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THE SYNTHESIS AND PROPERTIES OF 7H-NAPHTH[3,2,1-cd]AZULEN-7-ONES

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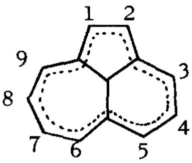
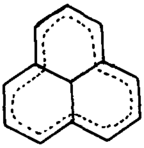
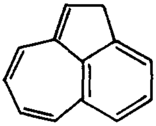
The benz[cd]azulenyl system (I) (1) is interesting theoretically, for it is isomeric with the phenalenyl system (II) (2) and is an 'odd' nonalternant hydrocarbon with a lower degree of symmetry. Recently, Boekelheide et al. have reported on the synthesis of the parent hydrocarbon (Ia) and on the formation of the corresponding cation, anion and radical (1). The stable ketonic derivatives, 6H-benz[cd]azulen-6-one (III) (1) and 2H-dibenz[cd,h]azulen-2-one (IV) (3) with this system were also synthesized. We now wish to report on the synthesis of 7H-naphth[3,2,1-cd]azulen-7-ones (VI) and (VII), which are tetracyclic non-benzenoid aromatic compounds with a new ring system corresponding to a benzlog of 3H-benz[cd]azulen-3-one, by intramolecular ring closure of diethyl 4-phenylazulene-1,3-dicarboxylate (V).



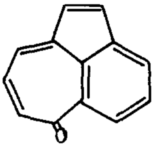
I



II



Ia



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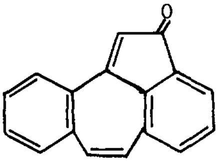

IV

It is known that the carboxyl or alkoxycarbonyl groups at the 1(or 3)-position of the azulene nucleus are easily eliminated upon heating with strong acid, such as sulfuric or phosphoric acid (4). However, it is expected that in the case of 4-phenylazulene derivatives possessing an alkoxycarbonyl substituent at

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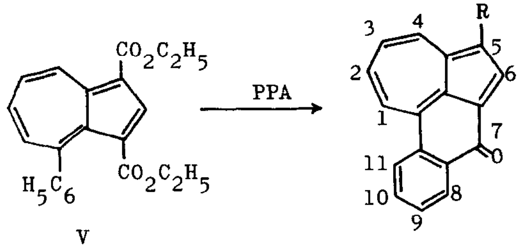
the 3-position, Friedel-Crafts-type intramolecular ring closure takes place easily instead of dealkoxycarbonylation, since the phenyl and the alkoxycarbonyl groups are located in a position favorable to ring formation.



V

VI: R=H
VII: R=$CO_2C_2H_5$

Thus, when a mixture of V (5) in polyphosphoric acid (PPA) was heated at about 100°C for 7 hr, then poured into ice-water, it gave two kinds of colored compounds, 7H-naphth[3,2,1-cd]azulen-7-one (VI); blue needles, mp 146.5-147°C; mass, m/e 230 (M^+); ir (KBr), $\nu_{c=o}$ 1629 cm^{-1} and ethyl 7-oxo-7H-naphth[3,2,1-cd]azulene-5-carboxylate (VII); violet needles, mp 185-187°C; mass, m/e 302 (M^+); ir (KBr), $\nu_{c=o}$ 1631, 1695 cm^{-1}, which were separated by chromatography on silica gel with chloroform in 10% and 60% yields, respectively (6). The structures of these compounds were substantiated by the ir and nmr data shown in Table 1 and the uv and visible spectra which are similar to those of the azulene derivatives as shown in Fig 1. Further, alkaline hydrolysis of VII, followed by decarboxylation upon heating at 300°C, gave VI.

In the ir spectra of VI and VII, the absorptions at 1629 and 1631 cm^{-1} are assigned to $\nu_{c=o}$ of the ring carbonyl. The lowering of the carbonyl frequency should arise from a high polarization of the carbonyl group. This is supported by the fact that VI and VII did not react with carbonyl reagents, such as hydroxylamine or phenylhydrazines.

