scrambling seems to take place in ions IIIa and IVa. This is suggested by the fact that quenching experiments prior to complete photoconversion of either III or IV failed to yield any neutral dienone other than the original one. A IIIa ⇄ VI ⇄ IVa equilibrium would be detected in the recovered neutral dienones. Since the rate of cyclopropane migration is very sensitive to the electron-donating ability of substituents on the cyclopropane bridge,[11] it is conceivable that the electron-withdrawing effects of the dichloromethyl group forces the thermal conversion of both IIIa and IVa entirely in the direction of VI, the most stable cation.[13]

The fact that both III and IV yield the same photoproduct strongly supports the suggestion of a common intermediate in both reactions. The absorption band centered at 258 nm in Figures 1a and 1b was associated with this intermediate, ion VI. Its presence in the III → V photoconversion (Figure 2) would be masked by the absorption of III. Furthermore, since the excitation light would be strongly absorbed by the intermediate, its concentration would remain small due to efficient conversion to V. The identity of VI is suggested by the isolation of bicyclo[3.1.0]hex-3-en-2-ones from photochemical rearrangements of other cyclohexadienones[14] and by the stabilizing effect of the $CHCl_2$ group in ion VI against thermal rearrangement. Since all spectra in Figures 1 and 2 remain unchanged in the dark it is obvious that an additional photon is required for rearrangement to VII.

The photoconversion of VI to VII is readily understood (see Scheme I). Theoretically, cyclopropane opening and methyl 1,2 migration can take place in the alternative direction to yield eventually 2-methyl-3-hydroxybenzaldehyde. The fact that none was isolated is consistent with the previous observed dependence of isomer distribution on acidity.[15]

Acknowledgment. This work was supported by National Aeronautics and Space Administration Grant No. NGL-09-010-008. Financial assistance from The Research Committee of George Washington University is also gratefully acknowledged.

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[13] Admittedly, hydrolysis of the dichloromethyl group could take place prior to formation of VII. The sequence shown is suggested by the known susceptibility of the $CHCl_2$ group toward hydrolysis when attached to an aromatic residue and the contrasting stability when connected to an alkyl moiety.

[14] P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967.

[15] H. E. Zimmerman, R. Keese, J. Nasielski, and J. W. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

[16] Postdoctoral Research Scientist, 1969–1970.

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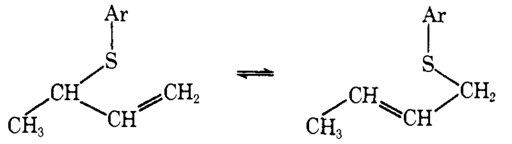
The Antipolar Mechanism of Thermal Allylic Rearrangements

Sir:

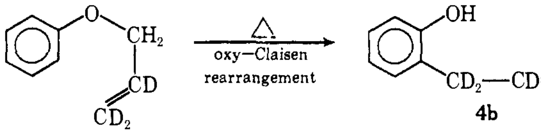
A striking example of 1,3-sigmatropic rearrangement[1] where a p orbital is binding the migrating group to the carbon skeleton[2] appears to have been established[3] for triallylboron ($E_a \cong 11$ kcal/mol). While it is possible that this does not qualify as a concerted process because it may involve a zwitterionic intermediate, it cannot be classified with mechanisms analogous to solvolytic allylic rearrangement, where an ion pair intermediate is formed.

A thioallylic rearrangement (eq 1) which is formally analogous to the triallylboron rearrangement has been previously invoked by us[4] to explain the course of the thio-Claisen rearrangement of **1** and **2** (and related compounds). This observation has been recently confirmed by others[5] studying the thermolysis of α-methylallyl 2-quinolyl sulfides. We are now able to discuss our studies of the thioallylic rearrangement of allyl aryl sulfides which suggest that the reaction course is unprecedented among allylic rearrangements[6] and warrants reexamination of the evidence upon which previous reports[3,7] of such thermally induced reactions have been based.



