

**Figure 1.** The  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$  molecule, with thermal ellipsoids scaled to 50% probability. The atom labeled H(4) was not located (see text). The intramolecular bond distances include Os(1)–Os(2) = 2.834 (6), Os(2)–Os(3) = 2.870 (7), Os(1)–Os(3) = 3.066 (6), Os(1)–C(1) = 2.15 (1), and Os(2)–C(1) = 2.15 (1) Å. The H–C–H angle is 106 (1)°.

$K_{\text{eq}} = 2.45$ ,<sup>14</sup> and  $d_1/d_2 = 0.20$ . The site populations determined by neutron diffraction were analyzed similarly with  $K_2$ ,  $d_1$ , and  $d_2$  variables.<sup>15</sup> The results were  $K_2 = 2.30$  (10) and  $d_1/d_2 = 0.17$ . The apparent difference in the  $K_2$  values determined by NMR and by neutron diffraction is not statistically significant.<sup>16</sup>

The equilibrium isotope effect observed for the partially deuterated tautomers is readily understood qualitatively in terms of zero-point energies. The C–H group has significantly higher vibrational frequencies than the Os–H–Os group, so that partial replacement by deuterium will lead to preferential placement of the lighter nucleus in the lower frequency site.<sup>17</sup> The vibrational data required for precise calculation of the isotope effect is not available; modes for bridging hydrogen are especially difficult to identify.<sup>18</sup> However, consideration of estimated frequencies leads to a range of calculated values from  $\sim 1.5$  to 3.5,<sup>19</sup> which is consistent with the experimental results. More importantly, because of the large disparity in zero-point energies, a value in this range should be characteristic of a fully equilibrated H/D distribution among carbon (or nitrogen or oxygen) and metal sites.<sup>22</sup> Therefore, the effect should be an important tool for detecting reversible hydrogen-transfer processes in organometal cluster compounds.<sup>23</sup> It should also be considered for such processes occurring on metal surfaces.

**Acknowledgments.** Work at Argonne National Laboratory was performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. Support of the neutron diffraction research by the National Science Foundation under Grant NSF CHE 77-22650 is gratefully acknowledged. Work at the University of Illinois was supported by NSF Grants DMR 76-01058 and CHE 77-24964 (S.L.S. and G.D.S.) and by NSF Grant CHE 75-14460 (R.B.C. and J.R.S.). We acknowledge a loan of osmium tetroxide from Englehard Industries.

## References and Notes

- (1) (a) University of Illinois; (b) Argonne National Laboratory.
- (2) (a) J. Roziere, J. M. Williams, R. P. Stewart, Jr., J. L. Petersen, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 4497 (1977); (b) A. J. Schultz, K. L. Stearley, J. M. Williams, R. Mink, and G. D. Stucky, *Inorg. Chem.*, **16**, 3303 (1977).
- (3) R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 3874 (1977).
- (4) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977).
- (5) The magnitudes of the coherent scattering cross sections are 1.74 barns for H and 5.64 barns for D and the coherent scattering lengths are  $b_{\text{H}} = -0.372 \times 10^{-12}$  cm and  $b_{\text{D}} = +0.67 \times 10^{-12}$  cm.

