white solid which remained was extracted with ligroin (2 × 5 mL), and the combined extracts were concentrated to 3 mL and then cooled in a refrigerator overnight. After this period, the white needles of **24** which separated were isolated by filtration (5 mg, 0.025 mmol, 28%), mp 70–71 °C, and found to have IR and ^{1}H NMR spectra which were superimposable with those of an authentic sample of **24**.[1]

Acknowledgment. This investigation was supported by U.S. Public Health Service Research Grant Number CA 17878 from the National Cancer Institute and such assistance is gratefully acknowledged.

Registry No.—**2**, 65523-04-8; **3**, 67464-81-7; **5**, 25472-44-0; **6**, 67464-82-8; **7**, 67464-83-9; **8**, 67139-78-0; **9**, 67411-04-5; **10**, 67464-84-0; **11**, 67464-85-1; **12**, 65523-03-7; **13**, 67411-05-6; **14**, 67464-86-2; **15**, 67464-87-3; **16**, 67464-88-4; **19**, 67464-89-5; **20**, 67464-90-8; **21**, 67464-91-9; **22**, 53912-79-1; **23**, 67464-92-0; **24**, 67411-02-3; diazomethane, 334-88-3; water, 7732-18-5; methanol, 67-56-1.

References and Notes

(1) S. W. Schneller, R. S. Hosmane, L. B. MacCartney, and D. A. Hessinger, *J. Med. Chem.*, **21**, 990 (1978).
(2) This approach is analogous to that used in the synthesis of 6-amino-1*H*-imidazo[4,5-*c*]pyridin-4(5*H*)-one (3-deazaguanine) (P. D. Cook, R. J. Rousseau, A. M. Mian, P. Dea, R. B. Meyer, Jr., and R. K. Robins, *J. Am. Chem. Soc.*, **98**, 1492 (1976)) and 6-amino-1*H*-pyrazolo[4,3-*c*]pyridin-4(5*H*)-one (K. W. Ehler, R. K. Robins, and R. B. Meyer, Jr., *J. Med. Chem.*, **20**, 317 (1977)).
(3) G. A. Swan and A. Waggott, *J. Chem. Soc. C*, 285 (1970).
(4) Although not conclusively proven, a similar reaction was believed (R. K. Robins, J. K. Horner, C. V. Greco, C. W. Noell, and C. G. Beames, Jr., *J. Org. Chem.*, **28**, 3041 (1963)) to have occurred when 4,6-dihydroxy-1*H*-imidazo[4,5-*c*]pyridine (3-deazaxanthine) was subjected to basic treatment.
(5) Although no reports of oxirane formation in the reaction of diazomethane with anhydrides could be found in the literature, oxiranes can result from the reaction of diazomethane with the carbonyl functionality of aldehydes and ketones (see C. D. Gutsche, *Org. React.*, **8**, 364 (1954)).
(6) If pH 6 is considerably exceeded, the product desired (i.e., **3**) is not obtained.
(7) Several attempts to note the exact melting point of **14** were unsuccessful because of a black fog accumulation inside the capillary tube near the sample as the temperature approached 200 °C.

Mass Spectral Studies of Unsymmetrical Dialkyl Disulfides. Intramolecular 1,2-, 1,3-, and 1,4-Hydrogen Migration Processes

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The mass spectra of several unsymmetrical dialkyl disulfides have been evaluated in terms of 1,2- and 1,3-hydrogen transfer mechanisms, using deuterium labeling and high-resolution analysis. Unprecedented 1,4-hydrogen shift in disulfides and novel electron impact induced skeletal rearrangements of alkyl and alkenyl hydrodisulfides are reported.