1 **2** (1)

Support for this claim stems from the synthesis of the appropriately deuterated allyl phenyl sulfide **3a** (C_6H_5—S—CD_2—CH=CH_2). The rate of its isomerization to the isotopic equilibrium composition (eq 3) could be readily pursued by nmr, and the activation parameters determined in this manner for reaction in a wide variety of solvent media are listed in the Table I. On the other hand, an oxygen analog of **1** (namely **4a**) showed no change of constitution after more than 5 hr of heating at 160°. Moreover, when this deuterated phenyl allyl ether was heated at 195° for 16 hr, the only product of Claisen rearrangement (eq 2) was **4b**, indicating that even at the elevated temperatures, no (prior) thermal oxyallylic rearrangement[8] had taken place.



4a **4b** (2)

The photooxyallylic rearrangement at ambient temperatures also could not be realized. Thus, when a

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[1] See for full discussion, R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[2] J. A. Berson, *ibid.*, **1**, 152 (1968).

[3] B. M. Mikhailov, V. S. Bogdonov, G. V. Lagodzinskaya, and V. G. Pozdnev, *Chem. Abstr.*, **65**, 595c (1966).

[4] H. Kwart and M. H. Cohen, *Chem. Commun.*, 319 (1968). This rearrangement (eq 1) had been previously investigated by A. C. Cope, D. E. Morrison, and L. Field (*J. Amer. Chem. Soc.*, **72**, 59 (1950)) and declared to have failed. We now can report direct measurement of the rate of rearrangement by glc separation of **1** and **2**. A full account of this work is being prepared for publication.

[5] Y. Makisumi and A. Murabayashi, *Tetrahedron Lett.*, 1975 (1969).

[6] E. A. Braude, *Quart. Rev., Chem. Soc.*, **4**, 404 (1950).

[7] M. Leguan, G. Guillerm, and A. Jean, *C. R. Acad. Sci., Ser. C*, **268**, 1542 (1969).

[8] Under more severe conditions γ-^{14}C allyl ether of 2,4,6-trimethylphenol experiences some distribution of its radioactivity between the α and γ carbons of the allyl group. This result was accounted for, not by an assumed oxyallylic rearrangement, but rather *via* a stepwise ortho–ortho rearrangement which is disallowed by the Woodward–Hoffmann selection rules;[1] see P. Fahrni and H. Schmid, *Helv. Chim. Acta*, **42**, 1102 (1959).

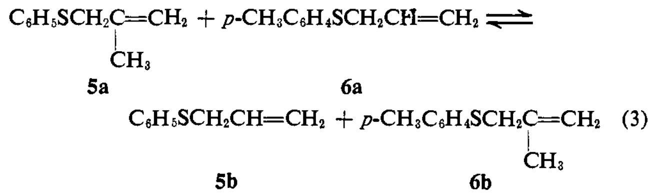
Table I. Activation Parameters in Thermal Allylic Rearrangements

Solvent	$\Delta H^{\ddagger}$, kcal/mol[b,c]	$\Delta S^{\ddagger}$, eu[b]	$\Delta G^{\ddagger}$, kcal/mol[c]	Dielectric constant[a]
	$\mathbf{3a} \underset{77-161°}{\rightleftharpoons} \mathbf{3b}^{e}$			
N-Methylacetamide (NMA)	33.2 ± 1.0	−0.5 ± 2.4	32.4	~200
Nitrobenzene	31.8 ± 0.5	−1.1 ± 1.2	32.3	34.1
o-Dichlorobenzene	24.2 ± 0.5	−21.0 ± 1.2	33.0	9.82
Decalin	23.2 ± 0.7	−23.2 ± 1.8	32.7	2.11
	$\mathbf{1} \underset{\text{gas phase}}{\rightleftharpoons} \mathbf{2}^{f}$			
	34.5 ± 0.4[d]	−7.9 ± 0.7		