- (6) R. Jungst, D. Sekutowski, J. Davis, M. Luly, and G. Stucky, *Inorg. Chem.*, **16**, 1645 (1977).
- (7) J. M. Williams, K. D. Keefer, D. M. Washecheck, and N. P. Enright, *Inorg. Chem.*, **15**, 2446 (1976).
- (8) International Tables for X-ray Crystallography, Vol. I, Kynoch Press, Birmingham, England, 1969.
- (9) The proposed position for H(4) was also suggested by the Os(2)–Os(3) bond length of 2.870 (7) Å compared with the Os(1)–Os(3) bond length of 3.066 (6) Å, and the fact that H(3) is in the plane of the osmium atoms. A complete neutron diffraction study of a larger crystal (14 mg) of  $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$  (undeuterated) recently has confirmed this assignment.
- (10) For a summary, see G. L. Delker, Yu Wang, G. Stucky, R. L. Lambert, Jr., C. K. Haas, and D. Seyferth, *J. Am. Chem. Soc.*, **98**, 1779 (1976).
- (11) R. A. Andersen, R. A. Jones, C. Wilkinson, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Chem. Commun.*, 865 (1977).
- (12) W. A. Herrman, C. Krüger, R. Goddard, and I. Bernal, *Angew. Chem., Int. Ed. Engl.*, **16**, 334 (1977).
- (13) All possible configurations of partially deuterated methyl and methylene tautomers were considered and their relative concentrations expressed in terms of  $K_1$ ,  $K_2$ ,  $K_{\text{eq}}$ ,  $d_1$ , and  $d_2$ . Expected  $^1\text{H}$  NMR intensities for a given site were then expressed as linear combinations of the appropriate configurations. The best values of the five variables were generated by computer minimization of the difference between the calculated and empirical  $^1\text{H}$  NMR intensities. The minimization program utilized was STEPT, J. P. Chandler, Computer Science Department, Oklahoma State University, Stillwater, Okla. Such a fit was required since  $K_2$  does not equal the inverse of the observed methylene/hydrate intensity ratio.
- (14)  $K_{\text{eq}} = 2.65 \pm 0.16$  ( $\text{CDCl}_3$ , 35 °C) was obtained by direct measurement on an undeuterated sample.
- (15) In this analysis the hydride site populations were averaged so that only one value of  $K_2$  was necessary.
- (16) It may be significant that the neutron crystal was grown at  $-2$  °C and the NMR data collected at  $+35$  °C. Adjusting the value of 2.30 obtained by neutron diffraction to reflect the value expected at  $+35$  °C, we obtained  $K_2 = 2.08$ .
- (17) C. D. Ritchie, "Physical Organic Chemistry—The Fundamental Concepts", Marcel Dekker, New York, N.Y., 1975, Chapter 8; M. Wolfsberg, *Acc. Chem. Res.*, **5**, 225 (1972).
- (18) C. B. Cooper, III, D. F. Shriver, and S. Onaka, *Adv. Chem.*, in press.
- (19) An antisymmetric stretch and two lower frequency deformation modes are expected for an Os–H–Os group.<sup>18</sup> The former has been observed for  $\mu_2\text{-H}$  in  $\text{H}_2\text{Os}_3(\text{CO})_{11}$  at  $1525$   $\text{cm}^{-1}$ ,<sup>20</sup> but the positions of the latter are unknown. Values of 1585 and 1290  $\text{cm}^{-1}$  (degenerate?) have been observed for  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ .<sup>21</sup> Assumptions of these values together with values of 2950, 1175, and 1175  $\text{cm}^{-1}$  for the C–H modes (1175  $\text{cm}^{-1}$  is the average of frequencies commonly found for the four  $\text{CH}_2$  bending modes) leads to a calculated value of 2.21 (300 K) for  $K_2$ .
- (20) J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, **97**, 4145 (1975).
- (21) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
- (22) An intermolecular example involving  $\text{HFe}_2(\text{CO})_8^-$ , which was detected by kinetics, has been reported and discussed recently: J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 1119 (1978).
- (23) The equilibrium isotope effect suffices to explain the apparently anomalous H/D distribution in partially deuterated  $\text{H}_2\text{Os}_3(\text{CO})_9\text{CCH}_3$ , which was prepared from  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CH}_2)$  and  $\text{D}_2$ : A. J. Deeming and M. Underhill, *J. Chem. Soc., Chem. Commun.*, 277 (1973).

