

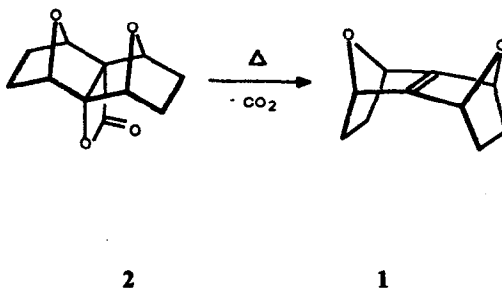
## Photoelectron Spectroscopic Evidence for Formation of *syn*-7,7'-dioxasesquinorbornene

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*Abstract: Photoelectron spectroscopic evidence for formation of novel 7,7'-dioxia analogon of syn-sesquinorbornene by pyrolytic decomposition of the corresponding  $\beta$ -lactone is presented*

Similarly to the *syn*-sesquinorbornene, its 7,7'-dioxia analogon (**1**)<sup>1</sup> is predicted to possess highly pyramidalized olefinic carbon atoms.<sup>2</sup> Hence, its physical and chemical properties are of considerable interest from both theoretical and experimental points of view. However, in contrast to its carbocyclic predecessor, which is a stable and thoroughly studied compound<sup>3</sup>, no example of *syn*-dioxasesquinorbornene isolation has been reported so far. Our current interest in fused 7-oxanorbornenes<sup>4,5</sup> and their saturated analogues<sup>6</sup> prompted us to investigate the possibility of generating **1** by thermolysis of the corresponding  $\beta$ -lactone **2**<sup>7,8</sup> by employing variable temperature photoelectron (PE) spectroscopy.<sup>9,10</sup>



The lactone **2** proved to be resistant to cleavage up to at least 600°C. By raising temperature to 900°C, however, formation of the sharp PE signal due to CO<sub>2</sub> (13.8 eV)<sup>11</sup> and a series of low-energy lying bands appeared which we assigned to the structure **1**. The PE spectra of the starting lactone and its

thermolytic products are shown in Fig. 1. The measured IE values are listed in Table 1, where also the energies of the highest occupied MO's for both compounds calculated by the semiempirical AM1<sup>13</sup> procedure and proposed assignment are given.<sup>14</sup>

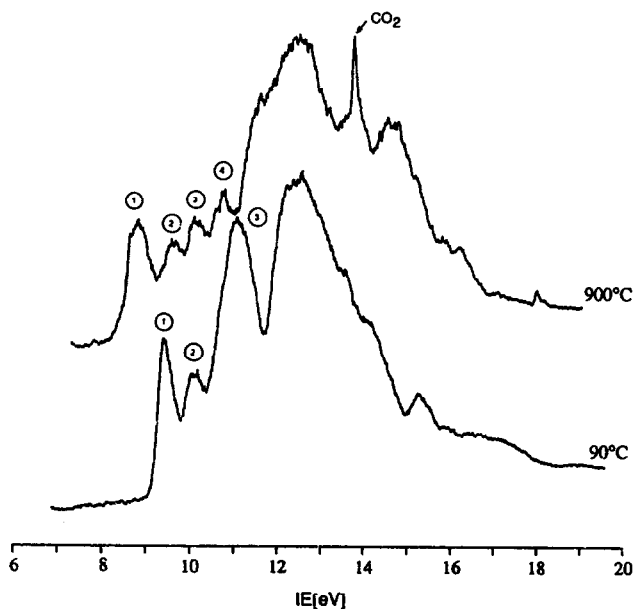


Figure 1. He(I) photoelectron spectra of 2 (bottom) and 1 (top).

Table 1. Comparison between the first vertical ionization energies ( $I_{v,j}$ ) and calculated orbital energies,  $\epsilon_j$ , by means of AM1 method for 1 and 2. All values in eV.

Compd.	Band	$I_{v,j}$	MO-type	$-\epsilon_j$ (AM1)
1	1	8.79	$\pi$	9.46
	2	9.62	$n_o$	10.86
	3	10.13	$n_+$	11.39
	4	10.79	$\sigma_{cc}$	11.48
2	1	9.47	$n_{-}^{a,b}$	11.00
	2	10.14	$n_{+}^{a,c}$	11.15
	3	11.13	$\sigma_{cc}^a, \sigma_{cc}^b$	11.55; 11.85

(a) ref. 12

(b) with considerable admixture of endocyclic lactone  $n_o$  orbital.

(c) with considerable admixture of lactone  $n_{co}$  orbital.

