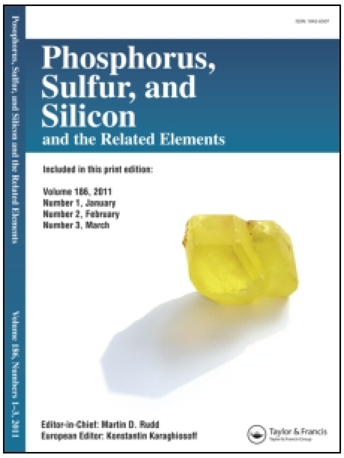

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GAS-PHASE THERMOLYSIS OF SULFUR COMPOUNDS. PART VI. ALLYL PROPARGYL AND ISOPROPYL PROPARGYL SULFIDES

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GAS-PHASE THERMOLYSIS OF SULFUR COMPOUNDS. PART VI. ALLYL PROPARGYL AND ISOPROPYL PROPARGYL SULFIDES

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Allyl propargyl and isopropyl propargyl sulfides were pyrolyzed in a stirred-flow system at temperatures in the range 312–402°C and pressures between 2 and 14 torr.

The allyl propargyl sulfide yielded as products a mixture of propene and allene and the corresponding propynethial and propenethial. The thioaldehydes react at room temperature to form polymers and the Diels-Alder adduct 1,3-dithia-2-ethynyl-cyclohex-5-ene. The reaction products from isopropyl propargyl sulfide were allene and thioacetone.

The reactions showed first order kinetics, with the rate coefficients following the Arrhenius equations
Allyl Propargyl Sulfide:

$$k\,(\mathrm{sec}^{-1}) = 10^{11.22 \pm 0.28}\exp(-139 \pm 3\ \mathrm{kJ/mol\ RT})$$

Isopropyl Propargyl Sulfide:

$$k\,(\mathrm{sec}^{-1}) = 10^{11.51 \pm 0.14}\exp(-155 \pm 2\ \mathrm{kJ/mol\ RT})$$

The kinetic deuterium isotope effect of 4-thia-5-deutero-5-methyl-hex-1-yne pyrolysis was studied over the temperature range 370–402°C.

INTRODUCTION

Previous work[1] on the pyrolysis of allyl sulfides showed that they decompose more readily than their oxygen and nitrogen homologues. Although these systems pyrolyze unimolecularly through mechanisms involving a six-centered cyclic transition state, the large substituent effect on reaction rate[1] and the temperature independence of the kinetic deuterium isotope effect[2] suggest a non-concerted mechanism in the allyl sulfides, whereby the αC—H bond should be nearly broken in the transition state.

As a continuation of this line of work, it was considered interesting to compare the reactivity and product distribution of the allyl propargyl sulfide with that of the diallyl sulfide.[1] For both systems, two equivalent reaction paths are available, however, some asymmetry in the reactivity would be expected for the former one.

With the purpose of measuring the kinetic deuterium isotope effect and observe the reactivity of the thioacetone generated as a reaction product, isopropyl propargyl sulfide and its monodeuterated homologue, 4-thia-5-deutero-5-methyl-hex-1-yne, were also studied in the present work.

