Thiosulfoxides. The Intermediates in Rearrangement and Reduction of Allylic Disulfides

Sir:

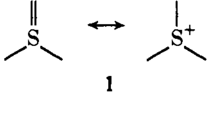
Although preparations of thiosulfoxides (**1**) have often been claimed physical, measurements always have shown that linear disulfide structures were involved.[1,2] However, the branched chain species difluoro disulfide[3] and thiono sulfites[4] have recently been isolated and so thiosulfoxides might in fact have independent existence. We now present evidence that such species (**1**) occur as intermediates in the rearrangement and desulfurizations of allylic disulfides.

We observed that α-substituted allylic desulfides **2**, R = H, and **2**, R = Me,[5] although stable below −20°, smoothly rearranged at room temperature in benzene to the more stable isomers **4**, R = H, and **4**, R = Me, respectively. This reaction proceeded entirely with double allylic inversion and was essentially quantitative (98% by nmr). The products were identical with authentic samples. In contrast to this facile transformation the mixed alkyl–allyl disulfides **5a** and **5b**[6] were thermally stable and could be purified by distillation (**5a**, bp 30–50° (oven) (0.2 mm); nmr (C_6H_6) δ 1.20 (d, J = 7 Hz, 3 H), 2.03 (s, 3 H), 3.30 (p, J = 7 Hz, 1 H), 4.7–5.0 (m, 2 H), 5.0–5.3 (m, 1 H); **5b**, bp 30–50° (oven) (0.2 mm); nmr (C_6H_6) δ 1.13 (s, 6 H), 2.04 (s, 3 H), 4.7–5.0 (m, 2 H), 5.6–6.0 (m, 1 H)).

This sharp difference in the stability of disulfides **2** and **5** is most simply rationalized by the operation, in the doubly allylic species **2**, of an intramolecular double [2,3]-sigmatropic rearrangement[7] proceeding through the intermediate thiosulfoxide as **3**. This reaction is closely related to the interconversion of allylic sulfoxides and sulfenates.[8] The rearrangements of **2** (R = H and R = Me) followed strictly first-order kinetics and measurement of the activation parameters by nmr spectroscopy for these conversions gave the values summarized in Table I. The negative entropy of activation is consistent with a cyclic transition state and is in good agreement with the values reported for the rearrangement of allylic sulfenates to sulfoxides (−5 to −10 eu),[8] which fact favors two consecutive [2,3]-sigmatropic processes, **2** to **3** and **3** to **4**, rather than the alternative single transition state **8**.

Table I. Rate Constants (at 24°) and Activation Parameters of the Rearrangement of **2** (0.2–0.3 M) in Benzene

	k, 10^{-4} sec^{-1}	Activation parameters
2 (R = H)	1.45	$\Delta H^{\ddagger} = 19.8 \pm 1$ kcal/mol; $\Delta S^{\ddagger} = -8.9 \pm 1$ eu
2 (R = Me)	8.0	$\Delta H^{\ddagger} = 18.7 \pm 1$ kcal/mol; $\Delta S^{\ddagger} = -9.7 + 1$ eu



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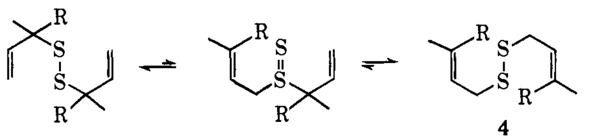
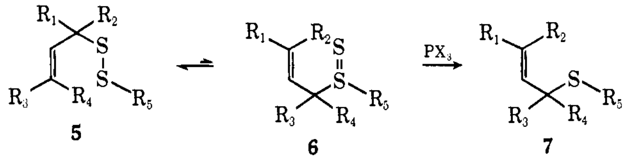
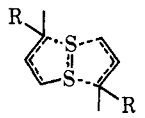


2 **3** **4**



5 **6** **7**



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	R_1	R_2	R_3	R_4	R_5
a	H	CH_3	H	H	CH_3
b	CH_3	CH_3	H	H	CH_3
c	H	H	CH_3	CH_3	CH_3
d	H	H	H	H	$CH_2CH{=}CH_2$
e	H	H	H	H	CH_3
f	H	C_6H_5	H	H	CH_3

In support of this interpretation we have obtained evidence for the intermediate **3** in these reactions by means of interception experiments. The desulfurization of polysulfides is a well-known process[9] and it has been demonstrated that allylic substituents provide an unusual enhancement of the rate of this reaction. Thus, allylic disulfides react with triphenylphosphine rapidly below 100°, whereas alkyl and aryl disulfides are stable to this reagent at 140° for long periods.[10,11] The mechanism of these processes and the origin of this difference is not clear[9,11] but it has been suggested[10,12,13] that branched chain intermediates may be involved. Briefly, the earlier work established that the desulfurization of allylic disulfides involves com-

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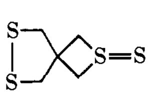
[1] O. Foss, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Elmsford, N. Y., 1961, pp 75–77.

