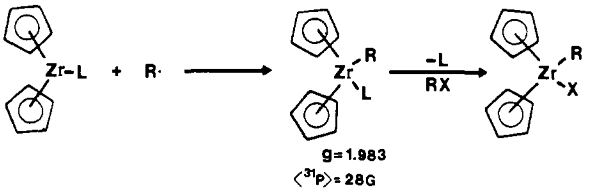
doublet is accordingly low.[9] Alkyl radical capture by Zr(II) would give a new paramagnetic species. Consistent with this notion, we find that EPR spectra recorded during the reaction between $Cp_2Zr(PPh_2Me)_2$ and *n*-butyl chloride display a pair of doublets which appear and decay consecutively with different kinetics (see Figure 2).[10] One is the halide-containing intermediate described above; the other (g = 1.983) has a hyperfine coupling constant of 28 G, consistent with greater unpaired spin density on phosphorus than is found for the initial doublet assigned to $Cp_2ZrCl(PPh_2Me)$. This behavior is consistent with changing the ligand on zirconium from an electron-withdrawing halide to an electron-donating alkyl group. This second signal is, therefore, attributed to $Cp_2Zr^{III}R(PPh_2Me)$.[11,12]

Monitored by EPR spectroscopy, the oxidation of $Cp_2Zr(PPh_2Me)_2$ by *sec*-butyl halides provides further evidence in support of Scheme I. At 29 °C reaction with *sec*-butyl chloride yields a mixture of Cp_2ZrCl_2 and $Cp_2Zr(Bu)Cl$ (68:32). Accordingly, the "initiation doublet" is observed, and a weak signal is found in the alkylzirconium(III) region. At 6 °C, however, no doublet attributable to the alkylzirconium(III) complex is noted in the reaction between $Cp_2Zr(PPh_2Me)_2$ and *sec*-butyl bromide (which produces Cp_2ZrRX/Cp_2ZrX_2 in the ratio 69:31). These observations are a function of relative rates for the two steps of the propagation sequence [addition step (k_1) vs. abstration step (k_2)] leading to oxidative addition. Fast R· capture (see reaction 2) (1° > 2° > 3°) relative to subsequent abstraction (I > Br > Cl) would result in a buildup of $Cp_2Zr^{III}RL$ and allow its detection by EPR spectroscopy. This situation would be maximized[1] for R = primary alkyl radical and X = Cl; Zr(II) capture of secondary alkyl radicals is slower and subsequent oxidation of Zr(III) to Zr(IV) can become competitive with this capture. The different intensities for the paramagnetic intermediates formed in the reactions of *sec*-butyl bromide and *sec*-butyl chloride with the bis(phosphine)zirconium(II) complex are readily understood: capture rates for each substrate should be the same; however, the subsequent abstraction should occur significantly faster for the bromide than for the chloride.



(2)

Classical product analysis studies originally enabled us to outline a mechanistic scheme to account for observed competitive oxidation of Zr(II) complexes by alkyl halides. Support for this scheme has been accomplished by EPR observation of reaction intermediates as noted herein, a result that demonstrates the utility of this spectroscopic technique for the elucidation of organometallic reaction mechanisms.

Acknowledgment. We acknowledge support for this work provided by the National Science Foundation (Grant CHE-79-00996). We also thank Professor C. Dismukes and D. Abramowicz for helpful comments and discussions.

Registry No. $Cp_2Zr(PPh_2Me)_2$, 71844-71-8; $Cp_2ZrCl(PPh_2Me)$, 80642-23-5; $Cp_2ZrBr(PPh_2Me)$, 80642-24-6; $Cp_2Zr(n\text{-}Bu)(PPh_2Me)$, 80642-25-7; Cp_2ZrCl_2, 1291-32-3; $Cp_2Zr(Bu)Cl$, 71844-78-5; $Cp_2Zr(sec\text{-}Bu)Br$, 80642-26-8; Cp_2ZrBr_2, 1294-67-3; *t*-BuCl, 507-20-0; *sec*-BuCl, 78-86-4; *n*-BuCl, 109-69-3; *sec*-BuBr, 78-76-2.

