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The Oxidation of Dimethyl 2-Hydroxy-5-isopropylazulene-1,3-dicarboxylat and Its 6-Isopropyl Isomer with Lead Dioxide - The First Formation of a Diethenodicyclopenta[*ef:kl*]heptalene Derivative -

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Oxidation of dimethyl 2-hydroxy-6-isopropylazulene-1,3-dicarboxylate (**1a**) with lead dioxide in acetic acid gave a 1,1'-bi-[2(1*H*)azulenone] derivative in good yield. The similar reaction of 5-isopropyl isomer of **1a** gave two 1,1'-bi-[2(1*H*)azulenone] and a novel diethenoazupyrene derivative, as the first example, through 1,6'-coupling reaction followed by intramolecular Diels-Alder type cyclization.

Oxidation of alkylphenols is one of synthetic strategies for quinones and quinonemethides.1) Dehydrogenation of dimethyl 2-hydroxy-6-isopropylazulene-1,3-dicarboxylate (**1a**)2) with 2,3-dichloro-5,6-dicyanobenzoquinone gave after quenching only the starting material without giving 2,6-azulenequinone 6-methide (**4**), which showed different result from the previous report on a 6-dicyanomethyl congener.3) On the other hand, it has been found that oxidation of phenols with lead dioxide gave benzoquinone methides,4) diphenoquinones and *p*-benzoquinones.5) This communication will describe that the oxidation of **1a** and the 5-isopropyl isomer (**1b**)2) with lead dioxide yielded novel dimers of azulene derivatives.

A typical procedure of oxidation of **1a** : A solution of **1a** in acetic acid was added to a 0.6 equimolar

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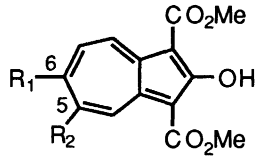
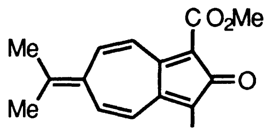
amount of lead dioxide. After the mixture was stirred at room temperature for 7 h, excess of lead dioxide was treated with a 3% hydrogen peroxide solution. The reaction mixture was extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate. The solvent was removed to give the residue which was chromatographed over silica gel to yield 1,1'-bi-[2(1*H*)azulenone] derivative (**2a**) in 70-80% yield.

Similar oxidation of **1b** gave diethenodicyclopenta[*ef*:*kl*]heptalene (diethenoazupyrene) derivative (**3**), 1,1'-bi-[2(1*H*)azulenone] derivatives (**2b**), and (**2c**), in 50, 18, and 11% yields, respectively.



1 a: R_1=$CHMe_2$, R_2=H
1 b: R_1=H, R_2=$CHMe_2$



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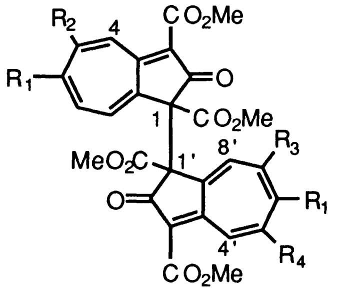
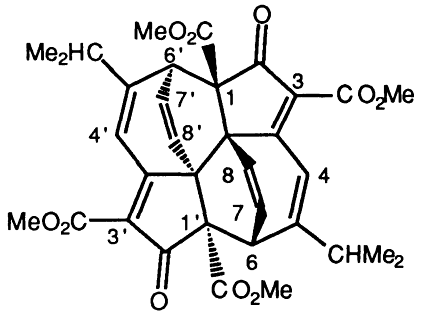


2 a: R_1=$CHMe_2$, R_2=R_3=R_4=H
2 b: R_1=R_4=H, R_2=R_3=$CHMe_2$
2 c: R_1=R_3=H, R_2=R_4=$CHMe_2$



3

The structures of **2a-c**, **3** were determined on the basis of their spectral data[6-9] and compound (**3**) was established by the single crystal X-ray analysis (Fig. 1).[10,11]