The literature abounds in reports on the chemistry and applications of symmetrical organic disulfides.[1] This family of compounds represents the most generally active class of chemicals for protection against lethal ionizing radiation,[2] and extensive studies about the physiological responses to these compounds have also been made. By contrast, unsymmetrical disulfides have been much less exploited as synthetic intermediates and industrial chemicals,[3,4] in spite of their ubiquitous presence in nature as organoleptic substances and constituents of essential oils, natural pesticides,[5,6a] and insect pheromones.[6b]

Since GC–mass spectrometry has become an expeditious technique for the study of mixtures of natural origin, the elucidation of fragmentation processes of individual components is of crucial importance. Previous investigations[7–13] have revealed two main decomposition pathways of organic disulfides upon electron impact besides simple bond disconnection: skeletal rearrangement and intramolecular hydrogen transfer. The former is evidenced by the appearance of $M^+ - S$, $M^+ - SH$, and $M^+ - 2S$ ions,[9,11] which become particularly noticeable in the mass spectra of dibenzyl, diphenyl,[9] dimethyl, and diallyl disulfides[11] to give alkyl hydrodisulfides[14] which decompose further to yield H_2S_2. That the mechanism involved is a 1,2- and 1,3-hydrogen transfer from vicinal and homovicinal carbons, respectively, has been supported by data put forth recently by Block et al.[13] for deuterium-labeled diethyl disulfide. These investigations, however, have limited their scope to symmetrical disulfides. We have now studied the fragmentation of a series of unsymmetrical disulfides which can provide two sets of hydrogen transfer derived fragment ions. This strategy allows for a more detailed analysis of competing processes taking place in each side of the unsymmetrical system to be put forward.

Results and Discussion

In spite of the considerable number of investigations bearing on the subject,[6a,c,15] a generalized and satisfactory synthetic procedure to obtain some of the hindered disulfides required in the present study is not yet available,[15c] the reason being probably that these methods utilize a sterically sensitive bimolecular attack of a nucleophilic form of sulfur onto a sulfur atom bearing a suitable leaving group.[6c] Forcing conditions lead usually to disproportionation[16,20] and polysulfide formation.[17a,b] The construction of the desired model compounds, however, was conveniently achieved in satisfactory yields and purity by modification[18] of the Bunte salt approach.[17b] In essence this change consisted of the addition of an organic cosolvent to the aqueous alkyl halide–sodium thiosulfate reaction mixture in order to prevent the formation of a two phase system; thus, smoother reaction conditions were required. The results are portrayed in Table I.

Compounds **1–15** were so constructed as to display an increasing α-substitution pattern on the R group in order to correlate its contribution to hydrogen transfer processes with changes on R′, whereas a set of four groups with various degrees of hydrogen availability were chosen for R′.

Examination of the mass spectra of compounds **1–15** (see supplementary material) suggests a consistent fragmentation pattern in which hydrogen transfer and bond breakage are predominant.[19] In Table II are collected the fragments cor-

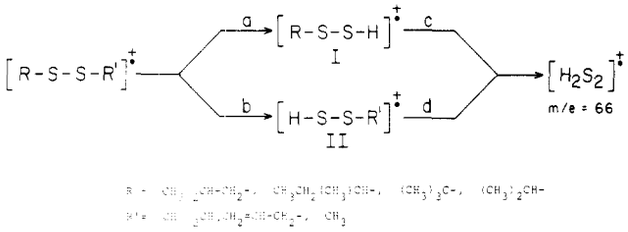
0022-3263/78/1943-4491$01.00/0

Table I. Unsymmetrical Dialkyl Disulfides Obtained from the Reaction $R'SSO_3^-,Na^+ + RS^-,Na^+ \rightarrow RSSR' + Na_2SO_3$. Distillation Conditions and Composition[a,b]

