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THE FORMATION OF CYCLOPENT[cd]AZULENE AND BENZ[cd]AZULENE DERIVATIVES BY A FRIEDEL-CRAFTS-TYPE RING CLOSURE OF DIETHYL 4-PHENYLETHYNYL- AND DIETHYL 4-STYRYLAZULENE-1,3-DICARBOXYLATES WITH POLYPHOSPHORIC ACID

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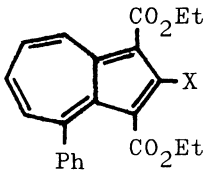
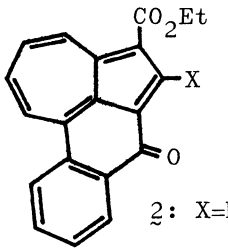
Diethyl 4-phenylethynylazulene-1,3-dicarboxylate (3) undergoes a Friedel-Crafts-type ring closure on treatment with polyphosphoric acid to give the cyclopent[cd]azulene derivative (5). In a similar manner, diethyl 4-styrylazulene-1,3-dicarboxylate (4) gives the benz[cd]azulene derivative (8) and the cyclopent[cd]azulene derivative (9). Some chemical properties of 5 are described.

As described in the previous papers,[1] it has been found that upon heating with polyphosphoric acid, diethyl 4-phenylazulene-1,3-dicarboxylates (1) undergo a Friedel-Crafts-type ring closure between the phenyl and the ethoxycarbonyl groups at the peri position to give the 7H-naphth[3,2,1-cd]azulen-7-one derivatives (2), which are the tetracyclic unsaturated compounds with a 5,6,6,7-ring system. Such a ring closure reaction in azulene derivatives is expected to be useful extensively for synthesizing polycyclic compounds containing the azulene nucleus. Of particular interest is that diethyl 4-phenylethynylazulene-1,3-dicarboxylate (3)[2] and diethyl 4-styrylazulene-1,3-dicarboxylate (4)[3] are expected to undergo ring closure between the ester group and the ethynylic or ethylenic carbon to give tricyclic compounds containing azulene nucleus. This communication describes that 3 and 4 undergo a Friedel-Crafts-type ring closure to give tricyclic compounds with a 5,5,7- and/or a 5,6,7-ring system, upon treatment with polyphosphoric acid.

Diethyl 4-phenylethynylazulene-1,3-dicarboxylate (3), when dissolved in polyphosphoric acid or 100% phosphoric acid and allowed to stand for 2 days at room temperature, gave a ring closure product (5), $C_{22}H_{16}O_4$[4] [orange needles, mp 209-210°C], in a 92% yield. The mass spectrum of 5, which shows a peak at m/e 105 ($C_6H_5CO^+$, 40%) as well as a parent peak at m/e 344 (100%), suggests the presence of the benzoyl group. The treatment of 5 with 48% hydrobromic acid in acetic acid at 95°C for 30 min. yielded two kinds of debenzoylation products, (6) [reddish violet prisms, mp 134-135°C] and (7) [red prisms, mp 159-160°C], which were isolated by an elution chromatography with benzene-chloroform over silica gel in 6.2 and 44% yields, respectively, together with benzoic acid. The compound, 6, shows the spectral data (Table 1) which are in accord with the structure of 2(1H)-cyclopent-



1: X=H or Cl



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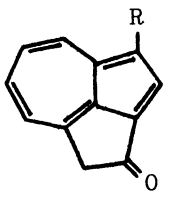
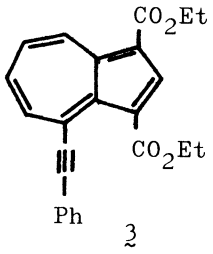


6: R=H
7: R=CO_2Et



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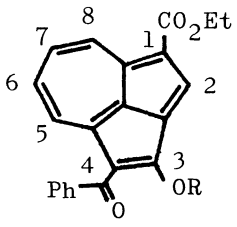
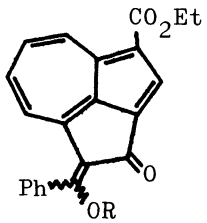
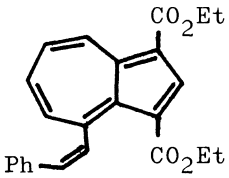