[a] Measured at 20°. [b] Determined from rate data at seven temperatures within the range indicated. [c] Calculated at 119° mean temperature. [d] Calculated at 350° mean temperature. At the extremely high dilutions, and short reaction time of the gas phase,[e] it is presumed that the pure unimolecular mechanism is experienced as the most rapid reaction. [e] The method employed for determination of gas-phase thermolysis kinetics involves a flow system which minimizes the possibility of catalytic wall reaction. The details of apparatus and procedure are discussed by H. Kwart, S. Sarner, and J. Olson, *J. Phys. Chem.*, **73**, 4056 (1969). [f] $k_1 = 6.76 \times 10^{11}e^{-36,700/RT}$ sec^{-1}.

thin layer (*ca.* 2 mm) of **4a** in a quartz cell, neat or in CCl_4 solution, was irradiated at room temperature with an xenon arc (Osram), no measurable reaction (of any kind) was noticed after 4 hr. Under exactly the same circumstances the analogous thio compound **3a** was completely isomerized to the equilibrium composition with **3b**. Apparently, thioallylic rearrangement is mobilized by both thermal and photochemical means, but the oxyallylic analog cannot be made to occur with comparable mobility, if at all.[8]

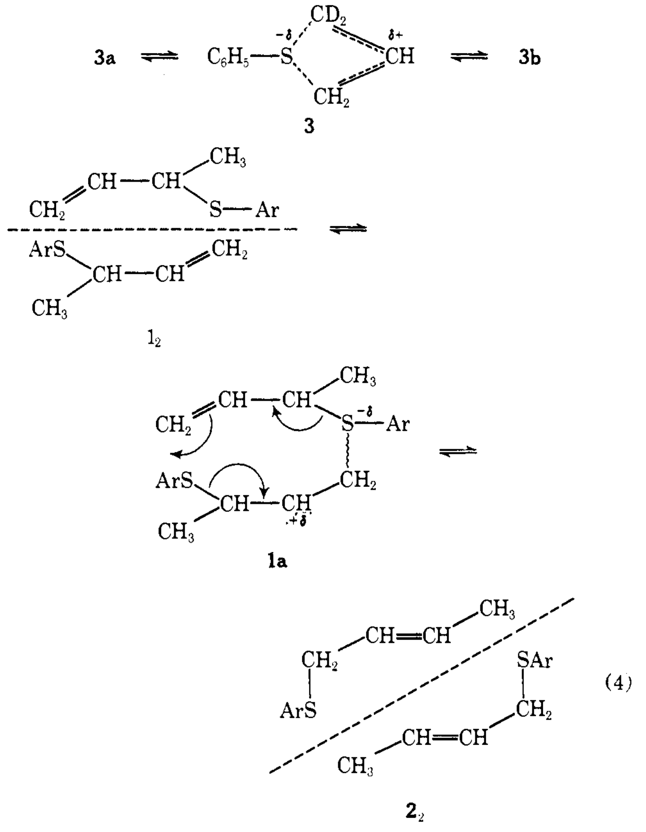
The kinetic order of rearrangement of **3a** was established as unimolecular by carrying out the reaction in widely varying concentrations. In *N*,*N*-dimethylacetamide, for instance, the rate was independent of $[\text{substrate}]_0$ over a *ca.* 50-fold range. However, when two different substrates (**5a** and **6a**) were isomerized in each other's presence, crossed products resulted (eq 3); that is to say, in addition to the two autorearranged products (which are identical with the starting materials in each case), two crossed products (**5b** and **6b**) were obtained in comparable yield under the usual reaction condition.



$$\underset{\mathbf{5a}}{C_6H_5SCH_2\underset{\displaystyle CH_3}{C}{=}CH_2} + \underset{\mathbf{6a}}{p\text{-}CH_3C_6H_4SCH_2CH{=}CH_2} \rightleftharpoons \underset{\mathbf{5b}}{C_6H_5SCH_2CH{=}CH_2} + \underset{\mathbf{6b}}{p\text{-}CH_3C_6H_4SCH_2\underset{\displaystyle CH_3}{C}{=}CH_2} \quad (3)$$