[2] H. J. Backer and N. Evenhuis (*Recl. Trav. Chem. Pay-Bas*, **56**, 129, 174 (1937)) have prepared some bicyclic polysulfides and on the basis of strong chemical evidence assigned the thiosulfoxide structure, *e.g.*, i. We determined by nmr spectroscopy that ii is the correct



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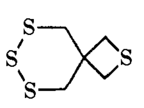

ii

structure.

[3] R. L. Kuczkowsky and E. B. Wilson, *J. Amer. Chem. Soc.*, **85**, 2028 (1963); F. Seel, R. Budenz, and D. Werner, *Chem. Ber.*, **97**, 1369 (1964).

[4] Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich, *J. Org. Chem.*, 30, 2969 (1965).

[5] These were obtained in quantitative yield by coupling (I_2–pyridine or I_2–$NaHCO_3$) the respective thiols at −40°. 3-Butene-2-thiol and 3-butene-2-thiol were obtained in 25–60% yield by cleavage of the respective butenyl methyl dithiolcarbonates with benzylamine or hydrazine at 120–140°, and distillation at 25° (10 mm). The dithiolcarbonates were obtained by rearrangement of the xanthates according to D. L. Garmaise, A. Uchyama, and A. G. McKay, *ibid.*, **27**, 4509 (1962).

[6] Prepared from butenethiols and methoxycarbonyl methyl disulfide (according to S. J. Brois, J F. Pilot, and H. W. Barnum, *J. Amer. Chem. Soc.*, **92**, 7629 (1970)) in high yield. These compounds gave correct combustion analyses.

[7] J. E. Baldwin, W. F. Erickson, R. T. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970), and references cited therein.

[8] R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 2100 (1970).

[9] D. N. Harpp and T. G. Gleason, *ibid.*, **93**, 2437 (1971), and references cited therein.

[10] F. Challenger and D. Greenwood, *J. Chem. Soc.*, 26 (1950).

[11] C. G. Moore and G. R. Trego, *Tetrahedron*, **18**, 205 (1962).

[12] D. Barnard, T. H. Houseman, M. Poeter, and B. K. Tidd, *Chem. Commun.*, 371 (1969).

[13] Values for **5a** and **5b** are extrapolated from several measurements at lower temperatures; all measurements by nmr, experimental error ±5–10%.

plete inversion of one allyl residue, that increasing volume of R_3, R_4, and R_5 in compound **5** strongly depresses the rate, increasing polarity of the medium slightly increases the rate, and finally, that no intermolecular interchange of groups occurs.[11]

These facts are completely in accord with the interception by triphenylphosphine of the intermediate **3**, postulated to occur in the conversions **2** to **4**, *vide supra.* Thus, in transformations of type **5** to **7**, increasing bulk of R_3, R_4, and R_5 would reduce the amount of thiosulfoxide (**6**) available for reduction to **7**, whereas increasing size of R_1 and R_2 would favor this intermediate and thereby enhance the rate of formation of **7**. We have verified this prediction by measurement of the rate of reduction of the allylic disulfides **5a–e**[6] by triphenylphosphine at 60°, Table II.[13] The thioether products **7a–e** were formed quantitatively and were identical with authentic samples.

Table II. Pseudo-First-Order Rate Constants of the Reduction of Disulfides **5a–e** with Triphenylphosphine (Benzene, 60°)

	5				
	c	e	d	a	b
k, 10^{-4} sec^{-1}	0.70	8.6	8.9	140	190

The great tendency of the thiosulfoxide intermediate **6** to expel the thionsulfur may be observed in **5e** and **5f**, which lose sulfur spontaneously at 25° to yield sulfides **7e** and **7f**, respectively. The direct observation of **6** has not been achieved since methanol solutions of **5e** and **5f** showed no additional signals (>2%) and decomposed faster than neat samples into **7e** and **7f**.

