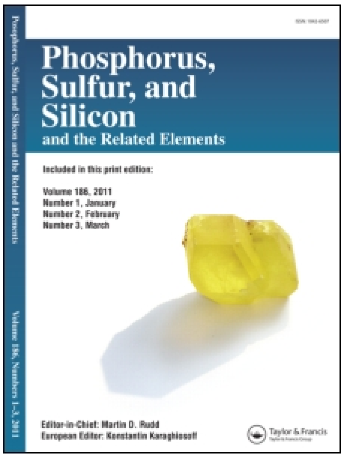

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MASS SPECTRA OF SULFUR COMPOUNDS. ASSESSMENT OF 1, X (X=2,3,4,5) HYDROGEN TRANSFER IN DIALKYL SULFIDES AND DISULFIDES UNDER ELECTRON IMPACT. A NOVEL 1,5-H SHIFT

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MASS SPECTRA OF SULFUR COMPOUNDS. ASSESSMENT OF 1, X (X=2, 3, 4, 5) HYDROGEN TRANSFER IN DIALKYL SULFIDES AND DISULFIDES UNDER ELECTRON IMPACT. A NOVEL 1,5-H SHIFT

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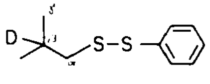
The transfer of hydrogen atoms from the *gamma* carbon of dialkyl disulfides upon electron impact is presented and its occurrence is formally shown by the electron ionization mass spectrum of 1-(2′,2′-dideuteriocyclohexyl)-2,3-dithiapent-1,1′-ene (**4b**). Also, the spectrum of 1-(2′,2′-dideuteriocyclohexyl)-2-thiahex-1-ene (**3b**) is analyzed in terms of hydrogen/deuterium transfer, where it is absent. This result is compared with selected mass spectral data of eighteen other dialkylthianes. Evidence is put forth to indicate that dialkyl sulfides are prone to undergo only 1,3-H shift upon electron inpact, whereas in dithianes 1,3- and 1,5-Hydrogen transfer take place. The evidence collected suggests that neither 1,2- nor 1,4-hydrogen transfer occurs in both sulfur derivatives.

INTRODUCTION

Organic sulfides and disulfides are an extended family of compounds with a wide spectrum of uses. In particular, dialkyl disulfides are not only common in nature, where they are responsible for, *inter alia*, ecologically meaningful organoleptic properties of plants and animals,[1] and some physiological responses relevant to human health,[2] but also their industrial applications are numerous.[3] Not surprisingly, the literature abounds with reports about ways of synthesis[4] and characterization of organic disulfides, gas chromatography in combination with mass spectrometry (GC–MS) being one of the most widely-used methods.[5]

Upon electron impact, dialkyl-1,2-dithianes decompose primarily by simple bond breakage and hydrogen transfer.[6–15] Frequently, the latter transfer accounts for either base peak or high relative intensity peaks,[14] while skeletal rearrangement is rarely observed.[10–12]

Thus far, two hydrogen transfer processes have formally been shown to generally occur in dialkyl 1,2-disulfides. Thus, Block *et al.*[12] studied hydrogen transfer of protons on the *alpha* and *beta* carbons to sulfur, using selectively deuterated diethyl disulfide as model. These shifts were interpreted as 1,2 and 1,3 hydrogen transfers. More recently, the transfer of protons from the *gamma* carbon (presumably 1,4-H shift) was suggested by the mass spectra of 1-phenyl-4-deuterio-4-methyl-1,2-dithiapentane (**1**), in studies from our laboratory.[13] How-



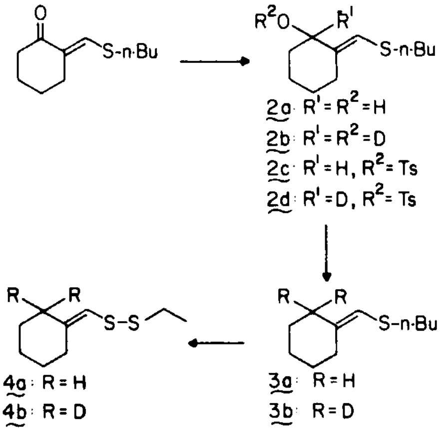
1

ever, formal evidence of this shift was not available. This current investigation is aimed at the development of such evidence, and at the same time to establish to which sulfur atom this hydrogen transfer takes place. To this end, the EI–MS of a *gamma* deuterated disulfide was examined, and a comparative analysis of the EI–MS of selected dialkyl sulfides was performed. Results are herewith described.

RESULTS

The model disulfide derivative was constructed so it would contain a deuterium atom on the *gamma* carbon relative to the nearest sulfur, and with minimal steric constraints that could restrict the approach of the involved atoms.[16] Also, two proton-bearing *gamma* carbons were included in the model. Only one of these carbons was deuterio-substituted to allow for a comparative D- vs H-transfer study. In order to prevent the obscuring effect of presumably more favorable hydrogen transfers from *alpha* and *beta* carbons a double bond between these two carbons was inserted in the model because it has been shown that hydrogens on vinyl and aryl carbons do not undergo transfer upon electron impact.[13] Finally, an ethyl group was substituted on the second sulphur atom of the model disulfide in view of the intense $[HSSEt]^{+}$ cation detected earlier in the EI–MS of ethyl-alkyl disulfides.[13] This feature would facilitate the observation of the *gamma* shift in our model. These conditions were met by compound **4**, which was synthesized by the sequence shown on Scheme I.[17]

SCHEME I



The isolation of compound **4** in the last step was hampered by its instability on various chromatographic supports and under those conditions required for its distillation. However, it was satisfactorily characterized by its PMR and MS spectrum and exact mass of the molecular ion (*vide infra*). Its isolation was accomplished by gas liquid chromatography at the time of the GC–MS experiments.