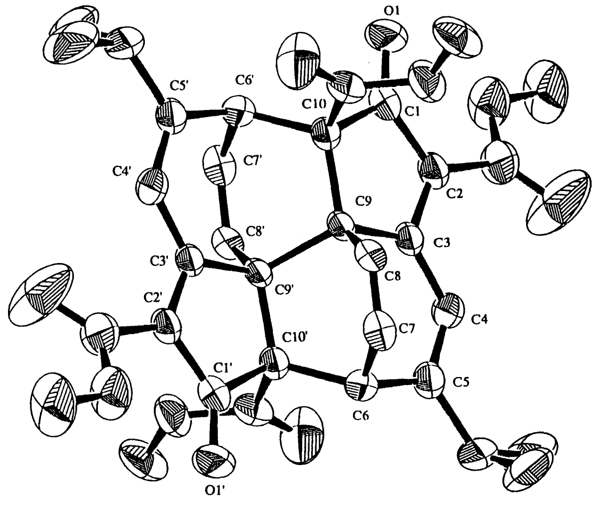
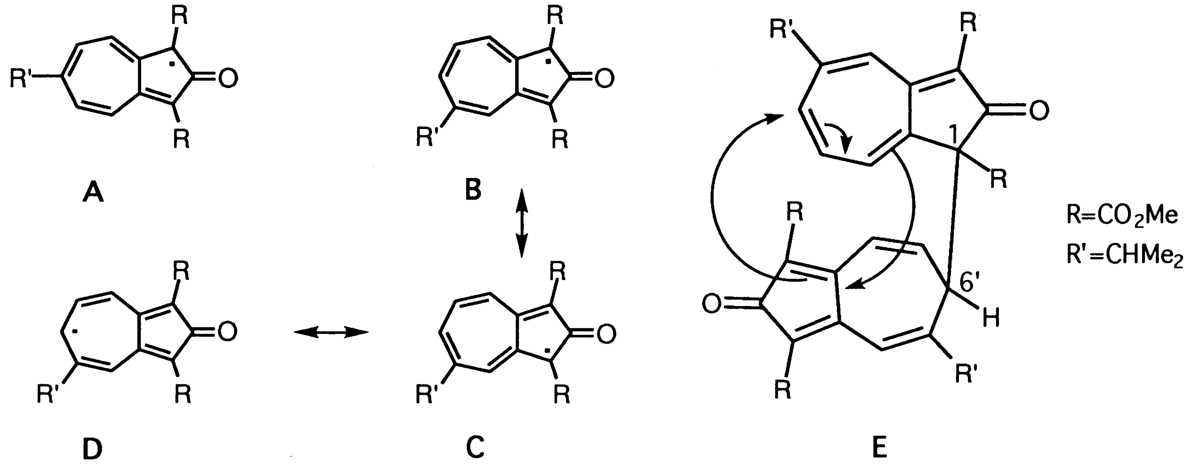


Fig. 1. ORTEP drawing of **3**.

Selected bond lengths and angles:

C1-C2, 1.456(4); C1-C10, 1.536(4); C1-O1, 1.210(4);
C2-C3, 1.357(5); C3-C4, 1.438(4); C4-C5, 1.336(5);
C3-C9, 1.553(4); C5-C6, 1.506(4); C6-C7, 1.509(5);
C6-C10', 1.555(4); C7-C8, 1.319(4); C8-C9, 1.506(5);
C9-C9', 1.617(6); C9-C10, 1.563(4) Å;
∠ C1-C2-C3, 110.9(3); ∠ C1-C10-C6', 104.7(3);
∠ C2-C3-C4, 122.7(3); ∠ C3-C4-C5, 125.8(3);
∠ C3-C9-C10, 102.2(3); ∠ C3-C9-C9', 111.4(3);
∠ C4-C5-C6, 121.0(3); ∠ C5-C6-C10', 114.8(3);
∠ C5-C6-C7, 110.2(3); ∠ C6-C7-C8, 119.5(4);
∠ C7-C8-C9, 118.3(3); ∠ C8-C9-C10, 117.9(3);
∠ C2-C1-C10, 108.0(3); ∠ C9-C10-C11, 113.6(3);
∠ C1-C10-C9, 106.1(3)°

