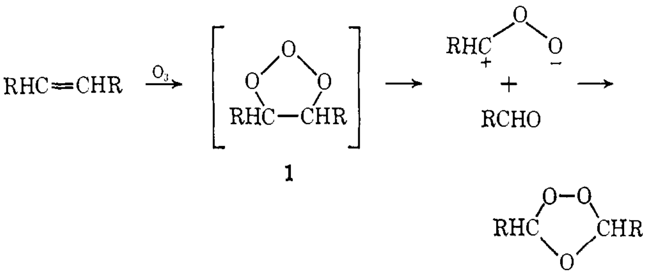
Communications to the Editor

Mechanisms of Ozonolysis. Reductive Ozonolysis with Aldehydes and Ketones

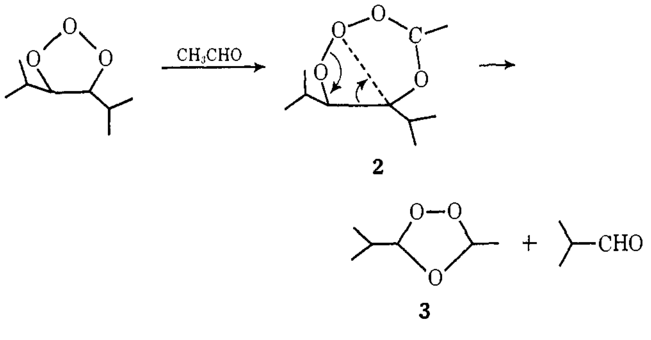
Sir:

We present evidence here which shows that in the ozonolysis of typical aliphatic olefins, the addition of an excess of certain aldehydes or ketones can completely eliminate ozonide formation. It is further demonstrated that the excess aldehyde or ketone effects a reductive ozonolysis.

For several years the ozonolysis of olefins was interpreted in terms of the Criegee zwitterion mechanism[1] which included the formation of a primary ozonide as the initial ozone–olefin adduct. This primary ozonide has been widely interpreted as having the 1,2,3-trioxolane structure (**1**).[1,2]



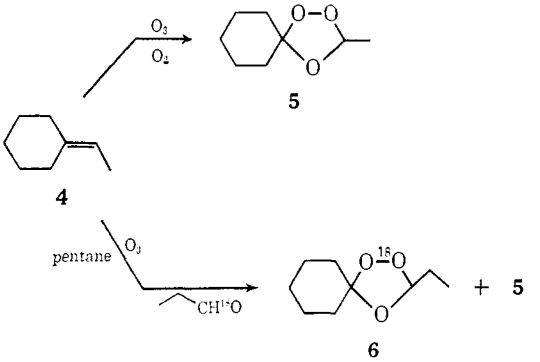
In 1966 it became necessary to question[3] the relative importance of ozonide formation by this mechanistic scheme and a new mechanistic proposal was published.[4] Because of the obvious dependence of ozonide cis/trans ratios on olefin geometry, we wrote an aldehyde interchange mechanism involving reaction of the molozonide with aldehyde to give a seven-membered ring intermediate **2** which subsequently fragmented to ozonide **3** and aldehyde, *e.g.*



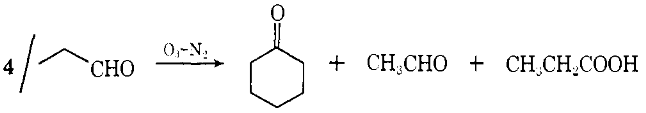
This mechanistic pathway was given substance by subsequent oxygen-18 labeling studies.[5,6]

Extension of these studies led to an investigation of the ozonolysis of several different types of olefins including ethylidenecyclohexane (**4**). Although this olefin might not be expected to yield an ozonide because it is trisubstituted,[7] it, in fact, gives the normal ozonide **5** in high yield; no cross-ozonide is observed.

Following the previously established procedure,[6] we carried out the ozonolysis of **4** in the presence of 1 molar equiv of propionaldehyde-^{18}O and found, as in the case of *trans*-diisopropylethylene, that most of the cross-ozonide, cyclohexylidene ethyl ozonide (**6**), was formed *via* a pathway which placed the oxygen-18 label in the peroxide bridge, consistent with the new mechanism.[6] None of the other possible cross-ozonide, methyl ethyl ozonide, was detected.



