Mechanism of Diphenyl Disulfide Catalysis of the Thermal Thia-allylic Rearrangement

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The effects of added concentrations of PhSSPh in solutions of deuterated allyl phenyl sulfide follow the rate law $k_0 = k_c[\text{cat}]^{1.0}$. Neither allyl cyclohexyl sulfide nor propyl phenyl sulfide shows a significant tendency to undergo thia-allylic rearrangement in the presence of an equivalent amount of PhSSPh. These and other pertinent considerations appear to disqualify all radical chain mechanisms or dissociation–recombination processes of catalysis. The evidence is arrayed in support of a mechanism involving initial formation of a trigonal-bipyramid complex of catalyst and substrate, followed by a rate-determining pseudorotation step which occurs over a lower barrier than in the uncatalyzed complex.

Since their discovery[1] in 1970, thermal thia-allylic rearrangements have found applications in synthesis.[2] Recent efforts to elucidate the mechanism of the thermal rearrangement, which is not experienced by first-row elements, have brought to light the necessity for an octet-expansion step,[3] presumably involving a trigonal-bipyramid intermediate undergoing the required act of permutational isomerism (pseudorotation) in the rate-determining step.[4]

Catalysis of the thia-allylic rearrangement has been the subject of considerable interest.[2,5] Warren and co-workers[6] have advocated a variety of catalytic mechanisms ranging from radical chain processes[6,7] to allyl cation-intermediated, dissociation–recombination processes.[8] Such speculations claim, in effect, that the catalyzed thia-allylic rearrangement represents a complete departure from the established sulfur octet-expansion mechanism of the uncatalyzed thermal reaction.[3,4] However, the lack of substantiation by careful kinetic studies and experimental controls raises some doubt as to the validity of such conclusions. Moreover, the converse conclusion, namely, that the essential features of the uncatalyzed mechanism are retained in the course of powerful catalysis by both singlet and triplet oxygen species, has been verified through kinetic studies discussed in a recent communication from these laboratories.[5] These results are closely consistent with the assumption of a trigonal-bipyramid intermediate complex in which the central sulfur atom enjoys a state of higher hypervalency stemming from initial coordination with the catalytic species. The catalytic effect is a derivative of the fact that the ease of permutational isomerism increases with increasing hypervalency of the central atom; for example, a >15 kcal lowering of the barrier to permutational isomerism in $C_6H_5SF_3$ is produced by traces of HF.[9]

All the catalysts of thermal thia-allylic rearrangement we have investigated thus far appear to follow the same rate law (eq 2), expressing clean first-order dependency on the initial concentration of the catalyst. That is to say, none of the catalysts studied previously is consumed or permanently altered in the course of exerting its influence, and all participate with the first-power concentration dependency expressed by this rate law.

Against this background we have undertaken to characterize the catalytic effect displayed by additions of diaryl disulfides on the rates and product compositions derived from thermal thia-allylic isomerizations.

Results

Addition of diphenyl disulfide to a thermally isomerizable solution of deuterated allyl phenyl sulfide (1 ⇌ 1a) increases the rate of reaction in accordance with the previously noted[5] relationship (eq 2), where $[S_e]$ is the equilibrium concentration of the thia-allylic substrate and $[S_0]$ is its initial concentration;

k_0, k_1, and k_2 are the respective observed, unimolecular, and bimolecular rate constants; k_c is the catalytic coefficient of the catalyst at constant concentration designated by [cat].
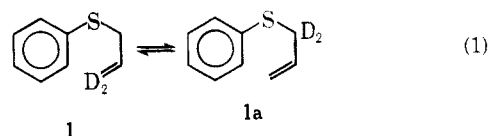

$$k_0 = -\ln ([S] - [S_e])/2t = (k_1 + k_2[S_0]) + k_c[\text{cat}]^{1.0} \quad (2)$$

