

## Stereochemical Assignment of Cyano-Substituted Ozonides by the NMR Spectroscopy

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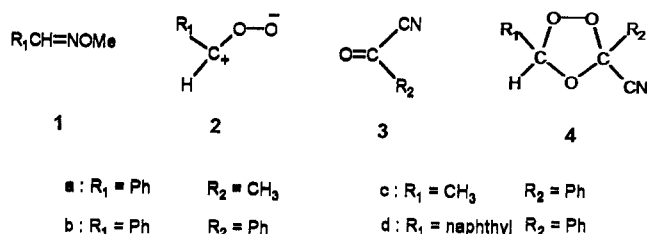
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The mechanism of the formation in the ozonolysis of alkenes in inert solvent was first proposed by Criegee<sup>1</sup> and later extended by others in order to include stereochemical effects.<sup>2</sup> More recently, attention was focused on conformational and stereochemical assignments of ozonides.<sup>3</sup> Few experimentally determined ozonide conformations have been reported, and only those of simple ozonides have been elucidated in detail by microwave spectroscopy.<sup>4</sup>

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.<sup>5</sup> More equivocal stereochemical assignments of *cis-trans*-ozonides have been made based on partial resolutions of the racemates of *trans*-isomers<sup>6</sup> and on deuterium isotope effects.<sup>7</sup>

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



Thus, ozonolysis of **1d** in the presence of **3d** gave two isomeric ozonides denoted **4d-I** and **4d-II**, which showed <sup>1</sup>H NMR signals for the CH groups in the ozonide rings at δ=6.52 and δ=6.91. Of these, only the ozonide which absorbed at δ=6.52 could be isolated as a crystalline material which melted at 100-101 °C without decomposition.<sup>9</sup> 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.<sup>10</sup>

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

In the <sup>13</sup>C 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 <sup>13</sup>C NMR

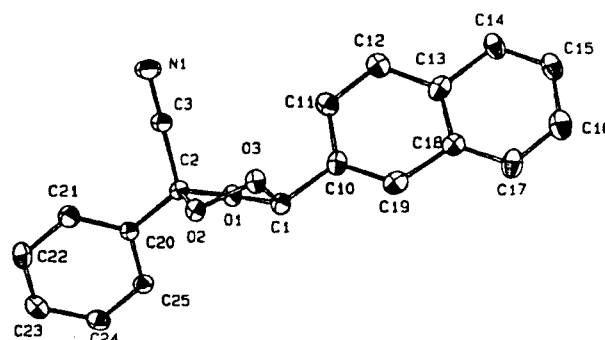
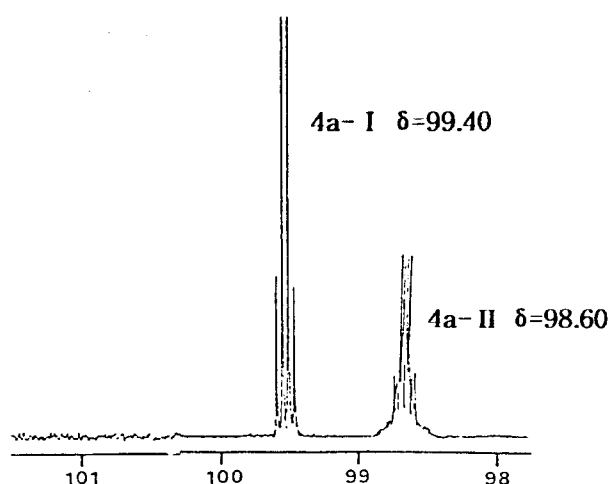


Figure 1. Molecular structure of *Z*-3-phenyl-5-(2-naphthyl)-1,2,4-trioxolane-3-carbonitrile (**4d-I**).