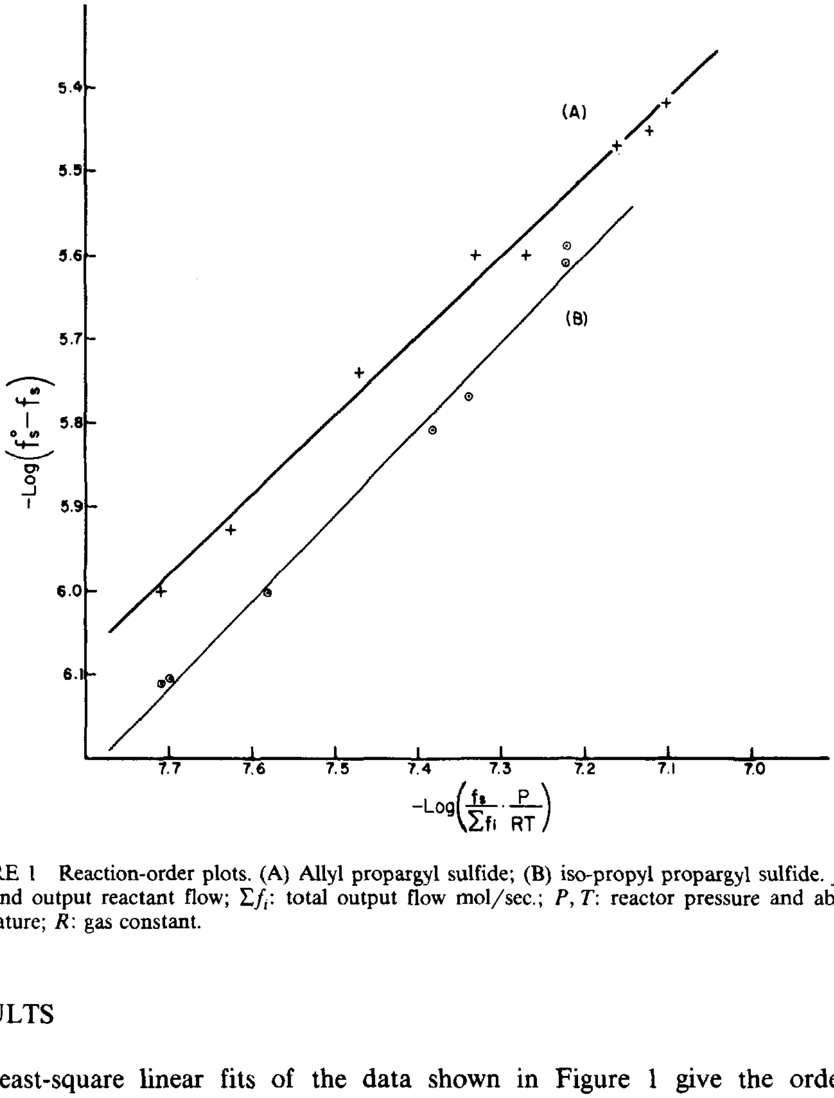

FIGURE 1 Reaction-order plots. (A) Allyl propargyl sulfide; (B) iso-propyl propargyl sulfide. f_S^0, f_S: input and output reactant flow; Σf_i: total output flow mol/sec.; P, T: reactor pressure and absolute temperature; R: gas constant.

RESULTS

The least-square linear fits of the data shown in Figure 1 give the order of consumption of allyl propargyl sulfide at 334°C and of isopropyl propargyl sulfide at 381°C as 0.95 ± 0.04 and 1.02 ± 0.06 respectively. These orders were examined at conversions ranging between 19 and 58% based on the amount of C_3 hydrocarbon formed as product.

In Table I are listed the experimental and kinetic data from runs made with allyl propargyl sulfide over the temperature range 312–345°C and pressures between 2 and 14 torr. There is a fair agreement between the percent conversion measured by gas chromatography of the unreacted sulfide ($\% r_{\mathrm{glc}}$) and by volumetric measurement of the total amount of C_3 hydrocarbon mixture formed as products ($\% r_{C_3}$). Over the whole temperature range studied, this mixture consisted of 50% each allene and propene. The only other reaction products observed in the pyrolysis of the allyl propargyl sulfide were two solids of quite different physical appearance. One was an amorphous polymer similar to that formed in the pyrolysis of allyl sulfide[1] whereas

