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THE SYNTHESIS AND SOME PROPERTIES OF 1,2-AZULENEQUINONE (1,2-AZULENEDIONE) AND ITS DERIVATIVES

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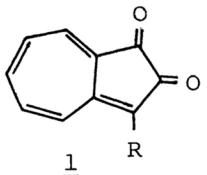
1,2-Azulenequinones (1,2-azulenediones) (1a-c) were synthesized by dehydrogenation of the corresponding 1,2-dihydroxyazulenes (5a-c) which were prepared from 2-acetoxyazulenes (2b,c) by benzoyloxylation followed by hydrolysis. Some chemical and physical properties of 1a-c are also described.

Azulenequinones (azulenediones) are non-benzenoid quinones having a unique azulene ring structure. Among azulenequinones, the highly annelated derivatives, 1,3-diphenyldibenz[e,h]azulene-2,8-dione[1] and tribenz[a,e,h]azulene-9,14-dione,[2] have been synthesized and shown to be stable. On the other hand, as reported in our previous paper,[3] the non-annelated 2,6-azulenequinone derivatives have been synthesized and shown to be so labile because of their high reactivities that they were isolated only in the form of dimers. This communication describes the synthesis of 1,2-azulenequnone (1a) and its derivatives (1b,c) as the first example of a stable non-annelated azulenequinone.

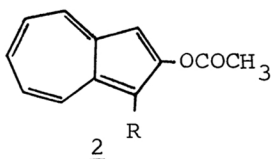
Benzoyloxylation[4] of ethyl 2-acetoxyazulene-1-carboxylate (2b)[5] with benzoyl peroxide (in C_6H_6 at 80 °C for 2.5 hr) gave, after an elution chromatography (Wako gel, C_6H_6), ethyl 2-acetoxy-3-benzoyloxyazulene-1-carboxylate (3b)[7] [violet needles, mp 140-141 °C; ν(KBr): 1771, 1728, and 1680 cm^{-1}; in a 65% yield] and ethyl 1,1-dibenzoyloxy-2(1H)-oxoazulene-3-carboxylate (4b)[red prims; mp 245-248 °C; ν(KBr): 1739, 1731-1719br, and 1700sh cm^{-1}; $\lambda_{max}(CHCl_3)$: 260 nm(log ε 4.27sh), 394 (4.24), and 406(4.21); in a 25% yield]. In a similar manner, benzoyloxylation of 2-acetoxy-1-cyanoazulene (2c)[8] gave 2-acetoxy-1-benzoyloxy-3-cyanoazulene (3c) [violet needles; mp 196-197 °C; ν(KBr): 2205, 1780, and 1740 cm^{-1}; in a 44% yield] and 1,1-dibenzoyloxy-3-cyano-2(1H)azulenone (4c) [brownish red prisms; mp 210 °C (dec); ν(KBr): 2205, 1740, and 1710; $\lambda_{max}(CHCl_3)$: 388 nm(log ε 4.40), 403(4.14sh); in a 33% yield]. In the nmr spectra of 4b,c, no signal due to the methyl protons of the acetoxy group is observed. The uv spectra of 4b,c are similar to those of 2H-cyclohepta[b]furan-2-ones[11] and diethyl 1-bromo-2(1H)-oxoazulene-1,3-dicarbxylate.[11] Further, reductive acetylation of 4b and 4c with Zn-AcOH-Ac_2O afforded 3b and 3c, respectively. From these findings the structures of 4b and 4c are assigned as 2(1H)-azulenone structures.

Treatment of 3b with 100% phosphoric acid at 90 °C for 50 min resulted in hydrolysis of acetoxyl and benzoyloxyl groups in accompany with deethoxycarbonylation to yield 1,2-dihydroxyazulene (5a)[12] as an ethyl acetate solution. Although 5a is so sensitive to air that it changes into a dark substance and could not be isolated



1

a series: R=H
b series: R=$COOC_2H_5$
c series: R=CN



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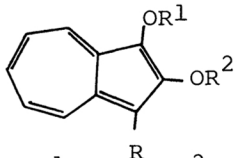
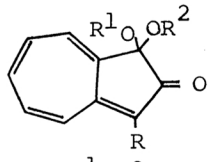
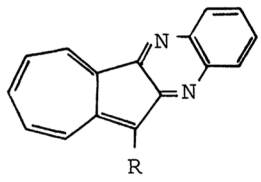


