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THE SYNTHESIS OF 2-HYDROXY-3H-DICYCLOHEPTA[b,d]PYRROL-3-ONE (6-AZAAZULENO[1,2-d]TROPOLONE) AND ITS METHYL ETHER

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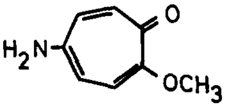
In a series of tricyclic systems containing azulene nucleus, 3H-dicyclohepta[b,d]pyrrol-3-one (6-azaazuleno[1,2-d]tropone) is of considerable interest as a pi-equivalent aza analogue of 3H-cyclohept[a]azulen-3-ones (azuleno[1,2-d]-tropones),[1,2] having a tricyclic carbon skeleton of 7,5,7-ring system. Following our synthesis of 5-azabenz[a]azulenes,[3] we have now synthesized 2-hydroxy-3H-dicyclohepta[b,d]pyrrol-3-one (6-azaazuleno[1,2-d]tropolone) (1) and its methyl ether (2). The results will be reported in this communication.

Tropylation[4] of 5-amino-2-methoxytropone (3)[5] with 7-ethoxytropylidene in ethanol in the presence of a catalytic amount of conc. hydrochloric acid yielded 5-amino-4-(cycloheptatrien-7-yl)-2-methoxytropone (4)[6,7] as pale brown prisms (from acetone); mp 149-149.5°C, or yellow scales[8] (from chloroform); mp 142-144°C, in a 82.4% yield. On thermal isomerization[9] under reflux in xylene for 3 hr, 4 gave 5-amino-4-(cycloheptatrien-3-yl)-2-methoxytropone (5)[6,7] as yellow needles[8] (from chloroform); mp 106-108°C, in a quantitative yield. When 5 was treated with 4 molar equivalents of trityl tetrafluoroborate in chloroform at room temperature,[3] a tetrafluoroborate (6) was obtained as violet micro-needles (from acetonitrile); mp 280°C (decomp.), in a 71.5% yield. The treatment of a solution of 6 dissolved in acetonitrile-chloroform with aq. sodium hydrogen carbonate afforded 2-methoxy-3H-dicyclohepta[b,d]pyrrol-3-one (2) as dark green micro-crystals (from methanol);



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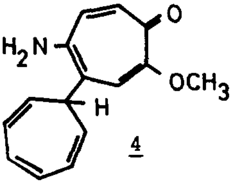

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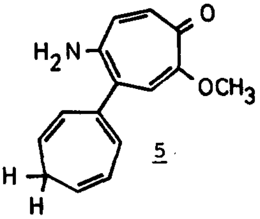

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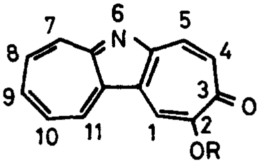
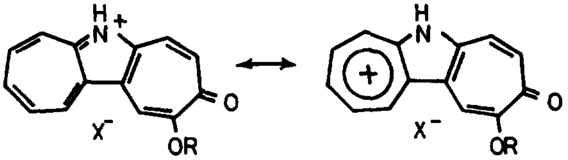


1: R=H
2: $R=CH_3$



1a: R=H
2a: $R=CH_3$
6 : $R=CH_3$, $X=BF_4$

mp 209.5-211.5°C, in a quantitative yield. Further, on heating with conc. hydrobromic acid in acetic acid at about 100°C, 2 was hydrolyzed to give 2-hydroxy-3H-dicyclohepta[b,d]pyrrol-3-one (1) as dark green micro-needles (from chloroform-benzene); mp over 360°C, in a 96.4% yield.

The spectral data of 1 and 2 are appropriate for their structures: The mass spectra of 1 and 2 show peaks at m/e 223 (78.5%, M^+) and 195 (100%, M^+-CO) and at m/e 237 (100%, M^+) and 209 (37.2%, M^+-CO), respectively. The IR spectra (KBr) of 1 and 2, showing absorption bands at 1620 (m), 1580 (s) and 1547 cm^{-1} (s), and at 1620 (m) and 1580 cm^{-1} (s), respectively, in the region of 1700-1500 cm^{-1}, as well as a band at 3270 cm^{-1} (OH) in that of 1, are comparable to those of tropolones and tropones,[10] respectively. Their electronic spectra in methanol are similar to those of 3H-cyclohept[a]azulen-3-ones[1,2] (Fig. 1). The nmr spectral data ($CDCl_3$) are also consistent with the structures (Table 1). Further, the chemical evidence also supported the structures: Thus, 1 is acidic to be soluble in aq. sodium hydroxide and showed positive ferric chloride coloration. Acetylation of 1 with acetic anhydride gave an acetate; violet micro-needles, mp 234.5°C, and methylation of 1 with diazomethane gave 2, although the isomeric methyl ether, which was expected to be formed,[2] could not be isolated.

Table 1. The nmr spectral data of 1 and 2 at 60 MHz; δ ppm (intensity, pattern, coupling constant, assignment).