A series of observed rate constants determined at different concentrations of diphenyl disulfide is listed in Table I. The plot of k_0 vs. [PhSSPh] was found to be perfectly linear over the entire range of catalyst concentrations studied ($0 \rightarrow 1.0$ M). The catalytic coefficient ($k_c = 7.25 \pm 0.05 \times 10^{-5}$ M^{-1} s^{-1}) was calculated from the slope of this plot (Figure 1) in the course of a regression analysis.[10]

When allyl p-tolyl sulfide (2) was rearranged in the presence of diphenyl disulfide, the crossed product (eq 3) could be identified in the product composition. Similarly the reverse reaction took place when the allyl phenyl sulfide was rearranged in the presence of some p-tolyl disulfide. Under exactly
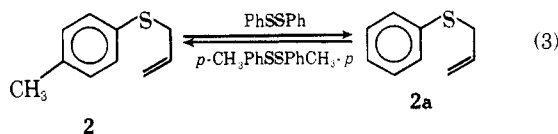
the same conditions the (nonallylic) propyl phenyl sulfide (3) did not undergo the exchange with p-$CH_3PhSSPhCH_3$-p to give 3a.
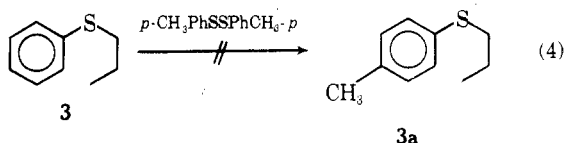
When phenyl is replaced by alkyl, as in allyl cyclohexyl sulfide (4), it has been previously shown that thia-allylic rearrangement does not occur to any significant extent under conditions which rapidly bring about the isomerization 1 ⇌ 1a. Attempts to exchange 4 with PhSSPh have resulted in less than 1% of 4a after a prolonged period of heating under con-

ditions which effect nearly complete exchange according to

Table I. Effect of PhSSPh on the Rate of Rearrangement (1 ⇌ 1a) at 0.954 M Substrate in Dichlorobenzene at 160.0 °C^a

$k_{obsd} \times 10^4\,s^{-1}$	[PhSSPh], M	$k_{obsd} \times 10^4\,s^{-1}$	[PhSSPh], M
0.162	0	0.530	0.491
0.192	0.071	0.675	0.701
0.248	0.100	0.860	0.972
0.380	0.312		

^{a} k_c = 7.25 ± 0.05 × 10^{-5} M^{-1} s^{-1} (calculated).

Figure 1. Plot of k_{obsd} vs. (PhSSPh) for the rearrangement of 1 to 1a in dichlorobenzene at 160.0 °C.

eq 3 in a fraction of the heating time at the same temperature.

Discussion

The Role of the Phenyl Group in Allyl Phenyl Sulfide Catalyzed Thermal Isomerization. The indispensability of the electronegative phenyl substituent on sulfur in bringing about the thia-allylic rearrangement has been correlated[4] with the requirements for octet expansion among third-row elements. In accordance with the preference rule,[11] the apical positions would be preferentially occupied by the more electronegative substituents in the stabilized trigonal-bipyramid intermediate implicated in the isomerization process. From many sources[12] it is now apparent that the barrier to pseudorotation parallels the apicophilicities of the TBP ligands; such electronegativity effects may control the ease of pseudorotation, though they may not entirely prevent its occurrence.

The fact that allyl cyclohexyl sulfide does not undergo rearrangement, or only very reluctantly, both in the uncatalyzed and disulfide catalyzed cases, would suggest that the catalyzed reaction is not strikingly different in its mechanistic requirements; i.e., pseudorotation (permutational isomerism)[13] is the rate-determining step in both cases. It therefore seems reasonable to assume that octet expansion is also involved in the disulfide-catalyzed process; this deduction is supported by analogy to the oxygen-catalyzed mechanism,[5] wherein an initially formed donor complex between catalyst and substrate is structured as a trigonal-bipyramid centered on a hypervalent sulfur atom. In the case of disulfide catalysis, this structure is capable of undergoing rearrangement, here accompanied by exchange, at a faster rate than was characteristic of the trigonal-bipyramid centered on a sulfur with less polar ligands.

