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THE SYNTHESIS OF DIETHYL 2,6-DIOXOAZULENE-1,3-DICARBOXYLATE, A DERIVATIVE OF 2,6-AZULENEDIONE (2,6-AZULENOQUINONE)

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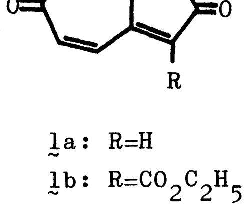
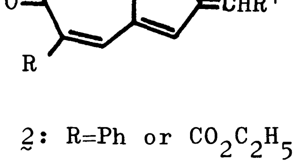
Diethyl 2,6-dioxoazulene-1,3-dicarboxylate (**1b**), a derivative of 2,6-azulenedione (2,6-azulenoquinone), was synthesized by dehydrogenation of diethyl 2,6-dihydroxyazulene-1,3-dicarboxylate (**5**), which was prepared from 2-diazo-6(2H)-azulenone (**4**), and was shown to be so reactive that it was isolated only in a form of the dimer (**7**).

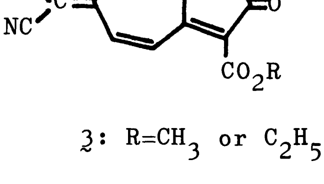
2,6-Azulenedione (2,6-azulenoquinone) (**1a**) is an extended quinone analogue having a unique structure of azulenic system. A highly annelated derivative, 1,3-diphenyldibenz[e,h]azulene-2,8-dione, has been synthesized by Ried et al.1) as an only example of such a quinone, but no detail has been described. 2-Methylen-6(2H)-azulenone derivatives (**2**), which are 2-methylene analogues with this quinoid system, have been synthesized by Hafner et al.2) and shown to be stable. On the other hand, as reported in the previous paper,3) 6-methylen-2(6H)-azulenone derivative (**3**), which are 6-methylene analogues with such a quinoid system, have been synthesized and shown to be so labile that they were isolated only in a form of dimer because of their high reactivity. This communication describes the synthesis of diethyl 2,6-dioxoazulene-1,3-dicarboxylate (**1b**), a non-annelated 2,6-azulenedione derivative.



1a: R=H
1b: $R=CO_2C_2H_5$



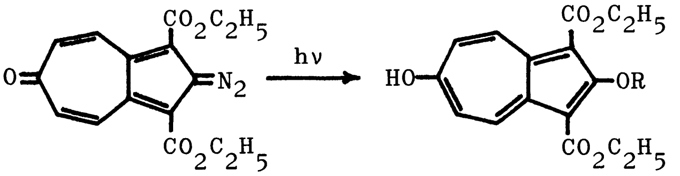
2: R=Ph or $CO_2C_2H_5$
$R'=OH$ or $N(CH_3)_2$



3: $R=CH_3$ or C_2H_5

Diethyl 2,6-dihydroxyazulene-1,3-dicarboxylate (5), which was used as a precursor for synthesizing 1b, was prepared from 2-diazo-6(2H)-azulenone (4)4) as follows: Photochemical decomposition of 4 in acetic acid with a high pressure mercury lamp yielded diethyl 2-acetoxy-6-hydroxyazulene-1,3-dicarboxylate (6)5) as pale yellow prisms, mp 183-184°C, in an 86% yield. Hydrolysis of 6 with aq. potassium hydroxide solution in acetone gave 5 as pale yellow prisms, mp 197-198°C, in an 84% yield.

Dehydrogenation of 5 was successful by the use of DDQ. Thus, the treatment of 5 with 1.1 equimolar amount of DDQ in benzene under reflux for 1 hr gave, after submission to an elution chromatography (Wakogel, chloroform), a dehydrogenation product (7) as colorless prisms, mp 260°C (decomp.), in a 65% yield. This compound gave satisfactory elemental analyses in accord with 1b. However, its mass spectrum, showing peaks at m/e 604 (M^+, 17.0%), 302 ($M^+/2$, 75.6%), 274 ($M^+/2$ -CO, 14.6%), 257 ($M^+/2$ -OC_2H_5, 51.2%), 144 (100%), suggests that 7 must be a dimer of 1b. Further, the ir spectrum of 7 exhibits absorptions corresponding to the strained five-membered ring ketone and the tropone nucleus6) as well as the non-conjugated ester group, and its uv spectrum is similar to those of tropone derivatives7) (Table 1). The nmr spectrum indicates 7 to be a highly symmetrical structure (Table 1). On the basis of these spectral data and the chemical evidences described below, 7 is assigned as the dimer of 1b, in which two azulene nuclei are joined at 1- to 1'- and 3- to 3'-positions. The conjunction between each azulene part in the dimer, 7, was reasonably determined to be *syn*, not but *anti*, on a dipole moment measurement, which gave



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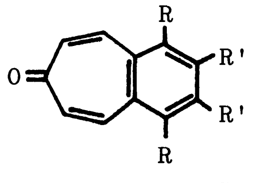
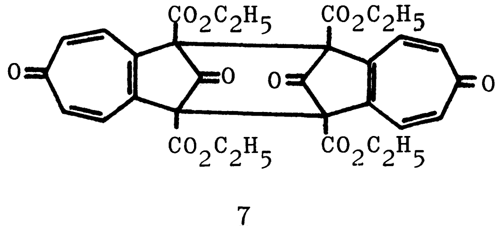
5: R=H