R. Bruce Calvert,<sup>1a</sup> John R. Shapley\*<sup>1a</sup>  
Arthur J. Schultz,<sup>1b</sup> Jack M. Williams\*<sup>1b</sup>  
Steven L. Suib,<sup>1a</sup> Galen D. Stucky\*<sup>1a</sup>

Department of Chemistry and  
Materials Research Laboratory, University of Illinois  
Urbana, Illinois 61801, and Chemistry Division,  
Argonne National Laboratory, Argonne, Illinois 60439

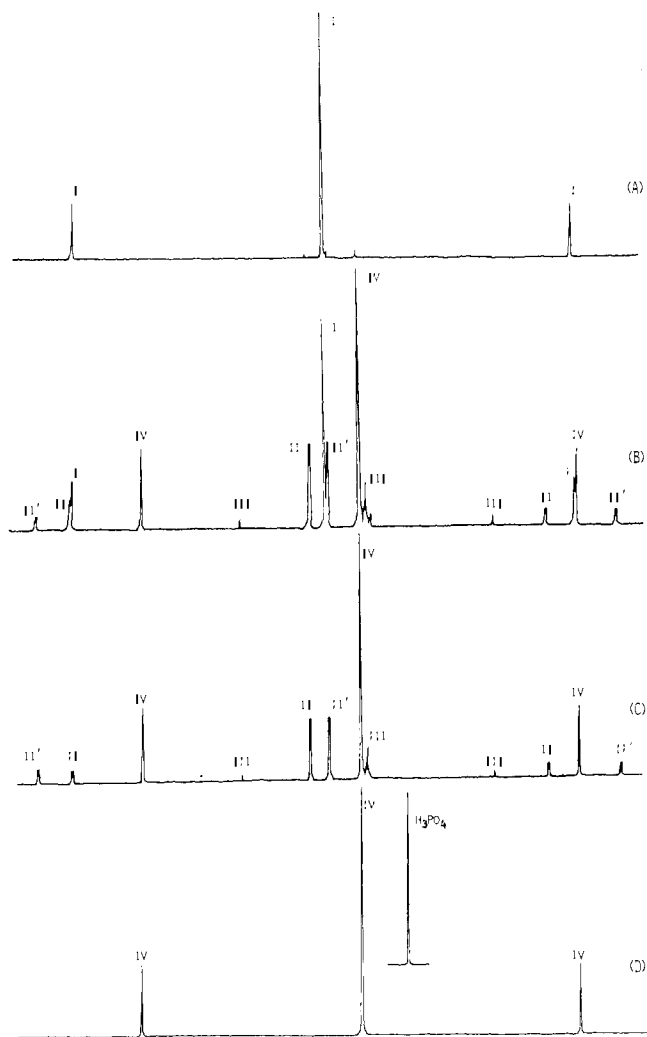
Received April 27, 1978

## Reactions of Dioxygen Platinum(II) Complexes with Activated Acetylenes

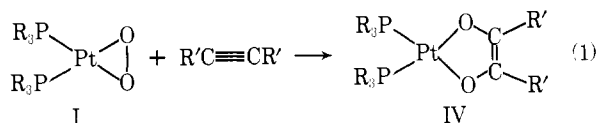
Sir:

Recently, we have synthesized a series of dioxygen platinum complexes, containing phosphine ligands having various degrees of bulkiness and basicity, which are useful intermediates in the preparation of the corresponding dihydrides.<sup>1</sup> We now wish to describe the interesting behavior of these dioxygen complexes toward activated acetylenes.

Dioxygen platinum complexes,  $\text{Pt}(\text{PR}_3)_2(\text{O}_2)$  ( $\text{PR}_3 = \text{PCy}_3$ ,  $\text{P}^i\text{Pr}_3$ ,  $\text{P}^i\text{Bu}_2^i\text{Bu}$ ,  $\text{P}^i\text{Bu}_2\text{Me}$ ,  $\text{PPh}_3$ ), react readily under ambient conditions with acetylenes such as hexafluorobut-2-yne ( $\text{C}_4\text{F}_6$ ) and dimethyl acetylenedicarboxylate (DMA) to give 1,2 addition of the dioxygen molecule across the acetylenic  $\text{C}=\text{C}$  bond (eq 1).



**Figure 1.**  $^{31}\text{P}$  NMR spectra of  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Pt}(\text{PCy}_3)_2\text{O}_2$  with excess DMA at  $-40$  (A),  $-20$  (B),  $-20^\circ\text{C}$  (after 90 min) (C) and room temperature (D).



