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THE SYNTHESIS OF 6-METHYLEN-2(6H)-AZULENONE (2,6-AZULENOQUINONE 6-METHIDE) DERIVATIVES

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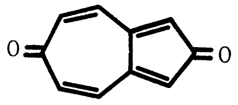
6-Methylen-2(6H)-azulenone (2,6-azulenoquinone 6-methide) derivatives (3a,b) were synthesized and shown to be so reactive that they could be isolated only in a form of dimers (4a,b).

2,6-Azulenedione (2,6-azulenoquinone) (1) is an extended quinone analogue having a unique structure of azulenic system. An 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 quinone, but no detail has been described. 2-Methylen-6(2H)-azulenones (fulvenotropones) (2), being a 2-methylene analogue with this quinoid system, have been synthesized by Hafner et al.$^{2)}$ and shown to be stable compounds. This communication describes the synthesis of 6-methylen-2(6H)-azulenone (2,6-azulenoquinone 6-methide) derivatives (3a,b), which are the 6-methylene analogue isomeric with 2, but could be isolated only in a form of dimers (4a,b) because of their high reactivity.



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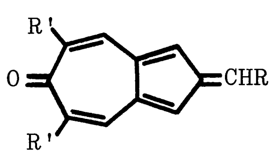
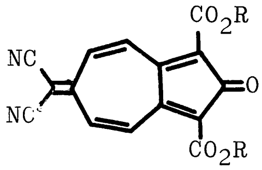


2: R=OH, NMe$_2$, NMePh, or piperidino
R'=Ph or CO$_2$Et

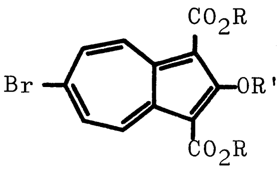


3a: R=Et
3b: R=Me

6-Bromo-2-hydroxyazulene derivatives (5a,b)$^{3)}$ were used as the starting materials for synthesizing 3a,b. The compounds, 5a,b, themselves did not react with sodiomalononitrile. On the other hand, the acetyl derivatives (6a)4) [red needles, mp 180°C; IR (KBr): 1776 (C=O), 1684 cm^{-1} (C=O)] and (6b)4) [red plates, mp 217-218°C; IR (KBr): 1770 (C=O), 1782 cm^{-1} (C=O)], derived from 5a,b, reacted easily with sodiomalononitrile in dimethoxyethane at room temperature to give substitution products (7a) [red needles, mp 158-159°C; IR (KBr): 2252 (C≡N), 1773 (C=O), 1689 cm^{-1} (C=O)] and (7b) [red needles, mp 165-167°C, IR (KBr): 2250 (C≡N), 1775 (C=O), 1690 cm^{-1} (C=O)] in quantitative yields respectively. Alkaline hydrolysis of 7a,b yielded 6-dicyanomethyl-2-hydroxyazulene derivatives (8a) [yellow needles, mp 147-148°C; IR (KBr): 3125 (OH), 2257 (C≡N), 1661 cm^{-1} (C=O)] and (8b) [yellow needles, mp 163.5-165°C; IR (KBr): 3060 (OH), 2250 (C≡N), 1655 cm^{-1} (C=O)] in 87% and 88% yields respectively.

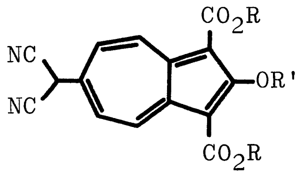
Treatment of 8a,b with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene under reflux for 1 hr gave after elution chromatography (Wakogel, chloroform) dehydrogenation products (4a) as orange needles, mp 223-225°C (decomp.), and (4b) as orange needles, mp 226-228°C (decomp.), in 88% and 60% yields respectively. These products gave satisfactory elemental analyses in accord with didehydro compounds (3a,b), respectively. The mass spectrum of 4a shows the highest mass peak at m/e 350 (50.0%), corresponding to the parent peak of 3a. However, a viscometric molecular weight of 684 5) was obtained for 4a; this is compatible with that of a dimer (M.W. 700) of 3a. Further, the infrared spectra of 4a,b exhibit absorptions corresponding to the strained five-membered ring ketone, as well as non-conjugated ester and conjugated cyano groups (Table 1). Their electronic spectra are closely similar to that of 8,8-dicyanoheptafulvene6) (Table 1). The nmr spectra suggest 4a,b to be highly symmetrical structures (Table 2). On the basis of these findings, 4a,b are assigned the dimeric structures bonded between the 1- and 1'-, and the 3- and 3'-positions, but not monomeric 6-methylen-2(6H)-azulenones, 3a,b. The conjunction between each azulene part in the dimers is reasonably determined to be *syn*, but not *anti*, on the basis of a dipole moment measurement which gave a large value of 6.26 D for 4a.7)