As predicted, 7H-naphth[3,2,1-cd]azulen-7-ones are readily soluble in strong acid such as conc. sulfuric acid and are regenerated on addition of a base. The uv and visible spectra of VI in acid are remarkably different from that in neutral solvents, but are similar to that of 6H-benz[cd]azulen-6-one (III). The nmr spectrum of VI in trifluoroacetic acid reveals a downfield shift of the ring protons, especially that of protons at the seven-membered ring. These findings indicate that VI exists in naphth[3,2,1-cd]azulenium ion (VIII) in an acidic medium. A larger downfield shift of the protons at the seven-mem-

Table 1. The nmr Chemical Shifts of 7H-Naphth[3,2,1-cd]azulen-7-ones (VI and VII) at 100 MHz. δ ppm (pattern, coupling constant Hz)

protons	VI in $CDCl_3$	VI in CF_3COOH	VII in $CDCl_3$
H-1	8.31 (bd, 10.0)	9.00 (d, 10.0)	8.27 (bd, 9.8)
H-2	7.78 (t,d, 10.0, 2.2)	8.90 (t, 10.0)	7.78 (bt, 9.8)
H-3	7.46 (bt, 10.0)	8.88 (t, 10.0)	7.56 (bt, 9.8)
H-4	8.26 (d,d, 10.0, 2.2)	8.94 (d, 10.0)	9.41 (bd, 9.8)
H-5	7.14 (d, 4.2)	7.53 (d, 5.2)	——
H-6	8.26 (d, 4.2)	8.41 (d, 5.2)	8.54 (s)
H-8	8.1-8.3 (m)	8.6-8.8 (m)	7.95-8.15 (m)
H-9 H-10	7.4-7.7 (m)	7.9-8.2 (m)	7.4-7.6 (m)
H-11	8.4-8.6 (m)	9.6-9.8 (m)	8.15-8.35 (m)
$OCH_2C\underline{H}_3$	——	——	1.46 (t, 7.0)
$OC\underline{H}_2CH_3$	——	——	4.37 (q, 7.0)

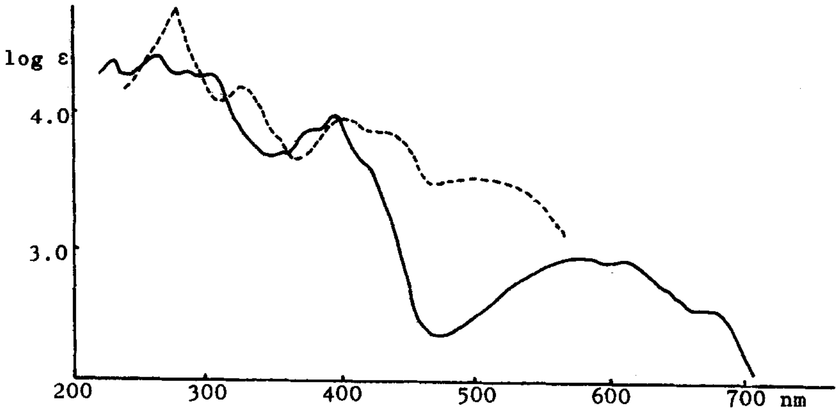


Fig 1. The uv and visible spectra of 7H-naphth[3,2,1-cd]azulen-7-one (VI) in $CHCl_3$; ——— , and in conc. H_2SO_4; ----- .

bered ring implies a larger contribution of the resonance form (VIIIc). This is also supported by a calculation (7, 8) which shows that the formal charge on the seven-membered ring (A) is +0.68, whereas that on the six-membered ring (D) is +0.18, as shown in Fig 2.

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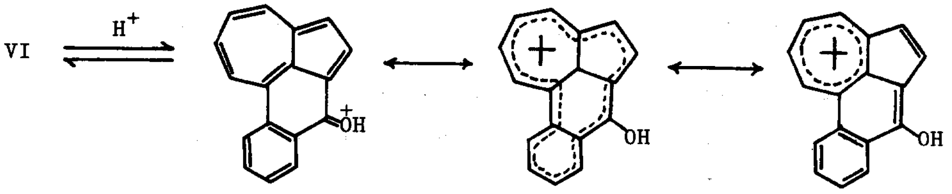

VIIIa VIIIb VIIIc

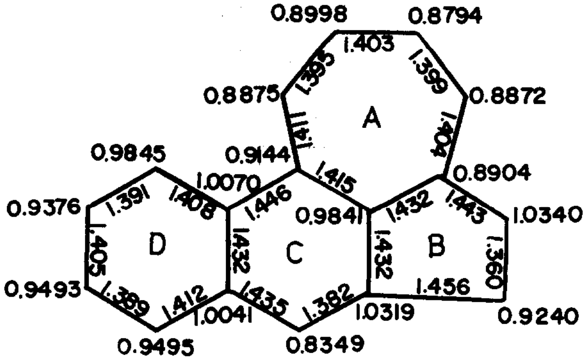

Fig. 2 π-electron density and bond length of 7H-naphto[3,2,1-cd]-azulenium cation (semi-empirical variable bond length SCF LCAO-π-MO method)

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