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THE SYNTHESIS AND SOME PROPERTIES OF 6-HYDROXY-7H-NAPHTH[3,2,1-cd]AZULEN-7-ONE

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In the previous paper,[1)] we have reported on the synthesis of 7H-naphth-[3,2,1-cd]azulen-7-one (1), which is a non-benzenoid aromatic compound with a new tetracyclic system. The ring carbonyl in 1 has been found to be highly polarized,[1)] so that it is expected that a hydroxyl derivative of 1, such as 6-hydroxy-7H-naphth[3,2,1-cd]azulen-7-one (2a), exists in a tautomeric mixture with its tautomer, 7-hydroxy-6H-naphth[3,2,1-cd]azulen-6-one (2b). In this communication we now wish to describe the synthesis and some properties of 2a.

Diethyl 4-phenylazulene-1,3-dicarboxylate has been found to give 1 and its ethoxycarbonyl derivative by Friedel-Crafts-type ring closure on heating in polyphosphoric acid at 100°C for 7 hr.[1)] In a similar manner, diethyl 2-chloro-4-phenylazulene-1,3-dicarboxylate (3)[2)] gave 6-chloro-7H-naphth[3,2,1-cd]azulen-7-one (4): blue green needles, mp 190-191°C, and its ethoxycarbonyl derivative (5): red violet needles, mp 202.5-204°C, in 15% and 60% yields respectively. When a monocarboxylic acid (6), derived from 3 by alkaline hydrolysis, was treated with polyphosphoric acid at 100°C for 3 hr, only 4 was obtained in a 90% yield. The chloro substituent of 4 was easily replaced with nucleophilic reagents to give the corresponding substitution products.[3)] Thus, the treatment of 4 in methanol with sodium methoxide under reflux for 1 hr yielded 6-methoxy-7H-naphth[3,2,1-cd]azulen-7-one (7): red needles, mp 218-219°C, in

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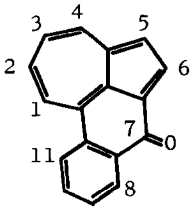

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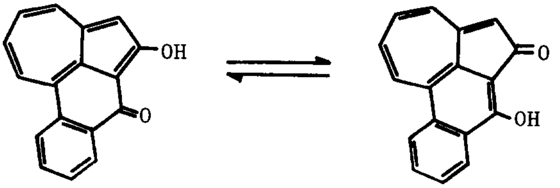
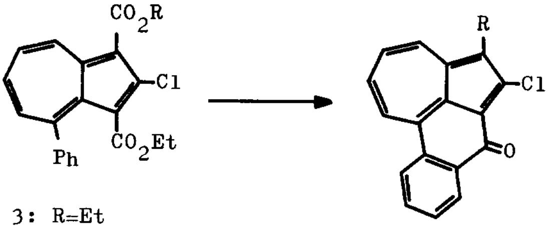
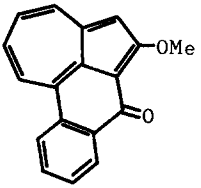


2a 2b



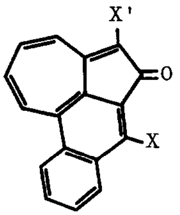
3: R=Et
6: R=H

4: R=H
5: R=CO_2Et
9: R=Cl



7

a quantitative yield. The structures of 4, 5 and 7 were substantiated on the basis of the electronic spectra, which are similar to that of 1, and the ir and nmr spectral data (Table 1), as well as the mass and elemental analyses.[4)]



8: X=OMe, X'=H
10: X=X'=Cl

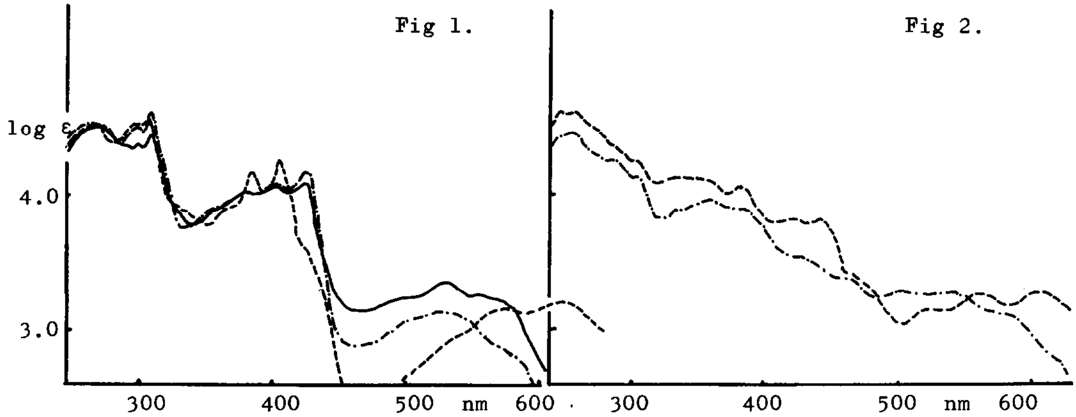
When heated with 48% hydrobromic acid at 90°C for 40 min., 7 was easily hydrolyzed to give an acidic compound (2):[4)] red needles, mp 198-199°C, in a quantitative yield. Its electronic spectrum, being similar to that of 1 (Fig 1), and its nmr spectral data (Table 1) are appropriate for the structure of 6-hydroxy-7H-naphth[3,2,1-cd]azulen-7-one (2a). On the other hand, its ir spectrum shows absorptions at 1627 (strong) and 1650 (medium) cm^{-1} corresponding to $\nu_{c=o}$ (Table 1). The former is assignable to $\nu_{c=o}$ of the ring carbonyl in 2a, while the latter is assignable to that in 7-hydroxy-6H-naphth[3,2,1-cd]azulen-6-one (2b), a tautomer of 2a; this assignment is reasonable since $\nu_{c=o}$ of the five-membered ring carbonyl in 1,2-dihydroazulen-2-one, a tautomer of 2-hydroxyazulene, appeared at 1642 cm^{-1}.[5)] These facts suggest that 2 exists in a tautomeric mixture between 2a and 2b, in