Ozonolysis of the same olefin in a 4 *M* or greater excess of propionaldehyde, however, was found to yield no ozonide product but gave, instead, cyclohexanone (85%), acetaldehyde (62%), and propionic acid in an amount (80%) roughly equivalent to the cyclohexanone formed



This effect was not limited to the ozonolysis of **4**, but has been observed for many olefins. For example, ozonolysis of a 0.25 *M* solution of *trans*-diisopropylethylene in freshly distilled propionaldehyde using ozone–nitrogen (to minimize aldehyde oxidation)[8] yielded none of the usual ozonide but gave isobutyraldehyde and propionic acid.

The ozonolysis of **4** and of *trans*-diisopropylethylene in acetone provided the normal ozonides in good yield, thus eliminating the possibility that the effect reported here is simply a consequence of solvent polarity.

By contrast, cyclohexanone as a solvent gave quite different results. Ozonolysis of **4** in cyclohexanone at −12° using ozone–nitrogen gave no ozonide product, but did yield 6-hexanolide and acetaldehyde. The lactone is, of course, in the Baeyer–Villiger sense, equiv-

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[1] 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.

[2] P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, 88, 4098 (1966).

[3] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, 88, 3143 (1966).

[4] P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, 88, 3144 (1966).

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

[6] P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

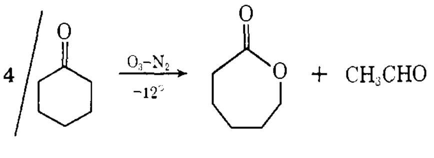
[7] R. W. Murray, P. R. Story, and L. D. Loan, *ibid.*, 87, 3025 (1965).

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

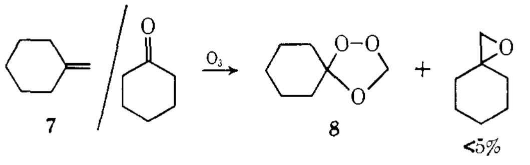
Table I. Ozonolysis of Olefins in the Presence of Excess Aldehydes and Ketones

Olefin	Concn, *M*	Solvent	*T*, °C	Ozone carrier	Normal ozonide yield, %	Cross-ozonide yield, %	Other products (yield, %)
4	0.25	Propionaldehyde	−70	N_2	None	None	Cyclohexanone (75) Acetaldehyde (62)
4	0.20	Acetaldehyde	−70	N_2	75		Cyclohexanone (low)
4	0.25	Butyraldehyde	−70	O_2	None	None	Not determined
4	0.15	Butyraldehyde	−70	N_2	None	None	Not determined (n.d.)
4	0.30	Butyraldehyde	−70	N_2	None	None	Butyric acid (high) Cyclohexanone (high) Acetaldehyde (high)
4	0.25	3,3-Dimethyl-2-butanone	Fp	O_2	None	N.d.	N.d.
4	0.25	Cyclohexanone	−15	O_2	None	None	6-Hexanolide (50) Acetic acid (low)
4	0.25	Cyclohexanone	−12	N_2	None	None	6-Hexanolide (50%)
7	0.31	Pentane	−70	O_3	85	N.d.	Cyclohexanone + cyclohexylidene epoxide (total = 5%)
7	0.25	Propionaldehyde	−78	N_2	Low	None	
7	0.20	Cyclohexanone	−15	O_2	75	None	None observed
7	0.20	Acetaldehyde	−70	N_2	40	42	
7	0.31	Acetone	−70	O_2	85	None	
cis-Diisopropylethylene	0.25	Propionaldehyde	−78	N_2	None	26	Propionic acid (23) Isobutyraldehyde (37)
trans-Diisopropylethylene	0.25	Propionaldehyde	−78	N_2	None	Trace	Propionic acid (~50)
8	0.25	Propionaldehyde	−78	N_2	Trace	Trace	Pivaldehyde (n.d.) Propionic acid (n.d.)
cis-Stilbene	0.1	CCl_4	−20	N_2	~50		Benzaldehyde (n.d.)
cis-Stilbene	0.1	Propionaldehyde	−20	N_2	None	~48	Benzaldehyde
trans-Stilbene	0.05	CCl_4	−20	N_2	~50		Benzaldehyde
trans-Stilbene	0.05	Propionaldehyde	−20	N_2	None	~40	Benzaldehyde

alent to the propionic acid resulting from ozonolyses conducted in propionaldehyde.



