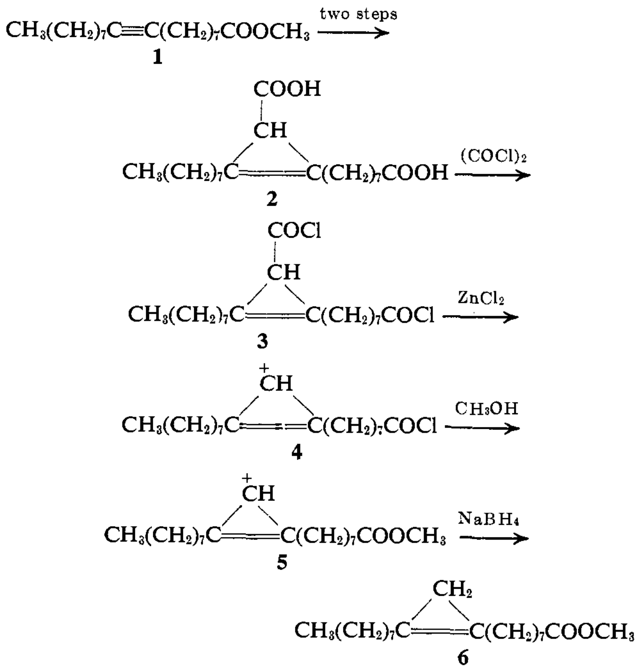
Direct decarbonylation of cyclopropene acids such as in **2** to give the cyclopropenium ion is a known



process.[7] However, to avoid using the potentially hazardous perchloric acid–acetic anhydride reagent we chose to operate *via* acid chloride **3**, which was obtained readily with excess oxalyl chloride. Treatment of diacid chloride **3** with zinc chloride selectively decarbonylated the chlorocarbonyl group in the cyclopropene ring to give **4** without affecting the second acid chloride grouping. Reaction with methanol converted the acid chloride, which is susceptible to borohydride reduction, to the ester **5**, which is not. The cyclopropenium ion ester **5** was then treated with sodium borohydride to reach the desired product, methyl sterculate (**6**), in 40% yield from diacid **2**.

Synthetic methyl sterculate [*Anal.* Calcd for $C_{20}H_{36}O_2$: C, 77.82; H, 11.76. Found: C, 77.83; H, 11.64] was obtained as a colorless oil sensitive to both heat and air. The material showed the expected features in its nmr and infrared absorption spectra, which were indistinguishable from those taken with pure methyl sterculate from *Sterculia foetida*.[8] The synthetic and natural materials gave single spots on thin-layer chromatographic plates, with the same R_f values. Gas–liquid partition chromatography with the two materials produced curves that were virtually superposable.[9,10] For further check on homogeneity and identity, the two materials were converted to their methylthiol adducts.[10,11] The adducts gave identical gas–liquid partition chromatography curves showing a single symmetrical peak. The infrared and the nmr absorption curves were also identical.

Work on the synthesis of ^{14}C-labeled malvalic acid (8,9-methano-8-heptadecenoic acid) is under way.

Walter J. Gensler, M. Brawner Floyd
Ryobun Yanase, Kenneth Pober
Department of Chemistry, Boston University
Boston, Massachusetts 02215

Received November 23, 1968

---

[7] F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964); A. W. Krebs, *Angew. Chem.*, **77**, 10 (1965).

[8] We are indebted to Alan R. Johnson, Commonwealth Scientific and Industrial Research Organization, Ryde, Australia, for a sample of pure methyl sterculate isolated from *Sterculia foetida*.

[9] See A. C. Fogerty, A. R. Johnson, J. A. Pearson, and F. S. Shenstone, *J. Am. Oil Chemists' Soc.*, 42, 885 (1965); F. G. Magne, *ibid.*, 42, 332 (1965); H. W. Kircher, *ibid.*, 42, 899 (1965).

[10] H. W. Kircher, *ibid.*, 41, 4 (1964).

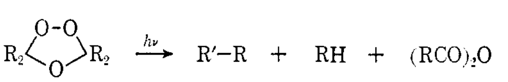
[11] P. K. Raju and R. Reiser, *Lipids*, 1, 10 (1966); N. K. Hooper and J. H. Law, *J. Lipid Res.*, **9**, 270 (1968).