Table 1. The ir and nmr spectral data of naphth[3,2,1-cd]azulenones

Compounds	ir (KBr) $\nu_{c=o}$ cm^{-1}	nmr ($CDCl_3$) δ ppm
2	1627, 1650	5.82 (1H, bs, OH), 6.43 (1H, s, H-5), 7.3-8.0 (4H, m, H-2,3,9,10), 8.1-8.7 (4H, m, H-1,4,8,11)
4	1631	6.98 (1H, s, H-5), 7.4-7.7 (3H, m, H-3,9,10), 7.81 (1H, td, J=10.0, 2.0 Hz, H-2), 8.0-8.5 (4H, m, H-1,4,8,11)
5	1637, 1692	1.50 (3H, t, J=7.2 Hz, $OCH_2C\underline{H}_3$), 4.47 (2H, q, J=7.2 Hz, $OC\underline{H}_2CH_3$), 7.3-8.4 (7H, m, H-1,2,3,8,9,10,11), 9.0-9.2 (1H, m, H-4)
7	1624	4.18 (3H, s, OCH_3), 6.55 (1H, s, H-5), 7.4-7.8 (4H, m, H-2,3,9,10), 7.9-8.7 (4H, m, H-1,4,8,11)
8	1657	4.43 (3H, s, OCH_3), 5.77 (1H, s, H-5), 6.3-7.0 (3H, m, H-2,3,4), 7.3-7.8 (3H, m, H-8,9,10), 8.0-8.5 (2H, m, H-1,11)
9	1630	7.4-8.3 (5H, m, H-2,3,4,9,10), 8.4-8.8 (3H, m, H-1,8,11)
10	1686	6.3-7.0 (3H, m, H-2,3,4), 7.3-7.8 (3H, m, H-8,9,10), 8.1-8.5 (2H, m, H-1,11)

which **2a** is predominant.

The existence of the tautomerism between **2a** and **2b** is also supported from the chemical evidence mentioned below. The methylation of **2** with diazomethane gave 7-methoxy-6H-naphth[3,2,1-cd]azulen-6-one (**8**): unstable dark red needles, mp 164-165°C, which should be derived from **2b**, in a 25% yield, besides the formation of **7** in a 75% yield. The structure of **8** was established on the basis of the spectral data, as well as the mass and elemental analyses.4) The electronic spectrum of **8** is apparently differing from that of **7** (Fig 2). The ir spectrum of **8** shows a absorption at 1657 cm^{-1} corresponding to $\nu_{c=o}$ (Table 1), which is comparable to that of 1,2-dihydroazulen-2-one.5) The nmr signals due to H-2,3,4,5 in **8**, which appear at a higher field than those in **7**, indicate **8** to have a heptafulvene-type structure.5,6) Further, the treatment of **2** with thionyl chloride yielded two kinds of dichloro derivatives, 5,6-dichloro-7H-naphth[3,2,1-cd]azulen-7-one (**9**): green needles, mp 297.5-298°C, and 5,7-dichloro-6H-naphth-[3,2,1-cd]azulen-6-one (**10**): green needles, mp 290-292°C, in 58% and 16% yields



The electronic spectra of naphth[3,2,1-cd]azulenones in $CHCl_3$.

Fig. 1; (2): ————————, (7): -·-·-·-·-·-, and (9): ----------.

Fig. 2; (8): -·-·-·-·-·-, and (10): ----------.

respectively. The structures of 9 and 10 were determined on the basis of the spectral data (ir, nmr and electronic spectra) (Table 1 and Figs. 1 and 2), as well as the mass and elemental analyses.[4)]

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REFERENCES

1) N. Abe, T. Morita, and K. Takase, Tetrahedron Lett., 1973, 4577.
2) N. Abe and K. Takase, Tetrahedron Lett., 1973, 4739.
3) The reaction of 4 with some nucleophilic reagents, such as alkoxides, amines or sulfides, easily proceeded with formation of the corresponding substitution products; the details will be reported in a full paper.
4) All new compounds showed the corresponding parent peaks (M^+) in the mass spectra and gave satisfactory elemental analyses in accord with the assigned structures.
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