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STRUCTURE AND CONFORMATION OF HETEROCYCLES V.[1a] ISOMERIC 1,1,2,2-BI(ETHYLENEDIOXY) DERIVATIVES OF CYCLIC 1,2-DIKETONES AND O-QUINONES : 2,2'-BRIDGED BI(DIOXOLAN-2-YLS) AND TETRAOXA[n,4,4]PROPELLANES[2].

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In continuation of a study of 1,4,5,8-tetraoxadecalins[1,3b] we became interested in the related compounds with the angular positions bridged by a third ring i.e. tetraoxapropellanes *II*[2]. We wish to report herein the results of a systematical effort to synthesize and characterize certain of these interesting compounds, and to investigate their behavior under electron impact.

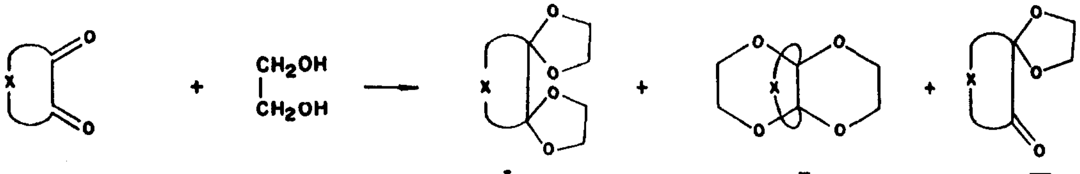
Of the methods available for synthesis of 1,4,5,8-tetraoxadecalins[3], only one was adaptable in this case, namely the classic[3a] condensation of cyclic 1,2-diketones with ethylene glycol under acid catalysis. The bi(dioxolan-2-yl) derivatives *I* and/or the isomeric tetraoxapropellanes *II* were thus formed accompanied sometimes by the monoketals *III*. In fact, this process had been realized by Jaeger and Smith[4] for the case X=$(CH_2)_4$ but the matter was not systematically investigated then or since.

Two types of cyclic 1,2-diketones were investigated. Simple alicyclic ones with X=$(CH_2)_3$, $(CH_2)_4$[4], $(CH_2)_6$, $(CH_2)_8$, $(CH_2)_{10}$ and fully conjugated ones i.e., o-quinones with X=o, o'-biphenylene, 1,4-tetrachlorobutadienylene and 1,8-naphthylene[5].

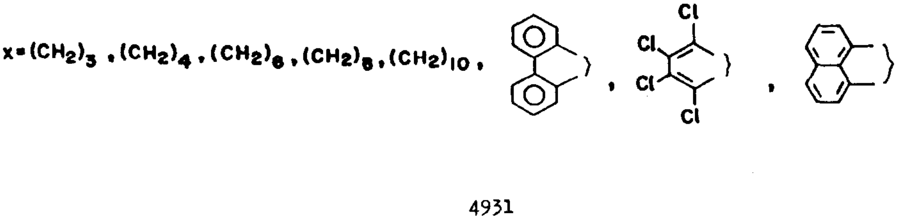
The salient data for both classes of compounds *I* and *II* are summarized in the Table.

As before,[6] IR studies were found to be largely uninformative for differentiating *I* from *II*. However NMR-and mass spectra were again[6] conclusive and exhibited characteristic behavior for each class of compounds.

Thus, the -O-CH_2-CH_2-O-protons absorb in the τ 6 region with different half-height-widths ($w_{\frac{1}{2}}$) similar to those found in the aliphatic series[6], namely the bi(dioxolan-2-yl) derivatives *I* exhibit relatively narrow multiplets ($w_{\frac{1}{2}}$=5-19Hz) whereas the tetraoxapropellanes *II* exhibit well resolved AA'BB'