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[9] These data were collected without use of an external calibration standard; exact quantitative conclusions, therefore, cannot be drawn. The fact that similar relative intensities for the Zr(III) species were observed for a large number of runs, performed at different times under the same conditions, justifies our conclusions qualitatively.

[10] Under these conditions both Cp_2ZrCl_2 and $Cp_2Zr(Cl)(Bu)$ are formed in the ratio 18:72.

[11] A third doublet has been noted (g = 1.986, $a\langle ^{31}P\rangle$ = 18 G), which forms and decays with a shorter lifetime than Cp_2ZrRL and remains unassigned. The relatively sharp lines for this doublet and the small hyperfine constant suggest that it is not an alkyl-containing metallic species. This last doublet was observed *only* for *n*-BuCl oxidation; it was not detected in reactions involving *tert* or *sec*-butyl chlorides or *sec*-butyl bromide.

[12] Proton hyperfine splitting (≈3 G) is not well resolved in this signal. A similar, low hyperfine splitting by alkyl group protons for an EPR study has been noted for a cyclopentadienyl(alkyl)zirconium species: Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

A Silicon-Mediated Homo-Claisen Rearrangement

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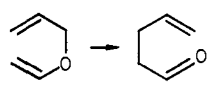
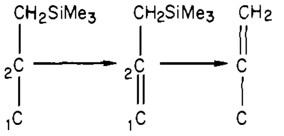
Received November 20, 1981

The Claisen rearrangement (reaction 1) is a well-known and exceptionally versatile reaction as evidenced, for example, by the number and frequency of its reviews.[1] The reaction is important in part because its high stereospecificity has found application in the construction of acyclic systems and trisubstituted olefins. The selectivity is a consequence of the highly ordered transition state in the Claisen rearrangement, a feature it has in common with the Diels–Alder reaction. We have now uncovered a variant of the Claisen rearrangement that leads to homologous products[2] and moreover has, we believe, significant and far-reaching consequences.



(1)

Our basic strategy for specific homologation involves silicon chemistry (reaction 2).[3-5] If a reaction can be conceived that



(2)

1 2 3

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[1] (a) Tarbell, D. S. *Chem. Rev.* **1940**, *27*, 495–546. (b) Tarbell, D. S. *Org. React.* **1944**, *2*, 1–49. (c) Alexander, E. R. "Principles of Ionic Reactions"; Wiley: New York, 1950; pp 292–295. (d) Fuson, R. C. "Reactions of Organic Compounds"; Wiley: New York, 1962; pp 672–676. (e) Rhoads, S. J. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Part 1, pp 655–706. (f) Schmid, H. *Osterr. Chemiker Ztg.* **1964**, *65*, 109–116; *Chem. Abstr.* **1964**, *61*, 2999g. (g) DeWolfe, R. H.; Young, W. G. In "The Chemistry of the Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; Vol. I, pp 681–738. (h) Krauch, H.; Kunz, W. "Organic Name Reactions"; Wiley: New York, 1964; pp 90–91. (i) Thyagarajan, B. S. *Adv. Heterocycl. Chem.* **1967**, *8*, 143–163. (j) Dalrymple, D. L.; Kruger, T. L.; White, W. N. In. "The Chemistry of the Ether Linkage"; Patai, S., Ed.; Interscience: New York, 1967; pp 635–660. (k) Shine, H. J. "Aromatic Rearrangements"; Elsevier: New York, 1967; pp 89–123. (l) Jefferson, A.; Scheinman, F. *Q. Rev., Chem. Soc.* **1968**, *22*, 391–421. (m) Denney, R. C. "Named Organic Reactions"; Plenum Press: New York, 1969; pp 65–68. (n) Hansen, H. J.; Schmid, H. *Chem. Br.* **1969**, *5*, 111–116. (o) Winterfeldt, E. *Fortschr. Chem. Forsch.* **1970**, *16*, 75–102. (p) MacKenzie, K. In "Chemistry of the Alkenes"; Patai, S., Ed.; Interscience: New York, *1970*; Vol. 2, pp 154–162. (q) Smith, G. G.; Kelly, F. W. *Prog. Phys. Org. Chem.* **1971**, *7*, 153–160. (r) Brandsma, L.; Schuijl, P. J. W.; Laros, D.; Meijer, J.; Wijers, H. E. *Int. J. Sulfur Chem. B* **1971**, *6*, 85–90. (s) Hansen, H. J. In "Mechanism of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, pp 177–236. (t) Faulkner, D. J. *Synthesis* **1971**, 175–189. (u) Stevens, T. S.; Watts, W. E. "Selected Molecular Rearrangements"; Van Nostrand Reinhold: New York, 1973; 181–190. (v) Rhoads, S. J.; Raulins, R. N. *Org. React.* **1975**, *22*, 1–252. (w) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227–232. (x) Bennett, G. B. *Synthesis* **1977**, 589–606. (y) Whiting, D. A. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; pp 837–839.