The EI–MS of *gamma* deuterated sulfide intermediate **3b** was first examined (Figure 1) by direct probe introduction. In addition to the intense molecular ion-radical at m/e 186, the base peak at m/e 129 corresponding to the expected *alpha* fragmentation of the n-butyl chain, was observed. Little difference was appreciable in comparing this spectrum with the EI–MS of non-deuterated sulfide **3a**, except for the two mass units difference of key fragments containing the two deuterium atoms. In both spectra, no $[RSH]^{+}$ cations attributable to H-transfer to sulfur were observed. This result is in contrast with the EI–MS of other dialkyl sulfides obtained under similar conditions (70 eV), in which $[RSH]^{+}$ fragment ions are clearly produced (see Table I).[18] In particular, ethyl, isopropyl, n-butyl, i-butyl, and t-butyl substitution favor hydrogen transfer to sulfur even over *alpha* fragmentation. This feature is apparent in the series **5–9**, **10–16**, and **17–22** (Table I). In these compounds, the relative intensity of the $[RSH]^{+}$ fragment increases to 100%.

Conceivably, the *exo-endo* isomerization of the double bond of 3b could have occurred during its vaporization inside the ionization chamber of the mass spectrometer. This possibility was assessed by comparison of the spectra of **3a** and of the independently synthesized endo-isomer **25** (see Scheme II).[19] The notable differences underscored by the relative abundance of the molecular ion, and of

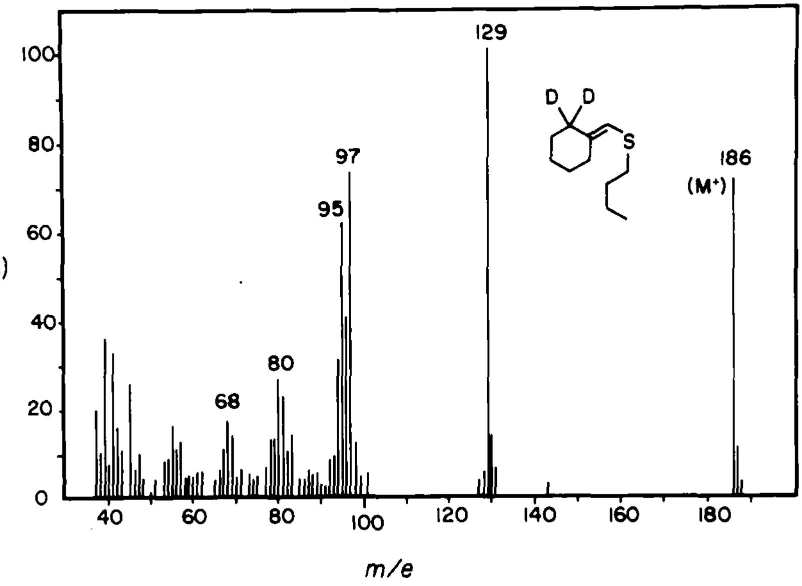


FIGURE 1 Electron impact mass spectrum of 1-(2′,2′-dideuterio-cyclohexyl)-2-thiahex-1,1′-ene (**3b**) at 70 eV.

TABLE I

Selected EI–MS data of alkyl sulfides. Fragment ions derived from intramolecular hydrogen transfer and alpha-breakage at 70 eV