TABLE I

Stirred-flow pyrolysis of allyl propargyl sulfide

T °C	k $\times 10^4$ sec^{-1}	a θ sec	b $\% r_{C_3}$	c $\% r_{glc}$	P Torr	d $f_S^0 \cdot 10^8$	e fc/f_S^0
345.4	3109	1.139	26.15	25.1	11.29	977	0
345.2	2949	0.8839	20.67	21.1	3.23	179	0
344.7	2996	0.6105	15.46	11.2	10.21	1090	1.9*
345.2	3052	2.3900	42.17	—	0.889	155	0
333.6	1703	1.395	19.20	—	9.39	495	7.0**
333.1	1970	2.435	32.40	—	3.08	576	0
333.8	1896	1.551	22.70	—	8.33	689	3.5**
334.3	1934	1.369	20.90	19.0	13.33	1107	4.1**
333.5	1972	1.797	26.16	25.4	3.46	962	0
333.0	1692	0.7925	11.82	—	2.37	1612	0
331.9	1851	4.258	44.07	46.5	2.73	268	0
332.7	1933	1.381	21.06	—	2.41	868	0
333.4	1848	1.269	18.99	—	13.89	757	7.5*
332.9	1678	0.5510	8.46	—	8.83	1602	4.9
323.1	1089	5.323	36.90	39.3	3.52	336	0
322.4	1147	4.249	32.76	35.6	2.58	281	0
322.5	1123	3.022	25.34	25.6	3.62	587	0
321.9	1090	2.918	24.14	—	8.50	334	4.1*
312.2	688	2.671	15.53	14.7	4.09	828	0
312.0	628	2.587	13.98	—	12.55	263	1.8*
312.0	671	2.725	15.46	—	3.87	769	0

[a] Residence time.
[b] Percent reaction from hydrocarbon measurement.
[c] Percent reaction from reactant measurement.
[d] Reactant inflow in mol/s.
[e] Ratio carrier to reactant flow; *Toluene; **Cyclohexene as carrier gas.

the other was a white crystalline solid easily separated from the amorphous material by vacuum sublimation, also highly soluble in organic solvents such as ether and acetone.

From the elemental analysis, NMR and mass spectra, its structure was confirmed to correspond to the Diels–Alder adduct 1,3-dithia-2-ethynyl-cyclohex-5-ene shown in Figure 2. The amount of adduct collected from six runs at 334°C indicated about 35% yield in relation to propene formation.

The rate coefficients given in Table I were estimated as usual[1,2] assuming that the thioaldehydes leave the reactor as monomers in the same proportion as the hydro-

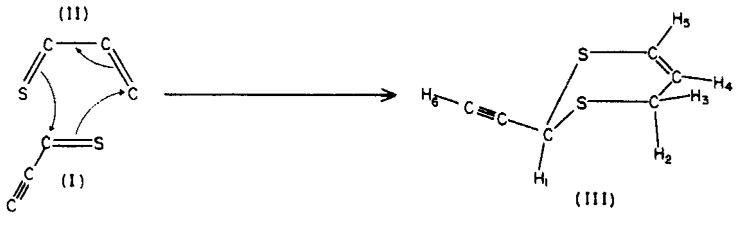

FIGURE 2 Diels-Alder adduct formation.