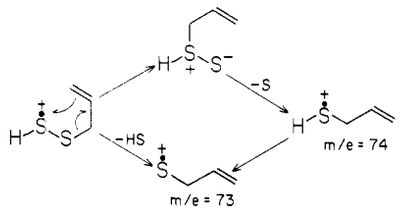
ref	compd no.	R	R′	bp, °C/ torr	yield, %	RSSR′ %	RSSR′ registry no.	RSSR, %	R′SSR′, %
	1	$(CH_3)_2CHCH_2$–	$(CH_3)_2CH$–	33–4/0.15	60	92	67421-82-3	6	2
	2	$(CH_3)_2CHCH_2$–	CH_3CH_2–	51/3	62	98	40126-66-1		1
26	3	$(CH_3)_2CHCH_2$–	CH_3–	52/8.5	65	97	67421-83-4		1.5
	4	$(CH_3)_2CHCH_2$–	CH_2=$CHCH_2$–	57.5/1.5	81	96	67421-84-5	2	1.5
27, 29	5	$(CH_3)_2CH$–	CH_3CH_2–	49/9	60	98	53966-36-2	<1	
28	6	$(CH_3)_2CH$–	CH_3–	37–38/11	72	98.5	40136-65-0	<1	
	7	$(CH_3)_2CH$–	CH_2=$CHCH_2$–	55.5/5	69	98.5	67421-85-6		<1
	8	$C_2H_5CH(CH_3)$–	$(CH_3)_2CH$–	40–41/0.2	73	96.5	67421-86-7	3	
29	9	$C_2H_5CH(CH_3)$–	CH_3CH_2–	47/1.5	64	98.5	54166-53-9	<1	<1
30, 31	10	$C_2H_5CH(CH_3)$–	CH_3–	46.5/6	71	99	67421-87-8		
	11	$C_2H_5CH(CH_3)$–	CH_2=$CHCH_2$–	51/1	71	98.5	67421-88-9	<1	
30, 32, 33	12	$(CH_3)_3C$–	$(CH_3)_2CH$–	30–32/2	53	96.5	43022-60-2	1	<1
11, 12, 27, 29, 30, 32	13	$(CH_3)_3C$–	CH_3CH_2–	43–44/5	52	97	4151-69-3	<1	2
28, 32	14	$(CH_3)_3C$–	CH_3–	46/12	49	98.5	35166-82-6	<1	<1
	15	$(CH_3)_3C$–	CH_2=$CHCH_2$–	53/2	54	99	67421-89-0		

[a] Determined by GLC analysis on a 12 ft 5% SE-30 on Chromosorb G column. [b] Satisfactory analytical data (±0.52% for C, H, S) were obtained for all compounds.

Scheme I



Scheme II

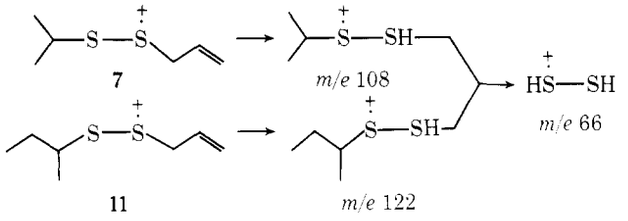


responding to hydrogen migration processes portrayed on Scheme I. These data allow for a correlation between the number of hydrogens available, their relative position within the molecular framework, and the occurrence of intramolecular hydrogen transfer to be advanced. On the one hand, H transfer takes place preferentially from the R group (route b of Scheme I) since in the great majority of cases the $[R'SSH]^+\cdot$ ion (II) is much more abundant than $[RSSH]^+\cdot$.[20] Metastable analysis, however, supports the occurrence of both decomposition pathways a and b. In addition, the position occupied by the migrating hydrogen is, not unexpectedly, of crucial importance. Primary evidence for this is found in the significant decrease of the relative intensities of type-I fragments in the series **1–3** and **8–10**. The possible H transfer mechanisms responsible for the appearance of fragments I and II are examined in the following discussion.

That 1,2-H shift is an unfavorable process is supported by the absence of type-I ions in the mass spectra of the methyl alkyl disulfides studied. Moreover, the transformation of hydrodisulfide intermediates into *m/e* 66 $[HSSH]^+\cdot$ via a

$$[CH_3SSR]^+\cdot \rightarrow [HSSR]^+\cdot$$
$$[CH_3SSH]^+\cdot \rightarrow [HSSH]^+\cdot$$
$$m/e\ 66$$