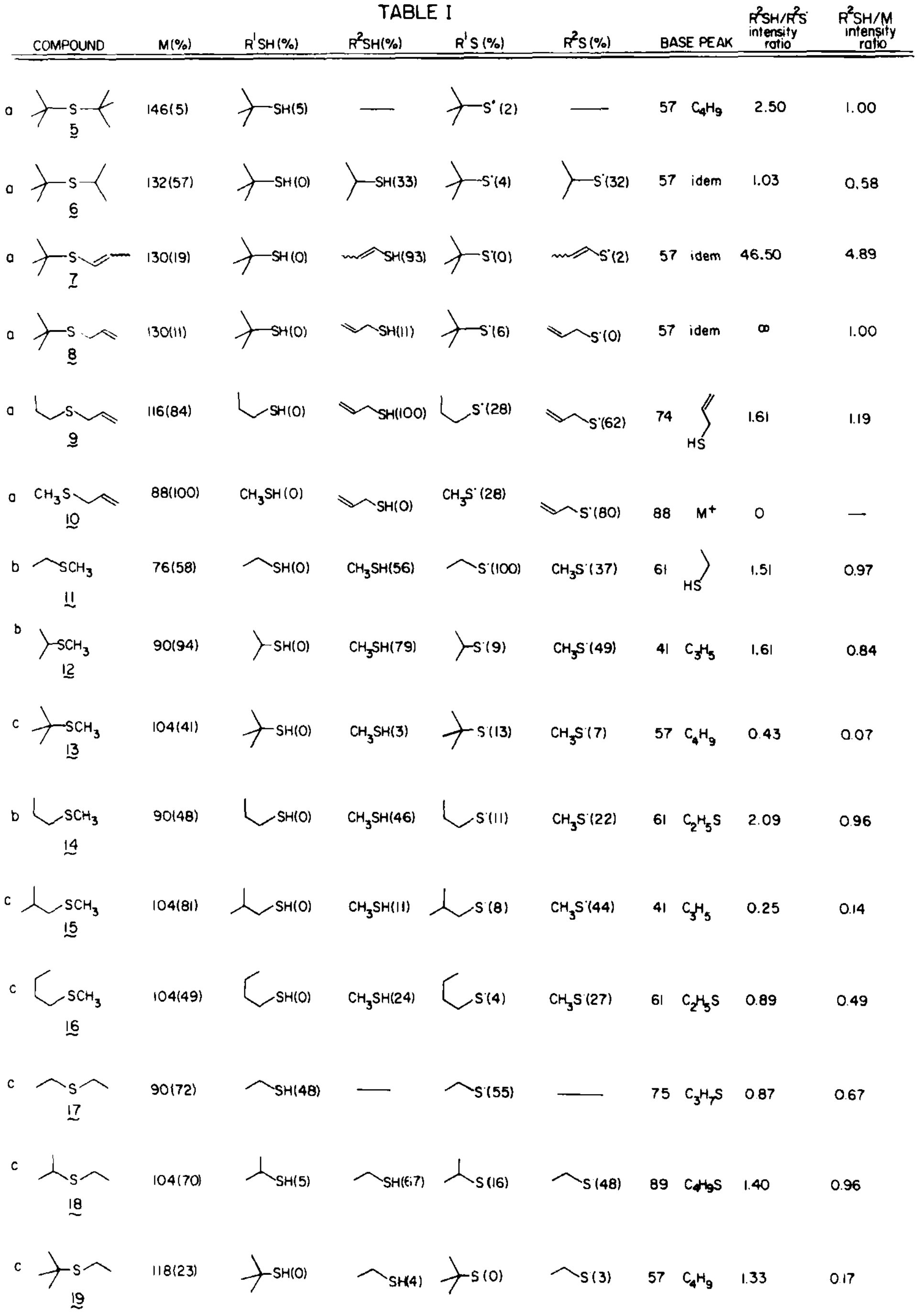
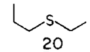
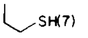
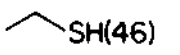
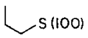
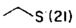
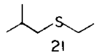
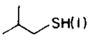
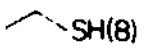
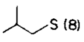
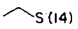
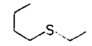
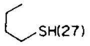
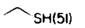
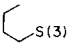
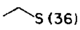


TABLE I

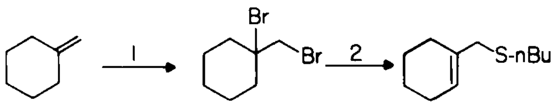
	COMPOUND	M(%)	R^1SH(%)	R^2SH(%)	R^1S(%)	R^2S(%)	BASE PEAK	R^2SH/R^2S· intensity ratio	R^2SH/M intensity ratio
a	5	146(5)	SH(5)	—	S·(2)	—	57 C_4H_9	2.50	1.00
a	6	132(57)	SH(0)	SH(33)	S·(4)	S·(32)	57 idem	1.03	0.58
a	7	130(19)	SH(0)	SH(93)	S·(0)	S·(2)	57 idem	46.50	4.89
a	8	130(11)	SH(0)	SH(11)	S·(6)	S·(0)	57 idem	∞	1.00
a	9	116(84)	SH(0)	SH(100)	S·(28)	S·(62)	74 HS	1.61	1.19
a	CH_3S 10	88(100)	CH_3SH(0)	SH(0)	CH_3S·(28)	S·(80)	88 M^+	0	—
b	SCH_3 11	76(58)	SH(0)	CH_3SH(56)	S·(100)	CH_3S·(37)	61 HS	1.51	0.97
b	SCH_3 12	90(94)	SH(0)	CH_3SH(79)	S·(9)	CH_3S·(49)	41 C_3H_5	1.61	0.84
c	SCH_3 13	104(41)	SH(0)	CH_3SH(3)	S·(13)	CH_3S·(7)	57 C_4H_9	0.43	0.07
b	SCH_3 14	90(48)	SH(0)	CH_3SH(46)	S·(11)	CH_3S·(22)	61 C_2H_5S	2.09	0.96
c	SCH_3 15	104(81)	SH(0)	CH_3SH(11)	S·(8)	CH_3S·(44)	41 C_3H_5	0.25	0.14
c	SCH_3 16	104(49)	SH(0)	CH_3SH(24)	S·(4)	CH_3S·(27)	61 C_2H_5S	0.89	0.49
c	S 17	90(72)	SH(48)	—	S·(55)	—	75 C_3H_7S	0.87	0.67
c	S 18	104(70)	SH(5)	SH(6.7)	S·(16)	S·(48)	89 C_4H_9S	1.40	0.96
c	S 19	118(23)	SH(0)	SH(4)	S·(0)	S·(3)	57 C_4H_9	1.33	0.17

TABLE I (*contd*)

COMPOUND	M(%)	R^{1}SH (%)	R^{2}SH(%)	R^{1}S (%)	R^{2}S(%)	BASE PEAK		R^{2}SH/R^{2}S intensity ratio	R^{2}SH/M intensity ratio
[c]  **20**	104(45)					75		2.19	1.02
[c]  **21**	118(33)					75	C_3H_7S	0.57	0.24
[c]  **22**	118(64)					75	idem	1.42	0.80

[a] This work;
[b] Calculated from data of reference 18b.
[c] Calculated from data of reference 18a.

