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AZULENO[1,8-bc] THIAPYRAN AND AZULENO[1,8-cd] AZEPINE

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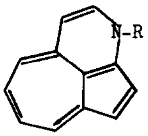
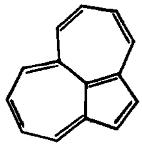
The synthesis and some properties of some alkyl derivatives of the 1*H*-cyclohepta[d,e]-1-pyrindine ring system (I) have been reported (1) recently. This nitrogen heterocycle (I) is iso-π-electronic with the interesting, nonbenzenoid, aromatic hydrocarbon cyclopenta[e,f]heptalene (II), (2) and the two have quite similar absorption spectra.

We wish to report in this communication the syntheses of derivatives of two new heteroanalogs of II. One heterocycle (III) contains the azuleno-[1,8-bc] thiapyran structure, and is of the π-excessive type, (3) and the other, IV, has the azuleno[1,8-cd] azepine structure, and is of the π-equivalent type. (4)



I



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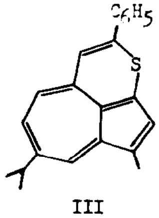
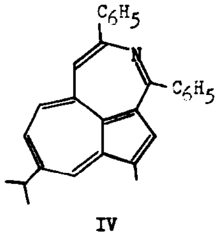
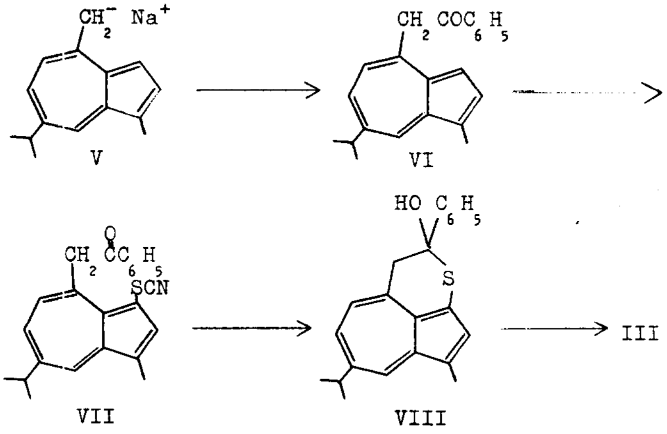


III



IV

The synthetic scheme for the preparation of the azuleno[1,8-bc]thiapyran involved the introduction of a sulfur atom at the 3-position of guaiazulene (1,4-dimethyl-7-isopropylazulene) and a carbonyl function on the 4-methyl group of the same molecule. The sodium salt of guaiazulene (V) was generated (5) and treated with benzonitrile to give, after acid hydrolysis, 7-isopropyl-1-methyl-4-phenacylazulene (VI), m.p. 116-117°, in 60% (89% net) yield. Visible: λ_{max} 608 mμ; infrared: 5.90 μ (C=O band). (6) Treatment of VI with thiocyanogen (7) gave a 70% (94% net) yield of the 3-thiocyano derivative VII, m.p. 123.5-125°. Visible: λ_{max} 583 mμ; infrared: 4.64 μ (SCN), 5.88 μ (C=O). When VII was treated with zinc and acetic acid, the thiocyano group was converted to a mercapto group which then added, intramolecularly, to the carbonyl group to give the presumed cyclic hemimercaptol VIII. Since VIII was a rather unstable green oil, it was not completely characterized, but it did show the expected spectral features: visible λ_{max} at 680 mμ, and the disappearance of bands at 4.6 and 5.9 μ with the appearance of a new band at 2.95 μ in the infrared. Dehydration of VIII with phosphoric acid in acetic acid yielded 6-isopropyl-8-methyl-2-phenylazuleno[1,8-bc]-



