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THE SYNTHESIS AND SOME PROPERTIES OF 3H-CYCLOHEPT[a]AZULEN-3-ONE

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3H-Cyclohept[a]azulen-3-one (azuleno[1,2-d]tropone) (1) was synthesized, starting from 2-styrylazulene (2). In trifluoroacetic or dil. sulfuric acid, 1 exists in hydroxycyclohept[a]azulenylium ion (A_1), while it exists in a dication (C) in conc. sulfuric acid.

Although the tropone derivatives fused with benzenoid aromatic rings and with heteroaromatic rings are well known,[1)] no tropone derivative fused with carbocyclic non-benzenoid aromatic rings has been synthesized to date. This communication will describe the synthesis of 3H-cyclohept[a]azulen-3-one (azuleno[1,2-d]tropone) (1), which is a tropone derivative fused with the azulene ring and a new type of non-benzenoid aromatic compound with a tricyclic carbon skeleton of 7,5,7-ring system.

The synthetic route of 1 is shown in Scheme 1. The starting material, 2-styrylazulene (2), was obtained by the condensation reaction of 2-methylazulene derivatives with benzaldehyde.[2)] The formylation of 2 with dimethylformamide-phosphoryl chloride gave 1-formyl-2-styrylazulene (3)[3,4)] as reddish violet needles, mp 125-126°C, in a 93% yield [ir (KBr): $\nu_{c=o}$ 1626 cm^{-1}]. Lemieux-Johnson oxidation[5)] of 3 in aq. dioxane and subsequent purification of the product by elution chromatography with benzene over an alumina column afforded 1,2-diformylazulene (4) as green blue needles, mp 155-156°C, in a 90% yield [ir (KBr): $\nu_{c=o}$ 1672 and 1643 cm^{-1}; nmr ($CDCl_3$): δ ppm 7.3-8.2 (3H, m, H-5,6,7), 7.77 (1H, s, H-3), 8.67 (1H, bd, J=10 Hz, H-4), 9.77 (1H, bd, J=10 Hz, H-8), 10.68 (1H, s, C$\underline{H}$O) and 10.91 (1H, s, C$\underline{H}$O)]. The condensation reaction between 4 and diethyl acetonedicarboxylate, being carried out in refluxing benzene in the presence of diethylamine,[6)] yielded diethyl 3-oxo-3H-cyclohept[a]azulene-2,4-dicarboxylate (5) as green needles, mp 136-137°C, in a 58% yield [ir (KBr): $\nu_{c=o}$ 1708 and 1655 cm^{-1}; nmr ($CDCl_3$): δ ppm 1.41 (6H, t, J=7 Hz, $OCH_2C\underline{H}_3$),

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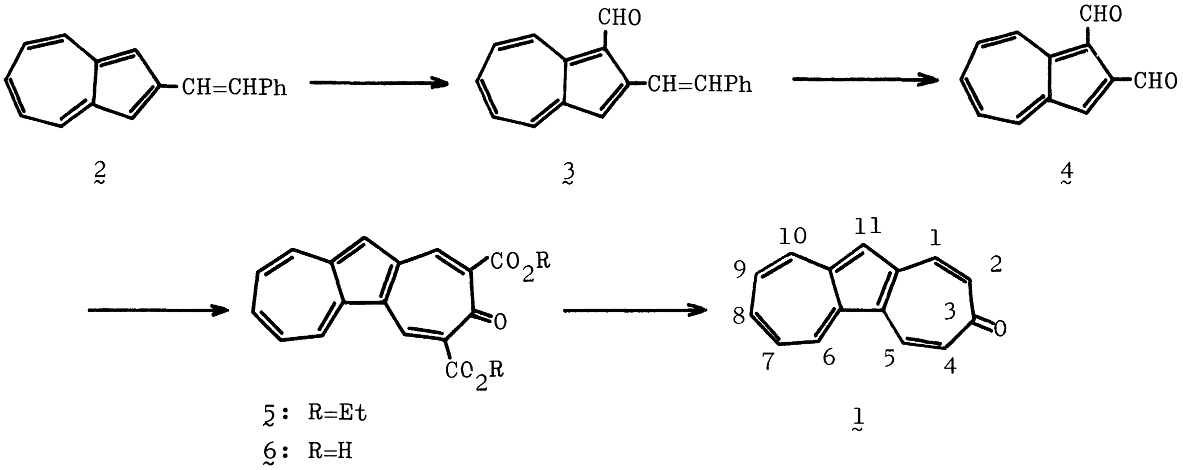
4.40 (4H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.44 (1H, bt, J=10 Hz, H-7 or 9), 7.50 (1H, bt, J=10 Hz, H-7 or 9), 7.53 (1H, s, H-11), 8.19 (1H, s, H-1), 8.42 (1H, bd, J=10 Hz, H-10), 8.70 (1H, s, H-5), and 8.73 (1H, bd, J=10 Hz, H-6); mass: m/e: 350 (19.6%, M^+) and 322 (100%, M^+-CO)].



Scheme 1. The synthetic route of 3H-cyclohept[a]azulen-3-one (1).

On hydrolysis with 70% sulfuric acid at 110-120°C, 5 gave a dicarboxylic acid (6) as brown green prisms, mp over 300°C, in a quantitative yield. The decarboxylation of 6 proceeded on heating at 190°C7) in the presence of copper powder. The sublimation of the product in vacuo and subsequent purification by elution chromatography with benzene over an alumina column afforded 3H-cyclohept[a]azulen-3-one (1) as green needles, mp 196-197°C, in a 31% yield. The spectral data of 1 are appropriate for its structure. The mass spectrum shows peaks at m/e 206 (38.8%, M^+) and 178 (100%, M^+-CO). The ir spectrum (KBr) shows absorption bands at 1590 (very strong) and 1615 cm^{-1} (medium) in the region of 1500-1700 cm^{-1}; this is comparable to those of tropones.8) The electronic spectrum in methanol is similar to those of azulene derivatives9) (Fig 1). The nmr spectral data ($CDCl_3$) are also consistent with the structure (Table 1).