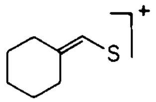
SCHEME II



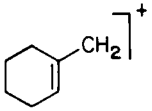
23 **24** **25**

1) $CuBr_2$, hν, CH_3CN, 91%
2) n BuSH, KOH, EtOH,Δ, 30%

key fragments m/e 127 (I) (100% for **3a**, 11% for **25**), and 95 (II) (67% for **3a**, 100% for **25**) suggest that little if any *exo-endo* isomerization occurs in **3b** prior to its ionization. However, it is likely that this isomerization does take place after *alpha* fragmentation.



I m/e 127



II m/e 95

By contrast, when **3b** was injected in the gas chromatograph prior to its introduction in the MS system, partial decomposition occurred. In fact, when **3b** was subjected to temperatures as low as 110°C in a glass-lined GC injector and a 12 ft Carbowax 10% on Chromosorb G column (temperature program: 75–170°C), compound **3b** furnished dibutyl sulfide, dibutyl disulfide, and endo-isomer **25**, while only 7% of **3b** survived this treatment. This decomposition was also

TABLE II

Thermolysis of sulfide **3b** during gas chromatographic analysis. Product composition

Compound	Column type Carbowax 10% (%)	Fused silica (%)
$(n\text{-Bu})_2$—S	10.9	4.0
$(n\text{-Bu})_2$—S_2	63.4	39.0
3b	7.3	26.0
DIDEUTERIO-**25**	14.0	21.0

[a] Identification by GC–EIMS. Injector temperature: 110°C. Column temperature program: 75–170°C (Carbowax) and 75–110°C (fused silica), 4°C/min.

[b] Part of the sample is converted to unrecorded polymeric material.

observed, though to a lesser extent, when a fused-silica capillary column (75–120°C) was used (see Table II).

Consequently, it was not surprising to observe partial decomposition during the GC separation that preceded the MS measurement of compounds **4a**,**b**. Nevertheless, whereas ethyl-butyl and dibutyl disulfides were in fact detected (Table III), no *exo-endo* isomerization of compound **4a** was observed. As much as 27% of unaffected **4a**,**b** still remained after the GC separation in Carbowax-packed columns and 44% in fused-silica capillary columns. This situation allowed for its mass spectral analysis.

TABLE III

Thermolysis of the mixture of **3b** (40%) and **4b** (60%) during gas chromatographic analysis. Product composition

Compound	Column type Carbowax 10% (%)	Fused silica (%)
Et-S—S-nBu	9.4	6.0
$(n\text{-Bu})_2$—S_2	3.0	<1.0
3b	28.0	36.0
4b	13.0	27.0

The initial composition of the mixture was determined by proton nmr spectroscopy. Injector temperature: 110°C. Column temperature program: 75–185°C (Carbowax) and 75–135°C (Fused silica), 4°C/min. Part of the sample is converted to intractable polymeric material.

The EI–MS of **4b** (Fig. 2) clearly shows hydrodisulfide[20a] fragments $[HSSt]^{\dot{+}}$ (m/e 94) and $[DSSEt]^{\dot{+}}$ m/e 95 (exact mass: calc: 93.9911 and 94.9974; found: 93.9921 and 94.9979, respectively) as strong signals of roughly equal relative intensity (86–88%). In all probability, both fragments are generated by transfer of hydrogen and deuterium substituted on the *gamma* carbons of the cyclohexyl ring. A metastable ion (broad signal with maxima at 46.5 and 47.5 mass units) confirms the precursor-product ion relationship. Thus, the *gamma* hydrogen