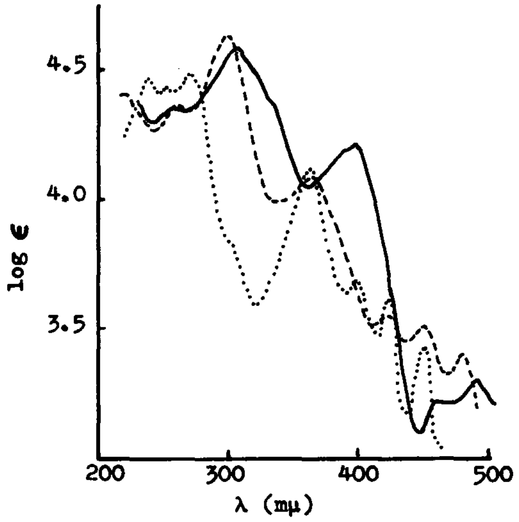


FIG. 1

Ultraviolet spectra of 6-isopropyl-8-methyl-2-phenylazuleno[1,8-bc]thiapyran (-----), 7-isopropyl-9-methyl-1,3-diphenylazuleno[1,8-cd]azepine (———), and 6-isopropyl-1,2,8-trimethylcyclohepta[d,e]-1-pyrindine (·····).

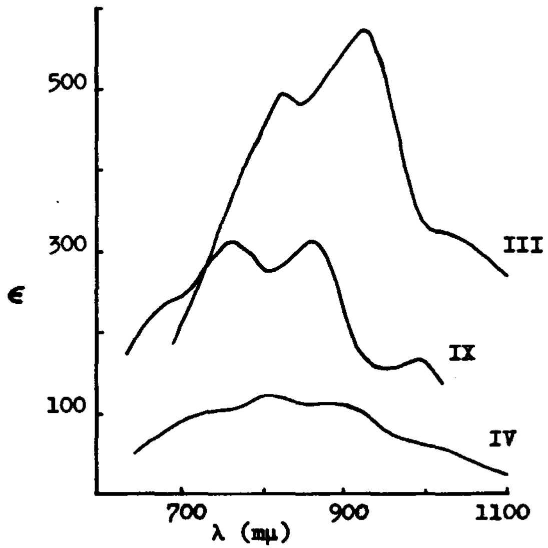


FIG. 2

Visible-near infrared spectra of 6-isopropyl-8-methyl-2-phenylazuleno[1,8-bc]thiapyran (III), 7-isopropyl-9-methyl-1,3-diphenylazuleno[1,8-cd]azepine (IV), and 6-isopropyl-1,2,8-trimethylcyclohepta[d,e]-1-pyrindine (IX).

