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MECHANISMS OF OZONOLYSIS. THE *cis, trans*-STILBENE SYSTEM

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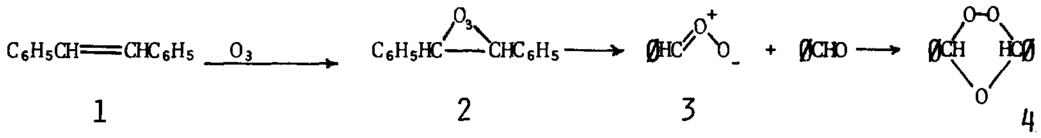
On the basis of the observation that cross ozonide *cis/trans* ratios from unsymmetrical, 1,2-disubstituted olefins were dependent upon olefin geometry *(1)*, we previously offered, as *part* of the framework of a mechanistic hypothesis *(2)*, the notion that ozonides could be formed by reaction of aldehyde with an unstable molozonide intermediate *(3)*. More recently, oxygen-18 labeling experiments have lent support to the new mechanism. *(4)(5)*

Fliszar and coworkers *(6)* have now used the results of oxygen-18 labeling experiments in stilbene ozonolyses to conclude that the molozonide-aldehyde mechanism *(2,4,5)* is unimportant in that system. Not unexpectedly, we find their conclusion is substantially correct, but the following points are to be considered:

(1) In the first place, it should be anticipated that the probable stability of a phenyl substituted zwitterion (3) would favor fragmentation of an olefin-ozone adduct intermediate (2) to give a Criegee zwitterion (3) and benzaldehyde. Ozonide (4) is then formed by zwitterion-aldehyde condensation.



(2) *cis*-Stilbene does not qualify as an unhindered 1,2-disubstituted olefin and, therefore, we would not, again, expect our mechanism to be operative. *(2,7)* This olefin, by simple analogy to similarly hindered aliphatic olefins, would be expected to give a predominance of *cis* ozonide.

(3) If our mechanism were operative, its effect should be reflected in a difference in ozonide *cis/trans* ratios for the isomeric olefins.

(4) No such variation exists. As seen in the Table, the *cis/trans* ratios are almost invariant. Fliszar did not report a determination of *cis/trans* ratios. The invariance of ozonide *cis/trans* ratios argues strongly for the Criegee zwitterion mechanism *(3)*.

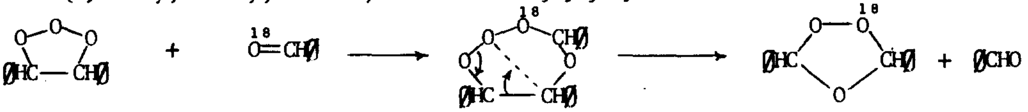
(5) According to the ozonide stereochemical assignment made by Fliszar, the *cis/trans* ratio from their data would appear to vary from greater than one to less than one, depending upon olefin geometry and the presence of added aldehyde [*cis/trans* ratio implied from isolation experiments]. This is inconsistent with the Criegee mechanism*(3)*.

(6) Fliszar's ozonide stereochemical assignment, in fact, is in error. The assignment was based on our earlier correlation of nmr chemical shift of the methine hydrogens for *aliphatic* ozonides.*(7)* Extension of this correlation to ozonides substituted with magnetically anisotropic groups, not surprisingly, would appear to be unreliable.

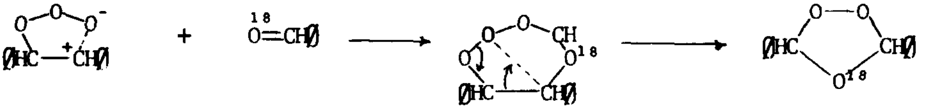
Fliszar and coworkers*(6)* ozonized *cis* and *trans* stilbene in the presence of benzaldehyde-O^{18} to generate labeled ozonide. On the basis of mass spectral analysis of the product ozonides, which showed that a minimum of 90% of the labeled ozonide contained label in the ether bridge, three possible mechanisms were evaluated and it was concluded that (1) and/or (3) may be operative:

