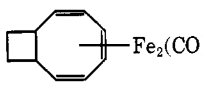

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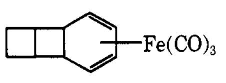

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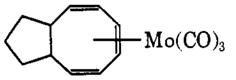

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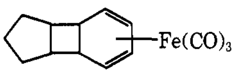

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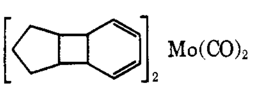

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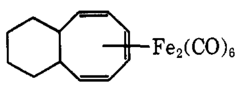

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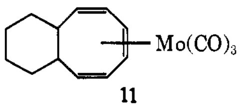

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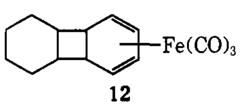

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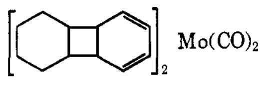

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characterized as to gross structure (connexity of bonds) by solution nmr.[7,7a]

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(7) This work was supported in part by the National Science Foundation.

(7a) Note Added in Proof. The structures of 5 and 8 have now been confirmed crystallographically.

(8) Address correspondence to this author at the Department of Chemistry, Texas A & M University, College Station, Texas 77843.

(9) On leave from Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi de Transizione del CNR, Bologna, Italy, during 1971.

F. A. Cotton,*[8] G. Deganello[9]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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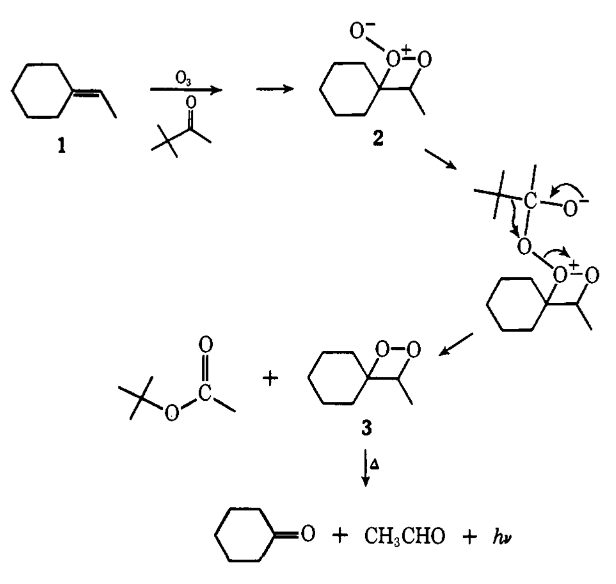
Mechanisms of Ozonolysis. Isolation of the Dioxetane Intermediate

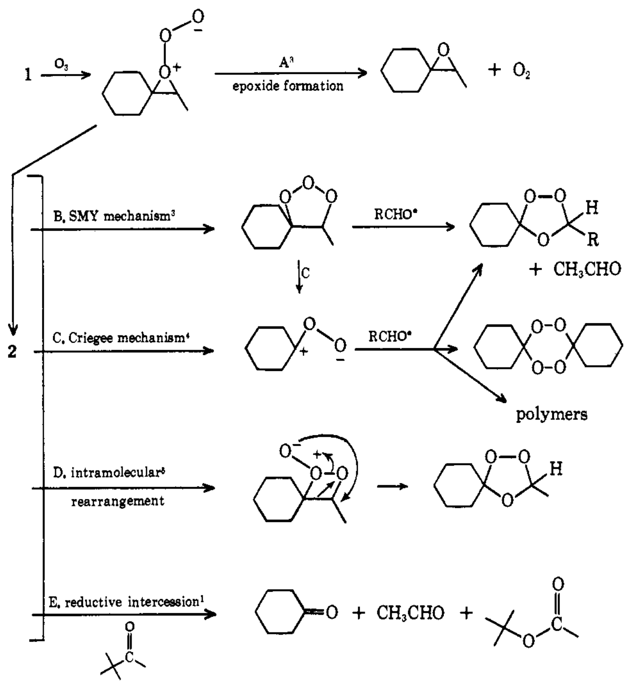
Sir:

