Compounds in which the existence of a single hydrogen bridge has been proposed include the adducts $NaBH_4 \cdot BH_3$, $LiH \cdot 2B(CH_3)_3$, and $LiH \cdot 2B(C_2H_5)_3$ whose stoichiometry was established in ether solutions.[4] As part of a broader investigation, we recently have examined the infrared spectra of these adducts in monoglyme or diglyme solutions and believe the results provide supporting evidence for the proposed structure.

It is well known that the presence of a hydrogen bridge in boron compounds is associated with a vibrational frequency in the general region between 1600 and 2100 cm^{-1}, the specific position depending on the molecular environment and symmetry of the motion. Terminal boron–hydrogen bonds on the other hand give rise to bands falling above 2300 cm^{-1}. Although the spectral range for bridge frequencies is rather broad, very few other molecular frequencies fall within it.

In the case of ethers, the spectral region between 1600 and 2600 cm^{-1} is free of infrared bands, and this has enabled us to observe clearly rather broad bands of moderate intensity at 2050, 2100, and 1915 cm^{-1} for solutions of the three adducts, respectively, mentioned above. These bands shift by a factor of approximately 0.7 upon substitution of deuterium for the nonmethyl hydrogen and clearly are due to hydrogen motions. To the extent that bands in this region are characteristic, we believe these data indicate the presence of B–H–B bridges. Although the structure in the case of the $B_2H_7^-$ ion may still be equivocal, the arrangement $[H_3B\text{–}H\text{–}BH_3]^-$ certainly is the most attractive; it is difficult to rationalize any other structure than a single bridging hydrogen in the alkyl compounds.

The diglyme solutions of the adducts were prepared on the vacuum line at temperatures below −20° using procedures described by Brown and Tierney.[4] The solutions were transferred without exposure to air directly into a specially designed infrared cell in which the samples could be maintained at temperatures down to −30°. Under these conditions, the solutions were stable for at least 24 hr and no difficulties were encountered in obtaining spectra. Comparison spectra of the reactants and other boron compounds such as $B_3H_8^-$ were obtained under the same conditions and shown to be different. Details will be published at a later date.

Acknowledgment. Support by the National Institutes of Health under Grant CA-07989-03 is gratefully acknowledged.

(4) H. C. Brown and P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958); A. Khuri Ph.D. Thesis, Purdue University, 1960; *Dissertation Abstr.*, **21**, 55 (1960).

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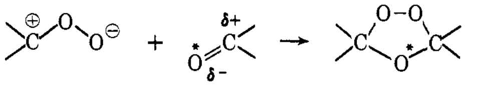
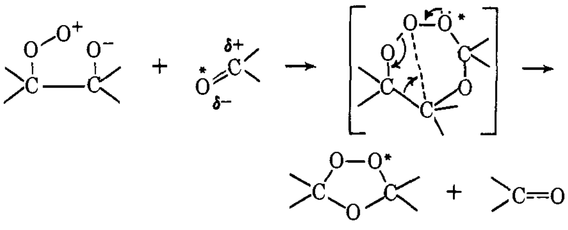
Received December 19, 1967

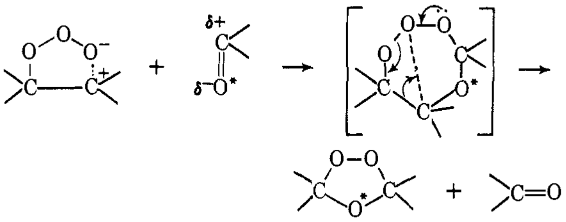
On the Ozonolysis of *cis*- and *trans*-Stilbene in the Presence of Benzaldehyde-^{18}O

Sir:

The object of this preliminary report is to compare, in the case of the *cis*- and *trans*-stilbenes, the mechanisms of ozonolysis proposed by Criegee[1] (1) and by Murray and coworkers[2,3] (2) and to suggest an alternative mechanism (3). The ozonolysis reactions reported below have been carried out in pentane solution in the presence of excess benzaldehyde-^{18}O. The following simplified schemes describe the various mechanistic theories and the corresponding expected labelings ($O^* = {}^{18}O$).