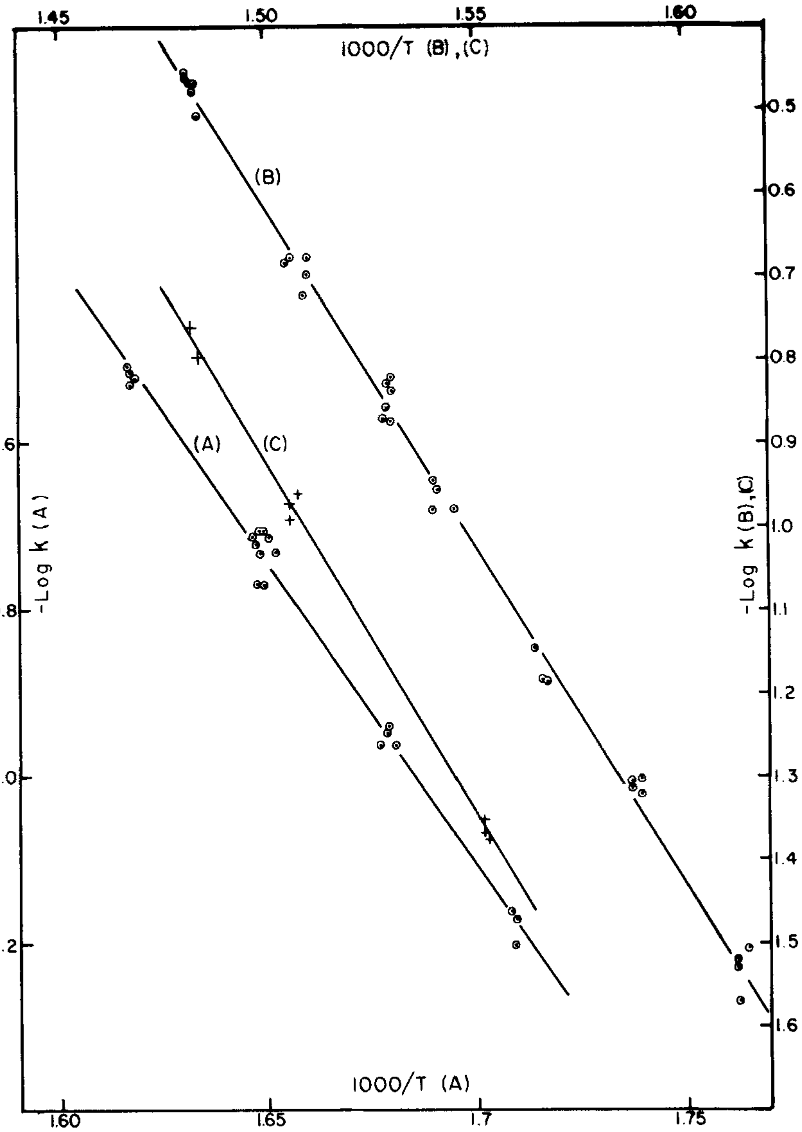

FIGURE 3 Arrhenius plots. (A) Allyl propargyl sulfide; (B) iso-propyl propargyl sulfide; (C) 4-thia-5-deutero-5-methyl-hex-1-yne.

carbon products. A least square fit of these rate coefficients gave the following Arrhenius equation for the allyl propargyl sulfide:

$$k\,(\mathrm{sec}^{-1}) = 10^{11.22 \pm 0.28}\exp(-139 \pm 3\ \mathrm{kJ/mol\ RT})$$

The corresponding plot is shown in Figure 3.

In Tables II and III are similarly listed the data pertaining to the pyrolysis of isopropyl propargyl sulfide and 4-thia-5-deutero-5-methyl-hex-1-yne, respectively. The former was pyrolyzed in the temperature range 347–402°C and pressures

TABLE II

Stirred-flow pyrolysis of isopropyl propargyl sulfide

	k	a	b	P	d	e
T °C	$\times 10^4$ sec^{-1}	θ sec	$\% r_{C_3}$	Torr	f_S^0	fc/f_S^0
347.2	267	4.722	11.19	13.46	522.69	2.6
347.5	303	5.816	15.00	12.39	392.60	2.6
347.2	295	5.745	14.50	11.83	306.00	3.5
357.0	499	5.388	21.04	12.10	523.47	1.7
357.1	489	4.872	19.23	13.20	445.52	2.9
356.3	477	5.110	19.59	13.09	446.17	2.7
365.2	698	3.503	19.65	12.95	660.98	2.5
365.6	653	4.514	22.76	2.574	309.15	—
366.4	715	3.866	21.66	4.737	669.48	—
375.8	1106	3.494	27.87	8.977	550.34	1.8
374.1	1051	3.462	26.68	10.67	689.43	1.7
376.5	1140	5.911	40.15	10.58	321.15	2.2
374.3	1060	4.987	34.58	12.15	619.36	1.2
380.4	1452	1.879	21.44	9.305	361.45	1.7
381.2	1389	1.718	19.27	12.80	796.86	4.9
380.2	1337	1.763	19.07	11.50	484.53	7.6
381.3	1391	1.623	18.41	12.89	917.07	4.4
381.0	1488	5.022	42.76	11.41	183.07	6.6
389.7	1891	2.902	35.43	2.887	471.09	—
389.1	2009	1.449	22.55	11.48	1663.7	1.8
389.3	2104	1.510	24.11	9.701	1156.4	2.3
391.4	2190	1.694	27.06	4.806	564.97	6.6
391.0	2092	1.788	27.23	10.99	409.60	8.3
401.6	3384	3.089	51.11	3.421	866.10	1.6
402.3	3451	3.835	56.96	10.07	468.99	1.9
401.5	3312	4.008	57.04	4.150	415.45	—
401.7	3392	4.239	58.98	3.448	322.21	—
401.0	3098	2.726	45.78	2.430	385.77	—

Headings as in Table I.
[e] Toluene as carrier gas.

