

Stereochemical Assignment of Cyano-Substituted Ozonides by the NMR Spectroscopy

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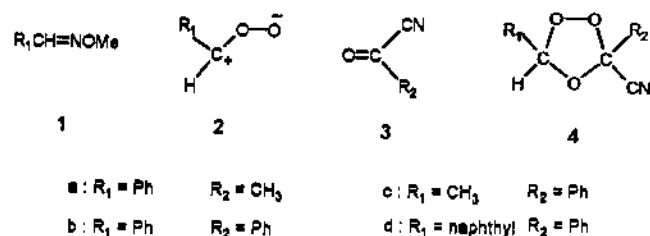
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The mechanism of the formation in the ozonolysis of alkenes in inert solvent was first proposed by Criegee¹ and later extended by others in order to include stereochemical effects.² More recently, attention was focused on conformational and stereochemical assignments of ozonides.³ Few experimentally determined ozonide conformations have been reported, and only those of simple ozonides have been elucidated in detail by microwave spectroscopy.⁴

Stereochemical assignments for *cis-trans*-isomeric ozonides, bearing H-atom at the ozonide rings, was based on the assumption that, the *cis*-isomer exhibited the longer chromatographic elution time.⁵ More equivocal stereochemical assignments of *cis-trans*-ozonides have been made based on partial resolutions of the racemates of *trans*-isomers⁶ and on deuterium isotope effects.⁷

Recently, we have found that ozonolyses of O-methyl oximes like **1** occur predominantly such that the corresponding carbonyl oxides like **2** are formed.⁸ The latter can be trapped with dipolarophiles like acyl cyanides **3** to give cyano substituted ozonides **4a-4d**.⁸



Thus, ozonolysis of **1d** in the presence of **3d** gave two isomeric ozonides denoted **4d-I** and **4d-II**, which showed ¹H NMR signals for the CH groups in the ozonide rings at $\delta=6.52$ and $\delta=6.91$. Of these, only the ozonide which absorbed at $\delta=6.52$ could be isolated as a crystalline material which melted at 100-101 °C without decomposition.⁹ We have now obtained single crystals of this ozonide (from pentane-ether) and determined its structure by X-ray diffraction.

This analysis showed (Figure 1) that the naphthyl and the phenyl group adopt a *Z*-arrangement, *i.e.* the crystalline material **4d-I** is the *Z*-isomer. The X-ray analysis of **4d-I** revealed the additional salient features: The atoms C(1), O(1), C(2) and O(2) of the ozonide ring are in a plane, whereas the second peroxidic oxygen atom O(3) is displaced from the plane by 70.1 pm. This half-chair conformation **4d-I** has been shown to be adopted by many ozonides in the absence of specific steric effects.¹⁰

The stereoisomeric ozonides of types **4d-I** and **4d-II** differ characteristically in their ¹H and ¹³C NMR spectra (Table 1): In the ¹H NMR spectrum, the CH signal for the *Z*-isomer **4d-I** appears upfield compared to those of *E*-isomer **4d-II**.

In the ¹³C NMR(GD) spectrum of the isolated *Z*-isomer **4d-I**, the signal for C(2) appears as a triplet, whereas in the spectrum of the non-isolated *E*-isomer **4d-II** it appears as a triplet of a doublet due to long-range coupling with the proton at C(1). Furthermore, the signal for C(2) in **4a-I** appears downfield from that of C(2) in **4a-II**.

Similar characteristic differences in the multiplicities of the signals for the carbon atoms in the ozonide rings and in the relative chemical shifts were observed in the ¹³C NMR

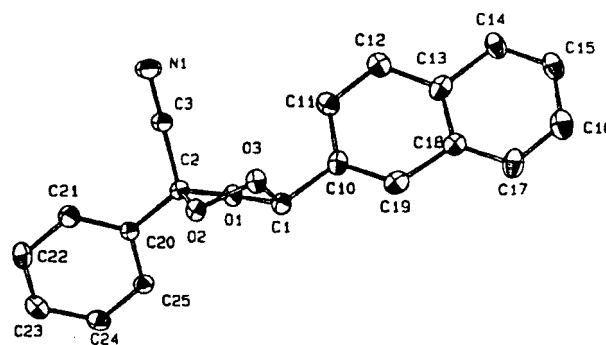


Figure 1. Molecular structure of *Z*-3-phenyl-5-(2-naphthyl)-1,2,4-trioxolane-3-carbonitrile (**4d-I**).