Mechanistic Possibilities. (A) The Radical Dissociation–Recombination Process. Considerable evidence[14] has been advanced suggesting that thermal homolysis of the S–S bond in diaryl disulfides proceeds at relatively low temperatures (30–150 °C), although some reservations have also been expressed.[15,16] For example, Leandri and Tundo[17] found clear evidence of unsymmetrical disulfides dissociating homolytically to give symmetrical diaryl at 170 °C. This can be accepted as the basis for assuming that, at the temperatures which bring about thermal isomerization and exchange of allyl phenyl sulfides in the presence of diphenyl disulfide, a certain extent of arylthiyl radical concentration does exist in the catalytically isomerizing solution; but do these thiyl radicals intermediate the course of the disulfide-catalyzed thia-allylic rearrangement?

This possibility has been considered in the work of Krusic and Kochi[18] who observed that when dimethyl disulfide is photolyzed in the presence of allyl methyl sulfide (6) in the cavity of an ESR spectrometer the symmetrical radical 6a is generated. The photochemical mechanism postulated is expressed by eq 6.

$$CH_3SSCH_3 \rightleftharpoons 2CH_3S\cdot$$

$$\underset{6}{CH_3S\cdot + CH_2\!\!=\!\!CHCH_2SCH_3} \rightleftharpoons \underset{6a}{CH_3SCH_2\dot{C}HCH_2SCH_3}$$

(6)

It is thus made conceivable that the disulfide-catalyzed thia-allylic rearrangement could involve attack of an arylthiyl radical in a Michael-type adduct with 1. This step could be the vehicle for (both) enhancement of the isomerization rate as well as the exchange reaction yielding crossed product, as expressed in eq 7.

$$ArS\cdot + CD_2\!\!=\!\!CHCH_2SPh \rightleftharpoons \underset{7}{(ArSCD_2\dot{C}HCH_2SPh)}$$

$$\rightleftharpoons ArSCD_2CH\!\!=\!\!CH_2 + PhS\cdot \quad (7)$$

This mechanistic scheme, however, can be discounted for several reasons stemming from the kinetic results presented above. One reason is that the Krusic–Kochi path[18] has been shown to be equally accessible to allyl alkyl and allyl aryl sulfides, since the effect of the sulfur substituent on the stability of the intermediate radical 6a is damped by separation from the carbon radical center. Consequently, this mechanism does not explain the indispensability of an electronegative aryl substituent on sulfur which has been found here to be characteristic of both the catalyzed and uncatalyzed thia-allylic cases.

The second and most telling argument against the radical dissociation–recombination pathway of catalysis is its failure to account for the catalytic kinetics as seen from the following kinetic analysis of this mechanism in the case of 1 ⇌ 1a in the presence of PhSSPh.

$$PhSSPh \overset{K_{eq}}{\rightleftharpoons} 2PhS\cdot$$

$$\underset{A}{PhS\cdot + CD_2\!\!=\!\!CHCH_2SPh} \overset{k_c}{\underset{k_{-c}}{\rightleftharpoons}} 7$$

$$\overset{k_c}{\underset{k_{-c}}{\rightleftharpoons}} \underset{B}{PhSCD_2CH\!\!=\!\!CH_2 + PhS\cdot}$$

$$-d[A]/dt = k_c[PhS\cdot][A] - k_{-c}[PhS\cdot][B]$$

where $k_c = k_{-c}$, and [B] = [A$_0$] − [A]

$$-d[A]/dt = k_c[PhS\cdot](2[A] - [A_0])$$

and at equilibrium

$$0 = k_c[\text{PhS·}](2[\text{A}_e] - [\text{A}_0])$$

where $[\text{A}_e]$ = equilibrium [A], and $[\text{A}_0]$ = initial [A]. Thus, by substraction:

$$-\text{d[A]}/\text{d}t = 2k_c[\text{PhS·}]([\text{A}] - [\text{A}_e])$$

and by integration

$$\ln ([\text{A}] - [\text{A}_e])/2t = k_0 = k_c[\text{PhS·}] + \text{constant}$$