We earlier reported[1] that certain aldehydes and ketones, when used as solvents, intercept and reduce a labile intermediate in the ozonolysis of olefins to the extent that no peroxidic products are isolable; however, the double bond is cleaved and the normal carbonyl products are obtained in high yield. This phenomenon is observed in solvents which will readily undergo Baeyer–Villiger oxidation; such solvents are henceforth termed "Baeyer–Villiger" solvents. On the basis of this observation we proposed that the intermediate so reduced in this sequence is most likely the Staudinger molozonide (2).[2] Reduction of the molozonide 2 in this way generates the corresponding dioxetane 3.

Accordingly, we wrote a unified concept for the ozonolysis reaction in which the key intermediate was the Staudinger molozonide 2 and the particular products of any given ozonolysis reaction were determined largely by competition among several possible reaction paths (B–E) involving this intermediate, 2. Using ethylidenecyclohexane (1) as a model, the overall scheme is illustrated here (Scheme I).



Scheme I[a]



[a] The asterisk indicates added foreign aldehyde or acetaldehyde produced in path C.

We can now report that we have isolated the dioxetane intermediate from the ozonolysis of several different olefins and it appears that this will be a general phenomenon for ozonolysis reactions. For ex-

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(1) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 3042 (1971).

(2) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *ibid.*, **93**, 3044 (1971).

(3) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966); P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

(4) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957); R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 29.

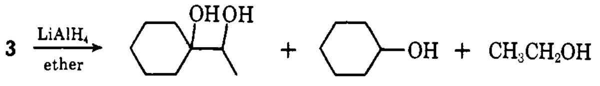
(5) P. R. Story and W. C. Ray, unpublished results.

ample, ozonolysis, to completion, of ethylidenecyclohexane (**1**) (0.25 molar) in pinacolone solvent at −45°, using ozone in nitrogen, yielded a colorless, viscous liquid after evaporative removal of most of the pinacolone at low temperature (0–10°). Gpc analysis of this residue indicated the presence of only cyclohexanone and acetaldehyde in approximately equal proportions, along with some remaining pinacolone and a trace of *tert*-butyl acetate. Analysis of the separated pinacolone revealed that it contained 1 equiv (relative to cyclohexanone) of *tert*-butyl acetate.

The neat residue, upon very rapid heating (placed in a hot bath at 170°), emitted a bluish-white light[6] (visible in a darkened room) and erupted violently to discharge acetaldehyde to the atmosphere. Similar heating of a decane solution containing the ozonolysis residue and 9,10-diphenylanthracene, 9,10-dibromoanthracene, or rubrene produced a very bright luminescence with a duration of 1–2 min.[7] Neither ozonides nor ketone diperoxides have been observed to luminesce during thermal decomposition.

The nmr of the crude residue also served to confirm the dioxetane structure. A multiplet centered at δ 5.2 compares well with the methine hydrogen quartet for trimethyl-1,2-dioxetane, reported[8] at δ 5.22. The methyl doublet for **3** at δ 1.22 also compares favorably with the corresponding doublet for trimethyl-1,2-dioxetane found at 1.35.[8] The crude residue was devoid of ozonide and acetaldehyde as determined by nmr, gpc, and infrared analysis. The yield of dioxetane **3** was estimated at 50–75%.

Lithium aluminum hydride reduction of the crude residue further served to confirm the assignment of structure **3** to the residue. Hydride reduction in ether yielded, in the proportions indicated (mole per cent), ethylidenecyclohexane glycol (**4**) (18%), cyclohexanol (40%), and ethanol (31%). For comparison, authentic glycol **4** was prepared by hydrolysis of the epoxide of ethylidenecyclohexane. By contrast, hydride reduction of ozonide[9] or of the presumed 1,2,3-trioxolane[10] does not yield glycols.