(1)


(2)


(3)

cis-Stilbene solutions (0.1 *M* in pentane) were ozonized in the presence of 0.1 *M* $PhCH^{18}O$ (9.8% ^{18}O) at −78 and 25° with ~70–90% of the theoretical amount of ozone. The ozonides were isolated (after evaporation of most of the solvent) by fractional crystallization and purified by recrystallization in CH_3OH. *trans*-Stilbene was studied in a similar way at −20 and 25°.

From the *cis*- and *trans*-stilbenes ozonized at 25° one obtains an ozonide, mp 74° (lit.[4] mp 74°), which is a 1:1 mixture of the *cis*- and *trans*-ozonides, as shown by the two nmr signals at τ 3.79 and 3.83 (methine protons) and by infrared spectroscopy (bands in CCl_4 at 914 and 952 cm^{-1}). The *cis*-stilbene, ozonized at −78° with excess benzaldehyde, yields (i) the ozonide mixture, mp 74°, and (ii) an ozonide, mp 94° (also observed by Criegee[4]), showing only the nmr signal at τ 3.83 and the infrared band at 914 cm^{-1}. The *trans*-stilbene, ozonized at −20 and 25° in the presence of excess aldehyde, yields two ozonides: (i) the mixture of mp 74° and (ii) an ozonide, mp 82°, which gives only the nmr signal at τ 3.79, but does give the two infrared bands at 914 and 952 cm^{-1}. By comparison with similar systems[3,5] it seems reasonable to assign the *trans*-ozonide configuration to the higher melting compound (τ 3.83) and the *cis* configuration to the compound of mp 82° (τ 3.79).

The mass spectra of the products of mp 74, 82, and 94° are practically identical; two possible fragmentation patterns (a and b) of the ozonide ring yielding *m/e* 122 and 106 are considered, as well as the fragmentation (c) yielding *m/e* 196.

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(1) R. Criegee, *Record Chem. Progr.*, (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(2) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143 (1966); P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966).

(3) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(4) R. Criegee, A. Kerckov, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 126.

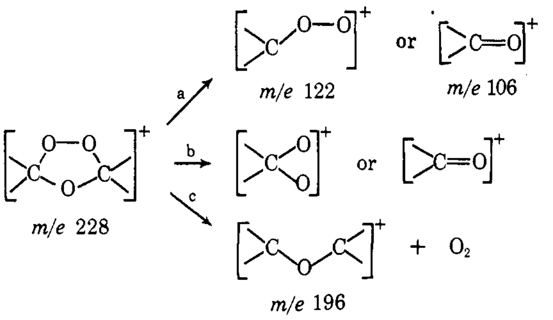

Table I shows the percentage of the molecules which have M + 2 (due to the replacement of ^{16}O by ^{18}O) in the *m/e* 196, 122, and 106 fragments. Whatever the mode of fragmentation[6] (a or b), the sum of the incorporations of ^{18}O in the *m/e* 122 and 106 fragments represents the total labeling of the ozonide ring. This sum can be greater than or equal to the labeling of the ether oxygen. If the total labeling in the *m/e* 122 and 106 fragments exceeds that of *m/e* 196, then ^{18}O incorporation in the peroxidic oxygens takes place, whereas equal labeling in the *m/e* 122 and 106 fragments and in the *m/e* 196 fragment means that all the ^{18}O is found in the ether oxygen.

Table I

Olefin isomer	Temp, ozonolysis, °C	Ozonide mp, °C	% ^{18}O at fragments		
			m/e 196	*m/e* 122	*m/e* 106
cis	−78	74	5.0 ± 0.3	4.5 ± 0.1	0.86 ± 0.06
		94	5.9 ± 0.5	4.2 ± 0.1	1.15 ± 0.05
	25	74	7.4 ± 0.3	5.7 ± 0.1	1.85 ± 0.05
trans	25	74	6.6 ± 0.2	5.4 ± 0.1	1.16 ± 0.08
		82	5.0 ± 0.4	4.2 ± 0.1	0.56 ± 0.05
	−20	82	5.1 ± 0.35	4.9 ± 0.1	0.67 ± 0.04

These results show that the total per cent labeling in the *m/e* 122, and 106 fragments does not (within experimental errors) exceed significantly the labeling in the *m/e* 196 fragment. We conclude therefore that the ozonolysis of *cis*- and *trans*-stilbenes under our experimental conditions leads to a major incorporation of ^{18}O in the ether oxygen. Thus the mode of attack given by (2) does not occur except perhaps to a small extent (~10% or less) at the lower temperatures.

