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ABNORMAL OZONOLYSIS OF 1-METHYL-3-STYRYL[3.3]PARACYCLOPHANE TO AFFORD 1-ALKOXY-3-METHYL[3.3]PARACYCLOPHANE

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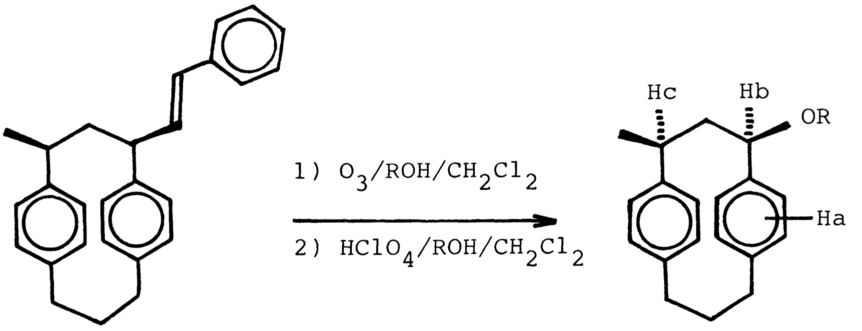
Ozonolysis of 1-methyl-3-styryl[3.3]paracyclophane in various alcohols, followed by the treatment with perchloric acid, produced the corresponding cyclophanyl ethers in 28.6 - 83.5% yields.

Cationic cyclocodimerization[1)] was recently discovered as a new synthetic method of [3.3]paracyclophane-derivatives and related phane-derivatives from α,ω-dienes and some comonomers. The cyclocodimers yielded by this method have a C=C double bond on the substituent of the methylene linkage, so that some oxidative cleavages of the double bond are envisioned to produce several phanes containing functional groups on their linkages.

In the ozonolysis of 1-methyl-3-styryl[3.3]paracyclophane, we found that the compound gave cyclophanyl ethers which had one carbon less than expected. This kind of abnormal ozonolysis often occurs for olefins conjugated with aryl group,[2)] but not so readily in such a non-conjugated olefin like the title compound.[3)] In this communication, we would like to report this intriguing ozonolysis.

Thus, 1-methyl-3-styryl[3.3]paracyclophane[1)] (500 mg, 1.42 mmol) was dissolved in an alcohol (35 mL) and methylene chloride (40 mL). Into the solution ozone was bubbled at 0 °C. After slightly excess ozone was expelled by a nitrogen stream, 4 ml of 60% perchloric acid was added into the reaction mixture. It was allowed to stand at r.t. until peroxide activity disappeared.[4)] The conditions were fundamentally the same as those of Kolsaker and Bailey.[2,5)] The mixture was poured into 200 ml of water and extracted by ether. The etherial solution was washed three times with water and then dried over sodium sulfate. After the evaporation of solvent, products were isolated by column chromatography (silica gel, benzene) or by vacuum distillation. Results are summarized in Table 1.

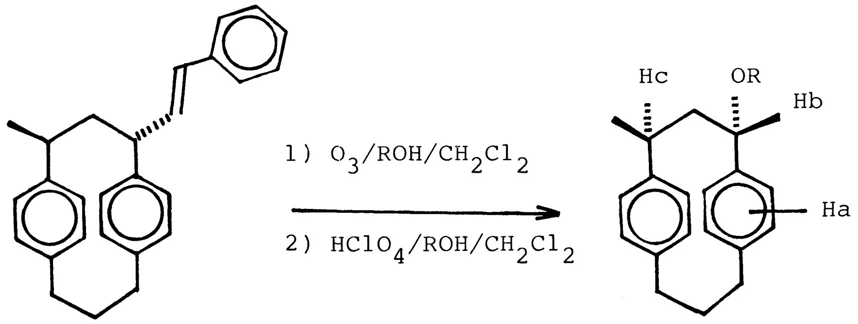
According to the proposed mechanism on the ozonolysis in protic solvents, the primarily formed alkoxyhydroperoxide **5** undergoes Baeyer-Villiger rearrangement to give formate **6** in acidic media, and then the formate is solvolyzed in the same acidic and alcoholic media to afford the ether.[6,7)] From the ozonolysis mixture of **1** in acetic acid, the formate was actually isolated together



1 (1)

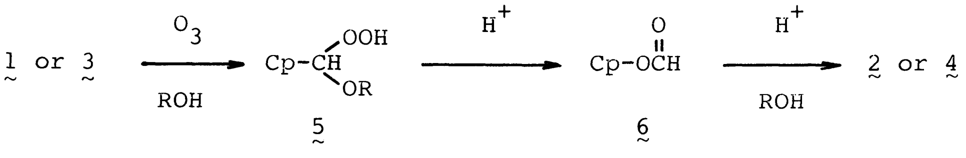
2	R
a	CH_3
b	CH_3CH_2
c	$C_6H_5CH_2$
d	p-$CH_3C_6H_4CH_2$
e	CH_3CO
f	CHO

(See 6 in Eq. 3.)