The conclusion to be inferred from this result is that the thioallylic rearrangement can take place by two different mechanisms, one a unimolecular and the other a bimolecular (crossed-product) process. In the unsubstituted allyl cases (**3a** or **6a**) the unimolecular process is much faster than the bimolecular, especially at ordinary concentrations (*ca.* 10% solution); but, where unimolecular rearrangement is undetectable (*i.e.*, **6a** ⇌ **6a** and **5a** ⇌ **5a**), the crossed-product result (eq 3) is the only one visible. Moreover, the concurrence of competing unimolecular and bimolecular processes can be readily perceived in the case of the α-methallyl → crotyl rearrangement (at equilibrium, 5% **1** ⇌ 95% **2**). Here we observe a clear dependence of rate on $[\text{substrate}]_0$; the plot of log $C - C_\infty$ *vs.* time is strongly curved at higher concentrations (*ca.* 1.0 *M*) and becomes nearly linear at high dilutions.

The simplest interpretation of these data requires initial formation of a transient complex, either intra- or intermolecularly, between the olefin and sulfur termini of the thioallylic system. Alkyl substitution on the allyl chain appears to hinder formation of a unimolecular complex like **3** and favor a bimolecular complex like **1a** (in eq 4).



An alternative picture involving prior ionization of the -C-S- bond and formation of ion pairs is inconsistent with the fact that the reaction proceeds nearly as rapidly in the gas phase,[9] without the benefit of solvent assistance.[10] On the other hand, the rate response to solvent (see Table I), and the activation parameters in the various solvents can be readily construed to support the structure of the intermediate

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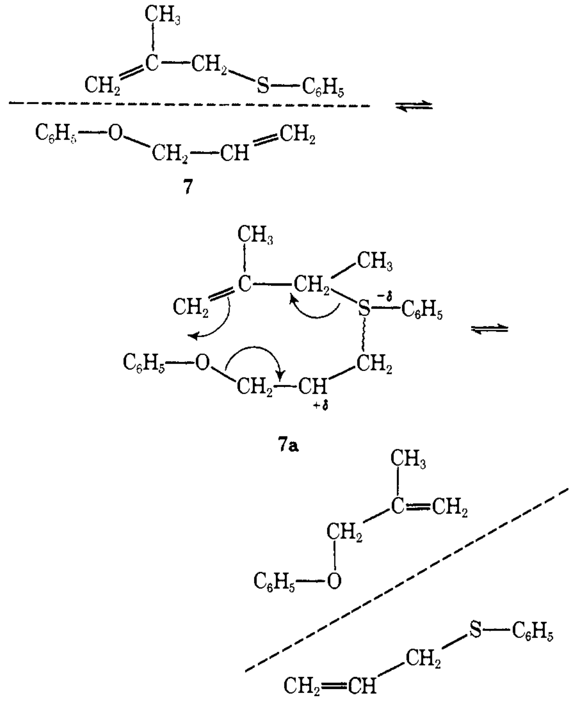
(9) H. Kwart and M. T. Waroblak, *J. Amer. Chem. Soc.*, **89**, 7145 (1967).

(10) A. Iliceto, A. Fava, U. Mazzucatto, and O. Rossetto, *ibid.*, **83**, 2729 (1961).

complex **3**. Thus, the conspicuously smaller values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the nonpolar solvent decalin (see Table I) compared to the polar solvents nitrobenzene and *N*-methylacetamide are quite inconsistent with a normal ionization mechanism.[11,12] Clearly, also, they are not characteristic of sigmatropic and electrocyclic rearrangements[1] in which solvent effects are normally absent. Rather than a nonpolar mechanism, these data indicate we are dealing with a unique transition state in which the charge separation of a lower lying intermediate is being destroyed (as illustrated in passing from **3** to **3a** or **3b**) (eq 4), and might be designated more appropriately as an antipolar mechanism. The negative $\Delta S^{\ddagger}$ values for such reactions taking place in the gas phase, and in decalin, are in keeping with the postulated mechanism.