In these oxidation, the 2-oxoazulen-1 (or 3)-yl radicals[12] (**A**, **B** or **C**) drived from **1a,b** coupled each other from less hinder sites to give 1,1'-bi-[2(1*H*)azulenone] derivatives (**2a-c**). The rate of 1,1'-coupling reaction of **A** seems to be faster than that of further oxidation for **4**. The radicals drived from **1a,b** have a large atomic spin population at positions 1, 3, 4, 6 , and 8.[13] On the other hand, 1,6'-coupling reaction of **B** with 2-oxoazulene-6-yl radical (**D**) presumed to generate an intermediate 2,2'(1*H*,6'*H*)-1,6'-biazulenedione (**E**) which undergoes intramolecular [4π+2π] cyclization to give **3**, finally.



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References

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6) **2a**: Yellow needles, mp 201-202 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.60 (12H, d, J=6.3 Hz, 2 x $(C\underline{H}_3)_2CH$), 2.70 (2H, sept, J=6.3 Hz, 2 x $(CH_3)_2C\underline{H}$), 3.60 (6H, s, 2 x $CO_2C\underline{H}_3$ at 1,1'), 3.62 (6H, s, 2 x $CO_2C\underline{H}_3$ at 3,3'), 6.81 (2H, dd, J=9.4, 1.5 Hz, H-7,7'), 7.03 (2H, dd, J=12.2, 1.5 Hz, H-5,5'), 7.64 (2H, d, J=9.4 Hz, H-8,8'), 8.31 (2H, d, J=12.2 Hz, H-4,4'); EIMS m/z (rel int.): 602 (M$^+$, 0.5), 302 (1/2M$^+$+1, 27), 270 (100), 239 (64), 212 (36); UV λ_{max} (CHCl$_3$) nm (log ε): 394 (4.54), 318 (3.42), 274 (4.47), 259 (4.20), 253, (4.13), 248 (4.06); IR (KBr): 1724, 1688 cm^{-1}.

7) **2b**: Yellow needles, mp 176-178 °C; ^{1}H NMR (300 MHz, CD_3CN): δ 1.09 (6H, d, J=6.8 Hz, $(C\underline{H}_3)_2CH$), 1.20 (6H, d, J=6.8 Hz, $(C\underline{H}_3)_2CH$), 2.57 (1H, sept, J=6.8 Hz, $(CH_3)_2C\underline{H}$), 2.80 (1H, sept, J=6.8 Hz, $(CH_3)_2C\underline{H}$), 3.64 (3H, s, $CO_2C\underline{H}_3$), 3.65 (3H, s, $CO_2C\underline{H}_3$), 3.69 (3H, s, $CO_2C\underline{H}_3$), 3.74 (3H, s, $CO_2C\underline{H}_3$), 6.77 (1H, d, J=7.6 Hz, H-6'), 6.93-7.12 (3H, m, H-5',6,7), 7.14 (1H, s, H-8'), 7.34 (1H, d, J=10.6 Hz, H-8), 8.12 (1H, d, J=12.0 Hz, H-4'), 8.28 (1H, s, H-4); EIMS m/z (rel int.): 602 (M^+, 1), 302 ($1/2M^+ +1$, 42), 270 (100), 239 (80), 212 (35); UV λ_{max} ($CHCl_3$) nm (log ε): 393 (4.59), 318 (3.30), 274 (4.64), 259 (4.50), 252 (4.44), 247 (3.39); IR (KBr): 1735, 1724, 1702, 1691,1682 cm^{-1}.