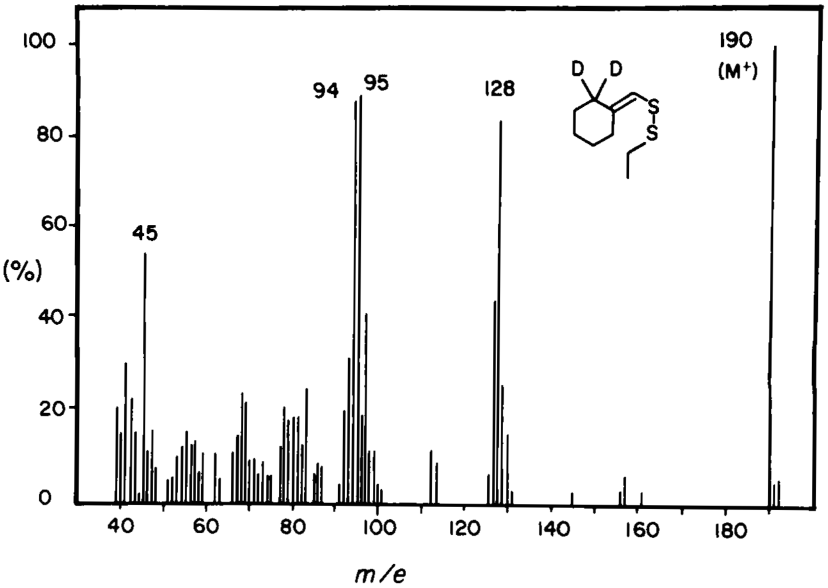
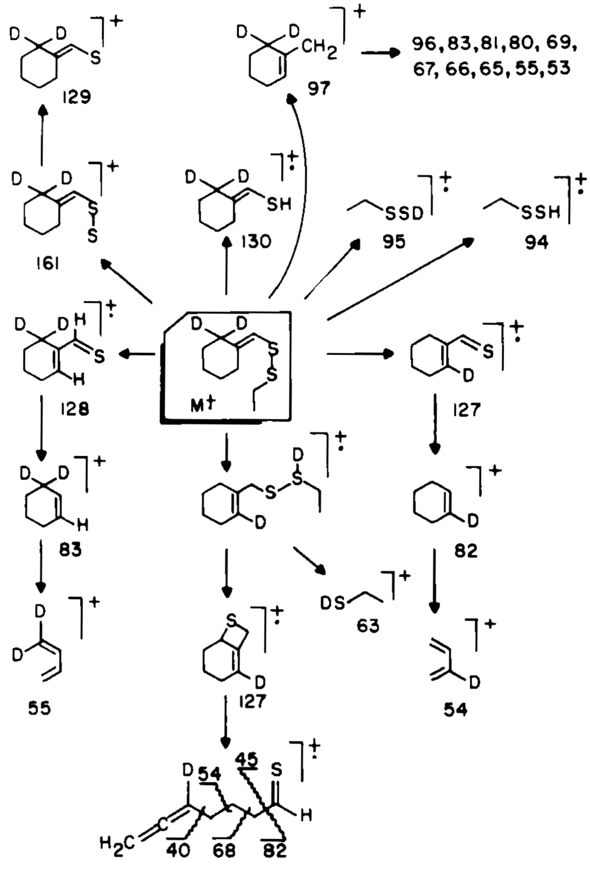
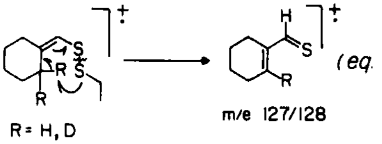


FIGURE 2 Electron impact mass spectrum of 1-(2′,2′-dideuterio-cyclohexyl)-2,3-dithiapent-1,1′-ene (**4b**) at 70 eV.

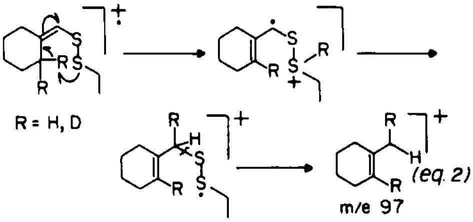
SCHEME III



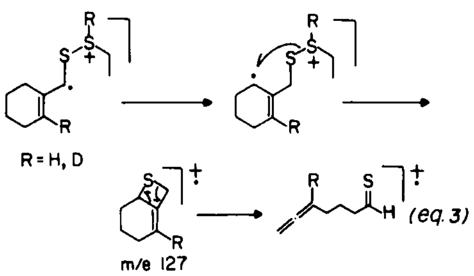
transfer appears formally demonstrated. Other important fragmentations of this spectrum are indicated in Scheme III. Simple S—S and S—C bond rupture leads to fragments m/e 161 and 129 whereas hydrogen transfer from the ethyl unit to the sulfur atoms yields the mercaptan fragment at m/e 130. The peaks at m/e 127 and 128 may be accounted for by means of allylic hydrogen/deuterium transfer to the sulphur atoms followed by scisson of the S—S bond, as indicated by Equation (1). The high relative intensity of these ions is suggestive of the importance of this process in disulfides.



The fragment m/e 97 finds a cursory explanation in the sequence portrayed in Equation (2), where a 1,5-H sift of the allylic hydrogen to that sulphur atom farthest removed from it followed by its 1,3-migration to the alpha carbon and finally allylic C—S bond disconnection are the key steps.



A tautomeric m/e 127 fragment that includes a thiooxetane structure (see Scheme III) may also be postulated to account for other important fragments such as m/e 82, 68, 54, 45, and 40. This tautomer may be derived from the molecular ion by appropriate hydrogen shifts which are indicated in equation 3. The ring strain associated with this structure would be compatible with the levels of energy expected under the conditions of the EIMS experiment.[20b]



DISCUSSION

The *gamma* hydrogen transfer process may be conceived to occur in at least three different ways, which are portrayed in Scheme IV. The absence of $[DSR]^{+}$ and

