CHEMISTRY LETTERS, pp. 441-444, 1975. Published by the Chemical Society of Japan

THE SYNTHESIS OF 2-HYDROXY-3H-CYCLOHEPT[a]AZULEN-3-ONE (AZULENO[2,1-d]TROPOLONE) AND ITS METHYL ETHERS

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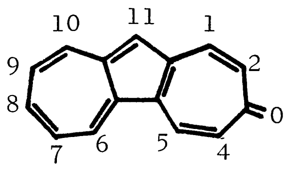
2-Hydroxy-3H-cyclohept[a]azulen-3-one (azuleno[2,1-d]tropolone) (2) was synthesized, starting from 1,2-diformylazulene (3). Methylation of 2 yielded two kinds of methyl ethers (4 and 6), differing from benzotropolones. In trifluoroacetic or dil. sulfuric acid, 2, 4 and 6 exist in cyclohept[a]azulenylium ions (2a, 4a and 6a).

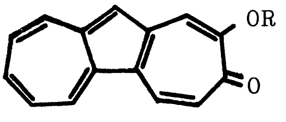
Although tropolone derivatives fused with benzenoid aromatic rings are well known,[1)] no tropolone derivative fused with carbocyclic non-benzenoid aromatic ring has been synthesized to date. In the previous paper,[2)] we have reported on the synthesis of 3H-cyclohept[a]azulen-3-one (azuleno[1,2-d]tropone) (1), a new tricyclic non-benzenoid aromatic compound with a 7,5,7-ring system. This communication will describe the synthesis and some chemical properties of 2-hydroxy-3H-cyclohept[a]azulen-3-one (azuleno[2,1-d]tropolone) (2), being a condensed system of azulene and tropolone rings.

The synthesis of 2 was achieved as follows: The condensation reaction of 1,2-diformylazulene (3)[2)] and methoxyacetone proceeded in the presence of aq. sodium hydroxide at room temperature, giving 2-methoxy-3H-cyclohept[a]azulen-3-one (4):[3)] green needles (from chloroform), mp 246-247°C, in a 74% yield. The spectral data are appropriate for the structure. The mass spectrum shows peaks at m/e 236 (81.3%, M^+), 208 (100%, M^+-CO), 178 (32.0%) and 165 (86.7%). The ir spectrum (KBr) shows absorptions at 1602 (shoulder), 1593 (vs), 1582(s) and 1530 (m) cm^{-1} in the region of 1700~1500 cm^{-1}; this is comparable to those of 1. The electronic spectrum of 4 is similar to that of 1 (Fig 1). The nmr data ($CDCl_3$) are also consistent with its structure (Table 1). Further, the methoxyl group in 4 is assignable to be at the 2-position, but not at the 4-position, by comparing its nmr data with those of 1, that is, the signals at δ 7.35, 7.02 and 8.24 ppm, corresponding to the protons at the tropolone ring of 4, are comparable to those corresponding to H-1, H-4 and H-5 of 1, respectively.

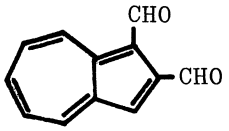
When hydrolyzed with conc. hydrobromic acid at 120-130°C, 4 gave 2-hydroxy-3H-cyclohept[a]azulen-3-one (2): green needles (from chloroform), mp 204-206°C, in a 65% yield. The spectral data appropriate for its structure. The mass spectrum shows peaks at *m/e* 222 (41.3%, M$^+$), 194 (100%, M$^+$-CO), and 165 (47.7%). The ir spectrum (KBr) shows absorptions at 3220 cm^{-1} (OH) and at 1616 (s), 1598 (m) and 1570 (vs) cm^{-1} in the region of 1700~1500 cm^{-1}. The electronic spectrum of 2 is similar to that of 4 (Fig 1) and the nmr data ($CDCl_3$) are also consistent with its structure (Table 1). The compound, 2, is acidic to give slightly soluble sodium salt on treating with sodium hydroxide solution and shows a red coloration on treating with ferric chloride solution, in analogy with tropolones. Acetylation of 2 with acetic anhydride yielded an acetyl derivative (5): green needles (from chloroform), mp 210-211°C, whose spectral data are consistent with its structure.