The spectroscopic parameters of IV, where  $\text{R}_3\text{P}$  = tricyclohexylphosphine and  $\text{R}' = \text{COOCH}_3$ , are consistent with this structure. Thus,  $\nu(\text{O}_2)$ , observed at  $817\text{ cm}^{-1}$  for the starting dioxygen complex, is not observed in the spectrum of IV, but a strong  $\nu(\text{C}=\text{C})$  absorption is found at  $1580\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum shows only one resonance (in addition to a broad resonance at  $\sim 1.5$  ppm due to the cyclohexyl protons) at 3.66 ppm for the methyl carboxylate groups indicating a symmetrical arrangement. The  $^{31}\text{P}$  NMR spectrum shows a single resonance at 9.61 ppm ( $J(\text{PtP}) = 3403\text{ Hz}$ ) consistent with a symmetrical cis disposition of two phosphine ligands. The other products IV showed very similar spectroscopic behavior. Further, in the mass spectrum of IV ( $\text{PR}_3 = \text{P}^i\text{Pr}_3$ ;  $\text{R}' = \text{CF}_3$ ), the parent ion,  $\text{Pt}(\text{PR}_3)_2$ , and  $\text{PtO}_2\text{C}_4\text{F}_6$  are observable, but the peak corresponding to  $\text{Pt}(\text{PR}_3)_2\text{O}_2$  is not detected.

The reactivity of these dioxygen complexes toward activated acetylenes has been observed to be dependent on the phosphine ligands, decreasing in the following order  $\text{P}^i\text{Pr}_3$ ,  $\text{PCy}_3 > \text{PPh}_3 > \text{P}^i\text{Bu}_2\text{Bu}$ ,  $\text{P}^i\text{Bu}_2\text{Me}$ . Under similar conditions, acetylenes, such as  $\text{CH}_3\text{C}\equiv\text{CCOOCH}_3$  and  $\text{PhC}\equiv\text{CPh}$ , and olefins, such as  $\text{CH}_2=\text{CH}_2$  and dimethyl maleate, were found to be inactive.

The mechanism of reaction 1 in  $\text{CH}_2\text{Cl}_2$  (with  $\text{R} = \text{Cy}$ ;  $\text{R}' = \text{COOCH}_3$ ) was studied by (a) following the kinetics spectrophotometrically at  $25^\circ\text{C}$  in the visible range  $400\text{--}320\text{ nm}$ , and (b) employing variable-temperature  $^{31}\text{P}$  NMR to detect the intermediate(s). (a)<sup>4</sup> The results indicate that reaction 1 consists of two stages (i) an initial step

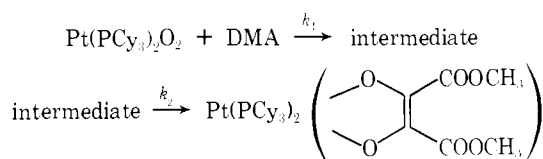
$$\frac{-d[\text{Pt}(\text{PCy}_3)_2\text{O}_2]}{dt} = k_1[\text{Pt}(\text{PCy}_3)_2\text{O}_2][\text{DMA}]$$

which is first order in both acetylene and platinum complex with  $k_1 = 1.9 \times 10^{-1}\text{ L M}^{-1}\text{ s}^{-1}$  and (ii) a second step

