Acetalization of Acenaphthenequinone

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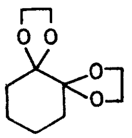
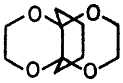
Summary The assignment of structures to the products of reaction of acenaphthenequinone with ethylene glycol is made chiefly on the basis of mass spectroscopy.

JAEGER and SMITH[1] examined the reaction between cyclohexane-1,2-dione and an excess of ethylene glycol, and isolated the bi(dioxolan-2-yl) (1) and a small amount (*ca.* 2%) of an isomeric product, assigned the bis-dioxan structure (2), which has also been isolated in *ca.* 1% yield from the acid-catalysed reaction of acraldehyde dimer with ethylene glycol.


(1)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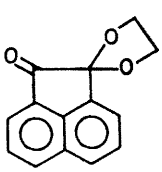
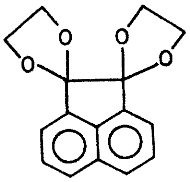
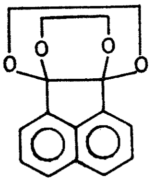
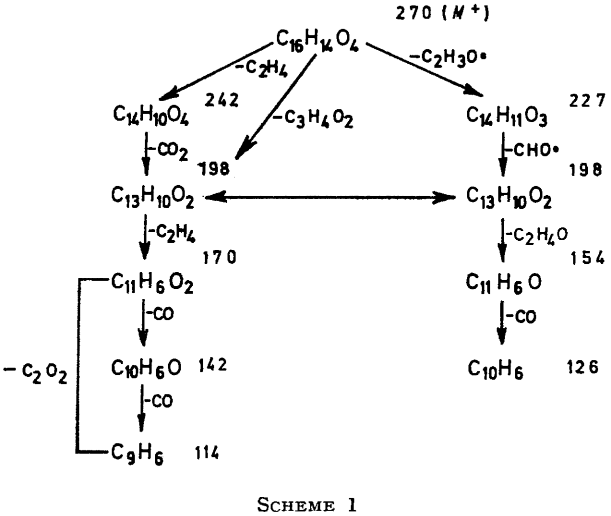

(3)


(4)

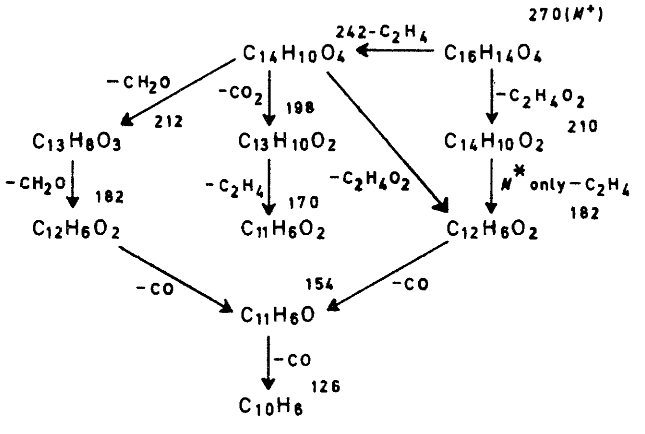

(5)

We report the structures of the products obtained from the reaction of acenaphthenequinone with an excess of ethylene glycol in benzene containing toluene-*p*-sulphonic acid. Preparative thick-layer chromatography of the crude reaction product on silica gel afforded three compounds in about *equal* amounts. The least polar compound was identified as the mono(dioxolan-2-yl) (3) by its i.r. spectrum [λ_{max} (KBr) 5·78 μm] and elemental analysis. Both the substance of intermediate polarity (m.p. 213·5—214°) and the most polar product (m.p. 147·5—148°) analysed satisfactorily for $C_{16}H_{14}O_4$. The low- and high-melting products have been assigned structures (4) and (5), respectively chiefly on the basis of mass spectrometry.[3]†



