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

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(7) An intermediate, $Pt(PCy_3)_2(DMA)$, formed by the displacement of the O_2^{2-} ligand by DMA cannot account for the observed ^{31}P NMR spectrum of the intermediates. Further, preformed $Pt(PCy_3)_2(DMA)$ does not react with H_2O_2 in CH_2Cl_2/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

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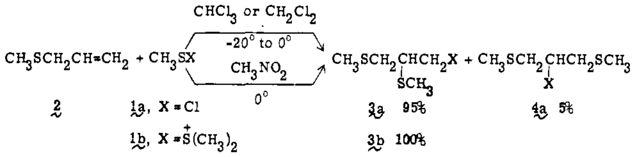
Methylthiolation of Allylic Sulfides. A Degenerate [2,3]-Sigmatropic Rearrangement

Sir:

Addition of sulfenyl halides to 1-alkenes is a well-studied reaction which is normally regiospecific and stereospecific when under kinetic control.[1] Not surprisingly, we have found that methanesulfenyl 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**.[2] Likewise, the sulfenyl salt $CH_3SS^+(CH_3)_2\ BF_4^-$ (**1b**)[3] reacts with **2** to form the adduct **3b** only.[4] 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*.



$$\mathrm{CH_3SCH_2CH{=}CH_2} + \mathrm{CH_3SX} \xrightarrow[\substack{\mathrm{CH_3NO_2}\\ 0^\circ}]{\substack{\mathrm{CHCl_3\ or\ CH_2Cl_2}\\ -20^\circ\ \mathrm{to}\ 0^\circ}} \mathrm{CH_3SCH_2\underset{SCH_3}{CH}CH_2X} + \mathrm{CH_3SCH_2\underset{X}{CH}CH_2SCH_3}$$

2 **1a**, X = Cl **3a** 95% **4a** 5%

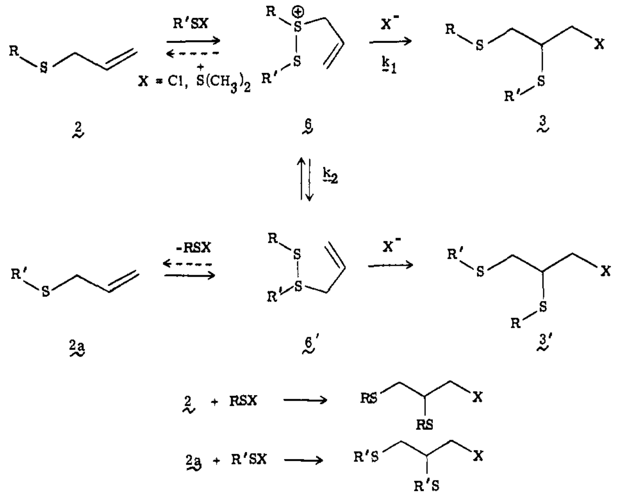
1b, X = $\overset{+}{S}(CH_3)_2$ **3b** 100%

Evidence of rearrangement was adduced from labeling studies. Addition of **1a** to 3-methylthiopropene-d_3 (**2**-d_3) at −20 °C in chloroform gave an adduct, **3a**-d_3, in which two thirds of the CD_3S label was at C-3 and one third at C-2. Addition of **1a** to 3-methylthiopropene-3-d_2 (**2**-d_2) gave **3a**-d_2 in which the CD_2 label was scrambled between C-3 and C-1 in the ratio of 2:1.[5] Scrambling of alkyl groups was also found in the adducts from reaction of 3-methylthiopropene with ethanesulfenyl chloride, and of 3-ethylthiopropene with methanesulfenyl chloride (Table I).

Reaction of **2**-d_3 with the sulfenyl salt **1b** gave a labeled adduct **3b** which, by NMR analysis, clearly showed that the 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.[6] 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 $C_5H_{10}S_2$ (*m/e* 134), $C_5D_3H_7S_2$ (*m/e* 137), and $C_5D_6H_4S_2$ (*m/e* 140). This result implies that the adduct **3b** derived from **2**-d_3 and **1b** is a mixture of unlabeled (12%), singly labeled (55%) and doubly labeled (33%) material (Table I).[7] A similar mix of alkylthio groups was observed in the adducts from **1b** and 3-ethylthiopropene.[7]

When excess allylic sulfide was used in reactions with alkanesulfenyl chlorides, unreacted sulfide showed (by NMR and mass spectrometry) *no* exchange of CD_3 for CH_3 in **2**-d_3, *no* scrambling of CD_2 in **2**-d_2, and *no* exchange of methyl for ethyl in **2** with ethanesulfenyl chloride (or in **5** with **1a**). In contrast, **1b** with excess sulfide led to recovery of unreacted sulfide showing extensive exchange of CD_3 for CH_3 in **2**-d_3 and scrambling of CD_2 in the allyl group of **2**-d_2. Also, reaction of **1b** with 3-ethylthiopropene (**5**) led to recovery of both **2** and **5** (Table I).