$$\frac{d[\text{product}]}{dt} = k_2[\text{intermediate}]$$

which is independent of acetylene concentration with  $k_2 = 3.9 \times 10^{-3}\text{ s}^{-1}$ . (b) On warming a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Pt}(\text{PCy}_3)_2\text{O}_2$  containing a large excess of DMA from  $-78$  to  $-20^\circ\text{C}$ , two intermediates were observed in the  $^{31}\text{P}$  NMR spectrum (Figure 1b): one contains two nonequivalent phosphorus nuclei, mutually coupled to each other ( $\delta_{\text{P}} 29.70$  ( $J(\text{PP}') = 7.3\text{ Hz}$ ),  $J(\text{PtP}) = 3693\text{ Hz}$ );  $\delta_{\text{P}} 23.47$  ( $J(\text{PtP}') = 4517\text{ Hz}$ )), and the other, a minor species, contains only one type of phosphorus ligand ( $\delta_{\text{P}} 10.95$  ( $J(\text{PtP}) = 1958\text{ Hz}$ )). On standing at  $-20^\circ\text{C}$  for 90 min, complete conversion of  $\text{Pt}(\text{PCy}_3)_2\text{O}_2$  to the intermediates and the product occurred (Figure 1c). On further warming to room temperature, only resonances corresponding to the final product IV were observed.

Results of (a) and (b) suggest the following mechanism for reaction 1:



The nature of the intermediates is not certain. In the minor species, III, the magnitude of the Pt-P coupling constant seems to suggest a five-coordinate structure with trans phosphines. In the major species, II, the  $J(\text{PtP})$  values are more consistent with a cis arrangement of the two phosphines (in comparison  $J(\text{PtP}) = 3552\text{ Hz}$  in  $\text{Pt}(\text{PCy}_3)_2\text{O}_2$ ). However, such structures assumes direct coordination of the acetylene to platinum. In a low-temperature  $^{19}\text{F}$  NMR study of the reaction between 1 and  $\text{C}_4\text{F}_6$ , only one intermediate was detectable which exhibited one singlet with no platinum satellites for the two  $\text{CF}_3$  groups. An alternative structure for the major intermediate may, therefore, be one in which the acetylene is attached directly to one of the coordinated oxygen atoms causing a non-equivalence of the two phosphine resonances.

This type of reaction of metal-dioxygen complexes with acetylenes is of interest from several standpoints. (1) It provides a convenient synthetic route to the hitherto unknown oxygen analogues of the well-known dithiolate ligands.<sup>5</sup> (2) In contrast to the catalytic oxidation of phosphines by  $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ ,<sup>6</sup> the mechanism of this reaction does not involve a displacement of the dioxygen ligand by the substrate, but rather a direct attack of the substrate on the dioxygen ligand.<sup>7</sup>

**Acknowledgments.** The continued financial support of the National Research Council of Canada is gratefully acknowledged.

## References and Notes

- H. C. Clark, A. B. Goel, and C. S. Wong, *J. Organomet. Chem.*, **152**, C45 (1978).
- C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 561 (1968).
- L. Malatesta and S. Cenini, "Zerovalent Compounds of Metals", Academic Press, London, 1974, p 69.
- Typically, the initial step of the reaction was studied at  $4 \times 10^{-4}\text{ M}$  of  $\text{Pt}(\text{PCy}_3)_2\text{O}_2$  and  $3 \times 10^{-3}$  to  $1.7 \times 10^{-2}\text{ M}$  of DMA; under this condition the

initial step is rate determining. The second stage of the reaction was studied at high concentration of DMA ( $1.3 \times 10^{-1}$  to  $7 \times 10^{-1}$  M) by following the spectral change accompanying the conversion of the intermediates to the final product.

- (5) G. N. Schrauzer, *Acc. Chem. Res.*, **2**, 72 (1969); J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).  
 (6) A. Sen and J. Halpern, *J. Am. Chem. Soc.*, **99**, 8337 (1977).  
 (7) An intermediate,  $\text{Pt}(\text{PCy}_3)_2(\text{DMA})$ , formed by the displacement of the  $\text{O}_2^{2-}$  ligand by DMA cannot account for the observed  $^{31}\text{P}$  NMR spectrum of the intermediates. Further, preformed  $\text{Pt}(\text{PCy}_3)_2(\text{DMA})$  does not react with  $\text{H}_2\text{O}_2$  in  $\text{CH}_2\text{Cl}_2/\text{EtOH}$ , nor does free DMA itself.