I II III



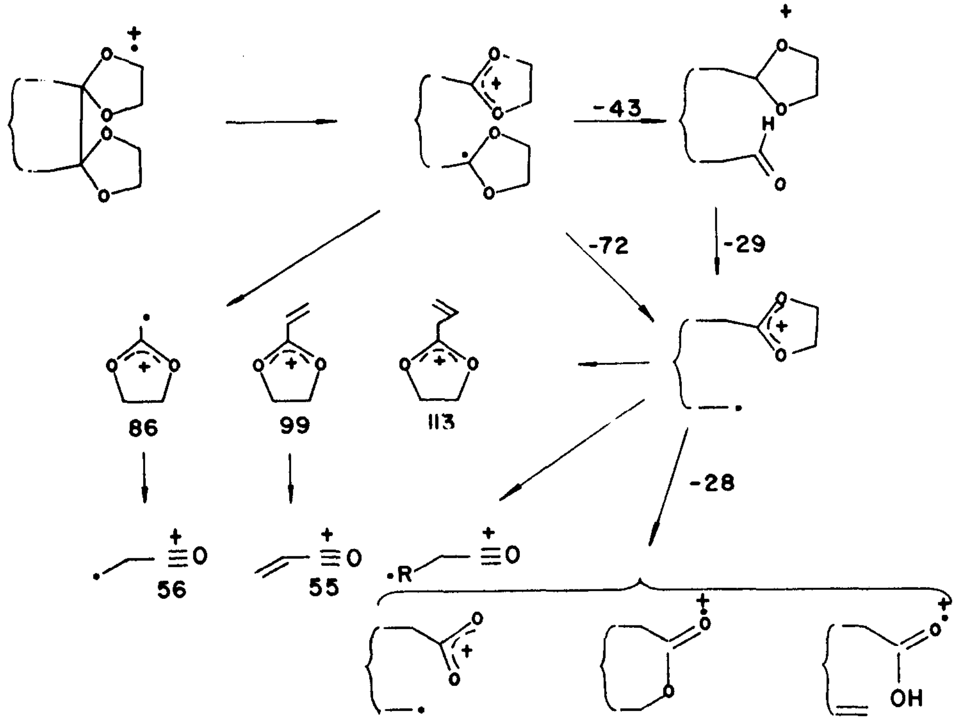
Table

Properties of 2,2'-bridged Bi(dioxolan-2-yl)s *I* and the isomeric Tetraoxapropellanes *II*