Scheme I



Direct alkylthiolation 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**.[8-10] Rearrangement of these ions is also documented.[8a] With this knowledge, it is possible to interpret the present results by the mechanistic sequence of Scheme I. The key steps involve alkylthiolation 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 CH_3SSCH_3, $CH_2{=}CHCH_2Cl$, and $AgBF_4$ in nitromethane at −20 °C gave **3b** in 90% yield when quenched with methyl sulfide.

Attack of alkanesulfenyl 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_3 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 alkylthiolation 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 *ethane*sulfenyl chloride with **2**-d_2 could give four distinguishable adducts by permutation of CH_3S, C_2H_5S, CH_2 and 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

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Table I. Product Distribution in the Addition of Sulfenyl Compounds to Allyl Sulfides

sulfide	RSX	temp, °C	solvent	products[a] (% compn)	recovered sulfide[b] (% compn)
$CD_3SCH_2CH{=}CH_2$ **2**-d_3	CH_3SCl **1a**	−20	$CHCl_3$	$CD_3SCH_2CH(SCH_3)CH_2Cl$ (65) $CH_3SCH_2CH(SCD_3)CH_2Cl$ (32)	$CD_3SCH_2CH{=}CH_2$ (100)
$CH_3SCD_2CH{=}CH_2$ **2**-d_2	**1a**	−20	$CHCl_3$	$CH_3SCD_2CH(SCH_3)CH_2Cl$ (63) $CH_3SCH_2CH(SCH_3)CD_2Cl$ (33)	$CH_3SCD_2CH{=}CH_2$ (100)
$C_2H_5SCH_2CH{=}CH_2$ **5**	**1a**	−55	CH_2Cl_2	$C_2H_5SCH_2CH(SCH_3)CH_2Cl$ (69) $CH_3SCH_2CH(SC_2H_5)CH_2Cl$ (24)	$C_2H_5CH_2CH{=}CH_2$ (100)
5	**1a**	35	CH_2Cl_2	$C_2H_5SCH_2CH(SCH_3)CH_2Cl$ (53) $CH_3SCH_2CH(SC_2H_5)CH_2Cl$ (41)	$C_2H_5CH_2CH{=}CH_2$ (100)
$CH_3SCH_2CH{=}CH_2$ **2**	C_2H_5SCl **1c**	−55	CH_2Cl_2	$CH_3SCH_2CH(SC_2H_5)CH_2Cl$ (66)[c] $C_2H_5SCH_2CH(SCH_3)CH_2Cl$ (22)	$CH_3SCH_2CH{=}CH_2$ (100)
2	**1c**	35	CH_2Cl_2	$CH_3SCH_2CH(SC_2H_5)CH_2Cl$ (42)[c,d] $C_2H_5SCH_2CH(SCH_3)CH_2Cl$ (40)	$CH_3SCH_2CH{=}CH_2$ (100)
$CH_3SCD_2CH{=}CH_2$ **2**-d_2	**1c**	0	CH_2Cl_2	$CH_3SCD_2CH(SC_2H_5)CH_2Cl$ (63)[e] $C_2H_5SCH_2CH(SCH_3)CD_2Cl$ (22)	$CH_3SCD_2CH{=}CH_2$ (100)
$CD_3SCH_2CH{=}CH_2$ **2**-d_3	$CH_3SS^+(CH_3)_2BF_4^-$ **1b**	25	CH_3NO_2 or CH_2Cl_2	$CD_3SCH_2CH(SCH_3)CH_2X$[f] (29) $CH_3SCH_2CH(SCD_3)CH_2X$ (26) $CH_3SCH_2CH(SCH_3)CH_2X$ (12) $CD_3SCH_2CH(SCD_3)CH_2X$ (33)	$CD_3SCH_2CH{=}CH_2$ (70) $CH_3SCH_2CH{=}CH_2$ (30)
$CH_3SCD_2CH{=}CH_2$ **2**-d_2	**1b**	−20	CH_3NO_2		$CH_3SCD_2CH{=}CH_2$ (68) $CH_3SCH_2CH{=}CD_2$ (32)
$C_2H_5SCH_2CH{=}CH_2$ **5**	**1b**	0	CH_3NO_2	$C_2H_5SCH_2CH(SCH_3)CH_2X$[f,g] (27) $CH_3SCH_2CH(SC_2H_5)CH_2X$ (19) $CH_3SCH_2CH(SCH_3)CH_2X$ (6) $C_2H_5SCH_2CH(SC_2H_5)CH_2X$ (~38)	$C_2H_5SCH_2CH{=}CH_2$ (78) $CH_3SCH_2CH{=}CH_2$ (22)