The ozonide-forming reaction is not so easily quenched in all olefinic systems, most notably in those which give high yields of ozonides and which we have long thought to form ozonides, at least in part, by an intramolecular rearrangement process.[4] One such example is provided by the ozonolysis of methylenecyclohexane (**7**), which in acetone, ether, or methylene chloride solvents gives cyclohexylidene ozonide (**8**) in 85% yield. In propionaldehyde solvent the yield of normal ozonide (**8**) is reduced to about 5% and no cross-ozonide is detectable. In cyclohexanone, however, there is little, if any, diminution in yield of the ozonide (**8**).



An especially important example is provided by the ozonolysis of *trans*-di-*tert*-butylethylene (**9**). Since the primary ozonide derived from this olefin is reported to be relatively stable,[1,2] we ozonized the olefin in pentane solution at −78°, flushed the system with cold nitrogen, and then introduced freshly distilled propionaldehyde precooled to the same temperature.[9] After about 15 min the solution was warmed to room temperature and found to contain pivaldehyde, propionic acid, and a low yield of normal ozonide (<10%). No cross-ozonide was in evidence.

By contrast, it is especially noteworthy that both *cis-* and *trans*-stilbene, which almost certainly give ozonide products *via* the Criegee zwitterion route,[10] give high yields of the cross-ozonide, phenyl ethyl ozonide, when ozonized in propionaldehyde.

The evidence presented here provides a new perspective on the ozonolysis reaction and requires reexamination of many interpretations placed on the data heretofore available. The formation of cross-ozonides with added, foreign aldehyde was, of course, one of the principal pieces of evidence which led Criegee to write the zwitterionic mechanism.[1] Fortunately, those early experiments utilized formaldehyde and acetaldehyde which, as we have seen here, do not curtail ozonide formation even when used in great excess. This is undoubtedly because both these aldehydes are so highly associated in solution that their effective concentrations are relatively low.[11] Propionaldehyde and butyraldehyde, however, are not highly associated and

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(9) Ozonolysis of *trans*-di-*tert*-butylethylene (**9**) in pentane at −78° results in the formation of a white precipitate which on warming in pentane or other solvent yields ozonide. Freshly distilled, precooled propionaldehyde was added to this white solid. It is unlikely that these observations conflict with those of Bailey[2] who observed the nmr spectrum of the primary ozonide of this olefin in solution and reported that it was most consistent with the 1,2,3-trioxolane structure. In other words, we believe that the white solid is a precursor to the 1,2,3-trioxolane, and is the material being reduced by propionaldehyde in our experiment.

(10) C. E. Bishop, D. D. Denson, and P. R. Story, *Tetrahedron Lett.*, 5739 (1968).

(11) J. C. Bevington, *Quart. Rev., Chem. Soc.*, **6**, 141 (1952).

their effective concentrations usually approach apparent concentrations. These aldehydes, as well as cyclohexanone and other ketones which readily undergo the Baeyer–Villiger rearrangement, may prevent ozonide formation when used in excess.

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Mechanisms of Ozonolysis. A New and Unifying Concept

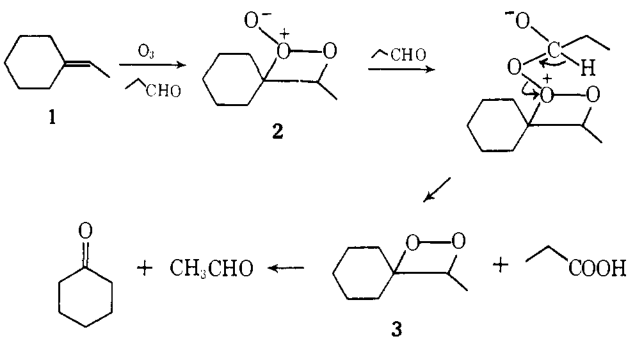
Sir:

In the preceding communication[1] we demonstrated that if the ozonolysis of typical aliphatic olefins is carried out in the presence of certain aldehydes and ketones, the formation of ozonides can be curtailed or prevented. The effect may be described as a reductive ozonolysis, with the added aldehyde or ketone being oxidized. An appropriate example is provided by the ozonolysis of ethylidenecyclohexane (**1**), which, in pentane or acetone solvent, at −78° using either ozone–oxygen or ozone–nitrogen, gives the normal ozonide, methyl cyclohexylidene ozonide, in 85% yield.