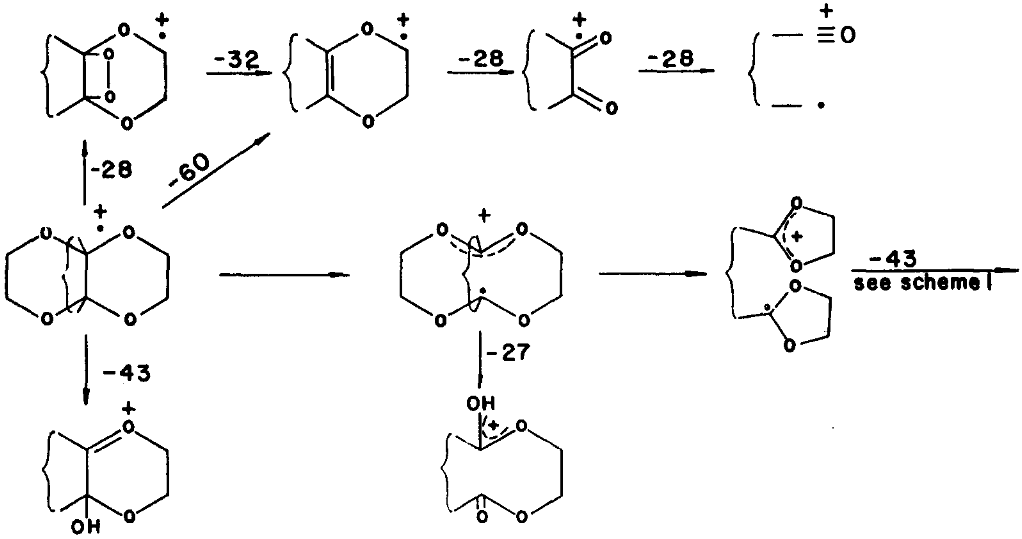
X	m.p., °C / Yield %[a]	($w_{\frac{1}{2}}$ Hz)[b]	m/e (rel. abundance)[c]
$(CH_2)_3$ (*I*)	Oil / 40[d]	6.0(6)	186(4), 143(2), 114(5), 100(4), 99(10), 98(4), 87(6), 86(100), 55(9)
$(CH_2)_4$ (*I*)	Oil / 95(82)	6.0(12)	200(4), 157(3), 128(6), 112(7), 100(16), 99(100), 86(6), 56(8), 55(16)
$(CH_2)_4$ (*II*)	102 / 0.5(5)	6.10(44)	200(47), 173(37), 157(12), 142(18), 140(20), 138(3), 136(12), 129(10), 128(3), 113(22), 112(60), 111(25), 101(11), 100(56), 99(41), 89(23), 86(24), 84(69), 56(33), 55(100)
$(CH_2)_6$ (*I*)	Oil / 30(7)[d]	6.12(19)	228(8), 185(4), 156(12), 155(7), 141(4), 128(3), 127(13), 125(4), 114(4), 113(50), 101(4), 100(35), 99(100), 86(33), 83(6), 69(10), 56(14), 55(71)
$(CH_2)_6$ (*II*)	80-81 / 30(10)[d]	6.13(43)	228(30), 201(30), 185(6), 172(4), 170(3), 168(4), 166(12), 157(25), 141(12), 140(20), 139(17), 138(48), 128(11), 127(6), 113(10), 112(19), 111(25), 110(16), 100(51), 99(100), 98(12), 97(20), 86(59), 84(25), 83(39), 68(55), 56(31), 55(96)
$(CH_2)_8$ (*I*)	Oil / 35[d]	6.06(12)	256(1), 213(2), 184(4), 156(4), 155(10), 141(12), 127(2), 113(10), 111(2), 100(14), 99(100), 86(34), 69(7), 67(6), 56(7), 55(29)
$(CH_2)_8$ (*II*)	170-173 / 10[d]	6.14(40)	256(4), 229(12), 213(6), 196(4), 195(6), 194(31), 185(10), 168(3), 167(3), 151(14), 140(4), 139(17), 138(21), 137(37), 125(17), 113(15), 112(14), 100(10), 99(74), 98(37), 97(22), 86(37), 84(22), 83(20), 82(21), 81(37), 69(31), 68(29), 56(24), 55(100)
$(CH_2)_{10}$ (*I*)	Oil / 10[d]	6.06(11)	284(2), 241(2), 212(3), 183(3), 169(8), 155(12), 141(6), 139(2), 127(2), 113(8), 100(9), 99(100), 86(16), 69(4), 56(3), 55(20)
$(CH_2)_{10}$ (*II*)	181-183 / 10[d]	6.16(42)	284(4), 257(7), 241(6), 224(2), 222(10), 213(6), 141(9), 137(12), 125(9), 113(13), 112(11), 111(13), 100(10), 99(100), 98(33), 97(15), 86(30), 84(21), 83(23), 81(21), 69(30), 68(19), 67(21), 56(25), 55(80)
1,8-naphthylene (*I*)	147-148 / 1[d,e]	5.72(10)	270(12), 242(8), 227(1), 199(12), 198(68), 197(7), 182(4), 170(100), 156(5), 155(12), 154(22), 153(7), 142(8), 139(4), 126(36), 114(45), 113(8), 99(4), 91(48), 77(25), 65(10), 63(26)
1,8-naphthylene (*II*)	215-216 / 59[d,e]	6.08(52)	270(76), 243(7), 242(39), 212(21), 211(11), 210(8), 199(11), 198(30), 183(9), 182(41), 171(5), 170(29), 155(15), 154(100), 127(11), 126(52), 114(7), 91(12), 77(10), 63(9)
o,o'-biphenylene (*II*)	236-237 / 41[f,g]	6.10(62)	296(40), 269(2), 268(11), 238(5), 236(41), 209(6), 208(8), 196(9), 181(18), 180(100), 152(32), 151(15), 104(10), 76(18)
1,4-tetrachloro butadienylene (*II*)	161-162 / 7[f]	6.10(49)[c]	332(12), 297(46), 272(5), 262(24), 244(8), 227(8), 216(61), 209(43), 192(10), 188(15), 181(40), 153(19), 116(31), 91(15), 89(100), 83(10), 71(6), 55(8)