Photochemistry of Ozonides. Generation of Tetramethylcyclobutadiene in Photolysis of Hexamethyl Dewar Benzene Monoozonide

Sir:

Photodecomposition of hexamethyl Dewar benzene monoozonide (**1**) has been found to give tetramethylcyclobutadiene (**2**) as evidenced by the isolation of tetramethylcyclobutadiene dimer, *syn*-octamethyltricyclooctadiene (**3**). This rather remarkable reaction is one of two particularly instructive examples which were chosen for defining the scope and applicability of ozonide photolysis.[1,2]

Most ozonides have been found to photolyze according to the general scheme outlined in eq 1 in which a double β scission follows homolysis of the oxygen–oxygen bond. Cage recombination of the resulting carbon radicals is reasonably efficient.[1,2] The examples described in this preliminary report, hexamethyl Dewar benzene ozonide and diphenylacenaphthalene ozonide, are ones for which double β scission should lead to interesting but unstable products.



(1)

By analogy to our earlier observation that irradiation of cyclopentene ozonide (**5**) gives good yields of cyclopropane,[1,2] it was anticipated that hexamethyl Dewar benzene monoozonide (**1**) may yield tetramethylcyclobutadiene (**2**) as a transient intermediate. This expectation appears to have been borne out. Using conditions previously described,[1] we photolyzed **1**, mp 53–54,[3] in pentane and obtained *syn*-octamethyltricyclooctadiene (**3**)[4,5] in 19% yield, mp 196–198°, along with the ketone **4** in 30% yield; infrared (**4**) (CCl_4, cm^{-1}): 1700 (s), 1628 (s); nmr (CCl_4, δ): 1.25 (s), 1.75 (s), 2.00 (s), 3.53 (d), 3.85 (d), in the ratio 3:6:3:1:1; mass spectrum: *m/e* 150, 107, 43. Isolation of the dimer **3** does not, of course, unequivocally establish the intermediacy of **2**.

That the presumed intermediate cyclobutadiene **2** is singlet is supported both by the exclusive formation of *syn* dimer **3**[6–8] and by virtue of the nature of the reaction, which we believe may lead directly to singlet product. Cyclopentene ozonide (**5**), for example, gives no more than a trace, if any, of propane or propene,[1,2]

---

[1] P. R. Story, W. H. Morrison, III, T. K. Hall, J-C. Farine, and C. E. Bishop, *Tetrahedron Letters*, 3291 (1968).

[2] P. R. Story, T. K. Hall, W. H. Morrison, III, and J-C. Farine, *ibid.*, 5397 (1968).

[3] H. Junker, W. Schafer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967).

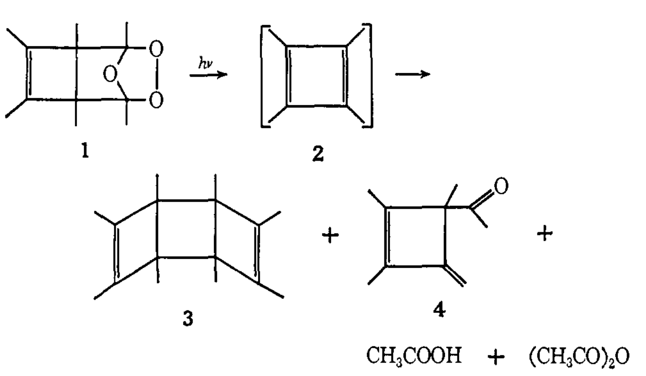
[4] R. Criegee and G. Louis, *ibid.*, 90, 417 (1957).

[5] R. Criegee, G. Schröder, G. Maier, and H-G. Fischer, *ibid.*, **93**, 1553 (1960).

[6] P. S. Skell and R. J. Peterson, *J. Am. Chem. Soc.*, **86**, 2530 (1964).

[7] L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); **88**, 623 (1966).

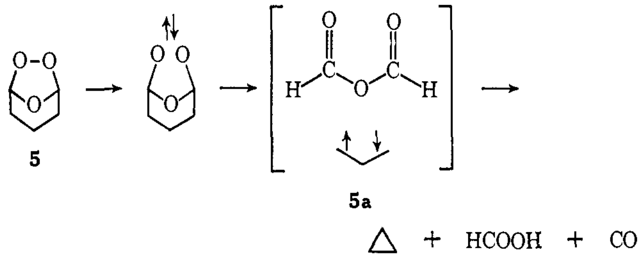
[8] M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965).