SCHEME 1

The significant ions (relative abundance shown in parentheses) in the low-resolution mass spectrum[4] of (4) occur at *m/e* 270(M^+)(28), 242(16), 227(2), 212(2), 210(1), 199(18), 198(81), 182(3), 170(100), 154(20), 142(5), 126(28), 114(42), 91(38), 77(34), and 63(24). Their elemental compositions were determined by high-resolution techniques and the fragmentation pathway, established by metastable ion de-focussing (Scheme 1).[5,6] The *m/e* 198 ion may be formed in three different ways: (1) by ring-cleavage, with successive losses of $C_2H_3O\cdot$ and $CHO\cdot$; (2) by loss of $C_3H_4O_2$; and (3) by loss of ethylene, followed by the elimination of carbon dioxide. The last two pathways are consistent with the elimination of the elements of 1,3-dioxolan from M^+. The *m/e* 198 ion is fragmented either through the loss of ethylene or of C_2H_4O, both modes being consistent with structure (4). Although the loss of carbon dioxide from the *m/e* 154 ion is expected, the double decarbonylation from the *m/e* 170 ion with loss of a nuclear carbon atom is explained as a rearrangement, in part, to 1,8-naphtholactone of the ion resulting from elimination of ethylene from the *m/e* 198 ion. Seibl described the fragmentation of 1,8-naphtholactone by double decarbonylation in a similar manner.[7]



SCHEME 2

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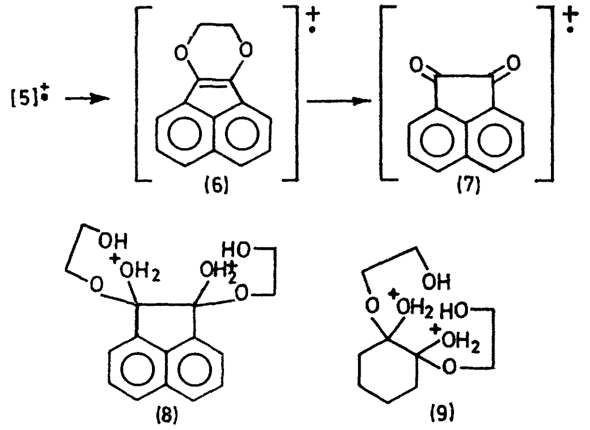
† The mass spectra were obtained with an AEI MS-902 double-focussing mass spectrometer (70 ev) equipped with a manually operated accelerating defocussing attachment and a Honeywell 7600 frequency-modulated analog tape recorder. The analog tape was processed on an IBM 1800 computer, using Squibb programs. The accuracy of high-resolution mass measurement was better than 10 p.p.m., while that of metastable ion defocussing was ±1 amu.

The ions of significant intensity in the low-resolution mass spectrum of (5) occur at *m/e* 270(M^+)(67), 242(28), 212(15), 210(10), 199(9), 198(19), 182(37), 170(24), 154(100), 142(1), 126(51), 115(7), 114(8), 91(20), 77(14), and 63(9). The mass spectrum and the fragmentation ion pathways, as determined by high-resolution techniques, are consistent with the structural assignment (Scheme 2).



SCHEME 3

The fragmentation pathway that demonstrates the bis-dioxan structure is the elimination of $C_2H_4O_2$ from the M^+ to form the stabilized unsaturated odd-electron ion (6) of *m/e* 210, which then eliminates ethylene to form the *m/e* 182 ion (7) (Scheme 3).

Upon further treatment under acetalization conditions, both (3) and (4) can be completely converted into (5). This result is in marked contrast to those in the cyclohexane-1,2-dione series, where (2) could not be converted into (1), and probably reflects the increased stability of the benzylic protonated intermediate (8) compared with that of the corresponding alicyclic ion (9).

(*Received, September* 30*th*, 1970; *Com.* 1683.)

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[1] R. H. Jaeger and H. Smith, *J. Chem. Soc.*, 1955, 160.

[2] T. D. J. D'Silva, *Chem. and Ind.*, 1970, 202.

[3] While this manuscript was in preparation, a communication appeared describing the use of low-resolution mass spectrometry to differentiate between bi(dioxolan-2-yl) and bisdioxan structures: B. Fuchs, *Tetrahedron Letters*, 1970, 1747. The fragmentation pathways described in Fuchs' work differ in some respects from those described here for (4) and (5), since his ethylene glycol adducts are derived from open chain α-dicarbonyl compounds.

[4] G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, 1969, **34**, 3618, have reported the mass spectrum of the ethylene glycol diacetal of phenylglyoxal.

[5] M. Barber and R. M. Elliott, ASTM E-14 Conference on Mass Spectrometry, Montreal, Canada, May 1964.

[6] J. H. Beynon, *Analyt. Chem.*, 1970, **42**, No. 1, A97.

[7] J. Seibl, *Experientia*, 1969, **25**, 1009.