(1) Criegee mechanism*(3)*,

(2) Story, Murray, Youssefyeh mechanism*(2,4,5,7)*,

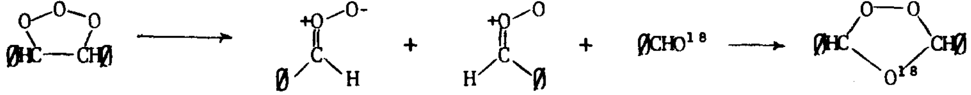


(3) Fliszar, et al*(6)*,



A fourth mechanism should also be considered:

(4) Bailey, et al*(8)*,



In the present study, the ozonolysis of *cis*-stilbene solutions (0.1 M in pentane) have been carried out both in the absence and in the presence of excess benzaldehyde at -78°, -20°

and 25° with 90% of the theoretical amount of ozone. *trans*-Stilbene solutions (0.05 M in pentane) were treated in the same manner at -20° and 25°. The *cis/trans* ratio in the product stilbene ozonides was obtained after stripping the pentane solvent (50 mm) at room temperature. The resulting solids were dissolved in a minimum amount of ether and the methine region of the nmr spectrum was subjected to multiple integration at a sweep width of 50 cps (100 mc). Two signals were present in the methine region corresponding to *cis* and *trans* stilbene ozonides, τ = 3.71 and τ = 3.77.*(9)* Fliszar, et al, have assigned the *trans*-ozonide configuration to the nmr absorption at τ = 3.83 (presumably in carbon tetrachloride).*(9)*

We have reversed this assignment on the following experimental evidence. Ozonolysis of *trans*-stilbene (0.1 M in ether) at 0° produces, in 25% yield, an ozonide which after repeated recrystallization from methanol melts at 74°. This ozonide proved to be a 1:1 mixture of *cis* and *trans* stilbene ozonide as shown by the nmr (CCl_4). τ = 3.79 and 3.83 (methine hydrogens) and by infrared spectroscopy [ν (CCl_4, cm^{-1}) = 909 and 948].

The 1:1 ozonide mixture was treated with triphenylphosphine (0.7 eq.) at room temperature to yield a single ozonide as shown by nmr (CCl_4, methine absorption at τ = 3.79). The ozonide (m.p., 83°) remaining after triphenylphosphine reduction was assigned the trans configuration on the basis of the work of Lorenz and Parks and work in our own laboratories which shows that triphenylphosphine very selectively reduces the *cis* ozonide isomer.*(10)(11)*

TABLE. Stilbene Ozonides [% *trans*]*

Temp., °C	*trans*-stilbene	*trans*-stilbene + benzaldehyde	*cis*-stilbene	*cis*-stilbene + benzaldehyde
+25°	57.5 ± 0.6	58.1 ± 0.5	58.7 ± 0.9	56.9 ± 0.4
-20°	55.7 ± 0.5	56.2 ± 0.8	53.1 ± 0.2	50.2 ± 0.2
-78°	----	-----	60.9 ± 0.3	60.4 ± 0.3

* All runs were carried out in triplicate. Each run was integrated a minimum of ten times using the nmr electronic integrator and mechanically by planimeter. The resulting data was treated statistically by computer program which applied the student's t-test at a 95% confidence level. *trans*-Stilbene was insufficiently soluble at -78° to allow ozonolysis.

These results indicate that the bulk of the ozonide in every case is formed from common intermediates. These common intermediates are most reasonably viewed as the Criegee zwitterion and benzaldehyde of mechanism (1). The other mechanisms would not be expected to lead to an invariant *cis/trans* ozonide ratio. Even mechanism (4) which involves zwitterionic intermediates cannot successfully account for the observations without modification.

The sum total of the available data indicate that the single most important mechanism in stilbene ozonolysis is the Criegee zwitterion mechanism. Further study is required to determine if this is generally the case in those systems which are capable of generating zwitterions which would be expected to have special stability.

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(9) These signals are observed at τ = 3.79 and 3.83, respectively, in carbon tetrachloride.

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(11) Triphenylphosphine reduction of ozonides correlates perfectly with our earlier nmr-vpc configuration correlation(ref. 7). In an attempt to make the configurational assignment completely unambiguous, we reacted the pure 83° ozonide (presumed *trans*) with brucine in order to effect a kinetic resolution as with *trans*-di-isopropyl ozonide [R.W. Murray, R.D. Youssefyeh, and P.R. Story, J. Am. Chem. Soc., 88, 3655 (1966)]. The ozonide proved to be too reactive, however, and was totally destroyed in every attempt.