0°. Results are summarized in Table III. Although the changes are small, the total observed variations in the amounts of products are well outside the experimental uncertainties (except possibly for the amount of recovered heptasulfurimide). The reaction at 0° was run several times over the course of 1 year with different batches of imide, base, solvent, and halide and led to the reproducibility indicated. Reactions at other temperatures were not carried out in duplicate but are presumed reliable to about the same degree. The trend was toward increasing the amounts of all by-products at the expense of alkylimide as the temperature was raised. While the amount of dialkyl polysulfides increased, the ratio of methyl to ethyl groups remained unchanged at 1:1. Reactions on a smaller scale in which only the yield of alkylimide was investigated suggested a more pronounced temperature effect when the addition of both methyl iodide and methyllithium were carried out at the same temperature; at 50° only 20% of N-methylheptasulfurimide was observed. Consequently a reaction was run in which base was added at −28.5° and methyl iodide at 50°. The yield of N-methylheptasulfurimide was low and the quantity of polysulfides high considering that the anion was generated under optimum conditions. The ratio of methyl to ethyl groups in the polysulfide mixture was 1.4:1 for this reaction.

Table III

Effect of Temperature on Anion Formation

Temp,[a] °C	Yield, % S_7NCH_3	Yield, g S[b]	R_2S_x[b]	S_7NH[b]
50	37	0.71	1.65	0.55
21	40	0.52	1.50	0.54
0	44 ± 1	0.48 ± 0.05	1.48 ± 0.07	0.41 ± 0.05
−28.5	49	0.39	1.04	0.36
[−28.5][c]	30	0.79	1.75	0.58

[a] Temperature at which ethyllithium was added. Methyl iodide was added at 0°. [b] From 5.00 g of heptasulfurimide. [c] For this reaction only, the temperature at which methyl iodide was added was 50°.

Synthesis of Alkylimides.—The reaction between lithium hydroxide and heptasulfurimide was employed in the synthesis of various alkyl derivatives of heptasulfurimide. Results are summarized in Table IV. Acceptable yields of products were observed with the four primary alkyl halides examined. In each of these cases the rate of reaction between the anion and the alkyl halide was fairly rapid. Ethyl iodide reacted most slowly of the primary halides requiring 3–4 hr at 0° for complete reaction. The secondary halide, isopropyl iodide, reacted appreciably more slowly requiring about 2 days at room temperature. The yield of alkylimide was significantly lower with this material and an increased quantity of sulfur was observed. With *t*-butyl iodide the characteristic blue color of the anion was discharged after 5 days but no trace of a substituted heptasulfurimide was obtained; sulfur was the only principal product. A significant amount (0.95 g) of heptasulfurimide was also recovered from this reaction. The recovered sulfur (0.087 g-atom) represented a 74% yield based on the 4.05 g of heptasulfurimide destroyed during the reaction.

Table IV

Synthesis of Alkylimides

Alkyl halide	Yield, % S_7NR[a]	Yield, g S[b]	R_2S_x[b]
CH_3I	85	0.09	0.12
CH_2CHCH_2I	79	0.12	0.75
$C_6H_5CH_2Br$	62	0.74	0.97
C_2H_5I	59	0.62	0.34
$(CH_3)_2CHI$	25	1.75	0.76
$(CH_3)_3CI$[c]	*d*	2.8	. . .

[a] Corrected for recovered heptasulfurimide (1–3%). [b] From 5.00 g of heptasulfurimide. [c] A 0.95-g amount of heptasulfurimide was recovered from this reaction. [d] None isolated—less than 0.1% would have been detected.

All derivatives were characterized by elemental analyses and molecular weight. Homogeneity of samples was verified by thin layer chromatography. Infrared and proton nmr spectra were in all cases consistent with the assigned structure. With the exception of the benzyl derivative the alkylated imides were all fairly stable oils which, in our hands, could not be induced to crystallize. N-Benzylheptasulfurimide, also initially obtained as a stable yellow oil, could be crystallized to a pale yellow, nearly colorless solid of mp 44–45° from hexane–benzene mixtures at low temperatures. Although *solutions* of the crystallized benzyl derivative in carbon tetrachloride did not change over a period of 1 month, the *solid* decomposed after a few days at room temperature to give several new species. These, however, also changed slowly, and after about 4 weeks the principal components were sulfur and a yellow substance identified as benzylidinimine tetrasulfide. Ammonia (0.25 mol/mol of benzylimide) was also produced. The other alkylimides were all fairly stable, surviving for 1 month or more at room temperature.