1 2 3 4

$CH_3COOH + (CH_3CO)_2O$

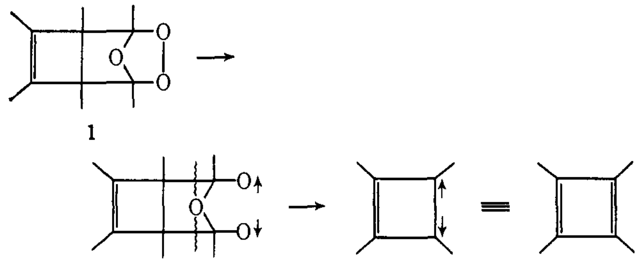
indicating that the 1,3-propane diradical **5a**–formic anhydride cage is singlet and that **5a** closes, therefore, with great efficiency to cyclopropane. Unequivocal establishment of the spin state of the initial product, however, will require additional data.



5 5a

+ HCOOH + CO

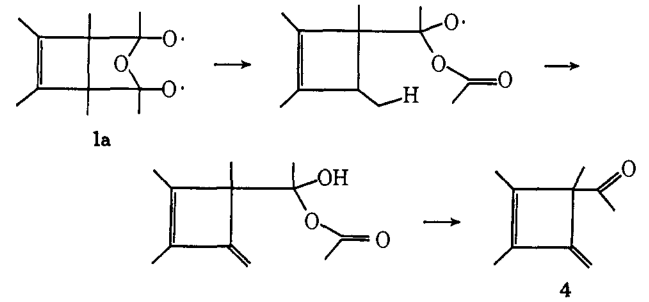
By analogy, we expect the direct formation of singlet cyclobutadiene. Application of this reaction to the



1 1a 2

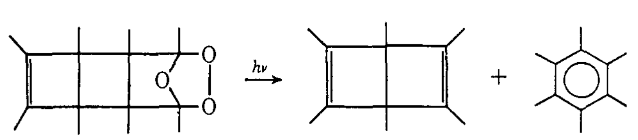
generation of monomeric tetramethylcyclobutadiene at low temperature, perhaps in a glass matrix, for the purpose of obtaining its electronic and epr spectra is under investigation.

Formation of the ketonic product **4** is easily understood in terms of a single β scission followed by an intramolecular hydrogen abstraction, for which there is an apparent analogy.[2]



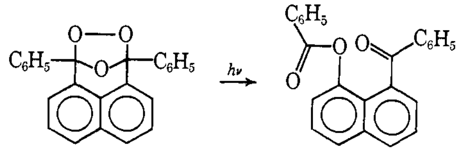
1a 4

Criegee has reported the successful application of ozonide photodecomposition to several other systems, *e.g.*[9]



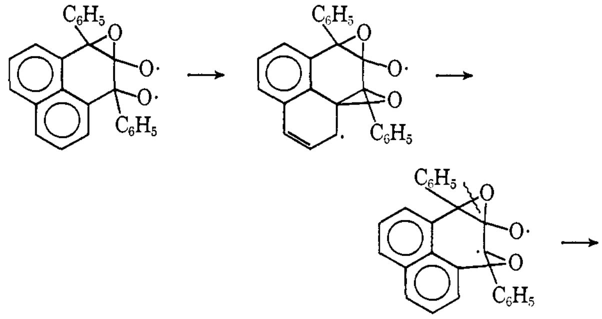
This sequence, interestingly, constitutes a reversal of the cyclobutadiene-forming reaction reported here.

Although most ozonides are photolyzed according to eq 1 in which oxygen–oxygen bond homolysis is followed by a double β scission, there are notable limiting exceptions. We have examined the photolysis of diphenylacenaphthalene ozonide (**6**)[10] and find no evidence of β scission. Instead, the reaction is, over-all, quite analogous to a Baeyer–Villiger rearrangement and gives the keto benzoate **7** in 60% yield, mp 125–126°;[11] infrared (CCl_4, cm^{-1}): 1680, 1750; mass spectrum: m/e = 352, 105, 77. Hydrolysis of **7** afforded benzoic acid. The rearrangement is very much like that observed by Criegee,[12] Bailey,[13] and Ullman and Henderson[14] for diphenylindenone ozonide which was found to give a high yield of a keto anhydride.