3: R^1=COPh, R^2=$COCH_3$
5: R^1=R^2=H
6: R^1=R^2=$COCH_3$



4: R^1=R^2=COPh
8: R^1=H, R^2=CH_3



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in a pure form, its formation was confirmed by acetylation in an ethyl acetate solution with Ac_2O-pyridine under N_2 atmosphere to give 1,2-diacetoxyazulene (6a) [blue oil; TNB complex: mp 107-108 °C; ν(neat): 1790-1770 cm^{-1}; in a 72% yield from 3b]. On the other hand, treatment of 3b and 3c with dimethylamine (in ethanol, at room temp, overnight) gave hydrolyzed products (5b and 5c), which were acetylated to give diacetates (6b) [violet needles; mp 89-90 °C; ν(KBr): 1781, 1777, and 1688 cm^{-1}; in a 99% yield from 3b] and (6c) [violet needles; mp 189-190 °C; ν(KBr): 2200 and 1780 cm^{-1}; in an 80% yield from 3c], respectively. The structural assignment of 6a, b, and c rests on the spectral data.[7)]

A solution of 5a in CH_2Cl_2, prepared by hydrolysis of 6a with 100% H_3PO_4, was treated instantly with DDQ at room temperature to give 1,2-azulenequinone (1a) [green needles; mp 130-135 °C(dec); in a 78% yield from 6a] after an elution chromatography (Wako gel, CH_2Cl_2). Similarly, treatment of solution of 5b and 5c in EtOAc, prepared from the benzoates, 3b and 3c, with DDQ gave 3-ethoxycarbonyl-1,2-azulenequinone (1b) [green needles; mp 157-158 °C; in an 82% yield] and 3-cyano-1,2-azulenequinone (1c) [green needles; mp 196-197 °C; in a 91% yield], respectively. The structures of 1a-c were determined from the following chemical evidence and the spectral data (Tables 1 and 2). Reductive acetylation of 1a-c with Zn-AcOH-Ac_2O afforded the corresponding 1,2-diacetoxyazulenes, 6a-c, respectively. Condensation of 1a-c with o-phenylenediamine gave azuleno[1,2]quinoxalines(7a: mp 185-186 °C; 7b: mp 173-174 °C; 7c: mp mp 268 °C), respectively, all as green needles. The mass spectra[13)] of 1a-c show the corresponding molecular ion peaks at m/e 158, 230, and 183, respectively. The IR spectra of 1a-c show three bands in the region of 1760-1630 cm^{-1} due to the α,β-diketone moity of five membered ring and $\nu_{C=C}$ (Table 1). The nmr spectrum of 1a reveals a singlet at δ 5.78 ppm assigned to H-3, being comparable to the H-3 (δ 5.79) of 2H-cyclohepta[b]furan-2-one,[10)] as well as a multiplet at δ 6.04-6.24 ppm assigned to ring protons (Table 2). The electronic absorption spectra of 1a-c show three principal band, involving a long tailed absorption in a region of 600-800 nm (Fig. 1). The polarographic half-wave potential[14)] of 1a-c were determined in anhydrous MeCN (at 25 °C, dropping-mercury electrode to SCE, supporting electrolyte 0.1M-NEt_4ClO_4). The E_1 and E_2 values of 1a are comparable to those 1,2-naphthoquinone (E_1 = -0.56, E_2 = -1.02 V vs. SCE)[15)] and those of 1b and 1c became more positive than those of 1a (Table 3). The results are

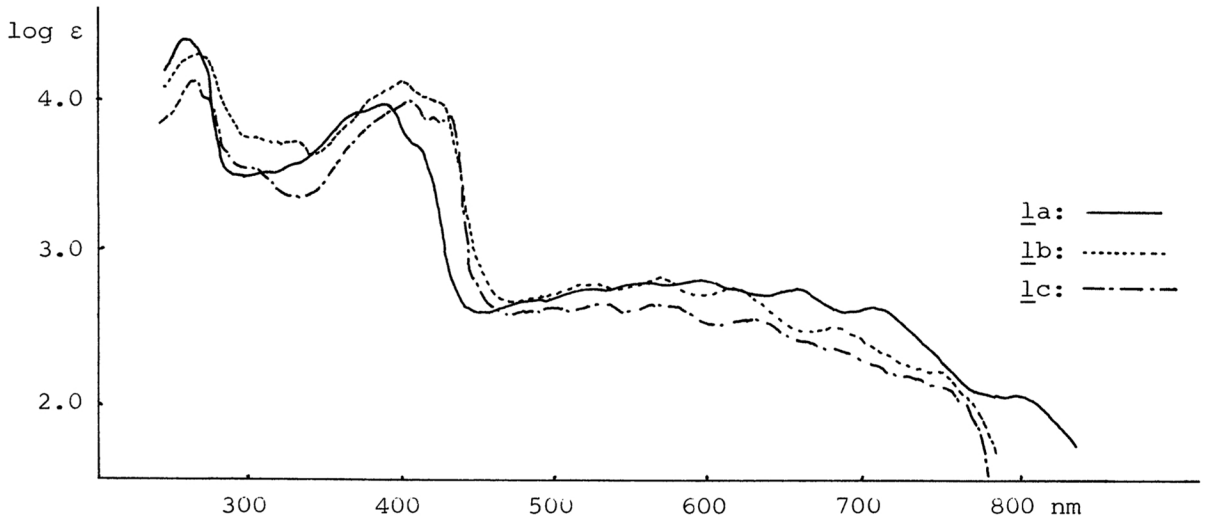

Fig. 1 Electronic spectra (in $CHCl_3$) of 1,2-azulenequinones(1a-c).