TABLE III

Stirred-flow pyrolysis of 4-thia-5-deutero-5-methyl-hex-1-yne

	k	a	b		d
T °C	$\times 10^4$ sec^{-1}	θ sec	$\% r_{C_3}$	Torr	$f_S^0 \times 10^8$
371.2	444	4.317	16.21	1.919	250.1
370.7	421	4.449	15.77	1.770	226.8
371.1	429	1.620	6.50	12.90*	948.2
390.8	979	3.298	24.41	2.998	467.7
390.1	1091	3.334	26.68	2.842	431.4
390.6	1062	3.634	27.85	2.623	361.5
401.6	1731	3.810	39.73	2.149	254.2
400.8	1596	2.110	25.19	5.603	133.7

Headings as in Table I.
*Toluene as carrier gas; $fc/f_S^0 = 4.5$.

between 2 and 13 torr. The only gaseous product observed was allene, and the NMR spectrum of the allene formed from the deuterated reactant clearly showed it to be monodeuterated. Similarly NMR and mass spectra of the unreacted material failed to reveal any deuterium scrambling. The only other reaction product formed in the pyrolysis of the isopropyl propargyl sulfide was thioacetone. Its presence was detected by mass and NMR spectroscopy in mixtures of its vapour with allene sampled from the products trap at room temperature. The thioacetone polymerizes rather slowly into a white solid.

The least-square fits of the rate coefficients shown in Tables II and III in the form of the Arrhenius equation, yielded the following relationships for the isopropyl propargyl sulfide (k_H) and its monodeuterated homologue (k_D), respectively:

$$k_H\,(\mathrm{sec}^{-1}) = 10^{11.51 \pm 0.14}\exp(-155 \pm 2\ \mathrm{kJ/mol\ RT})$$

$$k_D\,(\mathrm{sec}^{-1}) = 10^{11.71 \pm 0.34}\exp(-161 \pm 4\ \mathrm{kJ/mol\ RT})$$

The corresponding plots are also shown in Figure 3.

DISCUSSION

The values of k_H/k_D for isopropyl propargyl sulfide obtained in the present work are shown in Table IV together with those reported previously[2,3] for *n*-alkyl allyl sulfides. The figures for the propargylic system have been obtained from k_H and k_D estimated by using the respective Arrhenius equation. They can be considered to be temperature independent within the error limits of the measurements. The fact that k_H/k_D in the *n*-alkyl allyl sulfides is about 37% larger, suggests that in this system the stretching of α-C—H bond of the alkyl group is rate determining, thus giving rise to a "product like" transition state. In the propargylic system, the nucleophilicity of the terminal acetylenic carbon atom appears to be the more important factor in the mechanism, with a decreased influence of the degree of stretching of the α-C—H bond of the isopropyl group in the transition state.

The possible bending of the acetylenic chain to fit the appropriate angle in the transition state has been discussed in the literature in connection with the pyrolyses of propargylic ethers[4] and β-hydroxyacetylenes,[5] and related to a low energy bending mode at 336 cm^{-1}. Kwart[4,6] has argued that for the bending of that chain, so little energy is needed, that both acetylenic and allylic substrates can easily assume the same structure in transition states some 150 kJ/mol above their ground states.