but, since

$$[\text{PhS·}] = K_{eq}^{1/2}[\text{PhSSPh}]^{1/2} = [\text{cat}]^{1/2}$$

$$k_0 = k_c[\text{cat}]^{1/2} + \text{constant} \qquad (8)$$

This mechanism which, according to the derived eq 8, predicts that the catalytic coefficient k_c is dependent on the half-power of the catalyst concentration is completely at variance with the experimental data (Table I, Figure 1) which corroborate unequivocally a first-power dependency. In fact, it should be evident that any catalytic mechanism involving preliminary dissociation of diphenyl disulfide into phenylthiyl radicals cannot fit the observed kinetic dependencies. When taken in conjunction with the observation that propyl phenyl sulfide (3) does not undergo aryl exchange with p-tolyl disulfide, all mechanisms based on radical displacement on sulfur are also eliminated from consideration.

(B) The Process of Rearrangement in the TBP Structure of the Substrate–Catalyst Complex. The rapidly reversible formation of a donor complex between disulfide and the allyl aryl sulfide, pictured in eq 9, is fully supported by the
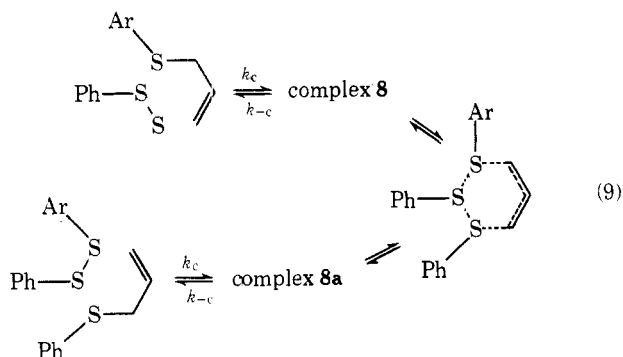
experimentally determined kinetic dependencies (eq 2). However, this is only a specious representation of the bonding changes which must occur and their thermodynamic consequences. Assuming that such a complex would have a TBP structure (although a square pyramid formulation (sp) or a distorted TBP are not excluded),[19-21] there must be at least two such complexes, one formed by apical attack of the disulfide on the reactant yielding complex **8** and the other formed analogously with the product yielding the complex **8a**. Since apical and basal bonds are of unequal energies, it is obvious that **8** and **8a** cannot be interconverted without the intervention of an energy-expending step. That is to say, since a complex arises by forming the appropriate apical bonds between the catalyst and substrate reaction centers, it can revert to these (equilibrium) components only by breaking the same kinds of apical bonds. The energy expenditure involved in the apical–basal bond transformations (**8** $\rightleftharpoons$ **8a**) corresponds to the familiar pathway of permutational isomerism; i.e., the rate-determining step in the disulfide-catalyzed reaction must occur as a polytopal rearrangement process.[13] An increase in rearrangement rate stemming from such catalysis is the consequence of lowering the so-called pseudorotation barrier of sulfur by creating a TBP complex between substrate and catalyst possessing ligands of higher apicophilicity.[12a-d]
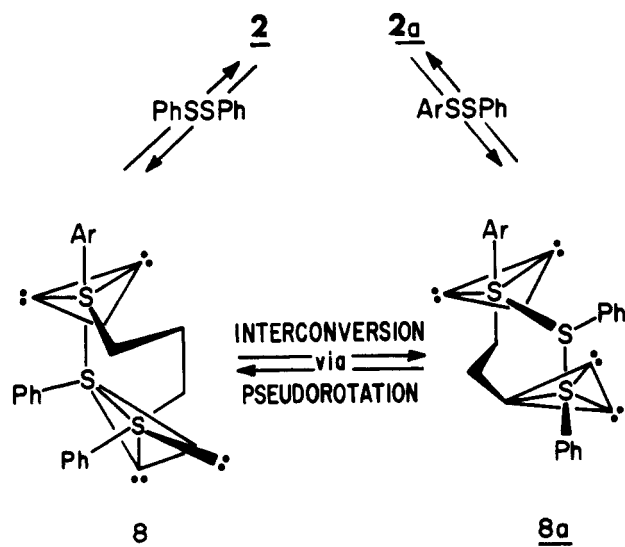
Finally, it must be clear that, although the action of diaryl disulfides in accelerating the thia-allylic rearrangement has here been identified as catalysis, these reagents are not truly catalysts; that is to say, a true catalyst would be a reagent that participates in the rate-determining step of the rearrangement and arrives at the product stage without experiencing an alteration of its structure. The title subject is therefore not to be regarded as a catalyzed thia-allylic rearrangement but rather as an analogous bimolecular reaction mechanism.