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(14) A. P. Sloan Fellow, 1969–1971.

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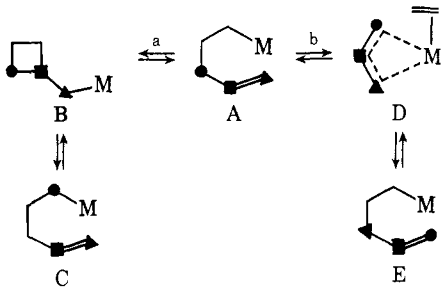
Homogeneous Catalysis of Diene Rearrangements *via* a Carbon–Metal β Elimination

Sir:

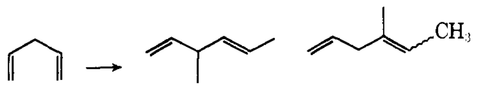
We wish to report extensive evidence for a new type of transformation in homogeneous catalysis, a carbon–metal β elimination. The nickel-catalyzed skeletal rearrangements of 1,4-dienes[1] are explained in terms of the chemistry of alkenylnickel species derived from 1,2 and 2,1 addition of nickel hydride to a terminal double bond.[2] The 1,4-pentadiene to isoprene rearrangement (herein referred to as the type I rearrangement) is pictured as involving a 2,1 nickel hydride adduct while the skeletal change exemplified by the 3-methyl-1,4-pentadiene to 1,4-hexadiene transformation (type II) is believed to involve a 1,2-nickel hydride adduct. For a given 1,4-diene, these are companion reaction paths, although in most cases only one type of reaction is detected. The competing route usually regenerates the carbon skeleton of the 1,4-diene reactant. We have reported evidence which suggests that the type I rearrangement proceeds *via* a cyclopropylcarbinylnickel derivative.[4]

Two reaction paths are considered to be serious candidates for the type II rearrangement (Scheme I). Path a entails the formation of a cyclobutylcarbinylnickel derivative, B, which on ring opening could afford rearrangement product C.[5] Path b is the reverse of the proposed addition step in the codimerization of alkenes and 1,3-dienes by nickel catalysts,[2a,3] a carbon–nickel β elimination. Scheme I describes the fates predicted by paths a and b for carbons in the 1,4-diene reactant.

Scheme I



While path a is intuitively attractive in view of results obtained in studies of the type I rearrangement, three lines of evidence have demanded serious consideration of path b. (1) Treatment of 3-methyl-1,4-pentadiene with the catalyst in the presence of propylene afforded significant quantities of 2-methyl-1,4-hexadiene,[1] the major product obtained when propylene is added to 1,3-butadiene by the same catalyst.[3] (2) We have discovered that product mixtures derived from treatment of 1,4-pentadiene with the catalyst over extended periods of time (1.5–3.0 hr) contain 3-methyl-1,4-hexadiene, 9–30% yields, and 4-methyl-1,4-hexadiene, 3–15% yields, in addition to the isomeric 1,3-pentadiene and isoprene. The yields of C-7 dienes were dependent upon the olefin-Ni ratio and reaction time employed. These C-7 dienes are those afforded by addition of ethylene to 1,3-pentadiene and isoprene, respectively, by the nickel catalyst.[3] (Thus, dienes seemingly derived from *both* path b hydrocarbon fragmentation products, methylallyl from observation 1, and ethylene from observation 2 have been isolated.) (3) We have never observed the formation of 1,5-dienes which, in addition to the observed 1,4-dienes, are expected prod-



(1)

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[1] R. G. Miller, *J. Amer. Chem. Soc.*, **89**, 2785 (1967).

[2] Support for our supposition[1,3] that nickel hydride transfer plays an important role in these reactions has recently been advanced: (a) C. A. Tolman, *ibid.*, **92**, 6777 (1970); (b) R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, *J. Organometal. Chem.*, **29**, C42 (1971); (c) L. W. Gosser and G. W. Parshall, *Tetrahedron Lett.*, 2555 (1971).

[3] R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Amer. Chem. Soc.*, **89**, 3756 (1967).

[4] R. G. Miller, P. A. Pinke, and D. J. Baker, *ibid.*, **92**, 4490 (1970).

[5] Evidence for this route in organomagnesium, sodium, and lithium chemistry: (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964).