8) **2c**: Yellow needles, mp 171-173 °C; ^{1}H NMR (300 MHz, CD_3CN): δ 1.19 (12H, d, J=6.8 Hz, 2 x $(C\underline{H}_3)_2CH$), 2.78 (2H, sept, J=6.8 Hz, 2 x $(CH_3)_2C\underline{H}$), 3.64 (6H, s, 2 x $CO_2C\underline{H}_3$ at 1,1'), 3.71 (6H, s, 2 x CO_2CH_3 at 3,3'), 6.85-6.88 (4H, m, H-6,6',7,7'), 7.14 (2H, d, J=10.9 Hz, H-8,8') 8.21(2H, s, H-4,4'); EIMS m/z (rel int.): 602 (M+1, 2), 302 ($1/2M^+ +1$, 38), 270 (100), 239 (82), 212 (43); UV λ_{max} ($CHCl_3$) nm (log ε): 394 (4.56), 318 (3.45), 273 (4.49), 259 (4.23), 253 (4.15), 247 (4.08); IR (KBr): 1742, 1685, 1673 cm^{-1}.

9) **3**: Colorless needles, mp 203-204 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (12H, d, J=6.9 Hz, 2 x $(C\underline{H}_3)_2CH$), 2.21 (2H, sept, J=6.9 Hz, 2 x $(CH_3)_2C\underline{H}$), 3.68 (2H, ddd, J=8.4, 1.2, 0.8 Hz, H-6,6'), 3.71 (6H, s, 2 x $CO_2C\underline{H}_3$), 3.81 (6H, s, 2 x $CO_2C\underline{H}_3$), 5.75 (2H, d, J=1.2 Hz, H-4,4'), 6.95 (2H, dd, J=10.5, 0.8 Hz, H-8,8'), 7.20 (2H, dd, J=10.5, 8.4 Hz, H-7,7'); EIMS m/z (rel int.): 602 (M^+; 38), 302 ($1/2M^+ +1$, 88), 270 (100), 239 (66), 212 (25); HRMS, Found: m/z 602.2175. Calcd for $C_{34}H_{34}O_{10}$: M, 602.2152; UV λ_{max} ($CHCl_3$) nm (log ε): 303 (4.48), 282 (4.83); IR (KBr): 1744, 1711, 1688 cm^{-1}.

10) Crystal data for **3**: $C_{34}H_{34}O_{10}$: M=602.64, monoclinic, space group $P2_1/n$, a=11.589(1), b=6.842(1), c=19.313(3) Å, β=91.458(1)°, Z=2. Data were collected on a Rigaku AFC6S diffractometer using Cu-Kα radiation. Reflections measured: 2636; reflections used: 2500. The final refinement converted with R=0.057 and Rw=0.038.

11) C. K. Johnson, "ORTEP II, Report ORNL-5138," Oak Ridge National Laboratory, Tennessee, USA (1976).

12) Such a 1,1'-coupling reaction of 2-azulenyloxy radical has been disclosed in the reaction of ethyl 2-hydroxyazulene-1-carboxylate with ferric chloride which generated a 1,1'-bi-[2(1*H*)-azulenone] derivative followed by enolization to give diethyl 2,2'-dihydroxy-1,1'-biazulene-3,3'-dicarboxylate: T. Morita, S. Kosuge, K. Suzuki, and K. Takase, to be published.

13) The molecular orbitals of 2-azulenyloxy radicals drived from **1a,b** were calculated by the PM3 method. J. J. Stewart, MOPAC Version 6.0, QCPE No. 455, Chemistry Department, Indiana University, Bloomington, IN, 1987; T. Hirano, MOPAC Version 6.01, JCPE Newslett., **2**, 26 (1991). Spin populations for the 6-isopropyl-1,3-bis(methoxycarbonyl)-2-azulenyloxy radical : 0.534, -0.120, 0.496, -0.353, 0.470, -0.453, 0.493, -0.457, 0.476, and -0.371 for the positions 1, 2, 3, 3a, 4, 5, 6, 7, 8, and 8a, respectively; spin populations for the radical of 5-isopropyl isomer : 0.532, -0.121, 0.504, -0.353, 0.476, -0.456, 0.495, -0.453, 0.486, and -0.367 for the positions 1, 3, 2, 4, 3a, 5, 6, 7, 8, 9, and 8a, respectively.

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