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We have examined the ozonolysis of a variety of olefins in pinacolone and other Baeyer–Villiger solvents and invariably find that ozonide is not formed and that the dioxetane is detectable. Routinely, the dioxetane is detected by light emission on sudden warming of the ozonolysis residue after removal of the solvent at low temperature. If the dioxetane is lower boiling than the solvent, it is concentrated by low-temperature distillation.[8] Ozonolysis of 2-methylbutene, cyclopentene, or indene in pinacolone results in light emission on warming the reaction residues and glycol formation on hydride reduction.

We have also prepared trimethyl-1,2-dioxetane and **3** by a conventional method[11] and find that hydride reduction yields the corresponding glycol in both cases. The dioxetanes so prepared are identical in all respects with those obtained by ozonolysis.

The observations reported here serve to place our earlier mechanistic proposal[2] on firm ground. It also appears that the technique employed here, *i.e.*, ozonolysis in Baeyer–Villiger solvents, represents a very useful synthetic procedure for the cleavage of double bonds. Rearrangements and abnormal ozonolysis products[12] are minimized and the work-up of peroxidic products is avoided. In addition, it now appears that ozonolysis of olefins in Baeyer–Villiger solvents at low temperature represents a superior method for the synthesis of dioxetanes.

Acknowledgment. We thank the National Air Pollution Control Office of the Environmental Protection Agency (HEW) for support of this work through Grant No. 00505.

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[6] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

[7] T. Wilson and A. P. Schaap, *ibid.*, **93**, 4126 (1971).

[8] E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970).

[9] C. E. Bishop and P. R. Story, *ibid.*, **90**, 1905 (1968).

[10] R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

[11] K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968); W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, **93**, 3996 (1971).

[12] P. R. Story and J. R. Burgess, *Tetrahedron Lett.*, 1287 (1968).

Paul R. Story,* Everest A. Whited, John A. Alford
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

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Diiron Enneacarbonyl Induced Rearrangement of Santonin

Sir:

Santonin (**1**) undergoes several remarkable rearrangements when photolyzed in solution[1] or in the solid state.[2] We now wish to report that treatment of santonin with diiron enneacarbonyl [$Fe_2(CO)_9$] results in a reaction showing the following novel features: (i) nonphotolytic rearrangement of santonin to the iron tricarbonyl complex of a compound believed to be formed on solid-state irradiation; (ii) the first reduction of a carbonyl group by $Fe_2(CO)_9$.

Reaction of santonin (1.17 g) with $Fe_2(CO)_9$ (3.45 g) in rigorously dried benzene at 40° (oil bath temperature) for 4.0–4.5 hr, followed by careful chromatography of the mixture on a Florisil column, gave a pale yellow solid [**2**, eluted with 7:3 petroleum ether (bp 38–52°)–ether] in 10.8–14.1% yield, unreacted santonin (eluted with 7:3 petroleum ether–ether or ether), and a pale yellow solid (**3**, eluted with 9.5:1.0 methylene chloride–ethanol) in 0.22–0.54% yield. The yields are based on the reaction being repeated four times. Both complexes were reasonably air stable.

The minor product, mp 109.0–110.5° (sealed tube), was assigned structure **3** on the basis of elemental analysis (*Anal.* Calcd for $C_{18}H_{18}O_6Fe$: C, 55.98; H, 4.70; Fe, 14.46. Found: C, 56.12; H, 4.69; Fe, 14.18) and spectral results. The ir spectrum (KBr) of **3** showed intense terminal metal carbonyl stretching bands at 2060, 2009, and 1983 cm^{-1} (shoulders at 2022 and 1994 cm^{-1}), lactone carbonyl stretching at 1771

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[1] P. J. Kropp, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

[2] T. Matsuura, Y. Sata, K. Ogura, and M. Mori, *Tetrahedron Lett.*, 4627 (1968).