5a: R=H
11: R=Me



5b: R=H
10: R=Me



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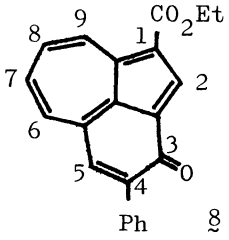

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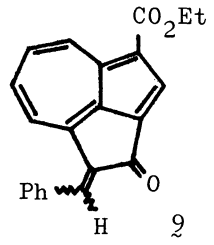

9

[cd]azulenone obtained by Hafner et al.[5] The compound, 7, is assumed to be ethyl 3(4H)-oxocyclopent[cd]azulene-1-carboxylate by its spectral data (Table 1). On the basis of these chemical evidences and the spectral data (Table 1), 5 is assigned the structure of ethyl 4-benzoyl-3-hydroxycyclopent[cd]azulene-1-carboxylate (5a) or its tautomer (5b), which is formed by ring closure between the α-carbon of the ethynyl group and the ester group at the peri-position. The enolic structure of 5, instead of the diketone form, is supported by the nmr spectrum which reveals a broad singlet at δ 15 ppm corresponding to the enolic OH and by the ir spectrum which shows an absorption at 1615 cm^{-1} corresponding to the conjugated chelated carbonyl group,[6] as well as the chemical evidences described later.

On the other hand, diethyl 4-styrylazulene-1,3-dicarboxylate (4), when treated with polyphosphoric acid at room temperature for 2.5 days, yielded two kinds of ring closure products, (8) [dark green needles, mp 176-177°C] and (9) [brownish orange needles, mp 179-180°C], which were isolated by a preparative thin-layer chromatography with cyclohexane-benzene over silica gel in 30 and 40% yields, respectively. The uv spectrum of 8 is similar to those of 3-oxo-3H-benz[cd]azulene derivatives,[7] while that of 9 is similar to that of the methyl ether (10) derived from 5 as described later. Further, the $\nu_{c=o}$ of 1615 cm^{-1} for 8 and 1670 cm^{-1} for 9 in their ir spectra indicates the presence of the conjugated six-membered ketone[1,7,8] in 8 and the conjugated five-membered ketone[8] in 9, respectively. On the basis of these findings as well as the nmr spectral data (Table 1), 8 and 9 are assumed to be the ethyl 3-oxo-4-phenyl-3H-benz[cd]azulene-1-carboxylate and ethyl 4-benzylidene-3(4H)-

Table 1. The spectral data of the compounds, 5, 6, 7, 8, 9, 10, and 11.
ir (KBr) cm^{-1}, uv λ_{max}(MeOH) nm (log ε), nmr ($CDCl_3$) δ ppm

5: ir 1695, 1615 (C=O).
uv 286 (4.31), 345 (4.49), 427 (3.33), 478 (3.20).
nmr 1.46 (t, J=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 4.45 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 7.4~7.9 (m, 8H, H-5,6,7,phenyl), 8.32 (s, 1H, H-2), 9.32 (m, 1H, H-8) [60 MHz].

6: ir 1667 (C=O).
uv 241 (4.66), 264 (4.71), 311 (4.80), 348 (4.30), 365 (4.29), 517 (2.77), 546 (2.78), 596sh (2.41) [$CHCl_3$].
nmr 4.09 (s, 2H, H-4), 7.37 (d, J=9.5 Hz, 1H, H-5), 7.44 (dd, J=10.0, 9.0 Hz, H-7), 7.48 (d, J=4.0 Hz, 1H, H-1), 7.87 (dd, J=10.0, 9.5 Hz, 1H, H-6), 7.89 (d, J=4.0 Hz, 1H, H-2), 8.37 (d, J=9.0 Hz, 1H, H-8) [100 MHz].

7: ir 1710, 1688sh, 1678 (C=O).
uv 283 (4.66), 308 (4.46), 339 (3.97), 365 (4.01), 520 (2.91) [$CHCl_3$].
nmr 1.46 (t, J=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 4.16 (s, 2H, H-4), 4.47 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 7.5~8.2 (m, 3H, H-5,6,7), 8.42 (s, 1H, H-2), 9.42 (dm, J=9.0 Hz, 1H, H-8) [60 MHz].