H. C. Clark,\* A. B. Goel, C. S. Wong

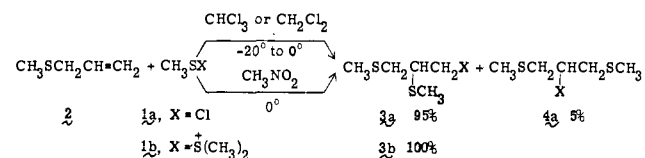
Guelph-Waterloo Centre for Graduate Work in Chemistry  
 Guelph Campus, Chemistry Department  
 University of Guelph, Guelph, Ontario, Canada, N1G 2W1

Received May 12, 1978

### Methylthiolation of Allylic Sulfides. A Degenerate [2,3]-Sigmatropic Rearrangement

Sir:

Addition of sulfenyl halides to 1-alkenes is a well-studied reaction which is normally regiospecific and stereospecific when under kinetic control.<sup>1</sup> Not surprisingly, we have found that methanesulfonyl chloride (**1a**) reacts with 3-methylthiopropene (**2**) to give 1-chloro-2,3-di(methylthio)propane (**3a**) and a minor amount of the regioisomer **4a**.<sup>2</sup> Likewise, the



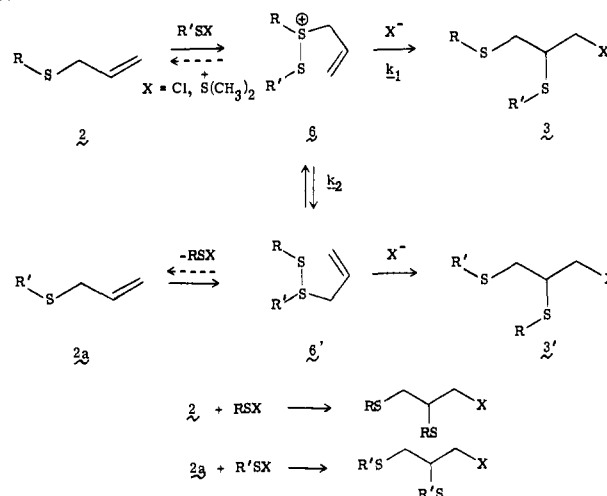
sulfenyl salt  $\text{CH}_3\text{SS}^+(\text{CH}_3)_2 \text{BF}_4^-$  (**1b**)<sup>3</sup> reacts with **2** to form the adduct **3b** only.<sup>4</sup> However, we wish to report that these reactions are not straightforward electrophilic additions to the double bond but involve an unsuspected sigmatropic rearrangement by way of attack of the sulfenating agent at *sulfur*.

Evidence of rearrangement was adduced from labeling studies. Addition of **1a** to 3-methylthiopropene-*d*<sub>3</sub> (**2-d**<sub>3</sub>) at  $-20^\circ \text{C}$  in chloroform gave an adduct, **3a-d**<sub>3</sub>, in which two thirds of the  $\text{CD}_3\text{S}$  label was at C-3 and one third at C-2. Addition of **1a** to 3-methylthiopropene-3-*d*<sub>2</sub> (**2-d**<sub>2</sub>) gave **3a-d**<sub>2</sub> in which the  $\text{CD}_2$  label was scrambled between C-3 and C-1 in the ratio of 2:1.<sup>5</sup> Scrambling of alkyl groups was also found in the adducts from reaction of 3-methylthiopropene with ethanesulfonyl chloride, and of 3-ethylthiopropene with methanesulfonyl chloride (Table I).

Reaction of **2-d**<sub>3</sub> with the sulfenyl salt **1b** gave a labeled adduct **3b** which, by NMR analysis, clearly showed that the  $\text{CD}_3$  label was distributed between the methylthio groups at C-2 and C-3 although a quantitative estimate of the distribution was not possible.<sup>6</sup> However, treatment of the adduct with sodium methoxide in methanol led to elimination of methyl sulfide and formation of neutral products that by mass spectral analysis gave molecular ions of composition  $\text{C}_5\text{H}_{10}\text{S}_2$  (*m/e* 134),  $\text{C}_5\text{D}_3\text{H}_7\text{S}_2$  (*m/e* 137), and  $\text{C}_5\text{D}_6\text{H}_4\text{S}_2$  (*m/e* 140). This result implies that the adduct **3b** derived from **2-d**<sub>3</sub> and **1b** is a mixture of unlabeled (12%), singly labeled (55%), and doubly labeled (33%) material (Table I).<sup>7</sup> A similar mix of alkylthio groups was observed in the adducts from **1b** and 3-ethylthiopropene.<sup>7</sup>