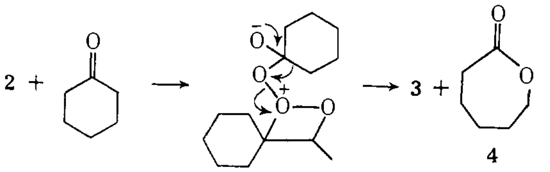
The addition of 1 molar equiv of propionaldehyde to the pentane–olefin solution prior to ozonolysis leads, as expected, to a good yield of both normal ozonide and the cross-ozonide, ethyl cyclohexylidene ozonide, in about equal quantities. Increasing the ratio of propionaldehyde to olefin, however, begins to decrease the total yield of ozonide until, finally, ozonolysis in propionaldehyde as the solvent gives no ozonide product. Cyclohexanone, acetaldehyde, and propionic acid are isolated, all in high yield.

This result appears incompatible both with the Criegee zwitterion mechanism[2] and with our aldehyde-interchange mechanism.[3] We submit, nonetheless, that these findings invalidate neither the Criegee mechanism nor our earlier mechanistic proposal,[3] but, in fact, provide for the first time the basis for a unifying mechanistic rationale, one which serves to tie together the many seemingly diverse elements of the ozonolysis reaction.

It is apparent that an intermediate formed during the ozonolysis is reduced in Baeyer–Villiger fashion by added aldehyde or ketone. The intermediate which can most reasonably provide the observed results is the Staudinger molozonide (**2**),[4,5] which see in the scheme below. Reduction of the molozonide (**2**) may occur, in what is essentially a Baeyer–Villiger oxidation of the aldehyde; the dioxetane intermediate **3** would, of course, be expected to cleave rapidly to cyclohexanone and acetaldehyde.



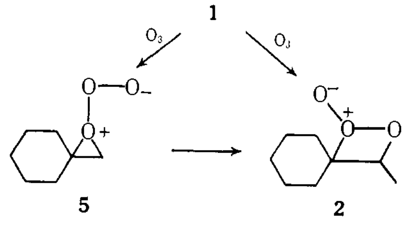
If the same reaction is carried out in cyclohexanone as solvent, 6-hexanolide (**4**) results from Baeyer–Villiger rearrangement of cyclohexanone, which is prone to undergo such rearrangement. Acetone, on the other hand, does not readily undergo Baeyer–Villiger rearrangement,[6] and in this solvent ozonide forms normally.



We must now deal with the observation that moderate concentrations of propionaldehyde do not prevent ozonide formation; *e.g.*, equimolar quantities of olefin and propionaldehyde in pentane solvent lead to good yields of both normal and cross-ozonides. This situation suggests the presence of more than one competing intermediate.

For some time now it has been assumed that ozone addition to an olefinic double bond is of the 1,3-dipolar type.[2,5,7] The results reported in the preceding communication are not consistent with that concept.[1]

From the data now available we can propose that the initial addition of ozone to an olefinic bond is to give the peroxy epoxide (**5**), which we have previously termed the σ complex.[3] The required Staudinger molozonide (**2**) is then formed from the σ complex. Alternatively, the Staudinger molozonide (**2**) may be produced directly through a 1,2-cycloaddition of ozone to the double bond; a concerted cycloaddition is not likely to be prohibitively forbidden.[8]



There are other reasons for preferring the initial formation of the peroxy epoxide (**5**). It is well known, for example, that many hindered olefins react with

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(1) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 0000 (1971).

(2) 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.

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

(4) H. Staudinger, *Chem. Ber.*, **58**, 1088 (1925).

(5) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958); see also, R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968), and P. S. Bailey and A. G. Lane, *J. Amer. Chem. Soc.*, **89**, 4473 (1967).

(6) P. A. S. Smith in "Molecular Rearrangements," P. deMayo Ed., Interscience, New York, N. Y., 1963, p 577.

(7) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963); P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966).

(8) D. R. Kearns, *ibid.*, **91**, 6554 (1969).