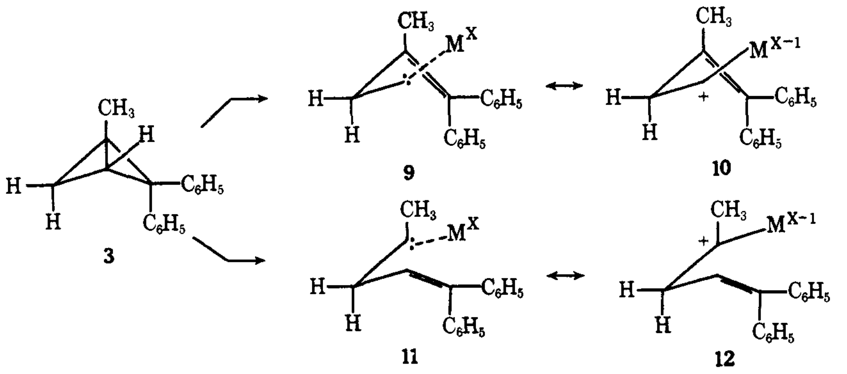
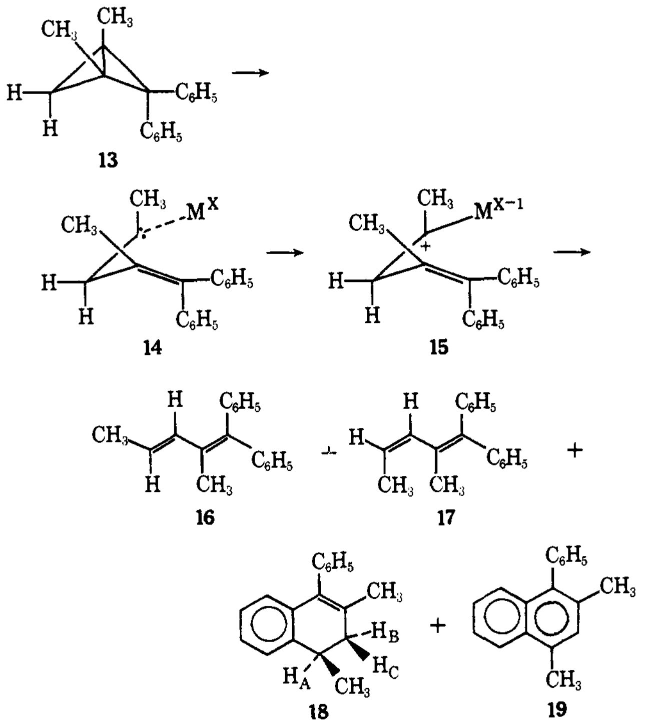


products, while **19** was a secondary product derived from the dehydrogenation of **18**. When the rearrangement of **13** was promoted by 4 mol % of pentafluorophenylcopper tetramer for 3 hr at 25°, we obtained a 60% yield of a mixture of **16** and **17** in the ratio of 7:3, respectively. No indication could be found for the formation of either **18** or **19** in the pentafluorophenylcopper tetramer promoted reaction. The formation of **18** and **19** when M^+ was rhodium(I) and the absence of **18** and **19** when M^+ was copper(I) indicated that *the formation of dihydroaromatic products from phenyl-substituted bicyclo*[*1.1.0*]*butanes was a function of the transition metal complex used to promote the isomerization*, and did not depend on the presence of the methyl group at the reactive site.



The conclusion reached above is not meant to imply that the methyl group was completely without influence. In relation to the rhodium(I) complex promoted rearrangement, the added methyl group was very important. Relative to the products formed in the rhodium(I) complex promoted rearrangement of **3**, the reaction of **13** with the same complex resulted in a significant increase in the amount of the dihydronaphthalene derivative and the complete absence of a dihydroazulene. Consideration of the intermediate resonance hybrid represented by **14** and **15** offered an insight into the origin of these changes. Addition of the bridgehead methyl group converts the "primary" reactive site of the **9** ↔ **10** resonance hybrid into the "secondary" reactive site of the **14** ↔ **15** resonance hybrid. The change from a "primary" to a "secondary" center would be expected to result in a greater contribution to the resonance hybrid by **15** than by **10**. Thus, the added methyl group makes the intermediate take on more cationic character at the expense of its carbenoid character. As a result, the formation of dihydroazulene derivatives stopped due to the lack of "carbenoid" addition to the aromatic ring, while the amount of the dihydronaphthalene derivative increased, presumably due to the increased Friedel-Crafts type alkylation of the phenyl group.[16]