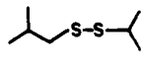
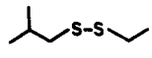
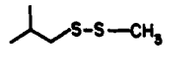
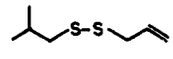
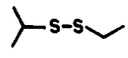
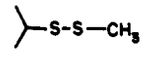
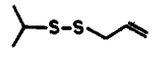
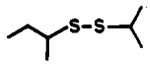
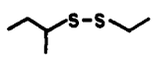
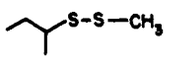
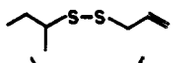
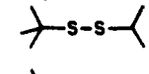
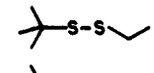
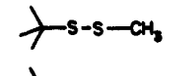
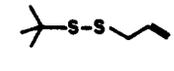
second H transfer (routes c and d of Scheme I) was not detected for methyl hydrodisulfide.[21] Nevertheless, 1,2-H transfer does take place to a small extent in favorable systems as witnessed by peaks at *m/e* 108 of compound **7** and *m/e* 122 of **11**.[13,22]



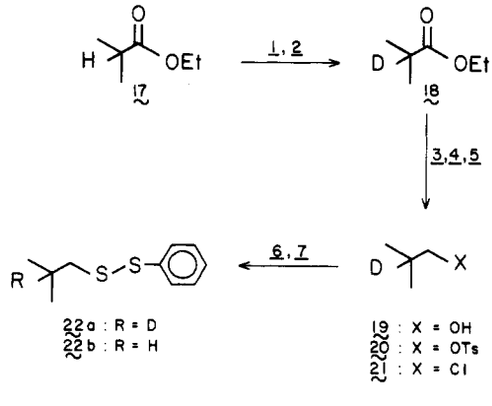
The migration of vinyl and aryl hydrogens does not occur as indicated by the lack of type-I fragments in the mass spectra of methyl ethenyl, ethyl ethenyl,[23] and methyl phenyl disulfides.[3] Allyl hydrodisulfide intermediates undergo preferentially skeletal rearrangement to furnish ions *m/e* 73 and 74. High-resolution analyses imply the operation of the mechanism portrayed on Scheme II. The thermal counterpart of this process has been reported for the unusually facile rearrangement of allyl disulfides and the high temperature sulfurization of allyl sulfides with S_8.[24]

The appearance of fragments *m/e* 94, 80, and 106 in the spectra of compounds **13**, **14**, and **15** with significant $R'SSH/M^+$ intensity ratios strongly suggests the contribution of a 1,3-H transfer process in congruence with Block's observations.[13] If a concerted 1,3-hydrogen migration having particular conformational requirements is assumed, then the 2-methylpropyl group of compounds **1–4** should be ill suited for this kind of transfer since there is only one β hydrogen flanked by two bulky substituents. Nevertheless, the type-II ion is not only present but also abundantly enough to suggest the operation of intramolecular hydrogen transfer phenomena other than 1,2- and 1,3-shifts. This point of view is substantiated by comparison of compound **9** with **5** and **11** with **7**; in spite of their possessing a larger molecular framework and thus being more prone to fragmentation, 2-butyl ethyl disulfide (**9**) and 2-butyl propenyl disulfide (**11**) display higher $R'SSH/M^+$ intensity ratios than the 2-propyl conterparts **5** and **7**. This fact may be attributed in principle to the additional six γ hydrogens present in the R group of compounds **9** and **11**.[25] In order to confirm these mechanistic speculations a model compound so constituted as to contain a unique β-deuterium atom plus several γ hydrogens of the same type was constructed. Thus, 1-phenyl-4-deuterio-4-methyl-1,2-dithiapentane (**22**) was synthesized following Scheme III as a 1:1 mixture of 4-D (**22a**) and 4-H (**22b**) compounds.[28]

Table II. Mass Spectral Data of Unsymmetrical Dialkyl Disulfides Fragment Ions Derived from Intramolecular Hydrogen Transfer Processes