For the systems benzyl allyl and benzyl propargyl ethers[4] and β-hydroxyacetylenes[5] and their olefinic homologues,[7] the acetylenic substrates are between 3 and 5 times more reactive than their olefinic counterparts. For the first system, the increased reactivity of the acetylenic compounds has been related to a less negative entropy of activation[4] whereas for the second it has been ascribed[5] to the greater nucleophilicity of the triple bond towards the hydroxyl proton. In the case of the allyl propargyl sulfide, whose two thermal cycloelimination pathways are represented in Figure 4, the experimental data indicate that $k_a/k_b = 1.0$. This means that in this molecule both allylic and propargylic hydrogen atoms show the same

TABLE IV

Kinetic deuterium isotope effect in alkyl allyl sulfides

Reactant[a]	T °C	k_H $\times 10^4$ sec^{-1}	k_D $\times 10^4$ sec^{-1}	k_H/k_D	Ref.
I(H)	281	5.84 ± 0.17		2.7 ± 0.2	3
I(D)	281		2.19 ± 0.09		3
I(H)	387	1430 ± 70		2.6 ± 0.4	2
I(D)	387		541 ± 30		2
II(H)	377	820 ± 10		2.6 ± 0.2	2
II(D)	377		310 ± 20		2
III(H)	370	839 ± 42		1.9 ± 0.2	*
III(D)	370		433 ± 15		
III(H)	390	2010 ± 80		1.9 ± 0.2	*
III(D)	390		1073 ± 62		
III(H)	400	3052 ± 106		1.8 ± 0.2	*
III(D)	400		1656 ± 113		

[a] I(H) = *n*-butyl allyl sulfide; I(D) = $CH_3(CH_2)_2CD_2S$-allyl.
II(H) = *n*-propyl allyl sulfide; II(D) = $CH_3CH_2CD_2S$-allyl.
III(H) = iso-propyl propargyl sulfide; III(D) = $(CH_3)_2CDS$-propargyl.

*The values for III(H) and III(D) were calculated by using the respective Arrhenius equation from this work.

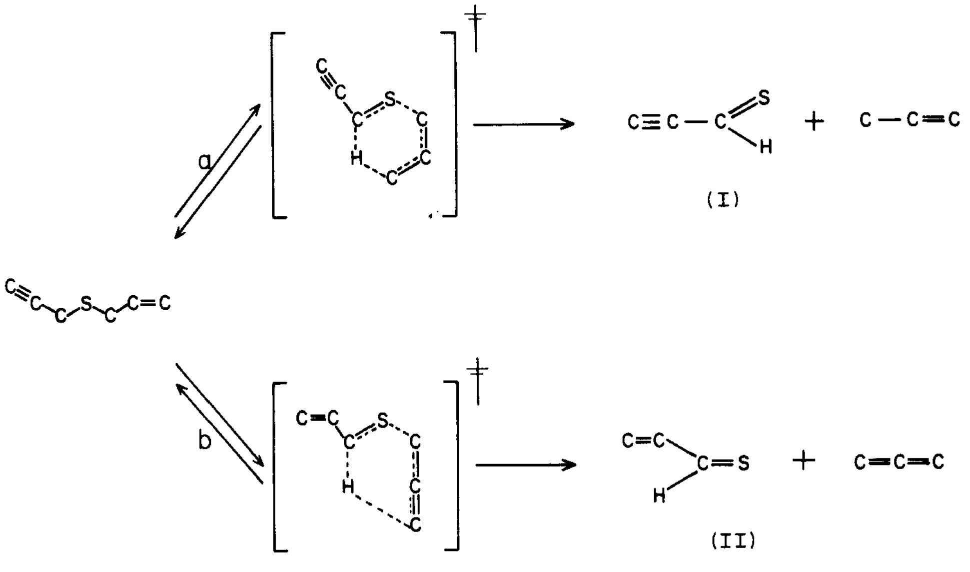

FIGURE 4 Allyl propargyl sulfide pyrolysis mechanism.

reactivity towards the doubly or triply bonded terminal carbon atoms. Furthermore, if one compares the values of the rate coefficients for diallyl sulfide pyrolysis[1] with those of allyl propargyl sulfide, the latter are about 40% larger indicating that the presence of the triple bond in this molecule enhances considerably the reactivities of the four α-H atoms available. As proposed previously,[1] the high polarizability of the sulfur atom should be the stabilizing factor if a partial negative charge is developed on the α-C atom in the transition state. The present results with allyl propargyl sulfide suggest that this charge dispersion, and consequently the acidity of the α-H atom, is the dominating factor in the reactivity and mechanism of the pyrolyses of the allyl sulfides.