In summary, we have shown that product formation depends on both the nature of the transition metal complex and on the substitution of the bicyclo[1.1.0]butane. In addition, we have shown that the change from a "primary" reactive site to a "secondary" reactive site dramatically changes the character of the reactive intermediate as demonstrated by a significant change in product ratios. We are continuing these studies in the hope of elucidating why different transition metal complexes promote the initial cleavage of different bonds of the substituted bicyclo[1.1.0]butanes.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

---

[15] The structures of **16**, **17**, **18**, and **19** were established on the basis of ir, uv, nmr, and mass spectral analysis. In addition, treatment of **18** with sulfur at 250° gave **19**. The extensive spectral data on **16**, **17**, **18**, and **19** will be presented in a full paper.

[16] If more cationic "carbenoids" are better at C–H insertion and poorer at adding to aromatic rings, the formation of dihydronaphthalene derivatives could also be interpreted in terms of a C–H insertion reaction of a very "cationic" carbene.

[17] The Ohio State University, Postdoctoral Fellow, 1970–1971.

Paul G. Gassman,* Takeshi Nakai[17]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received January 22, 1972

On the Formation of C_2O_4 in Chemiluminescent Reactions

Sir:

In a recent communication[1] to this journal, mass spectrometric evidence for the carbon dioxide dimer, C_2O_4, as a chemiluminescent intermediate was presented. Because of the interest of this laboratory in

---

[1] H. F. Cordes, H. P. Richter, and C. A. Heller, *J. Amer. Chem. Soc.*, **91**, 7209 (1969).

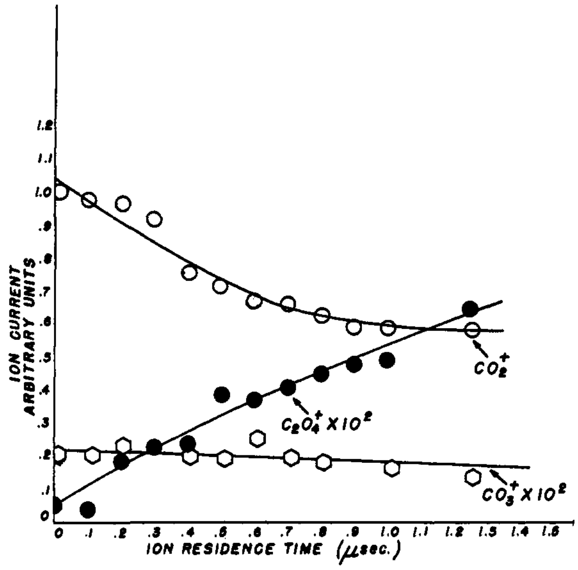


Figure 1. Relative concentrations [corrected for thermal drift: J. J. DeCorpo and F. W. Lampe, *J. Chem. Phys.*, **51**, 943 (1969)] of CO_2^+, CO_3^+, and $C_2O_4^+$ as a function of ion residence time.

chemiluminescent reactions, we have repeated this study.

As in the previous work, the gaseous products of hydrogen peroxide-oxalate ester reaction were allowed to flow directly into a Bendix Model 12 mass spectrometer. In the work reproduced in this laboratory, however, the products were not isolated behind a needle valve but were allowed to flow directly from the reaction vessel into the ionization region. This was made possible by fast differential pumping of the ion source in our mass spectrometer. This technique prevents any possible fractionation of the sample by the needle valve.

Another alteration effected in the study performed in this laboratory was the installation of a variable time-delay circuit. This circuit allows a variable time delay from 0 to 10 μsec between the end of the pulsed electron beam and the onset of the drawout pulse. The reaction or residence time is the sum of time delay and the time necessary for the ion to be withdrawn from the ionization chamber. The addition of the time-delay circuit permitted a study of the ions as a function of their residence time in the ion source. A Baratron Model 100A capacitance manometer was used to monitor the ion source pressure over a range of 0–50 μ and to study the ion current as a function of pressure.