6 7

Ozonides are, in a sense, Baeyer–Villiger intermediates,[15,16] and in many cases undergo acid-catalyzed rearrangement in Baeyer–Villiger style.[17] Although the rearrangement observed for **6** is formally of this type, we must conclude, in the absence of additional evidence, that the keto benzoate **7** probably results from a Wieland-type rearrangement[18] rather than from a photochemically induced and ionic Baeyer–Villiger rearrangement, *i.e.*



→ 7

The diphenylindenone ozonide rearrangement, both thermal[12–14] and photochemical,[14] is likely of the same type.

---

(9) R. Criegee, *Chimia*, **22**, 392 (1968).

(10) R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88**, 122 (1955).

(11) All new compounds gave satisfactory elemental analyses.

(12) R. Criegee, P. DeBruyn, and G. Lohaus, *Ann.*, **583**, 19 (1953).

(13) P. S. Bailey, *Chem. Ber.*, **88**, 795 (1957).

(14) E. F. Ullman and W. A. Henderson, *J. Am. Chem. Soc.*, **89**, 4390 (1967).

(15) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

(16) H. Kwart, P. S. Starcher, and S. W. Tinsley, *Chem. Commun.*, 335 (1967).

(17) P. R. Story, B. C. Clark, Jr., and C. E. Bishop, unpublished; E. Bernatek, H. Hagen, and T. Ledaal, *Acta Chem. Scand.*, **21**, 1555 (1967); E. Bernatek and F. Thorsen, *ibid.*, **13**, 342 (1959).

(18) H. Wieland, *Chem. Ber.*, 44, 2553 (1911); M. S. Kharasch, A. Poshkus, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 1458 (1951).

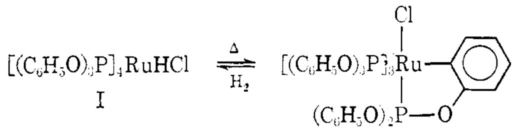
Acknowledgment. We thank the National Air Pollution Control Administration, Public Health Service, for support of this work through Grant AP 00580.

Paul R. Story, W. Herbert Morrison, III, James M. Butler
Department of Chemistry, The University of Georgia
Athens, Georgia 30601
Received December 30, 1968

Ligand–Metal Hydrogen Transfer in Phosphite Complexes

Sir:

A number of tertiary phosphine complexes of transition metals have been reported to exhibit interactions between the metal atom and C–H bonds of the phosphine ligand.[1] This communication describes related behavior for *phosphite* complexes. The reaction of tris(triphenylphosphine)ruthenium chlorohydride[2] with triphenyl phosphite in benzene at room temperature forms hydrogen and a mixture of tetrakis (triphenyl phosphite)ruthenium chlorohydride (I)[3] and an *ortho*-phenyl bonded, dehydrogenated derivative, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$ (II).[4] Both I and II are white, air-stable compounds which are soluble in aromatic hydrocarbons; they are readily interconvertible.


I

II

The dehydrogenation proceeds smoothly in refluxing methylcyclohexane from which crystalline II separates on cooling; the reversal occurs readily on exposure of hydrocarbon solutions of II to hydrogen. The ^1H nmr spectrum of I includes a hydride signal at τ 16.8, split into two multiplets. This is consistent with an octahedral structure in which the hydrogen is *trans* to phosphorus ($J_{P-H\ trans} = 176$ cps). The absence of hydrogen bonded to ruthenium in II has been established by nmr and infrared spectroscopy.

The ^{31}P nmr spectrum of II at 40.5 MHz consists of two pairs of overlapping triplets and one pair of overlapping doublets, indicative of an octahedral structure in which the ruthenium–carbon bond is *trans* to phosphorus and the *ortho*-bonded phosphite phosphorus is *trans* to chlorine.[5] The phenyl–ruthenium bond in II is assumed to be at an *ortho* position for steric reasons and by analogy with the deuteration of $[(C_6H_5O)_3P]_4CoH$, discussed below.

The reaction of II with deuterium leads to an *ortho*-deuterated analog of I. Participation of all the *ortho* positions in the equilibrium was demonstrated by an experiment in which 0.26 mmole of II was treated with 7.0 mmoles of deuterium for 2 days at ambient temperature in toluene. Analysis of the recovered gases showed 47.6% D_2, 41.7% HD, and 10.7% H_2, compared to a D_2:HD:H_2 ratio of 48.5:42.2:9.3 calculated for statistical distribution of the deuterium among all the 24 *ortho* positions of I.