Table 1. IR data of 1a-c (in $CHCl_3$)

	$\nu_{C=O}$		$\nu_{C=O}$
1a	1751m	1687vs	1643m cm^{-1}
1b	1752m	1699vs 1688*	1638m
1c	1757m	1707vs	1693m

* $\nu_{C=O}$ of ethoxycarbonyl group.
m: Medium. vs: Very strong.

Table 3. Half-wave potentials of 1a-c

	E_1	E_2
1a	-0.55	-1.17V vs SCE
1b	-0.40	-1.00
1c	-0.34	-0.88

Table 2. Nmr data of 1a-c ($CDCl_3$, 100 MHz, δ ppm from TMS)

1a	5.78(s, H-3), 6.04-6.24(m, H-4-8)
1b	6.72-7.12(m, H-5 - 8), 8.29(complex d, J=12 Hz, H-4) 1.40(t, J=7.0 Hz, $OCH_2C\underline{H}_3$), 4.36(q, J=7.0 Hz, $OC\underline{H}_2CH_3$)
1c	6.42-7.08(m, H-5 - 8), 7.20(dd, J=10, 1.4 Hz, H-4)

consistent with the view that electronegative substituents decrease the energy of LUMO's (electron affinities)[15, 16] of the parent compounds. As it is expected from their cross-conjugated systems, the tendency of C=O at the 1-position in 1 toward nucleophilic addition is influenced by the stability of the residual heptafulvene moiety Thus, when 1a was dissolved in methanol, addition of methanol upon 1a proceeded partially to afford an equilibrium mixture of 1a and the acetal (8a), while those upon 1b and 1c, in which the heptafulvene moity was stabilized by an electron-withdrawing groups (CO_2Et or CN) at the 3-position, proceeded completely to give the acetals (8b and 8c).[17]

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5) The compound, 2b (red prisms; mp 70-70.5 °C) was prepared from diethyl 2-hydroxyazulene-1,3-dicarboxylate (ref. 6) by partial deethoxycarbonylation (100% H_3PO_4, at 100 °C, for 10 min., in a 91% yield), followed by acetylation (Ac_2O-pyridine, at 80 °C, for 2 hr, in a quantitative yield).

6) T. Nozoe, K. Takase, and N. Shimazaki, Bull. Chem. Soc. Jpn., 37, 1644 (1964).

7) Satisfactory elemental analyses and spectral data (UV, IR, and nmr) are obtained for the all new compounds.

8) The compound, 2c (red needles; mp 196-197 °C) was prepared from ethyl 3-cyano-2-hydroxyazulene-1-carboxylate (ref. 10) by deethoxycarbonylation (100% H_3PO_4, at 95 °C; for 15 min., in a 60% yield), followed by acetylation (Ac_2O-pyridine, in a 98% yield).

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12) The keto-enol tautomerisms of 1,2-dihydroxyazulenes, 5's, are under investigation in our laboratory.

13) Mass spectral data of 1[(at 25 eV, prominent ions, m/e(rel. %)] 1a: 160(M^++2, 1.4), 159(M^++1, 4.8), 158(M^+, 30.4), 130(M^+-CO, 11.1), 102(M^+- 2 CO, 100); 1b: 232(M^++2, 9.8), 231(M^++1, 11.4), 230(M^+-CO, 60.7), 202(M^+-CO, 14.7), 174(M^+-2 CO, 21.3), 146(100); 1c: 185(M^++2, 2.1), 184(M^++1, 4.7), 183(M^+, 42.9), 155(M^+-CO, 28.7), 127(M^+- 2 CO, 100).

14) We thank Dr. Yoshikiyo Kato of our department for the measurements of polarographic data.

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17) The acetal, 8b, was formed as a methanolic solution, but could not be isolated in a pure form [λ_{max}(MeOH): 233 nm (log ε 4.22), 257 (4.13), and 400 (4.18); nmr(DMSO-d_6 + MeOH): δ 1.37 and 4.33 (OEt), 7.67-7.33 (4H, m, H-5 - 8), 8.07 - 8.53(1H, H-4), the signals of OH and OMe groups are overlapped with those of solvent]. The acetal, 8c, was obtained as red prisms; mp 119-121 °C [λ_{max} (in MeOH): 227 nm (log ε 4.18), 255 (3.73sh), and 396 (3.76); ν(KBr): 3360, 2201, and 1667 cm^{-1}; nmr(DMSO-d_6): δ 3.32 (3H, s, OMe), 7.12-7.48(5H, m, H-4 - 8), and 7.65 ppm (OH)].

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