Turning now to the Diels–Alder crystalline adduct (III in Figure 2) 1,3-dithia-2-ethynyl-cyclohex-5-ene, it has recently been reported[8] that its vinylic homologue is an oil, formed in 24% yield from the self condensation of the propenethial generated by photolysis of phenacyl allyl sulfide $C_6H_5COCH_2SCH_2CHCH_2$ in solution. This 1,3-dithia-2-vinyl-cyclohex-5-ene has been reported[9] to be formed also with 1,2-dithia-6-vinyl-cyclohex-3-ene. In the previous work on the pyrolysis of diallyl sulfide[1] it was only observed the formation of a highly stable solid polymer from propenethial condensation under vacuum.

EXPERIMENTAL

The allyl propargyl and isopropyl propargyl sulfides were synthesized by reaction of 2-propene-1-thiol[10] and 2-propanethiol (Phillips), respectively, with propargyl chloride (Aldrich) using a standard technique.[11] Both sulfides were purified by trap to trap distillation in a vacuum line (60–70% yield).

The 4-thia-5-deutero-5-methyl-hex-1-yne was synthesized from 2-deutero-2-propanethiol and propargyl chloride. The monodeuterated 2-propanethiol was obtained as follows: Dry acetone (0.53 mol, Merck) was treated with lithium aluminium deuteride (99% D, Merck, 0.13 mol) in 175 mL dry dioxane at 0°C. After addition, the mixture was refluxed for 22 hours under nitrogen. The complex was destroyed by titration with 10 mL D_2O and the solid material separated by filtration through a sintered glass funnel. The filtrate was distilled at ambient pressure through a 20 cm Vigreux column yielding 25 mL of a distillate composed of 68% 2-deutero-2-propanol, 28% dioxane and 4% acetone (by gas chromatography). This mixture was treated with 48% HBr, according to a standard technique[11] yielding 15 mL of pure 2-deutero-2-bromopropane. Treatment of the deuterated alkyl halide with 0.14 mol of thiourea[11] yielded 0.12 mol (84% yield) of 2-deutero-2-propyl thiol. Finally the reaction 0.07 mol of 2-deutero-2-propyl thiol with propargyl chloride yielded 0.05 mol of 4-thia-5-deutero-5-methyl-hex-1-yne. The deuterated sulfide was purified by trap to trap distillation in a vacuum line.

The purity of the synthesized sulfides was better than 98% by gas chromatography and their structures were confirmed by NMR and mass spectroscopy using the columns and instruments previously described.[3] These sulfides had to be kept in bulbs under vacuum and protected from direct light. For the analysis of allene and propene, the column used was 4-ft 1/8-in. outer diameter packed with 150/200 mesh porapak Q at 100°C. The stirred-flow technique has been described previously.[1,2,12]

1,3-dithia-2-ethynyl-cyclohex-5-ene (Figure 2) NMR (Varian EM-390, 90 MHz $CDCl_3$):
H_1: δ 4.80 (dm, $j_{1,6} = 2.0$; $j_{1,2} = 1.0$ Hz);
H_2: δ 3.33 (ddm, $j_{2,3} = 15.0$; $j_{2,4} = 4.5$; $j_{2,5} = 1.0$; $j_{2,1} = 1.0$ Hz);
H_3: δ 3.60 (ddd, $j_{3,2} = 15.0$; $j_{3,4} = 3.5$; $j_{3,5} = 1.5$ Hz);
H_4: δ 6.01 (ddd, $j_{4,5} = 9.5$; $j_{4,3} = 3.5$; $j_{4,2} = 4.5$ Hz);
H_5: δ 6.28 (dm, $j_{5,4} = 9.5$; $j_{5,3} = 1.5$; $j_{5,2} = 1.0$ Hz);
H_6: δ 2.66 (d, $j_{1,6} = 2.0$ Hz).

White needles, m.p. 62°C. Anal. calcd. for $C_6H_6S_2$: C, 50.67; H, 4.25; S, 45.1. Found: C, 50.71; H, 4.26; S, 44.6. Franz Pascher Mykroanalytisches Laboratorium, Bonn, Germany.

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