

NONTRIVIAL INTRAMOLECULAR INTERACTION IN OZONATION OF DIMETHYL ESTER OF
ENDO, *cis*-BICYCLO[2,2,1]HEPT-5-EN-2,3-DICARBONIC ACID IN DIETHYL ETHER

Viktor N. Odinokov, Olga S. Kukovinets*, Leonard M. Khalilov and
Genrikh A. Tolstikov

Institute of Chemistry, U.S.S.R. Acad. Sci. Bashkirian Branch, Ufa
and

Alexander Yu. Kosnikov, Sergei V. Lindeman, and Yury T. Struchkov
Institute of Organoelement Compounds, U.S.S.R. Acad. Sci., Moscow

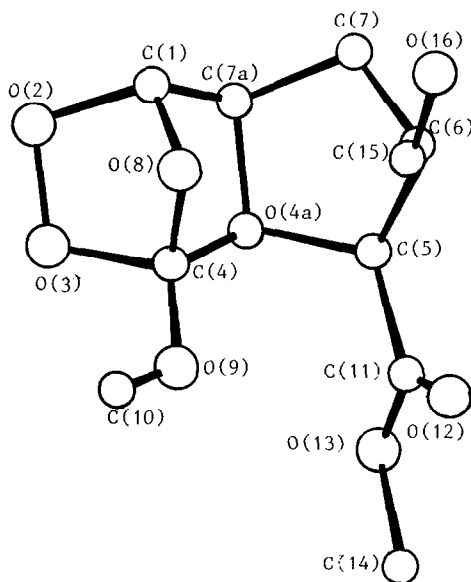
Summary: The formation of the product of intramolecular interaction of a zwitterion and a methoxycarbonyl group was observed in the process of ozonating dimethyl ester of endo, *cis*-bicyclo[2,2,1]hept-5-en-2,3-dicarboxylic acid in diethyl ether. The structure of racemic endo, *cis*-4-methoxy-5-methoxycarbonyl-6-formyl-1,4-epoxy-2,3-dioxacyclopenta[2,3-*d*]cyclohexane was established by an X-ray structure analysis.

The ozonation of cyclic olefins in inert solvents results in the formation of zwitterions which interact with the carbonyl fragment in both inter- and intra-molecular manners, thus leading to monomeric and oligomeric ozonides¹. The oligomeric peroxide was obtained by the ozonation of dimethyl ester of endo, *cis*-bicyclo[2,2,1]hept-5-en-2,3-dicarboxylic acid (1) in diethyl ether, the structure of the oligomeric peroxide being essentially different from that of the ozonide².

The report presented considers the unexpected formation of (2) as a product of the intramolecular interaction of a zwitterion and a methoxycarbonyl group by the ozonation of ester (1). The structure of (2) was determined by an X-ray structure analysis³. Crystals of (2) are monoclinic, $a = 7.27(1)$, $b = 11.27(1)$, $c = 13.81(2)$ Å, $\beta = 101.0(1)^\circ$, $V = 1111(2)$ Å³, $d_{\text{calcd}} = 1.54 \text{ g/cm}^3$, $\mu(\text{MoK}\alpha) = 1.41 \text{ cm}^{-1}$, $Z = 4$, space group $P2_1/n$ (at -120°C). The unit cell parameters and intensities of 540 reflections ($I > 4\sigma$) were measured with a "Syntex P2₁" four circle automatic diffractometer (λ MoK α , graphite monochromator, $\theta/2\theta$ scan, $\sin(\theta/\lambda)_{\text{max}} = 0.482$).

The structure was solved by direct methods and refined by the block-diagonal technique of the least squares in isotropic approximation for the skeletal atoms and in anisotropic approximation for other nonhydrogen atoms. The positional parameters of hydrogen atoms were recalculated after each cycle of refinement and included as fixed contributions in F_{calcd} with the fixed values of $B_{\text{iso}} = 4 \text{ \AA}^2$. The final values of discrepancy factors are 0.040 (R) and 0.038 (R_w). All calculations were carried out with an "Eclipse S/200" computer with the employment of INEXTL programmes. The molecular structure is shown in the Figure. Thus, compound (2) represents racemic endo, *cis*-4-methoxy-5-methoxycarbonyl-6-formyl-1,4-epoxy-2,3-dioxacyclopenta[2,3-*d*]cyclohexane. The five-membered carbocycle is endo-*cis*-fused with the ozonide bicycle and has an envelope conformation (displacement of C(6) from the plane of other four carbon atoms of the cycle is 0.578(6) Å). The aldehyde group occupies an axial position and the methoxycarbonyl group is in a pseudoequatorial position. A specific feature of ozonide (2) is a planar conformation of the peroxide group (torsion angle C-0-0-C = 2.7(6)°); the O-O peroxide bond length in (2) is 1.497(6) Å.