Mechanism 3 agrees with the presented results (as does mechanism 1) and may be retained as long as a reaction between molozonide and aldehyde needs to be considered. Mechanisms 2 and 3 differ by the mode of attack, but, since the seven-membered ring intermediate is the same, they are equally flexible in the attempt to explain the facts observed by Murray, *et al.*,[2,3] concerning the *cis*- and *trans*-ozonide distributions.

The mass spectra were recorded using a Hitachi RMU-6D mass spectrometer; the nmr spectra were recorded with a Varian A-60 spectrometer, using tetramethylsilane as internal reference.

Acknowledgment. The authors express their gratitude to Professor Y. Rousseau and to Mr. M. Bertrand for their analysis of the mass spectra. The financial support given by the National Research Council of Canada is gratefully acknowledged.

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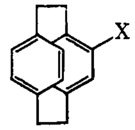
Transannular Directive Influences in Electrophilic Substitution of [2.2]Paracyclophane

Sir:

Chemical and spectral evidence indicates the presence of strong transannular electronic interactions in [2.2]-paracyclophane and its derivatives.[1] The electronic demands of electrophilic substitution are high and, as applied to monosubstituted [2.2]paracyclophanes (I),



I

should become manifest in transannular directive influences upon introduction of a second group into the system. Table I records the results of an investigation of such directive influences.

Table I. Pattern of Electrophilic Substitution of Monosubstituted [2.2]Paracyclophanes (I)[a]

Run no.	X	Reagent[b]	% *para*	% pseudo- *ortho*[c]	*para*[c]	*meta*[c]	*gem*[c]
1	CO_2CH_3	Br_2, Fe					89[d]
2	$COCH_3$	Br_2, Fe					56[e]
3	CO_2H	Br_2, Fe					63
4	NO_2	Br_2, Fe		2	6	8	70
5	CN	Br_2, Fe		16	25	26	
6	Br	Br_2, Fe	5[f]	16	26	6	
7	Br	CH_3COCl, $AlCl_3$	17[g]	5.6	41		

[a] The disubstituted compounds were separated by column chromatography and fractional crystallization unless indicated otherwise. Each compound gave a carbon and hydrogen analysis that deviated less than 0.3% from theory. No value listed indicates that none of that isomer could be detected. [b] Solvent was carbon tetrachloride, dichloromethane, or a mixture of the two. [c] The colloquial nomenclature is self-explanatory: pseudo-*gem* denotes the position directly below the substituent; pseudo-*ortho*, -*para*, and -*meta* denote the positions below the corresponding positions of the substituted ring. [d] Analysis by vpc indicated the product was approximately 98% pseudo-*gem*. [e] Analysis by nmr and vpc indicated that >99% of disubstituted product produced was pseudo-*gem*. [f] Determined by infrared analysis of a mixture with pseudo-*p*-dibromide. [g] Determined by nmr integration of a mixture with pseudo-*p*-bromoacetyl.

Structural assignments were made primarily on the basis of nmr spectra. As previously reported,[1b] a carbomethoxy, acetyl, or nitro group results in a substantial downfield shift of the *ortho* proton (0.6, 0.4, and 0.7 ppm, respectively, from the bulk of the aromatic protons). Similarly, 4-bromo[2.2]paracyclophane has one proton 0.7 ppm downfield, but the signal has a splitting pattern characteristic of a proton split by

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(6) A detailed study on the mass spectrometry of ozonides by Y. Rousseau, M. Bertrand, and S. Fliszár will be published shortly.

(1) (a) D. J. Cram, *Record Chem. Progr.*, **20**, 71 (1959); (b) L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963).