Discussion

The quantitative reaction of sodium hydride with heptasulfurimide to form hydrogen shows the presence of an active hydrogen but gives no indication of the species in solution once the hydrogen is removed. Taken with the observations that heptasulfurimide is regenerated upon addition to acid and that N-methylheptasulfurimide is formed when methyl iodide is added, however, this shows that the S_7N^- ion is present as a stable species in anhydrous tetrahydrofuran. This ion may be responsible for the observed color. The similar yields of recoverable imide (48%) and alkylated imide (47%) strongly suggest (although do not prove) that under the conditions employed, both of these reactions are fairly quantitative measures of the quantity of II present in solution. The balance of the starting material must either be lost in a competing reaction with the base or lost by formation of the imide anion and subsequent decomposition. The latter possibility can be partly eliminated since the yield of alkylimide does not decrease significantly when solutions of anion are allowed to stand up to 3 days at room temperature prior to addition of methyl iodide. Clearly the anion, once formed, is quite stable. The possibility of an equilibrium between II and some other species is, of course, not excluded by this observation.

The existence of a second reaction between heptasulfurimide and base is indicated, however, by the results of experiments in which different bases were used to generate II. Of those examined, the weakest (least nucleophilic, least reducing), lithium hydroxide, leads to the highest yield of anion, as evidenced by isolation of III in excess of 80%. Concurrently, the amount of both sulfur and alkyl polysulfides is quite low. From a synthetic point of view this base is clearly the best of those investigated. The success of lithium hydroxide as a base shows the proton of heptasulfurimide to be considerably more acidic than often supposed. The other bases all result in lower yields of anion. The relative amounts of the two major by-products vary somewhat from one base to another but both tend to decrease as yields of imide increase suggesting that they are formed in the competing reaction. The reaction with ethyllithium is of interest in identifying the nature of this competing reaction. The alkyl polysulfides formed contain both the methyl group originating from the methyl iodide and also an ethyl group which must come from the ethyllithium base. The competing reaction is therefore a nucleophilic substitution of the base on sulfur (*i.e.*, addition of base to either a sulfur–sulfur or a sulfur–nitrogen bond). This reaction must initially lead to an ethyl-substituted open-chain species containing a protonated nitrogen and a negative charge. Subsequent decomposition–disproportionation probably leads to diethyl polysulfides and to polysulfide ions (which on alkylation give dimethyl polysulfides) both of which are isolated. Nitrogen-containing materials were not observed among the principal products. Each addition of ethyllithium results in the incorporation of one ethyl group and one negative charge (and therefore eventually one methyl group) leading to an equimolar ratio of methyl and ethyl groups in the final polysulfides. The proton on the open-chain nitrogen decomposition product is probably still acidic and can consume a second mole of ethyllithium resulting in recovery of unreacted heptasulfurimide as observed in all reactions. This sequence predicts an increase in recovered heptasulfurimide with increasing dialkyl polysulfides—a result which appears to be borne out—but by an amount only barely outside the experimental error (Table III). In any case the evidence requires a competing substitution reaction between base and imide. This reaction becomes progressively more important at higher temperatures as evidenced both by the increased yields of sulfur and polysulfides and the decreased yields of alkylimide when base is added at higher temperatures.

An additional equilibrium between the S_7N^- ion and some other species, presumably an open chain of some kind, is also required. Three independent pieces of data are relevant. First, the yield of N-alkylheptasulfurimide is dependent on the temperature at which the methyl iodide is added as well as the temperature at which the alkyllithium is added. This requires one or more of the following: an equilibrium between S_7N^- and another species, two alternate competing reactions between anion and halide, or a decomposition of the anion at higher temperatures. The latter is eliminated since less than 25% of the anion initially formed is lost at room temperature (25°) in 70 hr.[32] The ion would not be 50% decomposed in 0.25 hr at 50°. However, the yield drops to nearly half simply by adding methyl iodide at this temperature. Second, all four of the primary halides react very much faster than the rate at which the anion is destroyed in their absence, yet the yield decreases significantly with increasing bulkiness of the alkyl group.[33] Even the isopropyl reaction is complete before a significant amount of anion would be lost in its absence, yet the yield is only one-third that of the methyl derivative. Again two paths for reaction of the anion are required. While a competing reaction is not rigorously excluded, an equilibrium between S_7N^- and an open-chain anion appears the more attractive choice. The open-chain species would be smaller and therefore less hindered in attacking a substituted methyl halide than the fairly large heptasulfurimide anion. The result is the gradual loss of heptasulfurimide by way of the open-chain species. The dialkyl polysulfides formed in these reactions (Table IV) give little information since the relative amounts reflect both the changing molecular weights of the alkyl groups and the changing amount of open-chain species reacted. The yield of sulfur, however, increases in direct proportion to the decreasing yields of alkylimides as required by this interpretation. Finally, the dialkyl polysulfides formed by addition of methyl iodide at 50° contain a substantial excess of methyl over ethyl groups. Since the original source of all ions (and therefore all methyl groups) is the ethyllithium, this result requires ethane [*i.e.*, S_7N^-] as a precursor to the *excess* methyl groups. Again equilibrium of S_7N^- with an open-chain sulfur anion is suggested. The position of this equilibrium at 0° must lie fairly far to the left since addition of methyl iodide or acidification at this temperature gives comparable yields of products. Indeed, if equilibrium can be achieved rapidly, even in the order of minutes at 0°, it is unnecessary to propose that more than a very small fraction of material is in the open-chain form. The following scheme summarizes what we feel to be the simplest satisfactory explanation of the available results.[34] Given this scheme the synthetic utility of the reaction appears limited to the preparation of deriva-