[2] A number of modified Claisen rearrangements have been reported including one claimed as a "homologous ester Claisen rearrangement": Ziegler, F. E.; Nelson, R. V.; Wang, T. F. *Tetrahedron Lett.* **1980**, *21*, 2125–2128. This process is actually a modification of the oxy-Cope rearrangement: cf. Viola, A.; Levasseur, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 1150–1151.

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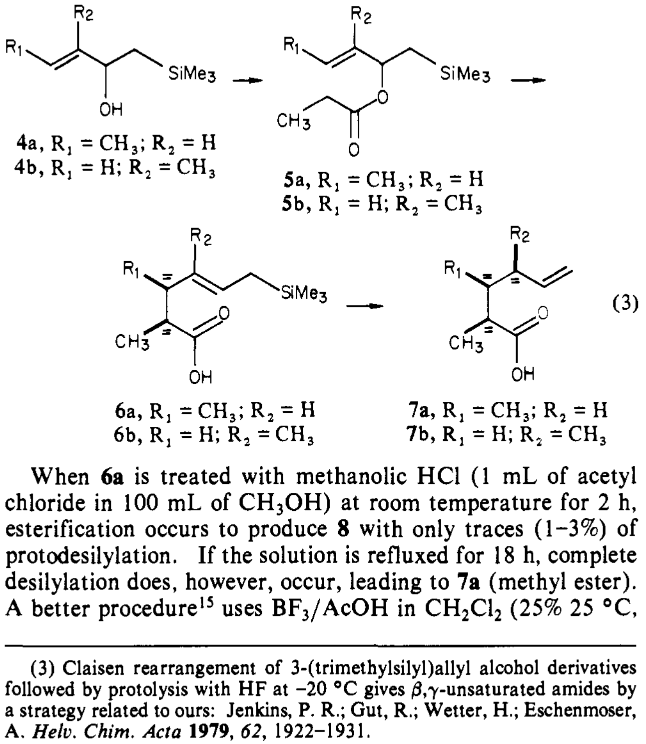
introduces a double bond between C_1 and C_2, the resulting allylsilane **2** will undergo protodesilylation leading to **3**. The silicon-mediated homo-Claisen rearrangement is outlined in reaction 3. Allylic alcohols **4a** and **4b**[6] were prepared from Me_3SiCH_2MgCl[7] and the corresponding aldehydes (80–85% yields). Such β-silyl alcohols have previously been studied as precursors to olefins via elimination of Me_3SiOH with acid or base.[8] The corresponding esters are not well-known; in fact one report[9] indicates they undergo spontaneous fragmentation to olefins. While allylic alcohols **4a** and **4b** are quite sensitive to acid (such as dilute aqueous mineral acid, pyridinium hydrochloride, or silica gel) esterification proceeds easily with propionic anhydride/triethylamine in the presence of 4-(dimethylamino)pyridine[10] in ether at 25 °C. Compound **5a** is produced in 80% yield and **5b** in 95% yield.[11] Ester enolate Claisen rearrangement[12] (LDA, −78 °C → room temperature) gave **6a** (61%) and **6b** (53%) respectively. As anticipated the selectivity of the rearrangement is high. Compound **6a** appears to be about a 9:1 mixture in favor of *trans-erythro*-**6a**.[13] Compound **6b** is greater than 95% *E*.[14]