[a] Isolated in 87–96% yield; sulfenyl chlorides gave 3–6% of the more stable adduct $RSCH_2CH(Cl)CH_2SR$. [b] Recovered from reactions using from 1.2–2.0 molar excess of sulfide to **1**. [c] About 7% of $CH_3SCH_2CH(SCH_3)CH_2Cl$ was formed. [d] Some 18% of the more stable isomer $CH_3SCH_2CH(Cl)CH_2SC_2H_5$ was formed. [e] About 9% of $CH_3SCH_2CH(SCH_3)CD_2Cl$ was formed.[11] [f] X is $-^+S(CH_3)_2\ ^-BF_4$. [g] Reference 7.

that at least 22% of the reaction involves rearrangement at 0° and that only two of the four possible labeled products were obtained, as expected of a concerted allylic rearrangement.[11]

These results emphasize the remarkable generality of symmetry-allowed [2,3]-sigmatropic rearrangements whereby allylic groups migrate to and from various atom types and charge types.[12-20] To this list we add the case of allylic rearrangement from S^+ to $\ddot{S}$. These results also reveal the facility with which S-S and C-S bonds cleave in molecules of the type $>^+S-S-$, which are formally alkylated disulfides or thiolated sulfides.

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(5) Label distribution was determined from NMR spectrum of products in benzene. **3a:** δ 1.68 (CH_3S at C-2, s), 1.81 (CH_3S at C-3, s), 2.65 (SCH_2CH, m), and 3.55 ppm (CH_2Cl, m).

(6) The chemical shifts of the two nonequivalent CH_3S groups cannot be resolved cleanly.

(7) Product composition was determined by demethylation of the adducts with trimethylamine to a mixture of tri(alkylthio)propanes which were analyzed by GPC, NMR, and mass spectrometry.

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(11) Composition was determined from 90-MHz and 220-MHz NMR spectra. A *single* ABX pattern was observed that was assigned to $CH_3SCD_2C\mathit{H}(SC_2H_5)C\mathit{H}_2Cl$ by comparison with authentic unlabeled material: δ_A 3.68, δ_B 3.52 ppm (J_{AB} = 7.6, J_{AX} = 3.6, J_{BX} = 4.6 Hz). No ABX signals corresponding to $C_2H_5SCD_2C\mathit{H}(SCH_3)C\mathit{H}_2Cl$ were evident.

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Jhong K. Kim, Margaret L. Kline, Marjorie C. Caserio*
Department of Chemistry, University of California
Irvine, California, 92717

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Photochemical Interconversion of Phenylnitrene and the Isomeric Pyridylmethylenes

Sir:

Recently we demonstrated that irradiation (>2160 Å) of phenyl azide matrix isolated in argon produces 1-aza-1,2,4,6-cycloheptatetraene (**1**).[1] The question whether phenylnitrene (**2**) was formed in competition with **1** prompted us to follow the irradiation of phenyl azide using electron spin resonance.[2] Irradiation (>2160 Å) of phenyl azide matrix isolated in argon at 12 K produced the characteristic, intense X,Y transition of the triplet phenylnitrene (Figure 1; D, 1,027 cm^{-1}; E, 0 cm^{-1}).[3,4] The excellent signal to noise ratio permitted observation of the weak $\Delta m = 2$ transition and the Z_1 transition which had not been observed in previous studies. Continued irradiation of the sample produced a new triplet species (Figure 1) with zero-field parameters (D, 0.537 cm^{-1}; E, 0.027 cm^{-1}) rather similar to those of phenylmethylene (D, 0.5098 cm^{-1}; E, 0.0249 cm^{-1}).[5] The similarity in zero-field parameters suggested that the new triplet species might be 2-pyridylmethylene (**3**). This possibility was confirmed by independent generation of 2-pyridylmethylene. Irradiation (λ > 2000 Å) of *vic*-triazolopyridine (**4**) matrix isolated in argon is known to give first 2-diazomethylpyridine then 1-aza-1,2,4,6-cycloheptatetraene.[1] When this irradiation is monitored by ESR, the signals characteristic of triplet 2-pyridylmethylene (**3**) are observed (Figure 2). Continued irradiation produces the signals of triplet phenylnitrene (Figure 2). Blank experiments showed the vacuum system and the ESR cell to be free of cross contamination.[6]