Experimental Section

General. NMR measurements were recorded on a Varian Associates A-60 spectrometer equipped with an electronic digital voltmeter. Spectral data are recorded in δ (ppm) with reference to Me_4Si in carbon tetrachloride solution. Mass spectral data were obtained using a Model C.E.C. 21-110B double-focusing, high-resolution, mass spectrometer. The GLC analyses were performed on an F & M Model 700 flame-ionization gas chromatograph. An injection-port temperature of 250 °C, detector temperature of 270 °C, and a flow rate of 40 mL/min were maintained throughout.

Kinetic Procedures. Sulfide and disulfide solutions of specified molarity were syringed into 5-mm o.d. Pyrex or NMR tubes. The contents were then thoroughly degassed on a high-vacuum line by freeze–pump–thaw cycling and the tubes sealed at 0.01–0.05 mm pressure. All tubes were thoroughly cleaned with chromic acid cleaning solution, rinsed with H_2O, dilute NH_4OH, and distilled H_2O, and annealed in an oven before use. The solvent, o-dichlorobenzene, was distilled twice before use. The disulfides (Aldrich) were purified by recrystallization from ethanol–water.

Kinetic runs were carried out at 160 °C in an oil bath equipped with a power-proportionating temperature controller. Temperatures were controlled to within ±0.05 °C. Rates and standard deviations were calculated on a Wang 700 programmable calculator equipped with a print-out system. Standard deviations were calculated on the basis of a 95% confidence interval and rate constants were reproducible to within ±2%.

Preparation of Allyl-*3,3-d₂* Chloride. Allyl-$3,3$-d_2 alcohol[22] (5 g, 0.0835 mol) and pyridine (7.1 g, 0.090 mol) were combined in a 25-mL flask equipped with a short distilling column and dropping funnel. The flask was cooled to −60 °C with dry ice–acetone and SOCl_2 (10.7 g, 0.090 mol) was added dropwise. After addition was complete, ca. 15 min, the contents of the flask were warmed to 45 °C with a small oil bath. The distillate, allyl-$3,3$-d_2 chloride (~4 g), was collected: bp 40 °C (760 mm) [lit.[23] undeuterated allyl chloride, 40 °C (760 mm)]; NMR δ 3.83 (2 H, d, J = 6 Hz), 5.49–6.18 (1 H, m), <5% 4.84–5.32 (2 H, m).

Preparation of Sulfides. The following modified procedure[24] was used to prepare all of the sulfide compounds. The corresponding thiophenol, or cyclohexyl mercaptan (0.10 mol), was added to sodium hydroxide (4 g, 0.10 mol) dissolved in 250 mL of H_2O and the mixture shaken vigorously in a separatory funnel until all of the mercaptan was dissolved. The aqueous solution was washed with methylene chloride to remove any unreacted mercaptan and disulfides which may have formed. The corresponding alkyl chloride (0.05 mol) was added and the solution again shaken vigorously. The aqueous solution

was extracted three times with 25-mL portions of methlene chloride and the combined extracts were washed twice with 5% NaOH, H_2O, dried over anhydrous Na_2SO_4, and concentrated under vacuum. Distillation through a short column under high vacuum yielded 80–85% of the corresponding sulfide. Molecular weights of all sulfides, as determined by mass spectroscopy, agreed with calculated values. The deuterated sulfides contained a minimum of 96% deuterium as determined by both proton NMR and mass spectroscopy.