When excess allylic sulfide was used in reactions with alkanesulfonyl chlorides, unreacted sulfide showed (by NMR and mass spectrometry) *no* exchange of  $\text{CD}_3$  for  $\text{CH}_3$  in **2-d**<sub>3</sub>, *no* scrambling of  $\text{CD}_2$  in **2-d**<sub>2</sub>, and *no* exchange of methyl for

Scheme I



ethyl in **2** with ethanesulfonyl chloride (or in **5** with **1a**). In contrast, **1b** with excess sulfide led to recovery of unreacted sulfide showing extensive exchange of  $\text{CD}_3$  for  $\text{CH}_3$  in **2-d**<sub>3</sub> and scrambling of  $\text{CD}_2$  in the allyl group of **2-d**<sub>2</sub>. Also, reaction of **1b** with 3-ethylthiopropene (**5**) led to recovery of both **2** and **5** (Table I).

Direct alkylation of the double bond of the allylic sulfides does not account for the observed scrambling of the deuterium labels or alkyl groups in the products and starting sulfides. However, sulfenyl compounds are known to react rapidly with sulfides to produce transient alkylthiosulfonium ions that are structural analogues of **1b**.<sup>8-10</sup> Rearrangement of these ions is also documented.<sup>8a</sup> With this knowledge, it is possible to interpret the present results by the mechanistic sequence of Scheme I. The key steps involve alkylation of **2** to give intermediate **6** which must rapidly rearrange to **6'**. This degenerate rearrangement effectively scrambles R and R' and the allylic methylenes. Collapse of intermediates **6** and **6'** by transfer of R'S or RS to the double bond carbons leads to the observed products **3** and **3'**.

In principle, intermediate **6** could be formed by alkylation of methyl disulfide with allyl chloride. Accordingly, an equimolar mixture of  $\text{CH}_3\text{SSCH}_3$ ,  $\text{CH}_2=\text{CHCH}_2\text{Cl}$ , and  $\text{AgBF}_4$  in nitromethane at  $-20^\circ \text{C}$  gave **3b** in 90% yield when quenched with methyl sulfide.

Attack of alkanesulfonyl chlorides at sulfur is evidently irreversible because the label in the starting sulfide remains undisturbed. Such is not the case with **1b**. The observed alkyl exchange and the label scrambling in the reaction of sulfides with **1b** means that the first step is *reversible*. This is supported further by the fact that all possible cross products of label-exchanged starting materials were formed from **2-d**<sub>3</sub> with **1b**, and **5** with **1b**. Table I shows that the degree of label scrambling varies with reaction temperature and with the alkyl group. Scrambling is also incomplete in the products from both **1a** and **1b**. For sulfenyl halides this could mean that some of the product is formed by direct alkylation at carbon. Alternatively, all the product could be formed by the sequence of Scheme I provided that the rate of rearrangement of **6** is competitive with the rate of formation of **3** ( $k_1 \sim k_2$ ).

The nature of the rearrangement step is of interest. Either it could involve a concerted [2,3]-sigmatropic shift or dissociation to an allylic cation and methyl disulfide. To distinguish between these possibilities, a double-labeling experiment was devised. Reaction of ethanesulfonyl chloride with **2-d**<sub>2</sub> could give four distinguishable adducts by permutation of  $\text{CH}_3\text{S}$ ,  $\text{C}_2\text{H}_5\text{S}$ ,  $\text{CH}_2$  and  $\text{CD}_2$ . If an allylic cation is formed, all four adducts would be expected. Only two would result from the concerted rearrangement. The results obtained (Table I) show