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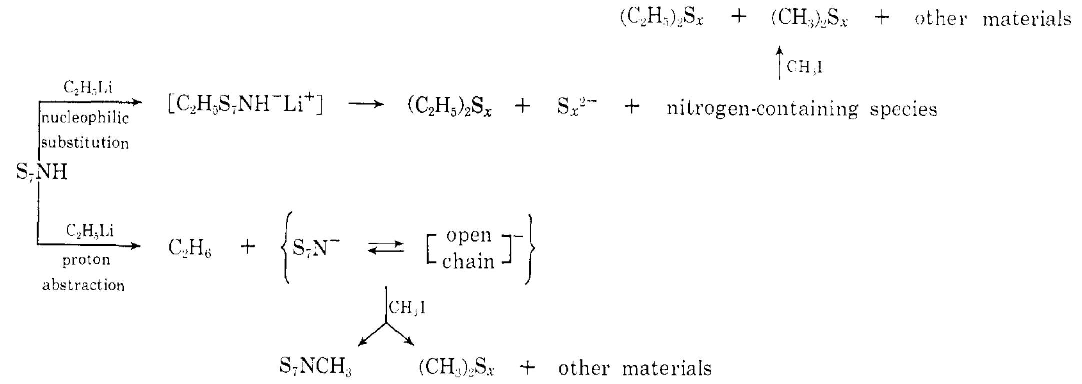
[32] No decomposition outside the experimental error was observed during this period.

[33] Use of ethyllithium as base rather than lithium hydroxide has the effect of lowering the yields of all products but does not change the relative amounts of each.

[34] G. P. Richter [Ph.D. Thesis, University of Minnesota, 1968] has recently suggested that S_7NH reacts with Lewis bases to give products derived from both ionic and free-radical processes. While free-radical reactions could conceivably provide an alternative explanation for certain side products, they are not required by any of our observations and do not provide a route to the alkylimides isolated.



tives of heptasulfurimide derived from fairly reactive (*i.e.*, sterically unhindered) halides.

Experimental Section

Materials.—Heptasulfurimide was prepared as previously described.[3] The product was recrystallized three to eight times from benzene and gave plates of mp 112.5–113° (lit.[35] mp 113°). Tetrahydrofuran was distilled from lithium aluminum hydride immediately prior to use. Lithium hydroxide was prepared by drying the monohydrate *in vacuo* at 100° for 24 hr over phosphorus pentoxide. Commercially available 40% sodium and 60% sodium hydride dispersions in mineral oil were used as obtained. Ethyllithium was 1.3 *M* in benzene and methyllithium was 1.88 *M* in ether. Silica gel, 100–200 mesh, was employed for chromatography. An average column was 30 mm in diameter and 45 cm tall.

General Data.—Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Molecular weights were obtained on a Mechrolab vapor pressure osmometer, Model 301-A, using a 37° probe and reagent grade benzene. Heptasulfurimide was used to establish the calibration curve. Proton nmr spectra were recorded on a Varian Model A-60 in carbon tetrachloride with tetramethylsilane as internal reference. Chemical shifts are reported as parts per million upfield from this reference. Infrared spectra were obtained on a Beckman IR-5 and were calibrated with polystyrene. Intensities are labeled s (strong), m (medium), w (weak), and sh (shoulder). Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Routine laboratory nitrogen analyses were run on a Coleman nitrogen analyzer, Model 29. R_f values are for hexane as eluent on 0.1-mm air-dried silica gel plates unless otherwise noted.

Reaction of Heptasulfurimide with Sodium Hydride.—Heptasulfurimide (0.293 g, 1.22 mmol) was placed in a flask with a side arm containing sodium hydride (0.25 g, 6.2 mmol) and a break-seal into which 30 ml of anhydrous tetrahydrofuran was distilled. The solution was cooled to liquid nitrogen temperature and the tube was evacuated, and sealed. Sodium hydride in the side arm was added by tipping the flask, and the solution was warmed to 0° for 30 min. The flask was returned to the vacuum line, the break-seal was opened, and the evolved gas was transferred to a calibrated volume where its pressure and temperature were noted. The amount of hydrogen gas evolved was calculated to be 1.21 mmol. The resulting solution was intensely blue-green.