a) From 1,2-diones (obtained commercially or following literature procedures) and excess ethylene glycol. Large variations in yields were recorded according to the reaction conditions. The given yields reflect experiments taken at random either from p-TsOH catalyzed reactions in boiling benzene with azeotropic water removal or (in parenthesis) from H_2SO_4 catalyzed reactions in chloroform at room temperature. In the alicyclic series, products were analysed and isolated by glpc. The aromatic reaction products were chromatographed on silica gel. b) Measured on a Varian HA-100 instrument at 100 MHz. The center of the symmetric AA'BB' multiplet is given and (in parenthesis) $w_{\frac{1}{2}}$ stands for half-height-width of the above pattern. c) Measured on a Hitachi-Perkin Elmer RMU-6 instrument at 70 eV. Significant ions and (in parenthisis) their relative abundances are given usually above 2%. For the tetrachloro derivative, only the lowest ions of the isotropic "clusters" are given i.e., with Cl^{35}. d) Varying amounts of mono-ketal were also isolated. e) Increased reaction time led to corresponding increase in the yield of the propellane. The latter was exclusively isolated at long reflux times or as in (f). f). These reactions had to be performed in boiling toluene whereby only the corresponding propellanes were isolated. g) ca. 1% of 9,10-dioxenophenanthrenene, m.p. 141-2°C was also obtained.

Scheme I



Scheme 2



patterns ($w_{\frac{1}{2}}$ = 40-62 Hz). This has been attributed[6] to the increased mobility (pseudorotation) of the five-membered rings as compared with the six-membered ones and is corroborated by the general behavior of 1,3-dioxolanes .

Although the mass-spectra were measured at low resolution and, at this stage, with the aid of no special techniques, interpretation was possible, based on comparative analysis of the various compounds in the series.

The result of this analysis is presented in Schemes 1 and 2 for the 2,2'-bridged bi(dioxolan-2-yl) *I* and for the tetraoxapropellane *II* systems respectively. Deuterium labelling, metastable ion defocussing and variable pressure measurements for further proof of the postulated fragmentation pathways will be reported in the full paper.

A final note concerning the formation and relative stabilities of *I* and *II*. The o-quinones, in contrast to the alicyclic 1,2-diketones, show both kinetic and thermodynamic preference for formation of the propellane structure *II*. To account for this[5] or for the dependence of the product composition on the proton concentration in the reaction[4a], a doubly charged positive ion due to benzylic stabilization has been invoked. We consider this hypothesis untenable because of the given reaction conditions and on grounds of other observations during our studies. For one, benzil forms only 2,2'-diphenyl bi(dioxolan-2-yl)[3,6]. Apparently, steric factors, such as ring strain and conformation of the 1,2-dione strongly govern the process along with electronic ones such as stabilization of a carbonium ion of a benzylic site and enolization proneness of the 1,2-diketone. A detailed discussion, though, is deferred to a later date together with conformational analytical studies, now in course.

Acknowledgements. Miss Pauline Lurie rendered skillful technical assistance. Mass Spectra were kindly measured at Bar Ilan University, Ramat Gan.

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2. This nomenclature was adapted according to J. Altman, E. Babad, J. Itzchaki and D. Ginsburg, Tetrahedron, Suppl. 8, Part 1, 279 (1966). Thus, for example, *II* (X=1,4-tetrachlorobutadienylene) is 11, 12, 13,14-tetrachloro-2,5,7,10-tetrachloro-2,5,7,10-tetraoxa[4.4.4]propella-11,13-diene but *II* (X=$(CH_2)_{10}$) is 13, 16, 17, 20-tetraoxa[10.4.4] propellane.

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   b. Y. Auerbach, M. Sprecher and B. Fuchs, Tetrahedron Letters, 5207 (1970) and previous papers in the series.

4. a. R.H. Jaeger and H. Smith, J. Chem. Soc., 160 (1955).

   b. Cf. Also T.D.J. D'Silva, Chem. Ind. (London, 202 (1970).

5. When this work had been completed[6,1b], a communication appeared: A.I. Cohen, I.T. Harper and S.D. Levine, Chem. Comm., 1610 (1970), on the ketalization of acenaphthoquinone. The structures of the acenaphthenequinone ketalization products and their fragmentation under electron impact were assigned using high-resolution mass-spectrometry and metastable ion defocussing.

6. B. Fuchs, Tetrahedron Letters, 1747 (1970).