Table 1. ¹H and ¹³C NMR (GD) data of the stereoisomeric cyanosubstituted ozonides **4a-4d**

compound	¹ H NMR (δ_{CH})	¹³ C NMR (δ_{C1})	¹³ C NMR (δ_{C2})	
4a	I	6.07	108.64 (d, t; $J=242$ Hz, $J=5.04$ Hz)	99.40 (q, $J=5.03$ Hz)
	II	6.48	106.64 (d, t; $J=227$ Hz, $J=5.04$ Hz)	98.60.64 (q, d; $J=5.03$ Hz, $J=2.52$ Hz)
4b	I	6.35	106.64 (d, t; $J=100$ Hz, $J=5.12$ Hz)	101.98 (t, $J=4.28$ Hz)
	II	6.70	105.64 (d, t; $J=97$ Hz, $J=5.13$ Hz)	101.16 (t, d; $J=4.28$ Hz, $J=2.33$ Hz)
4c	I	5.63	105.64 (d, q; $J=179$ Hz, $J=5.07$ Hz)	101.89 (t, $J=4.37$ Hz)
	II	6.06	104.64 (d, q; $J=182$ Hz, $J=5.07$ Hz)	101.63 (t, d; $J=4.37$ Hz, $J=2.11$ Hz)
4d	I	6.52	104.64 (d, t; $J=271$ Hz, $J=5.03$ Hz)	102.05 (t, $J=3.25$ Hz)
	II	6.91	103.64 (d, t; $J=269$ Hz, $J=5.04$ Hz)	101.12 (t, d; $J=3.25$ Hz, $J=1.71$ Hz)

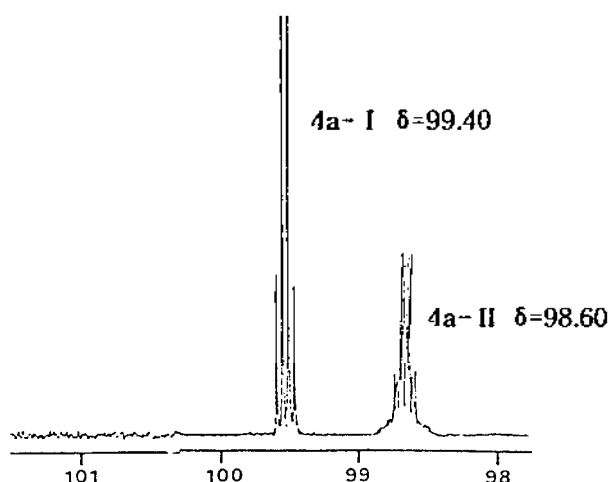


Figure 2. $^{13}\text{C}(\text{GD})\text{NMR}$ Signals C1 at C2 of the stereoisomeric ozonides **4a-I** and **4a-II**.

spectra of the previously obtained mixtures of the stereoisomeric ozonides **4a**, **4b** and **4c**, as summarized in Table 1. In particular, the ^{13}C NMR spectrum of **4a-I** exhibited a quartet for the signal of C(2) due to coupling with the CH_3 group, whereas the spectrum of the other isomer exhibited a quartet of a doublet due to long range coupling with the proton at C(1) (Figure 2). This prompted us to assign their stereochemical identities, although the isomers were not

separated. These assignments derive support from the fact, that the Z-isomer I exhibited the ^1H NMR signal for the CH group in the ozonide ring upfield from that of the corresponding E-isomer II.

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Electrophilic Substitution Reaction and A Novel [1,3] Rearrangement of 4-Lithio-5-*p*-toluenesulfonylpyrazoles

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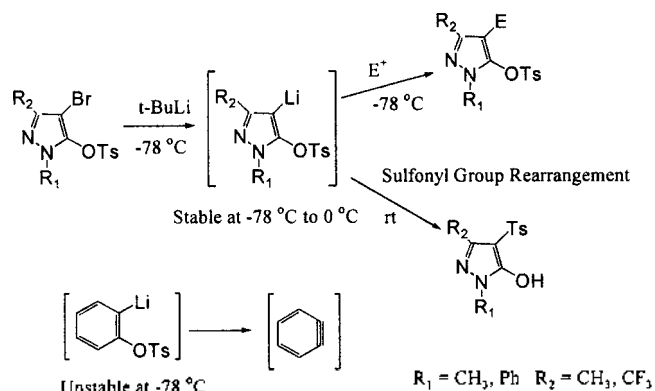
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Recently, we have reported a new synthesis of 4-benzoyl-3-trifluoromethyl-5-*p*-toluenesulfonylpyrazoles exhibiting herbicidal activities involving [1,3] rearrangement of benzoyl group in 5-benzoyloxy-4-bromo-3-trifluoromethylpyrazoles via lithium-bromine exchange reaction using *tert*-butyllithium.¹ In connection with this study, we wish to report the electrophilic substitution reaction and a new type of sulfonyl group rearrangement of the 4-lithio-5-*p*-toluenesulfonylpyrazoles.

It has been known that *ortho*-lithio-*p*-toluenesulfonylbenzene is unstable even at very low temperature leading to benzyne intermediate which results in the multimerized by-products.² However, the benzyne equivalents in the five membered aromatic heterocycles have not been known in the literature, and we assumed that 4-lithio-5-*p*-toluenesulfonylpyrazoles would be relatively stable and useful for the preparation of new pyrazole derivatives.

4-Bromo-5-*p*-toluenesulfonylpyrazoles were prepared by bromination of 5-*p*-toluenesulfonylpyrazoles or by tosylation of 4-bromo-5-hydroxypyrazoles.³ 4-Lithio-5-*p*-

toluenesulfonylpyrazoles as intermediates were prepared by lithium-bromine exchange reaction of 4-bromo-5-*p*-toluenesulfonylpyrazoles with *tert*-butyllithium in THF at -78°C .



Scheme 1. Use of 4-Lithio-5-*p*-toluenesulfonylpyrazole Derivatives.