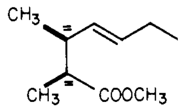
4a, $R_1 = CH_3$; $R_2 = H$
4b, $R_1 = H$; $R_2 = CH_3$

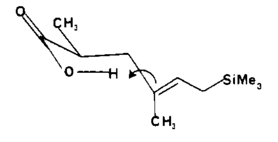
5a, $R_1 = CH_3$; $R_2 = H$
5b, $R_1 = H$; $R_2 = CH_3$

6a, $R_1 = CH_3$; $R_2 = H$
6b, $R_1 = H$; $R_2 = CH_3$

7a, $R_1 = CH_3$; $R_2 = H$
7b, $R_1 = H$; $R_2 = CH_3$

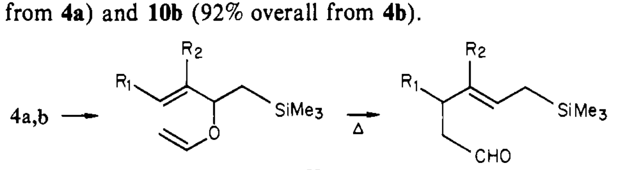
When **6a** is treated with methanolic HCl (1 mL of acetyl chloride in 100 mL of CH_3OH) at room temperature for 2 h, esterification occurs to produce **8** with only traces (1–3%) of protodesilylation. If the solution is refluxed for 18 h, complete desilylation does, however, occur, leading to **7a** (methyl ester). A better procedure[15] uses $BF_3/AcOH$ in CH_2Cl_2 (25% 25 °C, 5 min) to produce **7a** in quantitative yield. Compound **6b** also protodesilylates under the same conditions to give **7b** (85%).[16] We were very surprised to find that protonation of allylsilane **6b** is evidently *intramolecular*, leading to 1,3-asymmetric induction and





(2*S*),(4*R*)-2,4-dimethyl-5-hexenoic acid **7b** (>8:1 ratio by ^{13}C NMR spectroscopy).[18]

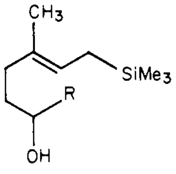
The homo-Claisen rearrangement of vinyl ethers has been explored as well. Alcohols **4a** and **4b** can be converted to their vinyl ethers **9a** and **9b** in the usual way [n-$BuOCH{=}CH_2/Hg(OAc)_2$]. Thermolysis at 110 °C (18 h) gave **10a** (85% overall from **4a**) and **10b** (92% overall from **4b**).



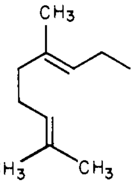
9a, $R_1 = CH_3$; $R_2 = H$
9b, $R_1 = H$; $R_2 = CH_3$

10a, $R_1 = CH_3$; $R_2 = H$
10b, $R_1 = H$; $R_2 = CH_3$

The *functionalized* allylsilanes available via this technology are valuable synthetic intermediates. We have converted **10b** to geranyltrimethylsilane[19] **12** (isopropylidene Wittig, 100%) and alcohols **11a** (LAH, 97%) and **11b** (vinyl Grignard). Alcohol **11b** on oxidation with PCC[20] gave enone **13** (68% overall from **10b**). When **13** was treated with $BF_3{\cdot}OEt_2$ in ether, intramolecular cyclization occurred readily to produce 4-methyl-4-vinylcyclohexanone **14** in 73% yield.