$[HSR]^{+\cdot}$ ($R = n$-Bu) ions in the EI–MS of **3b** indicates that either the transfer of *gamma* hydrogens does not take place in sulfides, or that it is vastly superseded by other fragmentations such as simple *alpha* rupture. Contrastingly, the favored formation of $[DSSR]^{+\cdot}$ and $[HSSR]^{+\cdot}$ species in the EI–MS of disulfide **4b** indicates that a second sulphur atom is essential for the transfer of *gamma* hydrogens. This finding, added to the production of fragments $[DSEt]^{+\cdot}$ (m/e 63) and $[HSEt]^{+\cdot}$ (m/e 62) in the mass spectrum of **4b**, alludes to the transfer of hydrogen from the carbon backbone to that sulphur atom farthest removed from the hydrogen-yielding carbon (options **B** and **C** of Scheme IV). Therefore *the apparent* 1,4-*hydrogen migration is actually a* 1,5-*H shift.* The appearance of $[HS\text{-}Ar]^{+\cdot}$ and $[DS\text{-}Ar]^{+\cdot}$ in the mass spectrum of compound **1** corroborates the same conclusion.[13] In addition, **VIII** type intermediates (option **C**) have been postulated to explain the skeletal rearrangement of dimethyl disulfide in EI–MS,[10,12a] although a non synchronous transfer as that portrayed by **VI** (option **B**) is probably more likely.

In this context, the EI–MS data of dialkyl sulfides 5–22 collected in Table I are pertinent.[18,21,22] A consistent fragmentation pattern emerges with the following outstanding points:

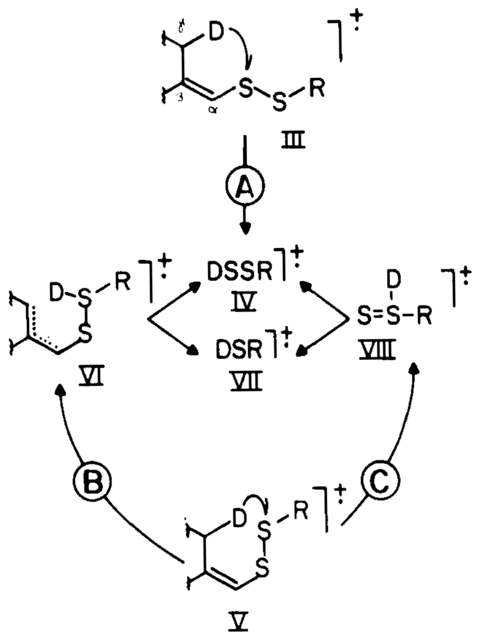
1) Hydrogen transfer and *alpha* cleavage are generally competitive processes in dialkyl sulfides, as indicated by the $R^2SH/R^2S^\cdot$ relative intensity ratios. Only when *alpha* fragmentation is disfavored (see compounds **7** and **8** in Table I) does this value depart significantly from 1.0. This behavior is opposed to that of dialkyl disulfides in which hydrogen migration is predominant.[13–15]

2) The lack of $[R^1SH]^{+\cdot}$ fragment ions in the EI–MS of methyl-alkyl and allyl-alkyl sulfides **8–16** rules out the transfer of *alpha* hydrogens in sulfides. It becomes clear then that the *alpha* deuterium transfer observed by Block *et al.*[12] in diethyl disulfide requires the intervention of the additional sulfur atom. Therefore, *the formerly postulated* 1,2-*H transfer in disulfides appears to be actually a* 1,3-*H shift,* a sequence that includes **VI**-type intermediates.

3) The *beta* hydrogen transfer does occur in sulfides because fragments of the type $[HS—CH_3]^{+\cdot}$ are recorded in the EI–MS of the series **11–13** and **17–19**. If it is true that a much debated[22] four-membered transition state participates in the *beta* transfer,[23] then steric obstruction may be introduced to hinder such hydrogen migration. This idea has been tested experimentally[13] using model compound **1**, in which two bulky methyl groups were placed on the *beta* carbon, thus causing a rotational barrier against the formation of the required transition state geometry due to the eclipsing of these two substituents with the C—H bonds of the *alpha* methylene group. As a result, the *beta* transfer was significantly retarded. Consequently, *transfer from the beta carbon may take place by a* 1,3-*H shift mechanism,* as previously postulated, because it requires only one sulfur atom to occur.

4) Although the introduction of *gamma* hydrogens increases the relative abundance of $[HSSR]^{+\cdot}$ fragment ions in disulfides,[13] a parallel behavior is not observed in alkyl sulfides. The lack of $[HSR]^{+\cdot}$ cations in the spectra of sulfides **3a,b**, **7** and **25**, and the low relative intensities of $[HS—CH_3]^{+\cdot}$ (m/e 48) and $[HS—C_2H_5]^{+\cdot}$ (m/e 62) fragments recorded for compounds **15** and **21** with respect to those observed for **11** and **17**, respectively, substantiate the contention that *gamma transfer does not take place in sulfides,* and as a consequence, *gamma*

SCHEME IV



hydrogen transfer in disulfides is actually a 1,5-*H shift.* This shift is likely to occur by way of a six-membered transition state such as that portrayed by **V** (Scheme IV, Figure 3).[21,22]

In conclusion, the transfer of hydrogen atoms located on *alpha* and *gamma* carbons relative to sulfur does not occur to a significant extent in the EI–MS spectra of *sulfides*. The only H-shift phenomena so far detected is that from the *beta carbon,* which is actually a 1,3-H shift. By contrast, the shift of hydrogen atoms on *alpha, beta,* and *gamma* carbons to sulfur in 1,2-*disulfides* is a predominant process in the EI–MS of these compounds. However, only 1,3 and 1,5-H shifts to the nearest and the farthest sulfur atom, respectively, appear to take place.