	COMPOUND	$[RSSH]^+$ (%)	$[R'SSH]^+$ (%)	R'SSH/M^+ INTENSITY RATIO	BASE PEAK	M^+ (%)	$[H_2S_2]$ (%)
1		122 (14)	108 (9)	0.31	57 $[(CH_3)_2CH\text{-}CH_2]^+$	164 (29)	(3)
2		122 (1)	94 (53)	1.04	57 idem	150 (51)	(17)
3		- -	80 (58)	1.04	57 idem	136 (56)	- -
4		- -	106 (27)	0.77	57 idem	162 (35)	(1)
5		108 (1)	94 (100)	1.49	94 $[HSS\text{-}C_2H_3]^+$	136 (67)	(50)
6		- -	80 (100)	1.79	80 $[HSS\text{-}CH_3]^+$	122 (56)	- -
7		108 (6)	106 (47)	1.24	41 $[CH_2{=}CH\text{-}CH_2]^+$	148 (38)	(2)
8		122 (9)	108 (57)	1.46	43 $[(CH_3)_2CH]^+$	164 (39)	(11)
9		122 (1)	94 (100)	2.50	94 $[HSS\text{-}C_2H_5]^+$	150 (40)	(24)
10		--	80 (100)	1.64	80 $[HSS\text{-}CH_3]^+$	136 (61)	- -
11		122 (2)	106 (73)	1.83	41 $[CH_2{=}CH\text{-}CH_2]^+$	162 (40)	(2)
12		- -	108 (15)	0.83	57 $[(CH_3)_3C]^+$	164 (18)	(3)
13		122 (2)	94 (15)	0.79	57 idem	150 (19)	(8)
14		- -	80 (12)	0.60	57 idem	136 (20)	- -
15		- -	106 (8)	0.67	57 idem	162 (12)	- -

Scheme III



1: $LiN(i\text{-}C_3H_7)(C_6H_{11})$, THF, HMPA, -20°[35]; 2: D_2O; 3: $LiAlH_4$, THF, 68°; 4: TsCl, C_5H_5N, 0°; 5: LiCl, DMSO, HMPA, 52°[36]; 6: $Na_2S_2O_3$, CH_3OH, H_2O, Δ[17,18]; 7: C_6H_5SH, NaOH, H_2O, 0-5°

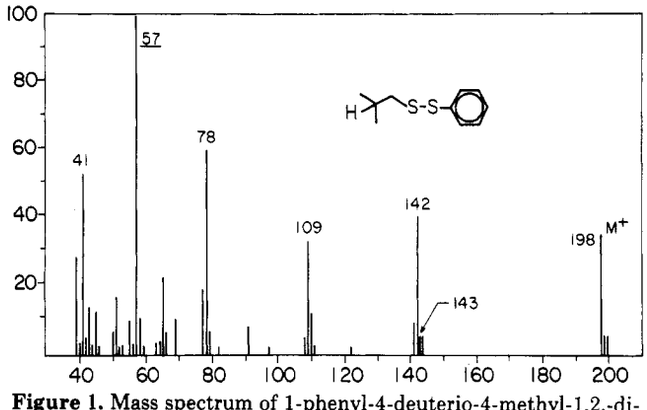


Figure 1. Mass spectrum of 1-phenyl-4-deuterio-4-methyl-1,2,-dithiapentane (**22a**).

That 1,2-H shift should not occur to a detectable extent in **22** was shown by the total absence of fragment *m/e* 142 $[C_6H_5SSH]^+\cdot$ in the mass spectrum of methyl phenyl disulfide (**16**). High-resolution mass spectra (Figures 1 and 2) and metastable analysis of **22a** and **22b**[34] confirmed the fragmentation pattern depicted in Scheme IV. The small relative intensity recorded for *m/e* 143 and the high relative abundance of peak *m/e* 142 in the mass spectrum of **22a** are consistent with the fact that the transition state required for a concerted deuterium migration should be retarded by eclipsing of the two secondary methyls with the methylene hydrogens as indicated in structure A of Scheme V, therefore providing a favorable situation for the hitherto unknown 1,4-hydrogen transfer to take place via conformation B.[37] In addition the loss of S and S_2 from hydrodisulfide intermediates *m/e* 143 and 142 observed in the fragmentation pattern of **22a** has never been reported before. The presence of fragment ions *m/e* 111 and 79 confirms solidly these skeletal rearrangement processes.