11a, R = H; 11b, R = CH = CH_2



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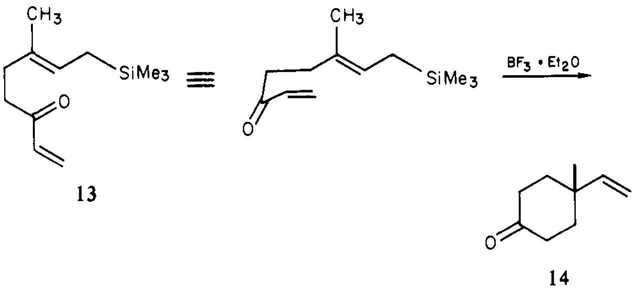

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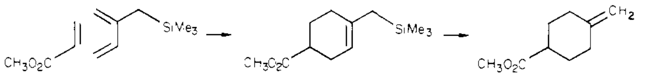
(3) Claisen rearrangement of 3-(trimethylsilyl)allyl alcohol derivatives followed by protolysis with HF at −20 °C gives β,γ-unsaturated amides by a strategy related to ours: Jenkins, P. R.; Gut, R.; Wetter, H.; Eschenmoser, A. *Helv. Chim. Acta* **1979**, *62*, 1922–1931.

(4) (a) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15–64. (b) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761–786.

(5) We exploited this strategy in the Diels–Alder cycloaddition which gives an allylsilane that can easily be eliminated to exomethylene: Wilson, S. R.; Phillips, L. R.; Natalie, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 3340–3344.



(6) All new compounds reported in this paper showed spectral data and combustion analysis in accord with their structures.

(7) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780–784.

(8) Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442–448.

(9) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264–3268.

(10) Hassner, A.; Krepski, L. R.; Alexanian, V. A. *Tetrahedron* **1978**, *34*, 2069–2076.

(11) An alternative procedure using an acid chloride on a slight excess of the lithium salt of the alcohol is also satisfactory. Esters **5a** and **5b** are thermally stable but are labile to acid treatment and cannot be chromatographed without losses.

(12) (a) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897–5898. (b) Wilson, S. R.; Myers, R. S. *J. Org. Chem.* **1975**, *40*, 3309–3331.

(13) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Org. Chem.* **1976**, *98*, 2868–2877.

(14) Faulkner, D. J. *Synthesis* **1971**, 175–189.

(15) This reagent was first reported by Fleming and serves to provide both a proton source and a good nucleophile (F^-) for silicon: Fleming, I.; Paterson, I. *Synthesis* **1979**, 446–448. This use of andyrous HF for the same purpose has been described.

(16) A small amount (15%) of a lactone isomeric with **6b** (15%) is also produced in this reaction. This side product is apparently the result of protonation of the allylsilane double bond "the wrong way" to produce a *tert*-carbonium ion rather than a β-silyl stabilized secondary carbonium ion.[17]

(17) Cf.: Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans 1* **1981**, 1421–1423.

(18) Both the 2*R*,4*S* and 2*R*,4*R* isomers have been synthesized: Bartlett, P. A.; Myerson, J. *J. Org. Chem.* **1979**, *44*, 1625–1627. The carbon-13 NMR spectra of the acids allow easy distinction of the isomers. Compound **7b** and its relatives have been used in several natural products syntheses (Monensin, multistriation, Prelog-Djerassi lactone) but have never been prepared from acyclic precursors.

(19) Brian, C.; Dunoques, J.; Calas, R.; Gerval, T. T. *Synthesis* **1981**, 220–222.

(20) Corey, E. J.; Suggs, J. W.; *Tetrahedron Lett.* **1975**, 2647–2650.

In conclusion we are convinced that the widely applicable chemistry of the Claisen rearrangement makes the homo-Claisen rearrangement and its concomitant possibilities important. We are currently investigating these questions.

Acknowledgment. We thank the National Institutes of Health (GM-29259) for financial support. We also thank Dr. Brian J. Willis (Fritzsche, Dodge and Olcott, New York) for a ^{13}C NMR spectrum of compound **7b**. NMR spectra were also obtained by using the 7 T spectrometer at The Rockefeller University purchased in part with funds from the National Science Foundation (PCM-7912083) and from the Camille and Henry Dreyfus Foundation.