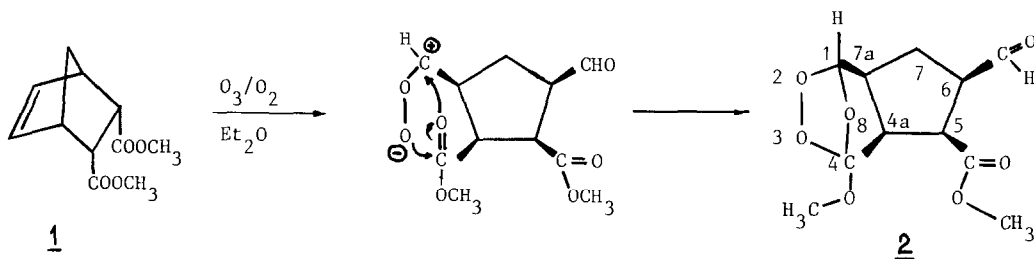
The PMR spectrum⁵ of ozonide (2) shows the characteristic narrow singlets of methoxyl



(3.61p.p.m.), methoxycarbonyl (3.73p.p.m.), methyne ozonide cycle (5.57p.p.m.), and formyl group (10.05 p.p.m.). The ^{13}C NMR spectrum⁵ has the signals of eleven carbon atoms. The most characteristic are the signals of methoxyl (q 51.50 and 51.63p.p.m.), carbonyl groups (s 170.70 and d 202.36p.p.m.) and of special interest are the signals of ozonide cycle: C(1) (d 103.98p.p.m.) and C(4) (s 124.42p.p.m.).

Ozonide (2) was obtained by the following procedure: the mixture of C_3 and C_2 was passed through the solution of 1.5g(7.1mmol) of (1) in 40ml of Et_2O (8.2 mmol O_3/h (4.5 l/h), 52min, -70°C). The residue of oligomeric peroxide (0.68g) was filtered off and (2) was gradually crystallized on cooling the mother liquor (0.28g, 15.2%, m.p. 111-112 $^\circ\text{C}$).

Figure: Molecular structure of (2).



REFERENCES AND NOTES

- Bailey, P.S. *Ozonation in Organic Chemistry*. Acad.Press, New York, S.Francisko, London, 1978, v.1, no.4.
- Odinokov, V.N.; Kukovinets, O.S.; Tolstikov, G.A. *Zh.Org.Khim.*, 1978, 14, 1209.
- Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication. Supplementary data available include Tables of bond lengths and angles.
- Gerr, R.G.; Yanovsky, A.I.; Struchkov, Yu.T. *Krisallografiya(Crystallography)*, 1983, 28, 1029(Russian).
- PMR spectrum of compound (2) (CDCl_3 , 100MHz, δ): m 1.6-3.5(6H, cyclo- C_5H_6), s(3.61 (3H, OCH_3), s 3.73(3H, CO_2CH_3), s 5.57(1H, OCHO), s 10.05(1H, CHO).
 ^{13}C NMR spectrum (CDCl_3 , 22.5MHz, δ): d 201.36(CHO), 170.70(OC=O), s 124.42(C^4), d 103.98(C^1), s 53.85(C^4a), q 51.63($\text{C}^4\text{-OCH}_3$), q 51.50(COOCH_3), s 48.96(C^7a), d 48.37(C^6), d 46.80(C^5), 29.64(C^7). Mass-spectrum (70eV, 150°C , m/z, I, %): ($\text{M-H}_2\text{O}$)⁺241(0.03), 183(0.38), 154(0.62), 126(0.83), 113(2.9), 74(2.4), 59(5.2), 44(83), 28(100).

(Received in UK 26 September 1985)