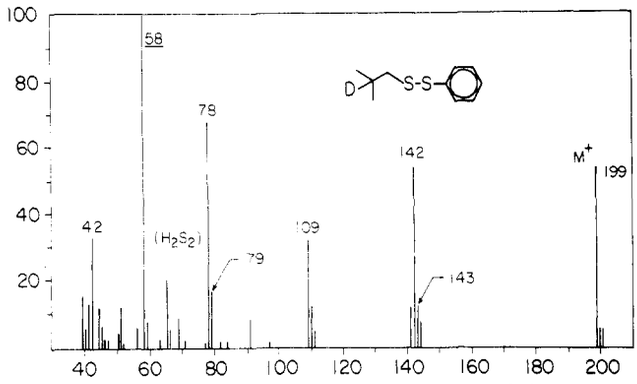


Figure 2. Mass spectrum of 1-phenyl-4-methyl-1,2-dithiapentane (**22b**).

Experimental Section

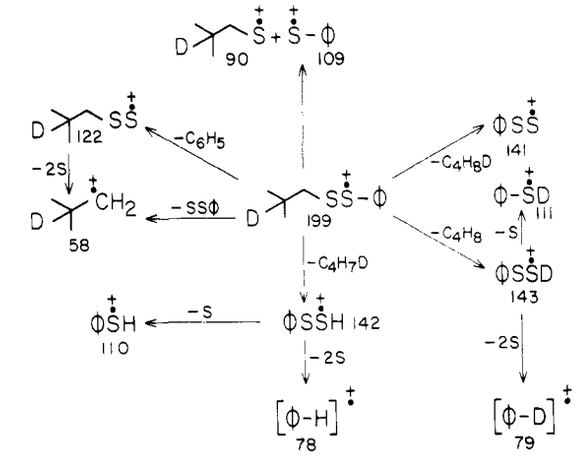
Mass spectra were determined on a DuPont 21-492 instrument at an ionizing voltage of 70 eV using an all glass inlet at 105–135 °C and on an AEI DS50S spectrometer at Manchester, England, operating under the same conditions. Infrared spectra were run on a Perkin-Elmer 337 spectrophotometer. NMR spectra were measured on a Bruker WP-60 instrument in deuteriochloroform using tetramethylsilane as an internal standard. VPC analyses were performed in a Varian Aerograph series 1400 gas chromatograph using a 5% 12 ft SE-30 on Chromosorb G column. Microanalyses were obtained from Franz Pascher Mykroanalytisches Laboratorium at Bonn, Germany. Methyl ethenyl, ethyl ethenyl, and methyl phenyl disulfides were prepared by known methods.[3,23]

Synthesis of Unsymmetrical Disulfides 1–15. A description of the generalized procedure follows. Water was added to a solution of 0.2 mol of freshly distilled alkyl halide in 240 mL of methanol until a slight turbidity (saturation in alkyl halide) developed. The mixture was brought to reflux temperature, and a solution of 0.25 mol of sodium thiosulfate pentahydrate in 50 mL of water was added dropwise during a 20-min period. Heating was continued for an additional 2-h period. The alcohol was then evaporated in vacuo and the aqueous solution brought to twice its volume with water. The mixture was washed with hexane, the organic extracts were discarded, and the aqueous layer was cooled to 0 °C. Sodium thiolate (0.2 mol) was prepared by adding the corresponding thiol to an aqueous concentrated sodium hydroxide solution. The mercaptide separated as a paste which was dissolved in a minimum amount of water and cooled to 0 °C. It was then added rapidly with efficient stirring to the alkyl thiosulfate solution at 0 °C. Stirring was stopped after 8 min, and the two layers that formed were separated. The organic layer was washed once with water, dried shortly over sodium sulfate, filtered, and distilled under vacuum to yield pure dialkyl disulfide. Results are collected in Table I.