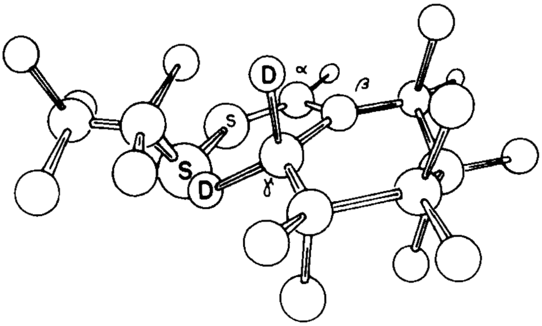


FIGURE 3 Molecular structure of disulfide **4b** in its most preferred conformation for 1,5-deuterium shift.

EXPERIMENTAL SECTION

Infrared spectra were determined on a Perkin Elmer 567 spectrophotometer, using potassium bromide disks and the 1601 and 1028 cm^{-1} bands of polystyrene for calibration. Proton nmr spectra were obtained from a Varian EM-390 instrument operating at 90 MHz, in carbon tetrachloride solutions unless otherwise stated, using 2 mm tubes (ca 1% tetramethylsilane at 0.00 ppm). Low resolution mass spectra were determined on a Dupont 21–492 instrument at an ionizing voltage of 70 eV using an all-glass inlet at 110°C, coupled to a Varian gas chromatograph model 1400. High resolution mass spectra were obtained from a AEI-Kratos MS-30 double-beam instrument operating under the same conditions, and coupled to a Shimadzu 9A gas chromatograph. Other gas chromatographic analyses were performed on a Hewlett–Packard 5710-A instrument. GLC columns utilized were Carbowax 10% on Chromosorb G, 12 ft, SE-30 3% on Chromosorb G, 12 ft, 1/8" packed metal columns, and a fused silica capillary column 60 m long, using nitrogen and helium as carrier gases. Lithium tetradeuteridoaluminate was purchased from Alpha-Ventron Corporation, Danvers, MA. 2,2,4-Trimethyl-3-thiapentane **6** was prepared as reported previously.[25] 5,5-Dimethyl-4-thia-hex-1-ene **7** and 5,5-dimethyl-4-thiahex-2-ene **8** and 4-thiahept-1-ene **9** were synthesized following literature reports.[26]

1-(2'-deuterio-2'-D-hydroxycyclohexyl)-2-thiahex-1-ene (2b)

A 250 mL, three necked, round-bottomed flask fitted with reflux condenser, 50 mL addition funnel, and a nitrogen inlet was flame-dried and charged with ether (150 mL) previously dried over sodium wire and distilled from lithium aluminum hydride and lithium tetradeuteroaluminate (LAD) (1.06 g, 0.0253 mole) under a nitrogen atmosphere. An anhydrous ether solution (25 mL) of n-butylthiomethylene derivative of cyclohexanone (10.0 g, 0.0505 mole)[27] was added dropwise at such a rate that the stirred mixture refluxed gently. Stirring was continued at reflux temperature for an additional two hour period. Excess LAD was destroyed by the addition of ethyl acetate and deuterium oxide. The crude mixture was dried over anhydrous magnesium sulfate, and the solvents were evaporated. The colorless oily residue (9.90 g, 98%) consisted of a carbonyl-free (ir) homogeneous (TLC, silica gel) substance, which was identified as the desired carbinol **2b** by comparison of R_f (TLC), retention time (GLC) of the trimethylsilyl derivative and ir and nmr spectral characteristics of non-deuterated carbinol **2a**, which was prepared under the same conditions using lithium aluminum hydride as reducing agent. Ir (neat) 3390 (s), 1015 (m) cm^{-1}; nmr δ 0.91 (t, 3H, J = 6.0 Hz, methyl), 1.20–1.95 (m, 12H, 6xCH_2), 2.50 (t, 2H, J = 6.0 Hz, CH_2—S),, 3.00 (broad s, 1H, OH, visible by exchange with water in **2b**). 3.96 (m, 1H, CH—OH in **2a** only), 5.80 (s, 1H, CH=C) ppm. A 100 mg sample was purified further by thick layer chromatography using petroleum ether/diethyl ether (1:6) as elution solvent, yielding pure alcohol **2a** as a colorless thick oil.

Anal. Calcd for **2a** ($C_{11}H_{20}OS$): C, 65.96; H, 10.07; O, 7.99; S, 15.98. Found: C, 65.84; H, 10.15; O, 8.09; S, 15.90.