The evidence for ascribing low ionization energy pattern of the examined pyrolytic product to olefin **1** is the following: (i) The first band appearing at 8.76 eV is of similar energy as the  $\pi$ -ionization band in the structurally related 3,7-dioxabicyclo[3.3.0]oct-1(5)ene.<sup>15</sup> Hence it is assigned to electron removal from an orbital predominantly double bond in character. Additional support for such assignment is found in vibrational spacing (1452 cm<sup>-1</sup>); (ii) The second and the third band appear in the region characteristic for ionization of 2p-type oxygen lone pairs in previously studied fused 7-oxanorborna(e)nes.<sup>4,6</sup> They are consequently assigned to the out-of-phase ( $n_-$ ) and in-phase ( $n_+$ ) linear combination of the etheric 2p-oxygen lone pair orbitals. It is worth of noting that the  $n_-,n_+$  splitting energy drops from ~1 eV in the latter compounds<sup>4,6</sup> to 0.51 eV in **1**. This is exactly what could be expected from the pronounced increase in the O...O distance occurring upon incorporation of the double bond within the central bridge. Consequently, the observed energy gap is solely due to through-bond<sup>16,17</sup> type of interaction. All these assumptions are fully corroborated by results of AM1 calculations (Table 1).

Finally, based on comparison with calculated MO energies and the PE data of related 7-oxanorbornene derivatives<sup>4,6</sup>, the fourth feature in the PE spectrum of pyrolyzed lactone commencing at 10.79 eV is expected to be due to ionization involving mainly skeletal  $\sigma$ -type orbitals.<sup>16,17</sup>

In conclusion, current results give a convincing evidence that **1** can be generated in the gas phase pyrolysis of the corresponding  $\beta$ -lactone, opening thus an avenue for investigation of this interesting class of compounds. Studies directed towards gas phase generation and spectroscopic characterization of *anti*-7,7'-dioxasesquinorbornene are currently under way in our laboratories.

#### Acknowledgements

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#### References and Notes

1. *exo-exo*-1,4:5,8-diepoxy-1,2,3,4,5,6,7,8-octahydronaphthalene
2. Spanget-Larsen, J. and R. Gleiter, *Tetrahedron*, **1983**, *39*, 3345-3350.
3. For recent comprehensive review articles see: *Stereochemistry and Reactivity of Systems Containing  $\pi$  Electrons* (Ed. Watson, W.H.) VCH International, Deerfield Beach, Florida, 1983.
4. Eckert-Maksić, M.; Maksimović Lj. and Hodošček, M. *Tetrahedron Lett.*, **1993**, *34*, 4245-4248.
5. Maksimović, Lj.; Novak, N. and Eckert-Maksić, M. *Synth. Comm.*, in press.
6. Eckert-Maksić, M. and Maksimović, Lj. *J. Org. Chem.* **1991**, *56*, 3719-3722.
7.  $\beta$ -lactone **2** was obtained by electrolytic decarboxylation of the corresponding diacid [8]

8. Margetić, D.; Eckert-Maksić, M.; Kiralj, R. and Kojić-Prodić, B. manuscript in preparation.
9. E.g. Schultz, R. and Schweig A., in: *Structure and Reactivity* (Eds. J.F. Liebman and A.Greenberg), VCH, N. York 1988, pp. 289-363 and references cited therein.
10. *PE Spectra*: were measured at UPG 200 spectrometer of Leybold-Heraeus equipped with a He(1) lamp (21.21 eV) as radiation source. The spectra were calibrated with the lines of xenon at 12.130 and 13.436 eV and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately  $\pm 0.03$  eV for the ionization potentials, for broad or overlapping signals it was only  $\pm 0.05$  eV. *Thermolysis* were carried out at 10-50 Pa in a molybdenum tube of 80 mm length and 4.5 mm inner diameter, which was placed between the sample inlet system and the ionization chamber. The distance between thermolysis tube and ionization chamber was about 35 mm. Temperatures are accurate to ca.  $\pm 5^{\circ}\text{C}$ .
11. Al-Joboury, M.I. and Turner, D.W. *J. Chem. Soc.* **1964**, 4434-4441.
12. Eckert-Maksić, M. and Margetić, D. unpublished results.
13. Dewar, M.J.S.; Zoebischs, E.G.; Healy, E.F. and Stewart, J.J.P. *J. Am. Chem. Soc.*, **1985**, *107*, 3902-3909.
14. The assumed correlation between vertical ionization energies and orbital energies rests on the validity of Koopmans' theorem; Koopmans' T. *Physica*, **1934**, *1*, 104-113.
15. Bloch, M.; Heilbronner, E.; Jones, T.B. and Ripoll, J.L., *Heterocycles*, **1978**, *11*, 443-453.
16. Hoffmann, R.; Imamura, A. and Hehre, W.J. *J. Am. Chem. Soc.*, **1968**, *90*, 1499-1509; Hoffmann, R. *Acc. Chem. Res.*, **1971**, *4*, 1-9; Gleiter, R. *Angew. Chem.*, **1974**, *86*, 770-775; *Angew. Chem. Int. Ed.*, **1974**, *13*, 696-701; Paddon-Row, M.N. *Acc. Chem. Res.*, **1982**, *15*, 245-251.
17. For a recent review consult Eckert-Maksić, M. in: *Theoretical Models of Chemical Bonding*, Part 3 (Ed. Maksić, Z.B.) Springer-Verlag, **1991**, pp. 154-198 and references cited therein.

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