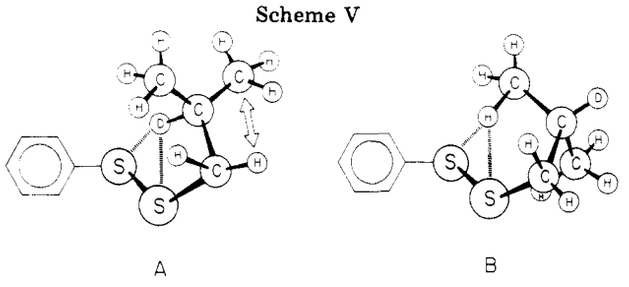
1-Phenyl-4-deuterio-4-methyl-1,2-dithiapentane (22a). A 1:1 mixture of ethyl 2-methylpropionate and ethyl 2-deuterio-2-methylpropionate[34,35] (5.75 g, 0.05 mol) dissolved in 10 mL of dry THF was added dropwise to a stirred suspension of lithium aluminum hydride (3.8 g, 0.1 mol) in 50 mL of dry THF at room temperature. The mixture was then refluxed for 6 h. After the usual workup and distillation of the residue, 3.60 g (97.7%) of a 1:1 mixture of 2-methyl-1-propanol and 2-deuterio-2-methyl-1-propanol, bp 97 °C (680 torr), was obtained: IR (neat) 3350, 2960, 1470, and 1040 cm^{-1}; mass spectrum, *m/e* 44 ($(CH_3)_2CD^+$·, 39). The mixture of alcohols was treated with *p*-toluenesulfonyl chloride (18.3 g, 0.096 mol) in 65 mL of anhydrous pyridine at 0 °C for 48 h. *p*-Toluenesulfonate ester **20** (9.1 g, 82.8%) was recovered as a yellowish oil: IR (neat) 2960, 1600, 1350, 1195, 1180, 1105, 980, 815, and 662 cm^{-1}. A mixture of compound **20** (6.0 g, 0.026 mol), lithium chloride (4.66 g, 0.11 mol), dimethyl sulfoxide (25 mL), and hexamethylphosphoramide (8 mL) was stirred at 52 °C for 72 h in a 100-mL flask connected to a trap cooled at −78 °C under 10-mm vacuum.[36] The volatile fraction collected in the trap was washed with 25 mL of 5% aqueous sodium carbonate and water and dried over granular anhydrous calcium chloride. Fractional distillation through a 12 cm Vigreux column furnished 1.98 g (81%) of a 1:1 mixture of 2-methylchloropropane and 2-deuterio-2-methyl-1-chloropropane (**21**): bp 90 °C (683 torr); IR (neat) 2955, 1455, 1375, 1360, 1240, and 650 cm^{-1}. Alkyl halide **21** was converted as described above into a 1:1 mixture of 1-phenyl-4-deuterio-4-methyl-1,2-dithiapentane (**22a**) [bp 95–96 °C (0.1 torr); IR (neat) 3070, 2960, 1590, 1490, 1480, 1450, 1065, 1020, 735, and 685 cm^{-1}; NMR δ 0.97 (t, 6, $2CH_3$, J = 0.7 Hz), 2.63 (t, 2, CH_2, J = 0.7 Hz); 7.28 (m, 5, C_6H_5)] and 1-phenyl-4-methyl-1,2-dithiapentane (**22b**) [NMR δ 0.97 d, 6, $2CH_3$, J = 7.5 Hz), 1.93 (m, 1, methyne), 2.63 (d, 2, CH_2, J = 7.5 Hz), 7.28 (m, 5, C_6H_5)].

Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.59; H, 7.12; S, 32.29. Found: C, 61.01; H, 7.20; S, 31.78.

Scheme IV



Scheme V



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Registry No.—20, 27135-66-0; **21,** 60640-37-1; **22a,** 67421-90-3; **22b,** 67421-91-4; RS^-,Na^+ (R = $CH_2CH(CH_3)_2$), 15449-18-0; RS^-,Na^+ (R = $(CH_3)_2CH$), 20607-43-6; RS^-,Na^+ (R = $C_2H_3CH(CH_3)$), 66783-99-1; RS^-,Na^+ (R = $(CH_3)_3C$), 29364-29-2; $R'SSO_3^-$, Na^+ (R = $(CH_3)_2CH$), 26726-19-2; $R'SSO_3^-$, Na^+ (R = CH_3CH_2), 6476,71-7; $R'SSO_3^-$, Na^+ (R′ = CH_3), 42254-80-8; $R'SSO_3^-$, Na^+ (R′ = $CH_2{=}CHCH_2$), 6363-01-5; ethyl 2-methylpropionate, 97-62-1; ethyl 2-deuterio-2-methylpropionate, 67421-92-5; 2-methyl-1-propanol, 78-83-1; 2-deuterio-2-methyl-1-propanol, 20440-13-5.