With zero delay time, the data cited by Cordes, *et al.*,[1] were reproduced. The major reaction product was CO_2; the ions at *m/e* 88 or 60 were also observed as reported previously. However, when either of the major components (ester or hydrogen peroxide) was not present in the reaction vessel the ion currents at *m/e* 88 and 60 were not observed. When the ion currents at *m/e* 88 ($C_2O_4^+$), 60 (CO_3^+), and 44 (CO_2^+) were investigated as a function of ion source residence time or pressure, it became apparent that $C_2O_4^+$ is a secondary ion formed by an ion-molecule reaction in the ion source itself and not as a product of the H_2O_2–oxalate ester reaction.

Examination of a plot of the relative concentration of $C_2O_4^+$, CO_2^+, CO_3^+ as a function of ion residence time, which is shown in Figure 1, reveals that simultaneously in the ion source the $C_2O_4^+$ ion is formed while the CO_2^+ ion is consumed. Thus, the ion observed at *m/e* 88 cannot be formed from the agent producing chemiluminescence as proposed earlier.[1] It should be noted that the ion current observed at *m/e* 60 (CO_3^+) exhibited the behavior of a species formed from the reaction mixture and thus its precursor is a possible chemiluminescent agent. When CO_2 was studied under similar conditions, *i.e.*, the same pressures and delay times used in these experiments, no *m/e* 88 was observed. This suggests that the ion-molecule reaction which produced *m/e* 88 in the chemiluminescent study was not between a CO_2 ion and a neutral CO_2 molecule. Two other possibilities exist: a reaction between CO_2^+ and some organic species (*e.g.*, the ester), or between $RCOO^+$ and CO_2. The first reaction is more likely and is supported by the decrease in the *m/e* 44 ion current shown in Figure 1. A comprehensive study of the formation of the *m/e* 88 ion current will be reported in a future publication.

Acknowledgment. We wish to thank Dr. A. B. Harvey for calling our attention to this problem and to Dr. T. Hall of the Naval Ordnance Laboratory for the chemical used in the reaction.

(2) NRL–NRC Postdoctoral Research Associate, 1970–1972.

J. J. DeCorpo,[2] A. Baronavski
M. V. McDowell, F. E. Saalfeld*
U. S. Naval Research Laboratory, Mass Spectroscopy Section
Chemistry Division, Code 6110, Washington, D. C. 20390
Received November 12, 1971

Facile Conversion of Oxiranes to Thiiranes by Phosphine Sulfides. Scope, Stereochemistry, and Mechanism

Sir:

We wish to report that thiiranes may be conveniently and rapidly synthesized from the corresponding oxiranes with phosphine sulfides.

In general, oxiranes can be converted to thiiranes by the use of thiocyanate ion, thiourea, or thioamides and related compounds.[1-4] Recently, it was reported that 2-hydroxyethyl disulfide reacted with triphenylphosphine to give ethylene sulfide and triphenylphosphine oxide.[5] A pentavalent phosphorus species I was proposed as the intermediate[5,6] (I, L_{1-3} = Ph; R_{1-4} = H). We reasoned that a thiophosphoryl compound might well react with an oxirane to form such an intermediate which would proceed to give a phosphoryl compound and a thiirane.[7] Formation of the phos-

---

(1) General reviews on thiiranes: D. D. Reynolds and D. L. Fields in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 576; L. Goodman and E. J. Reist in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, p 93; M. Sander, *Chem. Rev.*, **66**, 297 (1966).

(2) F. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969).

(3) D. L. Clason and L. E. Coleman, U. S. Patent 3,560,528 (1970); *Chem. Abstr.*, **75**, 20171*h* (1971).

(4) R. C. Vander Linden, J. M. Salva, and P. A. C. Smith, U. S. Patent 3,542,808 (1970); *Chem. Abstr.*, **74**, 53498*c* (1971).

(5) M. Grayson and C. E. Farley, *Chem. Commun.*, 831 (1967).

(6) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7031 (1969).

(7) An isolated example was provided by G. Schrader and W. Lorenz, German Patent 1,082,915 (1960); *Chem. Abstr.*, **55**, 25983 (1961), who reported the generation of thioglycidyl thiophosphate by conversion of epichlorohydrin with 2 mol of potassium dialkyl thiophosphate.