Rearrangement of Allyl-*3,3-d₂* Phenyl Sulfide in the Presence of Diphenyl Disulfide (1 ⇌ 1a). The deuterated allyl phenyl sulfide (0.954 m) and diphenyl disulfide (0.071–0.972 m) were dissolved in o-dichlorobenzene, syringed into an NMR tube, degassed, and sealed under vacuum. The tubes were heated to 160 °C in an oil bath for various time intervals, quenched in cold water, and analyzed by NMR. The disappearance of the S–CH_2 absorption (δ 3.30) and the appearance of the $C\!=\!CH_2$ absorption (δ 4.90) were monitored, and integration of the corresponding peak areas enabled calculation of the concentration of 1 at any time t. Triplicate runs were made for each concentration of diphenyl disulfide.

Analysis of Crossed Product Compositions. In general, a solution of the sulfide and disulfide dissolved in equimolar concentrations in o-dichlorobenzene (1.0 M) was syringed into Pyrex tubes. These were completely degassed and sealed under high vacuum before immersion in a 160 °C thermostated bath for given lengths of time. The product composition was analyzed on a polar ⅛ in. × 12 ft DEGA column and also on a ⅛ in. × 10 ft SE-30 column (10% liquid phase on 80/100 mesh Chromosorb WAW at 160 °C). The products of reaction were identified mainly by analytical comparison with authentic samples after isolation, as well as by retention times on the gas chromatograph.

Reaction tried	Disulfide reagent	Hours at 160 °C
2 ⇌ 2a	Diphenyl	6
4 ⇌ 4a	Diphenyl	16
3 ⇌ 3a	Di-p-tolyl	6

Registry No.—1, 61614-40-2; 1a, 62698-33-3; PhSSPh, 882-33-7.

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Reactions of Aromatic Radical Anions.[1] 13. Contributing Factors for the Partitioning Reaction of Sodium Naphthalene with Phenylacetonitrile

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The products, stoichiometry, and lack of reversibility of the partitioning reaction of sodium naphthalene and phenylacetonitrile have been studied. While the reaction has both reduction and hydrogen transfer pathways the latter dominate. The kinetic and product deuterium effect confirm this and indicate that the nitrile is the sole source of hydrogen. Structure variation of the nitrile indicates that only when the nitrile is not enolizable is reduction complete or even the predominant reaction. Solvent changes bring about a moderate change in reduction leading to a dampened ion-pairing effect. A proposal involving the intermediacy of the phenylacetonitrile radical anion is discussed. Additionally from competition experiments an extended scale of relative reactivities of many diverse reactions has been constructed.

Aromatic radical anions have an intrinsic duality of nature, and perhaps not surprisingly exhibit complex chemical behavior.[3] One widely exploited reaction is the ability to transfer electrons to another substrate, thus functioning as reducing agents. Examples of this mode of reaction include the reaction with metal halides,[4a] alkyl[1a,b,3c,4b] and aryl halides,[4c] alkyl and aryl tosylates,[4d] oxygen,[4e] sulfur dioxide,[4f] hydrogen,[4g] and nitrogen.[4h] Radical anions can also react as nucleophiles, abstracting a proton from a suitable acid or adding in a nucleophilic manner to a reactive center. Examples of these reactions include the reactions with water,[5a] alcohols,[5b] ethylene oxide,[5c] and trimethylsilyl chloride.[5d] In addition to these two primary reactions, radical anions exhibit some radical reactions such as radical–radical coupling. This reaction has been observed as a secondary process in the reactions of naphthalene radical anion with alkyl halides where the initially formed alkyl radical couples with a radical anion to yield an alkyl dihydronaphthyl anion.[6] Additionally hydrogen atoms are thought to couple with the naphthalene radical anion to give the dihydronaphthyl anion.[7]