8: ir 1695, 1615 (C=O).
uv 245 (4.29), 271 (4.47), 400 (4.07), 574 (2.99) [$CHCl_3$].
nmr 1.46 (t, J=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 4.43 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 7.3~8.0 (m, 3H, meta, para H of phenyl), 7.65~7.8 (m, 2H, ortho H of phenyl), 7.74 (s, 1H, H-5), 7.9~8.1 (m, 3H, H-6,7,8), 8.87 (s, 1H, H-2), 9.71 (dm, J=9.0 Hz, 1H, H-8) [100 MHz].

9: ir 1695, 1670 (C=O).
uv 267 (4.51), 305 (4.57), 342 (4.58), 427 (3.69), 505 (2.73).
nmr 1.45 (t, J=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 4.44 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 7.4~7.6 (m, 3H, meta, para H of phenyl), 7.68 (s, 1H, vinyl), 7.75 (t, J=9.5 Hz, 1H, H-7), 7.98 (d, J=9.5 Hz, 1H, H-5), 8.13 (t, J=9.5 Hz, 1H, H-6), 8.2~8.4 (m, 2H, ortho H of phenyl), 8.46 (s, 1H, H-2), 9.39 (d, J=9.5 Hz, 1H, H-8) [100 MHz].

10: ir 1680, 1670 (C=O).
uv 230 (4.31), 259 (4.39), 289 (4.71), 318 (4.62), 419 (3.76), 500 (2.79).
nmr 1.46 (t, J=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 3.73 and 3.84 (each s, rel. intens. 7:1, 3H, OCH_3), 4.44 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 7.4~7.6 (m, 5H, phenyl), 7.68 (dd, J=9.8, 9.5 Hz, 1H, H-7), 8.02 (dd, J=9.8, 9.5 Hz, H-6), 8.25 (s, 1H, H-2), 8.54 (d, J=9.8 Hz, 1H, H-5), 9.34 (d, J=9.5 Hz, 1H, H-8) [100 MHz].

11: ir 1693, 1670 (C=O).
uv 257 (4.52), 282 (4.81), 326 (4.45), 343sh (4.38), 578 (2.32).
nmr 1.48 (t, J=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 4.20 (s, 3H, OCH_3), 4.44 (q, J=7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 7.3~7.6 (m, 3H, meta, para H of phenyl), 7.65~7.85 (m, 2H, ortho H of phenyl), 8.12 (s, 1H, H-2), 8.04 (dd, L=10.0, 9.0 Hz, 1H, H-6 or 7), 8.20 (dd, J=10.0, 9.0 Hz, 1H, H-6 or 7), 9.02 (bd, J=9.0 Hz, 1H, H-5 or 8), 9.21 (bd, J=9.0 Hz, 1H, H-8 or 5) [100 MHz].

oxocyclopent[cd]azulene-1-carboxylate, respectively.

The compound, 5, is acidic enough to be soluble in aq. alkali and recovered from its solution by acidification. Methylation of 5 with diazomethane gave a mixture of methyl ethers, from which were isolated a 4-benzyliden-3(4H)-oxocyclopent[cd]azulene derivative (10) [brownish red needles, mp 175-177°C] and a 4-benzoyl-3-methoxycyclopent[cd]azulene derivative (11) [dark green needles, mp 186-187°C] by an elution chromatography with benzene over silica gel in 26 and 51% yields, respectively. Their structures are determined by the spectral data (Table 1). Further, the methyl ether, 10, is confirmed to be consisted of two kinds of stereoisomers with respect to phenyl and methoxyl group by the nmr spectrum which reveals two kinds of methoxyl proton signals at δ 3.73 and 3.84 ppm (relative intensity, 7:1). The methyl ethers, 10 and 11, were readily hydrolyzed on treatment with aq. potassium hydroxide in ethanol at room temperature, yielding the original compound, 5.

In summary, on treatment with polyphosphoric acid, diethyl 4-phenylethynylazulene-1,3-dicarboxylate, 3, undergoes ring closure to give the cyclopent[cd]azulene derivative, 5, the tricyclic unsaturated compound with the 5,5,7-ring system, while diethyl 4-styrylazulene-1,3-dicarboxylate, 4, undergoes ring closure to give the benz[cd]azulene derivative, 8, the tricyclic unsaturated compound with the 5,6,7-ring system, as well as the cyclopent[cd]azulene derivative, 9.

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* To whom correspondence should be addressed.

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