3 4 R = $C_6H_5CH_2$ (2)

with the corresponding acetate when any strong Brønsted acid was not employed. In methanol, ethanol, benzyl alcohol, and p-methylbenzyl alcohol, the corresponding 1-alkoxy-3-methyl[3.3]paracyclophanes were obtained in 28.6 - 83.5% yields. Generally, in highly nucleophilic alcohols, the cyclophanyl ethers were obtained in high yields. In bulky alcohols such as isopropyl and t-butyl alcohol, the ethers were not formed. These results are well consistent with the mechanism mentioned above.



$$\underset{\sim}{1} \text{ or } \underset{\sim}{3} \xrightarrow[ROH]{O_3} \underset{\underset{\sim}{5}}{\text{Cp-CH}\begin{smallmatrix}\text{OOH}\\ \text{OR}\end{smallmatrix}} \xrightarrow{H^+} \underset{\underset{\sim}{6}}{\text{Cp-O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H}} \xrightarrow[ROH]{H^+} \underset{\sim}{2} \text{ or } \underset{\sim}{4} \qquad (3)$$

Cp = cyclophanyl

Table 1. Ozonolysis of 1-Methyl-3-styryl[3.3]paracyclophane[a]

ROH	Time d	Product	Yield[b] %	Mp °C	IR ν_{C-O} / cm^{-1}
CH_3OH	7	**2a**	42.2[c]	107-9	1092
CH_3CH_2OH	7	**2b**	28.6	111-4	1096
$C_6H_5CH_2OH$	1	**2c**	67.8	94-5	1101
"	1[d]	**4**	51.2	h.l.[e]	1098
p-$CH_3C_6H_4CH_2OH$	1	**2d**	83.5	108-9	1075
CH_3COOH	7[f]	**2e**	44.8	124-5	1743[g]
		2f	31.2	149-0	1720[g]

a) All elemental analyses and high resolution mass spectrometric data of these products agreed well with their calcd. values. b) Determined by GC. c) Isolated yield. d) Trans isomer **3** was used. e) Heavy liquid. f) In the absence of $HClO_4$. g) $\nu_{C=O}$.

Table 2. NMR data of Cyclophanyl Ethers and Esters[a]

Substituent R-	Product	NMR chemical shift δ, ppm Ha	 Hb	 Hc	 Me (d, J in Hz)
CH_3	**2a**	6.63	3.97	2.65[b]	1.25(6.3)
CH_3CH_2	**2b**	6.61	4.10	2.70[b]	1.24(6.6)
$C_6H_5CH_2$	**2c**	6.66	4.06	2.70[b]	1.23(6.6)
"	**4**	6.60	4.43	3.06	1.19(6.6)
p-$CH_3C_6H_4CH_2$	**2d**	6.63	4.05	2.75[b]	1.26(6.6)
CH_3CO	**2e**	6.67	5.77	2.71[b]	1.26(7.6)
HCO	**2f**	6.72	5.70	2.60[b]	1.30(7.2)

a) Recorded by a Varian T-60A and XL-200FT NMR spectrometers in $CDCl_3$, using TMS as an internal standard. b) They overlap with the absorption of non-substituted methylene linkages.

The high nucleophilicity of the cyclophanyl group is a reason why it can readily migrate in this ozonolysis conditions. This high nucleophilicity has already been elucidated by the π-complex formation with TCNE8) and the direct spectroscopic observation of cyclophanyl cation.9)

The cis/trans assignment of the ethers was done by the chemical shift of proton Hc,1) and its designation is shown in Eq. 1 . The ozonolysis of cis-1-methyl-3-styryl[3.3]paracyclophane **1** in benzyl alcohol gave exclusively cis-1-benzyloxy-3-methyl[3.3]paracyclophane **2c** in 67.8% yield. The trans isomer **3** also afforded trans ether **4** in 51.2% yield. These results indicate clearly that the ozonolysis and the consecutive solvolysis occurred with a high stereoselectivity.10) This stereoselectivity is quite interesting, because it implies that the solvolysis of cyclophanyl formate proceeds most likely through a S_N1 mechanism, whereas the S_N2 mechanism is suppressed by the steric hindrance. We presume that a conformationally stable cyclophanyl cation may be generated. The elucidation of the structure and reactivity of this intriguing cyclophanyl cation by the solvolysis of the corresponding tosylates is now in progress.

References

1) J. Nishimura, K. Hashimoto, T. Okuda, H. Hayami, Y. Mukai, and A. Oku, J. Am. Chem. Soc., 105, 4758 (1983).

2) P. Kolsaker and P. S. Bailey, Acta Chem. Scand., 21, 537 (1967).

3) The compound has a conjugation of the C=C double bond with phenyl group in styryl moiety, but not with cyclophanyl group which migrates.

4) KI-starch paper was employed to test the peroxide activity.

5) When the ozonolysis of **1** was carried out in CCl_4, followed by the reduction with Zn-EtOH-AcOH, three abnormal ozonolysis products, 1-methyl-3-oxo-[3.3]paracyclophane, **2b**, and **2e** were obtained in 6, 8, and 3% yields, respectively, in addition to the normal product cis-1-formyl-3-methyl[3.3]-paracyclophane (37%).

6) P. S. Bailey, Chem. Rev., 58, 925 (1958).

7) The direct formation of the cyclophanyl cation from the alkoxyhydroperoxide is also conceivable.

8) D. J. Cram and R. H. Bauer, J. Am. Chem. Soc., 81, 5971 (1959).

9) J. Nishimura, Y. Ishida, S. Yamashita, K. Hasegawa, M. Sawamoto, and T. Higashimura, Polym. J., 15, 303 (1983).

10) At present, there are no chromatographic methods to separate the cis/trans isomers from their mixture so that the conclusion was led by the ^{1}H-NMR spectroscopic analysis: in spectra of **2c** and **4**, no resonances belonging to the other isomer were found (see Table 2).

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