Regeneration of Heptasulfurimide.—Heptasulfurimide (5.00 g) was allowed to react with excess sodium hydride in 150 ml of anhydrous tetrahydrofuran. The solution was poured slowly onto excess ice-cold 10% hydrochloric acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated *in vacuo* to give 3.33 g of a beige solid of mp 94–97°. An additional 0.58 g of sulfur was insoluble in both the ether and the aqueous layers. Chromatography of the beige solid separated sulfur (0.54 g) and heptasulfurimide (2.41 g, 48%).

Stability of Anion.—Heptasulfurimide (10 g) was dissolved in approximately 500 ml of anhydrous tetrahydrofuran and cooled to 0° whereupon 32 ml of 1.3 *M* ethyllithium was added by syringe. After 10 min at 0° the flask was allowed to warm to room temperature. Aliquots (45 ml) were periodically withdrawn by syringe and transferred to a separate flask. Methyl iodide (1.5 ml) was added to each aliquot and the solutions were allowed to stand overnight. Work-up and chromatography as described below gave the following quantities of N-methylheptasulfurimide: after 1.0 hr, 0.29 ± 0.03 g; 6 hr, 0.22 g; 47 hr, 0.27 g; 71 hr, 0.25 g.

N-Alkylheptasulfurimides.—Heptasulfurimide (5.00 g, 20.8 mmol) was treated with approximately 0.6 g of lithium hydroxide in 150 ml of anhydrous tetrahydrofuran at 0°. A green solution developed slowly which gradually changed to intense blue. After stirring for 20 min, 1 equiv of alkyl halide was added. The solution was allowed to warm to room temperature and was observed to become red-orange or yellow. Utilizing color change to indicate destruction of the anion, the most rapid reaction with methyl iodide was complete within 0.5 hr at 0° while isopropyl iodide (the slowest) took 2 days at room temperature. After the reaction was complete (no further color change), the solvent was removed *in vacuo*, and the residual oil was distributed between ether and water. The ether layer was dried over anhydrous sodium sulfate and the ether was removed *in vacuo*. Chromatography of the residue on silica gel with hexane eluted first sulfur, then the product, N-alkylheptasulfurimide, and finally alkyl polysulfides. Eluting with more polar solvents (benzene, ether, methanol) gave some unreacted heptasulfurimide and decomposed products in great profusion. Yields of the above three products are summarized in Table IV. Analytical data for the N-alkylheptasulfurimides prepared are given in Table V. Physical properties are summarized below.

N-Methylheptasulfurimide, a yellow oil, had R_f 0.42 (*vs.* 0.52 for sulfur); nmr: τ -3.18 (sharp singlet); infrared spectrum (neat oil): 760 (s), 1063 (s), 1120 (m), 1425 (s), 1450 (sh), 2890 (sh), 2910 (m), 2950 (sh) cm^{-1}.

N-Ethylheptasulfurimide, a yellow oil, had R_f 0.42; nmr: τ -1.33 (triplet), -3.43 (quartet) (J = 7 Hz); infrared spectrum (neat oil): 752 (s), 827 (m), 918 (w), 1055 (s), 1090 (m), 1340 (m), 1375 (m), 1440 (m), 1450 (sh), 2850 (sh), 2900 (sh), 2955 (w) cm^{-1}.

N-Benzylheptasulfurimide, a yellow oil which could be induced to crystallize from hexane–benzene at low temperature as a pale yellow solid of mp 44–45°, had R_f 0.19; nmr: τ -4.32 (CH_2 protons), -7.24 (aromatic protons as a single peak); infrared spectrum (Nujol mull): 697 (s), 745 (s), 783 (m), 847 (m), 910 (w), 1018 (m), 1343 (w) cm^{-1}—others hidden by Nujol.

N-Allylheptasulfurimide, a yellow oil, had R_f 0.38; nmr consistent with substituted allyl group:[36,37] τ -3.91 (methylene on

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(35) M. Becke-Goehring, H. Herb, and W. Koch, *Z. Anorg. Allgem. Chem.*, **264**, 137 (1951).

(36) The spectrum of allyl sulfide[37] is nearly identical in gross appearance with that of N-allylheptasulfurimide.

(37) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Varian Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, spectrum no. 136.

TABLE V

ANALYTICAL DATA FOR N-ALKYLHEPTASULFURIMIDES

Compound	% C		% H		% N		% S		Mol wt	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	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.

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[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]

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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 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

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[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).