The compound, 1, is soluble in acids, such as trifluoroacetic acid or dil. and conc. sulfuric acid, and regenerated on dilution with water. The electronic spectrum of 1 in trifluoroacetic acid exhibits an intense absorption at λ_{max} 494 nm (log ε 4.33) (Fig 1); this is different from that of 1 in methanol and also from that expected for an 11H-azulenium ion (B).9) A similar spectrum is also obtained in 10% sulfuric acid [λ_{max} 492 nm (log ε 4.24)]. Further, the nmr spectrum of 1 in trifluoroacetic acid reveals no signal corresponding to the methylene protons expected

Table 1. The nmr spectral data of 3H-cyclohept[a]azulen-3-one (1) at 100 MHz. chemical shifts; δ ppm [coupling constants Hz]

protons	H-1	H-2	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11
in $CDCl_3$	7.82	7.01	6.82	8.15	8.77	7.46	7.80	7.38	8.44	7.56
	[$J_{1,2}$=12.0, $J_{2,4}$=2.5, $J_{4,5}$=12.0, $J_{6,7}$=8.4, $J_{7,8}$=9.5, $J_{8,9}$=9.0, $J_{9,10}$=9.0]									
in CF_3CO_2H	8.94	7.97	7.83	9.53	9.61	8.20	8.46	8.13	9.01	8.15
	[$J_{1,2}$=12.0, $J_{2,4}$=2.7, $J_{4,5}$=10.7, $J_{6,7}$=8.5, $J_{7,8}$=9.5, $J_{8,9}$=9.5, $J_{9,10}$=10.5]									

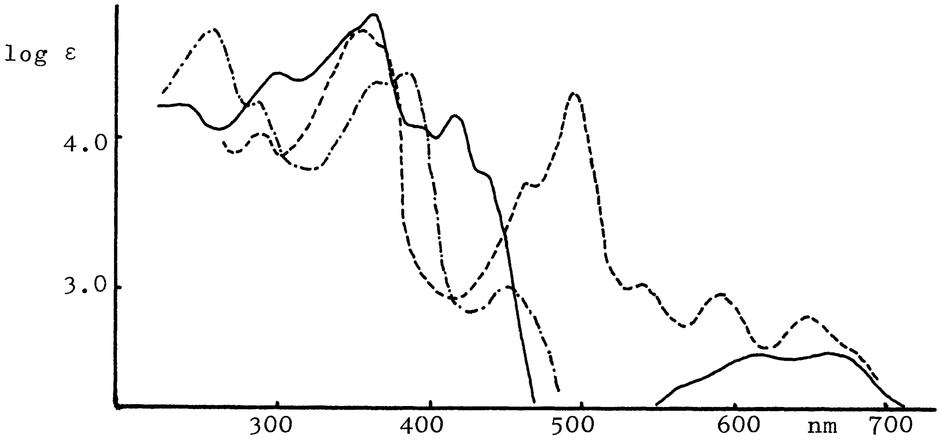
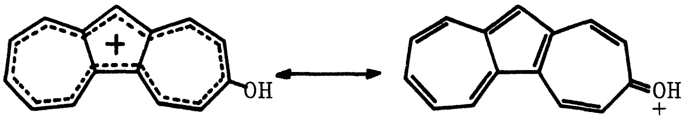
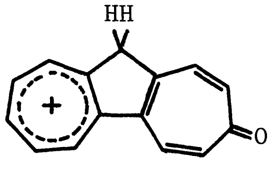


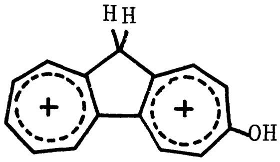
Fig 1. The electronic spectra of 3H-cyclohept[a]azulen-3-one (1) in MeOH; ————, CF_3CO_2H; --------, and conc. H_2SO_4; -·-·-·-·- .



(A_1) (A_2)



(B)



(C)

for (B) (Table 1). These findings indicate that in trifluoroacetic acid or dil. sulfuric acid, 1 exists in a structure (A), protonated at the carbonyl oxygen, but not the azulenium ion (B). Further, the observation in the electronic spectrum, exhibiting a characteristic absorption band near 500 nm,[10] and in the nmr spectrum, showing a downfield shift of the all signals due to the ring protons (Table 1), implies a larger contribution of the resonance form of hydroxycyclohept[a]azulenylium ion (A_1), having a 14 pi-electron system, in (A).

On the other hand, the electronic spectrum of 1 in conc. sulfuric acid is markedly different from those in methanol or dil. sulfuric acid, and is similar to that of ditropylium dication.[11] Further, the nmr spectrum of 1 in conc. sulfuric acid reveals a two-proton singlet at δ 5.43 ppm due to the methylene protons, besides multiplets at δ 7.9-8.3 (2H) and 8.7-9.5 ppm (7H) due to the ring protons. These facts suggest that 1 exists in a dication (C) in conc. sulfuric acid.

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10) Cyclohept[a]azulenylium tetrafluoroborate has recently been synthesized in our laboratory and its electronic spectrum in CF_3CO_2H exhibits a characteristic absorption at λ_{max} 506 nm; T. Amemiya, M. Yasunami, and K. Takase, unpublished data.

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