Registry No. 4a, 80399-28-6; **4b**, 80399-29-7; **5a**, 80399-30-0; **5b**, 80399-31-1; **6a**, 80399-32-2; **6b**, 80399-33-3; **7a**, 80399-34-4; **7a** methyl ester, 80399-35-5; **7b**, 67279-65-6; **8**, 80399-36-6; **9a**, 80399-37-7; **9b**, 80399-38-8; **10a**, 80399-39-9; **10b**, 80399-40-2; **11a**, 80399-41-3; **11b**, 80399-42-4; **12**, 80399-43-5; **13**, 80399-44-6; **14**, 4111-01-7; $TMSCH_2Cl$, 2344-80-1; 2-butenal, 4170-30-3; 2-methyl-2-propenal, 78-85-3.

Single-Collision Chemiluminescent Reactions of Ozone with Hydrogen Sulfide and Methyl Mercaptan

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Received August 21, 1981

The reactions of ozone with a wide range of molecules have provided insight into many novel chemical processes. Ozonolysis of olefins is, of course, extremely important synthetically,[1] while reactions of ozone with metal atoms, M, yield information about the refractory MO species via chemiluminescence.[2] The reaction of O_3 with certain small molecules, e.g., NO,[3] is known to produce electronically excited products that can fluoresce on a single collision. Other molecules such as olefins and small sulfur-containing compounds react with ozone to produce chemiluminescent products possibly via multistep pathways.[4-6] We are interested in the dynamics of reactions of ozone with various organic molecules and began our studies with mercaptans.[7] We have previously studied the reaction of ozone with H_2S and CH_3SH to produce electronically excited SO_2. This work was carried out at low pressures but still under multiple-collision conditions. In this communication, we present single-collision studies[8] of the chemiluminescent reactions of ozone with H_2S and CH_3SH.

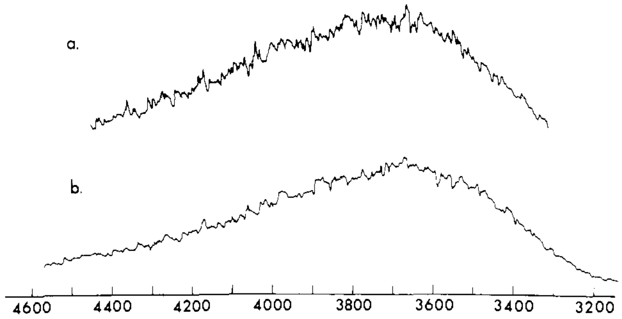

Figure 1. Continuous chemiluminescence spectra of SO_2 from ozone reactions under multiple-collision conditions. The short wavelength cutoff is due to the Pyrex window. (a) Chemiluminescence spectrum recorded from the reaction of 10-μm O_3 (beam) with 5-μm CH_3SH. (b) Chemiluminescence spectrum recorded from the reaction of 40-μm O_3 (beam) with 10-μm H_2S; 1 $\mu m = 10^{-3}$ torr.

The reactions were studied in our beam-gas chemiluminescence apparatus which has been previously described.[7] Briefly, an evacuated chamber (base system pressure $<1 \times 10^{-6}$ torr) is filled to a certain pressure with a background gas. A molecular beam of ozone is injected into the chamber, and the ozone molecules undergo collisions with the background gas. Due to the large exoergicity of the reactions, products can be generated in electronically excited states. These molecules can fluoresce, and the emitted photons are detected perpendicular to the beam axis through a Pyrex viewing window.[9] The photons are spectroscopically analyzed by using an 0.75-m Spex monochromator and are detected by a cooled photomultiplier tube (EMI 6256 B). Due to the low cross section for photon production, photon-counting techniques must be employed. The output of the photomultiplier tube was sent to an Ortec pulse counting system. The pressure was determined by an ion gauge for pressures $<10^{-3}$ torr and by a Granville–Phillips Convectron gauge for pressures $>10^{-3}$ torr. These measurements should be accurate to 50%. Ozone, produced in a commercial ozonizer, was collected on silica gel at −59 °C. The ozone container was flushed with helium to eliminate as much O_2 as possible and then warmed gradually to room temperature. The background reagent gases, H_2S and CH_3SH, were obtained from commercial sources and were used without further purification.