The reaction of $[(C_6H_5O)_3P]_4CoH$ with deuterium also results in deuteration of the phenyl rings although no intermediate similar to II has been isolated. At 220 MHz, the spectra of the deuterated and undeuterated complexes are well resolved and permit unambiguous identification of the *ortho* positions as the sole sites of deuteration. Presumably complexes similar to II are involved as reaction intermediates.

Recently the reaction of $[(C_6H_5O)_3P]_3Rh(CO)H$ with triphenyl phosphite was reported to give $[(C_6H_5O)_3P]_4RhH$ in refluxing ethanol[6] and $\{[(C_6H_5O)_3P]_4Rh\}_2$ in refluxing *n*-alkanes.[7] The evidence presented for the dimeric nature of the latter consisted of the observed diamagnetism of the complex and an inability to detect hydride ligands. It is suggested here that "$\{[(C_6H_5O)_3P]_4Rh\}_2$" and the analogous "$\{[(C_6H_5O)_3P]_4Ir\}_2$"[7] are actually *ortho*-phenyl bonded species, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4M}$, analogous to II above. In support of this it was noted that the infrared spectrum of $[(C_6H_5O)_3P]_4RhH$ is virtually identical with that of I, and that refluxing this rhodium complex in *n*-heptane gives a new species with an infrared spectrum very similar to that of II. This transformation is readily reversed by hydrogen at atmospheric pressure, analogous to the transformation of II to I. Additionally, treatment of $[(C_6H_5O)_3P]_4RhH$ with deuterium resulted in extensive deuteration of the *ortho*-phenyl positions.

The mechanism of the reversible hydrogenation and other aspects of this chemistry will be discussed in a forthcoming article.

---

[1] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965); M. A. Bennett and D. C. Milner, *Chem. Commun.*, 581 (1967); G. W. Parshall, *J. Am. Chem. Soc.*, 90, 1669 (1968); A. Sacco and M. Rossi, *Inorg. Chim. Acta*, 2, 127 (1968); W. Keim, *J. Organometal. Chem.*, 14, 179 (1968); G. Hata, H. Kondo, and A. Miyaki, *J. Am. Chem. Soc.*, 90, 2278 (1968); W. H. Knoth, *ibid.*, 90, 7172 (1968); S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968); A. Sacco and M. Aresta, *ibid.*, 1223 (1968).

[2] P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *ibid.*, 305 (1967).

[3] *Anal.* Calcd for $C_{72}H_{61}ClO_{12}P_4Ru$: C, 62.7; H, 4.5; Cl, 2.6; P, 9.0. Found: C, 62.9; H, 4.4; Cl, 2.6; P, 8.4.

[4] *Anal.* Calcd for $C_{72}H_{59}ClO_{12}P_4Ru$: C, 62.8; H, 4.3; Cl, 2.6; O, 14.0; P, 9.0. Found: C, 62.8; H, 4.4; Cl, 2.6; O, 13.8; P, 8.8.

[5] A referee has requested comment on the fact that the ^{31}P nmr pattern of II is also consistent with a structure in which the ruthenium–carbon bond is *trans* to chlorine. We prefer the structure proposed in the text because of the chemical shift and coupling constant data, which will be discussed in detail in a forthcoming paper. Also, the structures proposed for I and II in the text are mutually consistent, whereas the alternate structure for II would require that a rearrangement occur in the equilibrium between I and II.

[6] J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1405 (1968).

[7] S. D. Robinson, *ibid.*, 521 (1968).

W. H. Knoth, R. A. Schunn
Contribution No. 1552, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898
Received February 6, 1969

Synthesis of Ethylenediamine-N,N,N′-triacetic Acid and Its Cobalt(III) Complexes

Sir:

Past attempts to prepare ethylenediaminetriacetic acid have been generally unsuccessful and recent reports of the acid's existence could not be confirmed.[1–3]

---

[1] K. A. Schroeder and R. E. Hamm, *Inorg. Chem.*, 3, 391 (1964).

[2] R. E. Hamm and M. A. Suwyn, *ibid.*, 6, 139 (1967).

[3] D. L. Venezky and W. B. Moniz, *Anal. Chem.*, 41, 11 (1969).