The assumption of an intermediate complex such as **3** or **1a** in thermal allylic rearrangements is compelled by another crossed-product experiment (**7** $\rightleftharpoons$ **8**). Thus, while the oxyallylic rearrangement does not occur in pure allyl phenyl ether, a crossed-product isomerization does take place in the presence of allyl phenyl sulfide (eq 5). Presumably, the principal reason for the (observed) slower reactions here lies in the nature of the mixed complex **7a**. Though its formation is made possible by the ability of (one) sulfur to expand its octet,[13] the presence of oxygen instead of a second sulfur (as in **7a**) enforces sigmatropic change with a stricter requirement for concertedness.



7

7a

8

(5)

A point of further interest is the effect of the substituent[13] on the sulfur atom. It is found that rearrangement of the homologous compound $C_6H_5CH_2SCH_2CD{=}CD_2$ occurs at a (more than) 50 times slower rate both thermally and photochemically. Apparently the efficiency with which sulfur accepts electronic charge by octet expansion, a necessary step which oxygen cannot accommodate, is somewhat dependent on the nature of the sulfur substituents.

Finally, we have considered the possibility of a radical pathway analogous to what has been established for certain 1,3-thermal sigmatropic rearrangements occurring in homoallylic systems.[14] The search for identifying emissions in nmr nuclear polarization experiments with substrates like **1** and **3** in solution at various temperatures up to 180° have been unfruitful. Moreover, the total lack of disulfide and other characteristic side products under any of the reaction circumstances discussed in this report comprises the most telling argument against the operation of a radical dissociation–recombination process. Any occurrence of aryl thiyl radicals in the (even neat) bimolecular reaction should certainly have led to some diphenyl disulfides, but no such products, even in traces, were observable. We know of no cases[15] where aryl thiyl radical intermediates have been implicated in which corresponding diaryl disulfides and related side products are not formed. Having applied all presently available criteria to eliminate a radical mechanism of thioallylic rearrangement, we conclude that this hitherto unknown reaction proceeds by a previously unfamiliar reaction course.[16]

Acknowledgment. We are obliged for advice and helpful suggestions made by Professor P. D. Bartlett in the preparation of our manuscript. Support through a grant by the donors of the Petroleum Research Fund of the American Chemical Society is also gratefully acknowledged.

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(11) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

(12) W. H. Saunders, Jr., and J. C. Ware, *J. Amer. Chem. Soc.*, **80**, 3328 (1958). The data presented by these authors demontrate that, in a thermal rearrangement involving charge development in the transition state rather than charge destruction, the opposite order of solvent effect is to be observed; *i.e.*, the more polar solvent is associated with smaller $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

(13) The assumption that the sulfur acquires *negative charge* through octet expansion in the complex **7a** is supported by two lines of evidence: (1) the oxygen analog in which such octet expansion is not possible does *not* undergo allylic rearrangement except with the assistance of a mole of allyl thiophenyl ether, and (2) substituent effect studies in para-substituted allyl thiophenyl ethers show measurable rate enhancement by electron-withdrawing substituents, $\rho_H \cong +1.0$; these latter results will be considered in detail in a future publication.

(14) J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, **91**, 3647 (1969).

(15) See for examples H. Kwart and M. H. Cohen, *J. Org. Chem.*, **32**, 3135 (1967).

(16) Note Added in Proof. The possibility that a thioallylic rearrangement could be made to occur *via* free-radical intermediates involving reaction circumstances other than those discussed in this report is currently under investigation in these laboratories.

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Nitrogen-15 Magnetic Resonance Studies. Further Evidence for the Dependence of $^1J(^{15}NH)$ on the Hybridization of Nitrogen

Sir:

Recently we reported[1] a substituent effect on the one-bond ^{15}N–H coupling constant in a series of aniline derivatives where $^1J(^{15}NH)$ in dimethyl sulfoxide (DMSO) solution was found to vary from 79.4

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(1) T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Amer. Chem. Soc.*, **91**, 3681 (1969).