6: R=$COCH_3$



8: R=$CO_2C_2H_5$, R'=CO_2CH_3



7

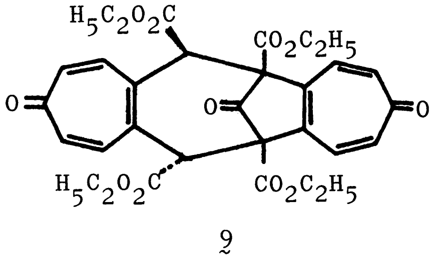


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Table 1. The spectral data of the compounds, **5**, **6**, **7**, **8**, and **9**: ir (KBr) cm^{-1}; uv λ_{max}(MeOH) nm (log ε); nmr (CDCl$_3$) δ ppm

5:	ir	3190 (OH), 1642 (C=O).
	uv	225 (4.31), 269 (4.35), 283 (4.10), 327 (4.65), 334 (4.62), 372sh (3.99), 415 (3.54).
	nmr	1.42 (t, J=7.0 Hz, 6H, $OCH_2C\underline{H}_3$), 4.44 (q, J=7.0 Hz, 4H, $OC\underline{H}_2CH_3$), 7.43 (d, J=11.0 Hz, 2H, H-5,7), 9.23 (d, J=11.0 Hz, 2H, H-4,8), 10.82 (s, 1H, OH at C-2) [60 MHz, acetone-d_6].
6:	ir	3100 (OH), 1774, 1693 (C=O).
	uv	214 (4.27), 250 (3.78), 284 (4.37), 325 (4.77), 352sh (4.14), 390sh (3.23), 420 (3.11).
	nmr	1.45 (t, J=7.0 Hz, 6H, $OCH_2C\underline{H}_3$), 2.48 (s, 3H, $COC\underline{H}_3$), 4.43 (q, J=7.0 Hz, 4H, $OC\underline{H}_2CH_3$), 6.87 (d, J=11.0 Hz, 2H, H-5,7), 9.10 (d, J=11.0 Hz, 2H, H-4,8) [60 MHz].
7:	ir	1793sh, 1789, 1728 (C=O), 1612, 1579 (tropone).
	uv	245.5 (4.53), 311 (4.15), 323 (4.09).
	nmr	1.36 (t, J=7.0 Hz, 12H, $OCH_2C\underline{H}_3$), 4.46 (q, J=7.0 Hz, 8H, $OC\underline{H}_2CH_3$), 7.04 (d, J=12.5 Hz, 4H, ring protons), 7.56 (d, J=12.5 Hz, ring protons) [100 MHz].
8:	ir	1739, 1727 (C=O), 1628, 1569 (tropone).
	uv	245 (4.50), 280 (4.70), 310sh (4.10), 350 (3.60).
	nmr	1.45 (t, J=7.0 Hz, 6H, $OCH_2C\underline{H}_3$), 3.93 (s, 6H, $OC\underline{H}_3$), 4.55 (q, J=7.0 Hz, 4H, $OC\underline{H}_2CH_3$), 7.11 (d, J=12.0 Hz, 2H, ring protons), 7.75 (d, J=12.0 Hz, 2H, ring protons) [60 MHz].
9:	ir	1764, 1740, 1733 (C=O), 1643, 1639, 1593 (tropone).
	uv	242 (4.73), 307 (4.46), 316sh (4.43), 360 (3.00).
	nmr	1.40 (t, J=7.0 Hz, 12H, $OCH_2C\underline{H}_3$), 4.18 (s, 2H, methine protons), 4.25 (q, J=7.0 Hz, 4H, $OC\underline{H}_2CH_3$), 4.33 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 4.36 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 6.66 (d, J=13 Hz, 2H, ring protons), 6.86 (d, J=13 Hz, 2H, ring protons), 6.94 (d, J=13 Hz, 1H, ring proton), 6.96 (d, J=13 Hz, 1H, ring proton), 7.11 (d, J=13 Hz, 2H, ring protons) [100 MHz].

a large value of 3.76 D for 7.8)

The dimer, 7, was rather stable on standing for a long time at room temperature or upon heating at about 100°C. However, the treatment of 7 with zinc in acetic acid yielded the original dihydroxyazulene, 5, in a 48% yield. Further, heating of 7 with dimethyl acetylenedicarboxylate in xylene under reflux gave a benzotropone derivative (8), whose structure was substantiated by the spectral data (Table 1), as colorless prisms, mp 178-179°C, in a 14% yield. The compound, 8, must be formed by decarbonylation from the adduct of the monomer, 1b, and acetylenedicarboxylate. These chemical evidences indicate that the dimer, 7, should dissociate in the solution to exist partly in the monomeric form, 1b, which reacts with the reagents. On the other hand, 7, when treated on a silica gel column for a long time, gave a decarbonylation product (9) as colorless prisms, mp 268-269°C (decomp.), in a 50% yield [mass: *m/e* 578 (M^+, 32.4%), 550 (M^+-CO, 8.1%), 275 (100%)]. The structure of 9 was established on the basis of the spectral data (Table 1). This compound may be formed by hydration upon the ketonic carbonyl followed by the ring opening and then decarboxylation.

From the above-mentioned results, it has been found that 2,6-azulenedione, 1b, produced from the dihydroxyazulene, 5, by dehydrogenation with DDQ, was so reactive that it was isolated in a form of the dimer, 7. It is noteworthy that 1b is similar to the 6-methylene analogue, 3, but is different from the 2-methylene analogue, 2, in reactivities.

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8) The dipole moment was measured by Dr. Kaoru Kuriyama of Shionogi Research Laboratory, Shionogi Co., Ltd., for which we thank him.

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