The continuous spectra obtained for $O_3 + CH_3SH$ and $O_3 + H_2S$ under multiple-collision conditions are shown in Figure 1, a and b, respectively. This spectrum corresponds to the fluorescent spectrum of SO_2 and is essentially identical with that recorded by Halsted and Thrush[10] from the reaction

$$SO + O_3 \rightarrow SO_2 + O_2 \qquad (1)$$

and with the low-pressure luminescent spectrum obtained by Strickler et al.[11] Due to the complicated manifold of electronic states for SO_2, the individual vibrational lines have not been resolved.[12] In figure 2, a and b, we show the digital spectra obtained for the reaction of O_3 with H_2S and O_3 with CH_3SH at very low pressures. At this pressure (4×10^{-4} torr), the mean free path is on the order of 10 cm; within the region viewed by the monochromator, this corresponds to single-collision conditions. The bar spectra follow the general shape seen in the higher pressure spectra, and we attribute the spectra to SO_2. A digital spectrum obtained at a pressure of 6×10^{-5} torr (definitely in the single-collision regime) is shown in Figure 2c for the reaction of H_2S. It is again similar to the higher pressure spectra. In another

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[‡] Alfred P. Sloan Foundation Fellow (1977–1981); Camille and Henry Dreyfus Teacher–Scholar (1978–1983); DuPont Young Faculty Grantee (1978).

(1) (a) Murray, R. W. *Acc. Chem. Res.* **1968**, *1*, 313. (b) Criegee, R.; *Angew. Chem.*, Int. Ed. **1975**, *14*, 745.

(2) Gole, J. L. *Annu. Rev. Phys. Chem.* **1976**, *27*, 525.

(3) Redpath, A. E.; Menzinger, M.; Carrington, T. *Chem. Phys.* **1978**, *27*, 409.

(4) (a) Finlayson, B. J.; Pitts, J. N., Jr.; Akimoto, H. *Chem. Phys. Lett.* **1972**, *12*, 495. (b) Finlayson, B. J.; Pitts, J. N., Jr.; Atkinson, R. *J. Am. Chem. Soc.* **1974**, *96*, 5356. (c) Schurath, U.; Gusten, H.; Penzhorn, R.-D. *J. Photochem.* **1976**, *5*, 33.

(5) (a) Akimoto, H.; Finlayson, B. J.; Pitts, J. N., Jr. *Chem. Phys. Lett.* **1971**, *12*, 199. (b) Kummer, W. A.; Pitts, J. N., Jr.; Steer, R. P. *Environ. Sci. Technol.* **1971**, *5*, 1045. (b) Pitts, J. N., Jr.; Kummer, W. A.; Steer, R. P.; Finlayson, B. J. *Adv. Chem. Ser.*, **1972**, *No. 113*, 246. (d) Becker, K. H.; Inocêncio, M. A.; Schurath, U. *Int. J. Chem. Kinet., Symp.* **1975**, *1*, 205.

(6) Toby, S.; Toby, F. S.; Kaduk, B. A. *J. Photochem.* **1977**, *6*, 297.

(7) Glinski, R. J.; Sedarski, J. A.; Dixon, D. A. *J. Phys. Chem.* **1981**, *85*, 2440.

(8) The mean free path, l, for various pressures based on a cross section of 3.7 Å^2: $P = 1 \times 10^{-5}$ torr, $l = 500$ cm; $P = 5 \times 10^{-5}$ torr, $l = 100$ cm; $P = 1 \times 10^{-4}$ torr, $l = 50$ cm; $P = 5 \times 10^{-4}$ torr, $l = 10$ cm. The single-collision regime occurs when l is greater than the dimensions of the apparatus. In this case the chamber is a cylinder ($r = 18$ cm $\times$ $L = 60$ cm).

(9) The Pyrex window imposes a short wavelength cutoff of ~3300 Å.

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