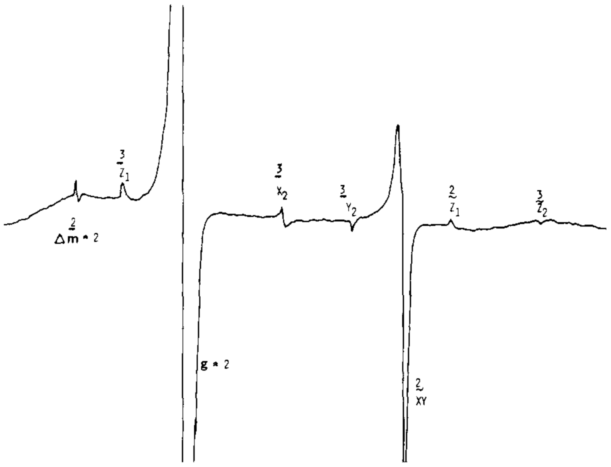

Figure 1. ESR spectrum produced upon irradiation of phenyl azide (>2160 Å) matrix isolated in argon at 10 K. The observed field positions for **2** are Δm = 2, 1668 G; XY, 6914 G; Z_1, 7639 G. The field positions for **3** are Z_1, 2377 G; X_2, 4934 G; Y_2, 6057 G; Z_2, 9068 G. The g = 2 region is due to the adventitious formation of free radicals.

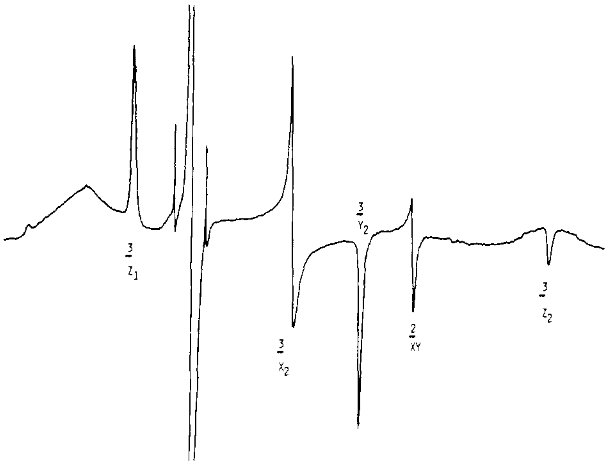

Figure 2. ESR spectrum produced on irradiation of *vic*-triazolopyridine (**4**, >2000 Å) matrix isolated in argon at 10 K. The field positions are identical with those given in Figure 1. The sharp signals symmetrically disposed about the g = 2 signal are due to hydrogen atoms.

Irradiation (>2000 Å) of 4-diazomethylpyridine[6,7] matrix isolated in argon at 12 K gave triplet 4-pyridylmethylene (**5**: D, 0.533 cm^{-1}; E, 0.0248 cm^{-1}). Continued irradiation produces 3-pyridylmethylene (**6**, vide infra), 2-pyridylmethylene (**3**), and phenylnitrene (**2**) as well (Figure 3). Similar irradiation of argon matrix isolated 3-diazomethylpyridine[6,7] gives 3-pyridylmethylene (**6**: D, 0.513 cm^{-1}; E, 0.0241 cm^{-1}), 4-pyridylmethylene, 2-pyridylmethylene, and phenylnitrene (Figure 4). The three isomeric pyridylmethylenes can be clearly distinguished in the Z_1 and Y_2 transitions. The Z_1 transition of 3-pyridylmethylene is complex owing to the presence of two conformers.[8] Only one conformer is possible for 4-pyridylmethylene, and only one of the two possible conformers is observed for 2-pyridylmethylene. This observation is probably due to an effect of the nitrogen lone pair. When the irradiation of either 4-diazomethylpyridine or 3-diazo-

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