1-(2′,2′-dideuteriocyclohexyl)-2-thiahex-1-ene (3b)

The crude deuterated carbinol **2b** (9.30 g, 0.047 mole) was dissolved in anhydrous pyridine (100 mL) containing freshly recrystallized p-toluenesulfonyl chloride (18.0 g, 0.0946 mole) and stirred at 0°C for six days. The mixture was poured over 400 g of water-ice and the oily crude material extracted several times with cold ether. The organic layer was washed repeatedly with 8% aqueous copper sulfate until no change in the blue color was observed. After solvent evaporation at room temperature, the residual light-yellow oil (11.9 g, 71%) proved to be homogeneous (TLC, silica gel), and consisted of unstable tosylate **2d** that could not be crystallized. Again, comparison of this material with tosylate **2c** prepared in a similar fashion from **2a** allowed its identification as p-toluenesulfonate ester **2d**. Ir (neat) 1193 (s), 1181 (s) $\mathrm{cm^{-1}}$. Compound **2d** thus prepared (8.0 g, 22.5 mmole) was immediately taken up in anhydrous ether (30 mL) and added to a stirred suspension of LAD (800 mg, 18.6 mmole) in anhydrous ether (10 mL) at room temperature under a nitrogen atmosphere and rigorous exclusion of moisture. Stirring was continued for a 48 hours and after the work-up procedure described above for **2b**, a yellowish oil (3.2 g) was obtained. Repeated column chromatography through neutral alumina act III and elution with petroleum ether furnished pure sulfide **3b** (0.8 g, 20%). A similar procedure applied to **2c** using lithium aluminum hydride furnished pure non-deuterated sulfide **3a** as a light-yellow oil in 29% yield. Ir (neat) 810 (s) $\mathrm{S{-}CH{=}C}$ $\mathrm{cm^{-1}}$; nmr δ 0.90 (t, 3H, $J = 6.0$ Hz, methyl), 1.53 (m, 10H, $5\mathrm{xCH_2}$), 2.0–2.5 (m, 2H, $\mathrm{CH_2{-}C{=}}$), 5.50 (s, 1H, —CH=) ppm.

Anal. Calcd for **3a** $\mathrm{C_{11}H_{20}S}$: C, 71.69; H, 10.95; S, 17.36. Found: C, 71.63; H, 11.00; S, 17.40.

1-(2′,2′-dideuteriocyclohexyl)-2,3-dithiapent-1,1′-ene (4b)

Dideuteriosulfide **3b** (790 mg, 4.2 mmole) was reacted with lithium metal (0.12 g, 0.017 g-atom) in liquid ammonia (100 mL) and ethyl thiocyanate (0.37 g) using the reported procedure.[29] After evaporation of ammonia, the brownish residue was taken up in ethyl ether and washed twice with 20 mL portions of water. Moisture was removed with the aid of anhydrous magnesium sulfate. Filtration and evaporation gave 110 mg of light-brown liquid which consisted of a 2:3 mixture of **3b** and **4b** (90%) along with unidentified impurities (10%) according to nmr data using dimethyl pthalate as internal standard. Isolation of **4b** by thick layer or column chromatography, or by distillation under high vacuum could not be accomplished without extensive decomposition. Reaction conditions could not be modified to improve the conversion of **3a** into **4a** in parallel experiments. However, compound **4b** could be characterized by selected nmr data of the mixture and its mass spectrum. Nmr (**4a**) δ 1.30 (t, 3H, $J = 7.0$ Hz, methyl), 2.67 (q, 2H, $J = 7.0$ Hz, $\mathrm{CH_2}$ of ethyl group), 5.75 (broad s, 1H, —HC=), ppm. Exact mass calcd for $\mathrm{C_9D_2H_{14}S_2}$: 190.0817. Found: 190.0823. For its mass spectrum, see Figure 2 in the text.

1-(cyclohexen-1′-yl)-2-thiahexane (25)

To a solution of n-butylthiolate in water (15 mL) and ethanol (2 mL) prepared from n-butylthiol (0.35 g, 3.9 mmole) and potassium hydroxide (3.9 mmoles) was added 1-bromomethyl-1-bromocyclohexane[28] (0.5 g, 1.9 mmole) with stirring at room temperature over a period of two hours. Then the mixture was heated to 80°C for an additional seven hours. The cold reaction mixture was poured into ice-cold water (50 mL) and extracted twice with 25 mL portions of ether. The organic extract was washed with water to neutral pH, dried over anhydrous magnesium sulfate and evaporated under reduced pressure to yield a light yellow oil (210 mg) consisting chiefly of allylic sulfide **25**. This compound was purified further by thick layer chromatography using petroleum ether/diethyl ether 1:1 as elution solvent. This allowed for the recovery of 190 mg of pure sulfide **25**. Ir (neat) 805 (s) C═C cm^{-1}; nmr 0.95 (t, 3H, J = 6.0 Hz, methyl), 1.20–1.80 (m, 8H, 4xCH_2), 2.0–2.4 (m, 4H, allylic endocyclic CH_2), 2.68 (t, 2H, J = 6.0 Hz, C_3H_7—CH_2—S), 2.98 (broad s, 2H, ═C—CH_2—S—), 5.50 (m, 1H, —HC═). EI-mass spectrum m/e (%) 184 (26%, M^+), 127 (11%, M^+—C_4H_9), 95 (100%, M^+—C_4H_9—S), 94 (52%).

Anal. Calcd for $C_{11}H_{20}S$: C, 71.69; H, 10.95; S, 17.36. Found: C, 71.66; H, 10.97; S, 17.39.

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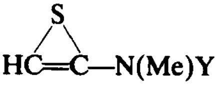

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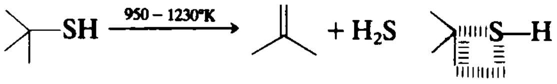

$$k = 10^{13.3} e^{-55000/RT}$$

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