Supplementary Material Available: Complete infrared, NMR, and mass spectral data of compounds **1–15** (17 pages). Ordering information is given on any current masthead page.

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(19) Skeletal rearrangement of the molecular ion with loss of S, SH, and 2S does not become apparent even in allyl alkyl disulfides **4**, **7**, **11**, and **15** in contrast with previous reports.[11]
(20) Instability of the $[RSSH]^{+\cdot}$ fragment (I) upon electron impact cannot account for the low intensities observed as shown by comparison of 2-propyl ethyl disulfide (**5**) and 2-butyl 2-propyl disulfide (**8**) in which peaks *m/e* 108 $[(CH_3)_2CH\text{–}SSH]^{+\cdot}$ show 1 and 57% relative intensities, respectively.
(21) This inability to decompose by a pathway other than bond disconnection might explain the high relative abundance of *m/e* 80 $[CH_3SSH]^{+\cdot}$ in the spectra of methyl alkyl disulfides studied.
(22) These disulfides contain the allyl moiety in which the availability of α protons may be spurred by their being sandwiched between the sulfur atom and the vinyl group.
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(37) The addition of radical inhibitors did not produce any noticeable change in the spectrum of **22a**. Therefore, radical propagation cannot account for the presence of the *m/e* 142 species.

Triplet–Singlet Energy-Transfer Parameters from Tetramethyl-1,2-dioxetane Chemi-Energized 9,10-Dibromoanthracene Fluorescence in Polymer Matrices[1]

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The binary chemiluminescent system consisting of tetramethyl-1,2-dioxetane (TMD) and 9,10-dibromoanthracene (DBA) was investigated in polystyrene (PST) and poly(methyl methacrylate) (PMMA). Since collisional triplet–triplet energy transfer is negligible in rigid phases, our experimental results confirm that the main physical event is long-range triplet–singlet energy transfer from excited triplet acetone ($^3K^*$), thermally generated from TMD, to DBA affording singlet excited DBA, whose fluorescence is observed. From this enhanced chemiluminescence data the long-range triplet–singlet energy-transfer parameters $k_{K,DBA}{}^{TS} = (1.05 \pm 0.14) \times 10^9\ s^{-1}\ m^{-1}$ and $\phi_{K,DBA}{}^{TS} = 0.27 \pm 0.07$ were extrapolated. Furthermore, the activation energies for the enhanced DBA chemiluminescence are the same in the PST and PMMA matrices, i.e., $E_a \sim 18 \pm 1$ kcal/mol. These results are in good agreement with earlier data obtained in liquid phases or more complex solid-phase systems.

The biological function of the thyroid hormones has been speculated[3] to be an enhancement of the spin-forbidden triplet–singlet energy transfer between a chemigenerated triplet energy donor and a singlet energy acceptor by means of the heavy-atom effect of the iodine substituents of these hormones. As a chemical model system we may consider the TMD sensitized DBA fluorescence,[4] in which TMD is the excited state donor and DBA the triplet–singlet energy transfer mediator. For example, it is well established[5] that TMD is a selective and efficient source (ca. 50%) of triplet acetone since only 0.1% singlet acetone is formed.[6] Furthermore, it was recently shown[7] that in polymer matrices the rate of thermal decomposition of TMD remains unaltered. This represents a unique opportunity to isolate and elucidate the noncollisional, spin-forbidden, triplet–singlet energy-transfer process, since the collisional triplet–triplet energy transfer process should be inhibited due to immobilization of the excited states. Use of polymer matrices of different hardness, e.g., PST and PMMA, should enable us to assess how effectively triplet–triplet energy transfer is inhibited. Presently

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