Compounds	in $CDCl_3$	in CF_3CO_2H
1	7.55 (1H, d, J=12 Hz, H-4)	8.23 (1H, d, J=12.5 Hz, H-4)
	8.38 (1H, d, J=12 Hz, H-5)	8.70 (1H, d, J=12.5 Hz, H-5)
	8.39 (1H, s, H-1)	8.93 (1H, s, H-1)
	7.83-8.45 (3H, m, H-8,9,10)	8.83-9.23 (3H, m, H-8,9,10)
	8.88 (1H, bd, J=10 Hz, H-7)	9.24 (1H, bd, J=10 Hz, H-7)
	9.44 (1H, bd, J=10 Hz, H-11)	10.02 (1H, bd, J=10 Hz, H-11)
2	4.05 (3H, s, OCH_3)	4.58 (3H, s, OCH_3)
	7.32 (1H, d, J=13 Hz, H-4)	8.53 (1H, d, J=12 Hz, H-4)
	7.50 (1H, s, H-1)	9.26 (1H, s, H-1)
	7.65-8.24 (3H, m, H-8,9,10)	8.85-9.35 (3H, m, H-8,9,10)
	8.00 (1H, d, J=13, H-5)	9.10 (1H, d, J=12 Hz, H-5)
	8.75 (2H, bd, J=10.0 Hz, H-7,11)	9.51 (1H, bd, J=10 Hz, H-7)
		10.30 (1H, bd, J=10 Hz, H-11)

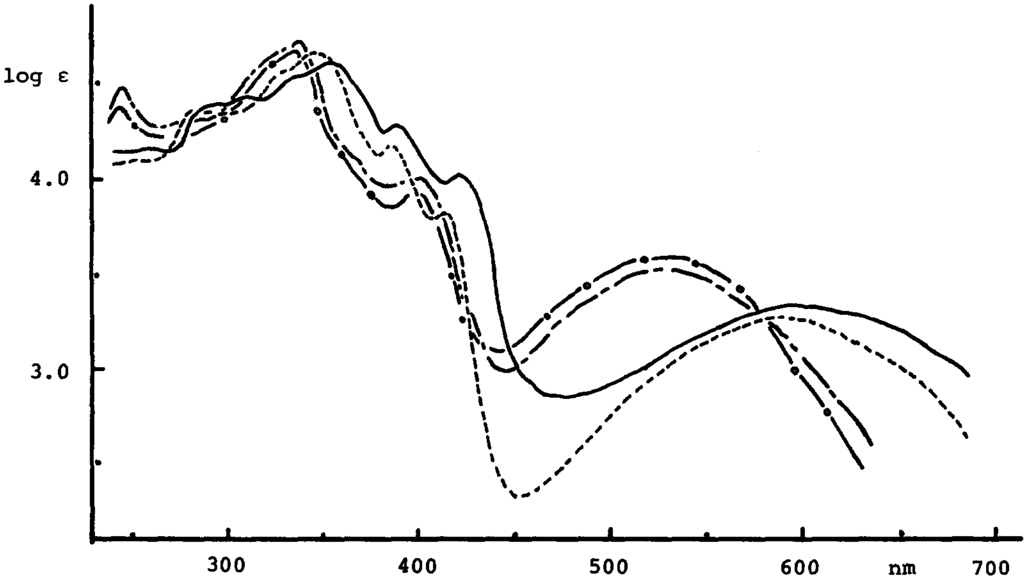


Fig. 1. The electronic spectra of 1 in MeOH ; ——— , and in 3M H_2SO_4 ; - - - -, and 2 in MeOH ; —-—, and in 3M H_2SO_4 —•—.

The compound, 2, is soluble in acids such as dil. sulfuric acid and gave 6, on treatment with tetrafluoroboric acid. The electronic spectrum of 2 in 3M sulfuric acid (Fig.1), which is identical with that of 6 in the same solvent, is similar to that of 5-azabenz[a]azulene in the same solvent although the absorption bands of the former show some bathochromic shifts compared to that of the latter, but is markedly different from that of cyclohept[a]azulenylium ion.[1,11] These findings indicate that, in 3M sulfuric acid, 2 exists in 6H-6-azacyclohept[a]azulenium ion (2a), protonated at the nitrogen, and therefore, 6 is its tetrafluoroborate. The nmr spectrum of 2 in trifluoroacetic acid, which is identical with that of 6 in the same solvent, is also consistent with the structure of 2a (Table 1). A downfield shift of the all signals due to the ring protons compared to that of 2 in chloroform implies a delocalization of the positive charge over the ring system in 2a. The compound, 1, is also soluble in 3M sulfuric acid to yield 6H-6-azacyclohept[a]azulenium ion (1a), whose electronic spectrum is similar to that of 2a. The nmr spectrum of 1 in trifluoroacetic acid also consistent with the structure of 1a (Table 1).

REFERENCES AND NOTES

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6) All new compounds gave satisfactory analyses in accord with the assigned structures.
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11) 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, to be published.