The dimers, 4a,b, are rather stable on standing for a long time at room temperature or upon heating at about 100°C. On the other hand, 4a gave the azulene, 8a, when treated with sodium hydrogen sulfite solution. Further, treatment of 4a with dimethyl acetylenedicarboxylate in xylene under reflux yielded a benzoheptafulvene derivative (9) as yellow prisms, mp 226-227.5°C, in a 75.4% yield. The structure



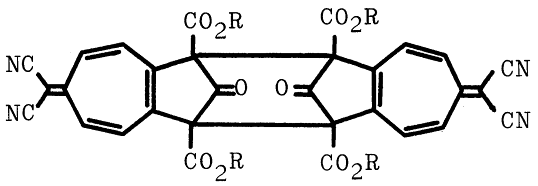
5a: R=Et, R'=H
5b: R=Me, R'=H

6a: R=Et, R'=Ac
6b: R=Me, R'=Ac



7a: R=Et, R'=Ac
7b: R=Me, R'=Ac

8a: R=Et, R'=H
8b: R=Me, R'=H



4a: R=Et
4b: R=Me

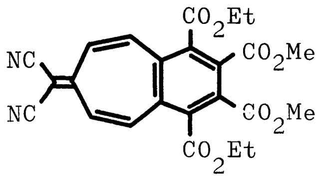


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Table 1. The IR and electronic spectral data of 6-methylen-2(6H)-azulenone dimers (4a,b) and benzoheptafulvene (9).

compounds	IR absorptions (KBr) cm^{-1}	electronic absorption maxima (MeOH) nm (log ε)
4a	2210 (C≡N), 1787 (C=O), 1740 (C=O)	258 (4.59), 264 (4.62), 401 (4.77), 422 (4.62)
4b	2208 (C≡N), 1788 (C=O), 1736 (C=O)	261 (4.50), 400 (4.80), 420 (4.71)
9	2215 (C≡N), 1740 (C=O), 1727 (C=O)	315 (4.53), 327 (4.59), 395 (4.43), 413 (4.38)

Table 2. The nmr data of 6-methylen-2(6H)-azulenone dimers (4a,b) and benzoheptafulvene (9) at 100 MHz. δ ppm

compounds	solvent	
4a	$CDCl_3$	1.69 (12H, t, J=7.0 Hz), 4.87 (8H, q, J=7.0 Hz), 7.19 (4H, d, J=12.5 Hz), 7.35 (4H, d, J=12.5 Hz)
4b	DMSO-d_6	3.87 (12H, s), 7.38 (8H, s)
9	$CDCl_3$	1.42 (6H, t, J=7.0 Hz), 3.92 (6H, s), 4.47 (4H, q, J=7.0 Hz), 7.20 (2H, d, J=6.0 Hz), 7.32 (2H, d, J=6.0 Hz)

of **9** was established on the basis of the electronic spectrum, which is similar to that of 10,10-dicyanobenzo[c]heptafulvene[8] (Table 1), and the nmr data (Table 2). The chemical evidence described above indicates that the dimer, **4a**, should dissociate into the monomer, **3a**, to react with these reagents, although the monomer could not be isolated.

From the above-mentioned results, it has been found that 6-methylen-2(6H)-azulenones, **3a,b**, produced from **8a,b** by dehydrogenation, are so reactive that they dimerize rapidly into the dimers, **4a,b**. It may be noteworthy that **3a,b** are markedly different from 2-methylen-6(2H)-azulenones, **2**, in reactivity. Further, such easy thermal dimerization of **3a,b** is surprising because both 4-pi-electron components must be joined in a manner suprafacial[9] and such unusual dimerization may involve a stabilized diradical intermediate.

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* To whom correspondence should be addressed.

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7) 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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