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

compound		<sup>1</sup> H NMR (δCH)	<sup>13</sup> C NMR (δC1)	<sup>13</sup> C NMR (δC2)
<b>4a</b>	I	6.07	108.64 (d, t; <i>J</i> =242 Hz, <i>J</i> =5.04 Hz)	99.40 (q, <i>J</i> =5.03 Hz)
	II	6.48	106.64 (d, t; <i>J</i> =227 Hz, <i>J</i> =5.04 Hz)	98.60.64 (q, d; <i>J</i> =5.03 Hz, <i>J</i> =2.52 Hz)
<b>4b</b>	I	6.35	106.64 (d, t; <i>J</i> =100 Hz, <i>J</i> =5.12 Hz)	101.98 (t, <i>J</i> =4.28 Hz)
	II	6.70	105.64 (d, t; <i>J</i> =97 Hz, <i>J</i> =5.13 Hz)	101.16 (t, d; <i>J</i> =4.28 Hz, <i>J</i> =2.33 Hz)
<b>4c</b>	I	5.63	105.64 (d, q; <i>J</i> =179 Hz, <i>J</i> =5.07 Hz)	101.89 (t, <i>J</i> =4.37 Hz)
	II	6.06	104.64 (d, q; <i>J</i> =182 Hz, <i>J</i> =5.07 Hz)	101.63 (t, d; <i>J</i> =4.37 Hz, <i>J</i> =2.11 Hz)
<b>4d</b>	I	6.52	104.64 (d, t; <i>J</i> =271 Hz, <i>J</i> =5.03 Hz)	102.05 (t, <i>J</i> =3.25 Hz)
	II	6.91	103.64 (d, t; <i>J</i> =269 Hz, <i>J</i> =5.04 Hz)	101.12 (t, d; <i>J</i> =3.25 Hz, <i>J</i> =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  $^{13}\text{C}$  NMR spectrum of **4a-I** exhibited a quartet for the signal of C(2) due to coupling with the  $\text{CH}_3$  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  $^1\text{H}$  NMR signal for the CH group in the ozonide ring upfield from that of the corresponding *E*-isomer II.

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### References

1. Criegee, R.; Wenner, G. *Justus Ann. Chem.* **1949**, *561*, 9.
2. Lattimer, P. R.; Kuczkowski, R. L.; Gallies, C. W. *J. Am. Chem. Soc.* **1974**, *96*, 348.
3. Bailey, P. S.; Ferrel, T. M. *J. Am. Chem. Soc.* **1978**, *100*, 899.
4. Mazur, W.; Kuczkowski, R. L. *J. Mol. Spectroscopy* **1977**, *65*, 84.
5. Loan, L. D.; Murray, R. W.; Story, P. R. *J. Am. Chem. Soc.* **1965**, *87*, 737.
6. Criegee, R.; Kober, H. *Chem. Ber.* **1971**, 104
7. Choe, J.-I.; Choe, H.-S.; Kuczkowski, R. L. *Magnetic Reson. Chem.* **1986**, *24*, 1044.
8. Huh, T. S.; Lee, M. K.; Kim, M. J.; Griesbaum, K. *Erdol Erdgas Kohle* **1996**, *112*(6), 264.
9. Griesbaum, K.; Ovez, B.; Huh, T. S.; Dong, Y. *Liebigs Ann.* **1995**, 1571.
10. Jung, I. C.; Yun, H. S.; Huh, T. S. *Bull. Kor. Chem. Soc.* **1996**, *17*(4), 307.

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

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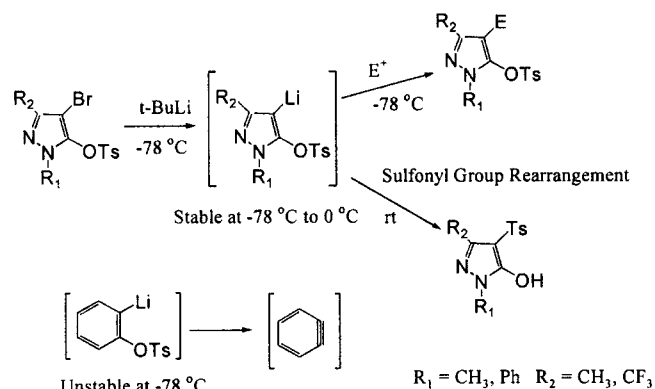
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Recently, we have reported a new synthesis of 4-benzoyl-3-trifluoromethyl-5-*p*-toluenesulfonyloxy-pyrazoles exhibiting herbicidal activities involving [1,3] rearrangement of benzoyl group in 5-benzoyloxy-4-bromo-3-trifluoromethylpyrazoles via lithium-bromine exchange reaction using *tert*-butyllithium.<sup>1</sup> 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*-toluenesulfonyloxy-pyrazoles.

It has been known that *ortho*-lithio-*p*-toluenesulfonyloxy-benzene is unstable even at very low temperature leading to benzyne intermediate which results in the multimerized by-products.<sup>2</sup> 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*-toluenesulfonyloxy-pyrazoles would be relatively stable and useful for the preparation of new pyrazole derivatives.

4-Bromo-5-*p*-toluenesulfonyloxy-pyrazoles were prepared by bromination of 5-*p*-toluenesulfonyloxy-pyrazoles or by tosylation of 4-bromo-5-hydroxypyrazoles.<sup>3</sup> 4-Lithio-5-*p*-

toluenesulfonyloxy-pyrazoles as intermediates were prepared by lithium-bromine exchange reaction of 4-bromo-5-*p*-toluenesulfonyloxy-pyrazoles with *tert*-butyllithium in THF at  $-78^\circ\text{C}$ .



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