1



2: R=H
4: R=Me
5: R=Ac



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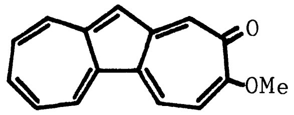
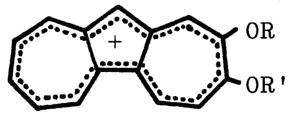


6



2a: R=R'=H
4a: R=Me, R'=H
6a: R=H, R'=Me

On methylation with diazomethane, 2 gave two kinds of methyl ethers, 4 and 3-methoxy-2H-cyclohept[a]azulen-2-one (6): brownish yellow needles (from ethanol), mp 183-184°C, in respective 49% and 29% yields. The spectral data of 6 are appropriate for its structure. The mass spectrum shows peaks at *m/e* 236 (30.8%, M$^+$), 208 (100%, M$^+$-CO), 178 (23.0%) and 165 (84.6%). The ir spectrum (KBr) shows absorptions at 1612 (m), 1594 (m), 1570 (s), 1534 (vs) and 1515 (s) cm^{-1} in the region of 1700~1500 cm^{-1}. The electronic spectrum of 6 in chloroform exhibits absorption bands

Table 1. The nmr spectral data of 2-hydroxy-3H-cyclohept[a]azulen-3-one (2) and its methyl ethers (4 and 6) at 100 MHz. δ ppm

compounds		2		4		6	
solvents		$CDCl_3$	CF_3CO_2H	$CDCl_3$	CF_3CO_2H	$CDCl_3$	CF_3CO_2H
	H-1	7.79 (s)	8.67 (s)	7.35 (s)	8.60 (s)	7.57 (s)	8.63 (s)
	H-4	7.20 (d)	8.06 (d)	7.02 (d)	8.08 (d)	6.92 (d)	7.84 (d)
	H-5	8.49 (d)	9.40 (d)	8.24 (d)	9.55 (d)	8.00 (d)	9.52 (d)
	H-6	8.67 (bd)	9.30 (bd)	8.68 (bd)	9.48 (bd)	7.45 (m)	9.37 (bd)
protons	H-7	7.46 (bt)	7.9 ~ 8.3 (m)	7.43 (bt)	8.0 ~ 8.4 (m)	6.5 ~ 6.8 (m)	8.0 ~ 8.4 (m)
	H-8	7.70 (bt)		7.69 (bt)			
	H-9	7.35 (bt)		7.33 (bt)			
	H-10	8.32 (bd)	8.71 (bd)	8.35 (bd)	8.89 (bd)	7.23 (bd)	8.73 (bd)
	H-11	7.50 (s)	7.91 (s)	7.52 (s)	8.13 (s)	6.71 (s)	7.97 (s)
	OMe	--	--	4.05 (s)	4.52 (s)	4.05 (s)	4.42 (s)
coupling constants Hz							
	$J_{4,5}$	12.0	11.0	12.0	11.0	10.4	11.0
	$J_{6,7}$	8.8	10.0	9.0	10.0	-	10.0
	$J_{7,8}$	9.5	-	9.0	-	-	-
	$J_{8,9}$	9.0	-	9.0	-	-	-
	$J_{9,10}$	10.0	10.0	10.0	10.0	10.0	10.0

s: singlet, d: doublet, bd: broad doublet, bt: broad triplet, m: multiplet

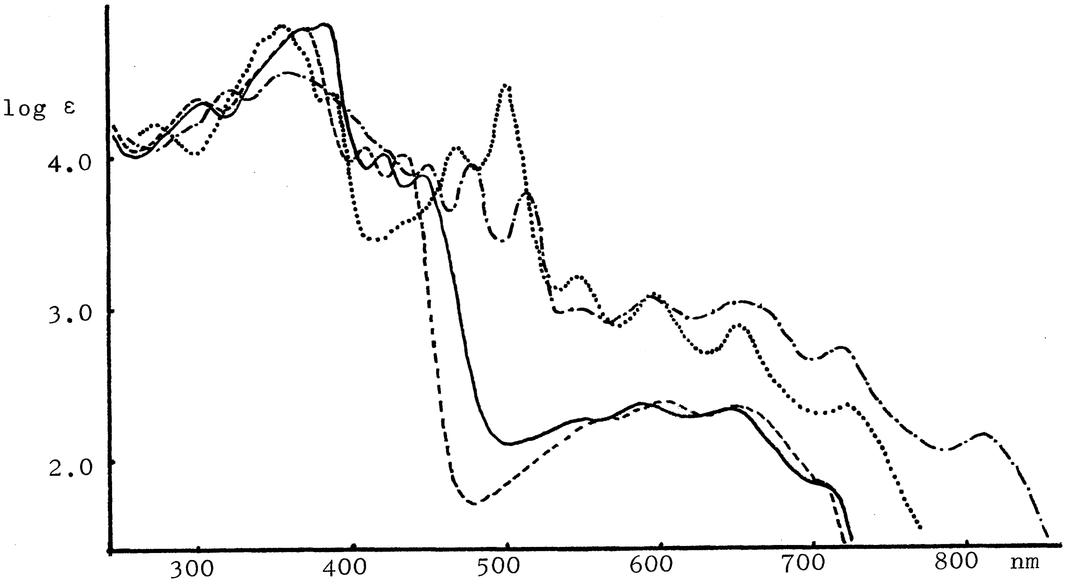


Fig 1. The electronic spectra of 2-hydroxy-3H-cyclohept[a]azulen-3-one (2) in $CHCl_3$; ————, and in CF_3CO_2H; ············, and its methyl ethers (4) in $CHCl_3$; ----------, and (6) in $CHCl_3$; -·-·-·-·-.

in a longer wavelength region in comparison with those of 2 and 4, supporting the quinoid structure of azulene ring in 6 (Fig 1). The nmr spectrum ($CDCl_3$) of 6 reveals signals corresponding to H-6~11 at a somewhat higher field than those of 4 (Table 1). This is assumed to be due to a decrease of the aromaticity in azulene ring because of its quinoid structure in 6. A smaller coupling constant of $J_{4,5}$= 10.4 Hz in 6, compared with that of $J_{4,5}$=12.0 Hz in 4, also supports 6 to be the structure of 2H-cyclohept[a]azulen-2-one in which the C_4-C_5 bond has a single bond character.[4] It is noteworthy that the methylation of 2 yielded two kinds of isomeric methyl ethers since tropolone derivatives fused with aromatic rings, such as benzotropolones, are known to give only a kind of methyl ether in which the fused aromatic ring remains to keep its aromatic stability.[1]

The compounds, 2, 4 and 6, as well as 1,[2] are soluble in trifluoroacetic or dil. sulfuric acid to yield cyclohept[a]azulenylium ions (2a, 4a and 6a). Thus, the electronic spectra of 2, 4 and 6 in trifluoroacetic acid or 10% sulfuric acid are similar to that of 1 in the same solvents, exhibiting intense absorption maxima at 500 nm (log ε 4.47), 500 (4.43) and 502 (4.45), respectively, characteristic to cyclohept[a]azulenylium ion.[2,5] Further, the nmr spectra of 2, 4 and 6 in trifluoroacetic acid show down-field shifts of the all signals corresponding to the ring protons, compared with those in deuteriochloroform (Table 1); this fact also supports the structure of cyclohept[a]azulenylium ions (2a, 4a and 6a).

This research has been financially supported by grants of the Japanese Ministry of Education and the Sankyo Co., Ltd.

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2) M. Saito, T. Morita, and K. Takase, Chem. Lett., 1974, 955.

3) All new compounds gave satisfactory elemental analyses in accord with the assigned structures.

4) 2-Methoxytropone shows coupling constants of $J_{3,4}$=10.1 and $J_{6,7}$=12.5 Hz in its nmr spectrum ($CDCl_3$); cf H. Sugiyama, Thesis of Ph.D., Tohoku University (1963).

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

(Received March 22, 1975)