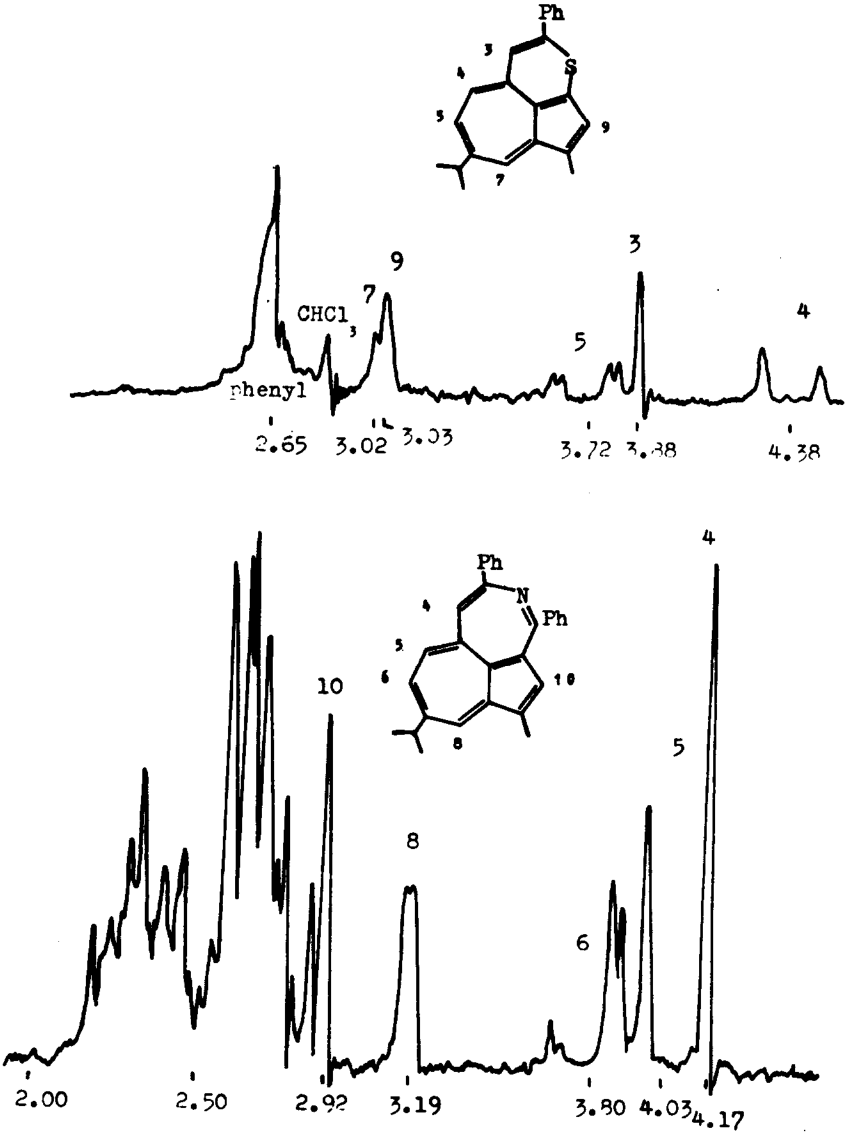


FIG. 3

The ring proton n.m.r. spectra of III (top) and IV (bottom) in deuterochloroform.

thiapyran (III) as a reddish-brown crystalline solid, m.p. 88.5-89.5°. The thiapyran was obtained in 93% yield (from VII).

The ultraviolet (Figure 1) and visible-near infrared (Figure 2) spectra of III are seen to be quite similar to those of the corresponding nitrogen heterocycle, (1) 6-isopropyl-1,2,8-trimethylcyclohepta[d,e]-1-pyrindine (IX); however the bands of the sulfur heterocycle are shifted somewhat to longer wavelengths. A proton n.m.r. spectrum of III was consistent with the proposed structure, showing the same general pattern (except for the phenyl protons signal at τ=2.65) as that of IX. (1). Thus the H-4 and H-5 signals are seen as doublets (J=12 cps) centered at 4.38 and 3.72, respectively (8). The latter is split (J=2 cps) by cross-ring coupling with H-7, whose chemical shift is at 3.02. Singlets at 3.88 and 3.03 are assigned to H-3 and H-9, respectively.

In one of the preparations of the ketone V, when a large excess of benzonitrile was unintentionally used, a significant amount of a crystalline compound was isolated from the dilute acid fraction. Recrystallization of this solid from ethanol yielded golden-brown needles, m.p. 152.5-153.5°. On the basis of its ultraviolet (Figure 1) and visible-near infrared spectra (Figure 2), elemental analysis and molecular weight (found for $C_{29}H_{25}N$: C, 89.80; H, 6.64; N, 3.58; MW, 366), and origin, this compound is believed to be 7-isopropyl-9-methyl-1,3-diphenylazuleno[1,8-cd]azepine (IV). The ring proton n.m.r. spectrum (Figure 3) of IV is similar to that of III except for the complex multiplet at 2.2-2.9 which is presumed to be due to the two phenyl groups. The H-5 and H-6 doublets (J=12 cps), which correspond to H-4 and H-5 of III, are centered at 4.03 and 3.80, respectively. The peaks of the H-6 doublet are further split by the characteristic cross-ring coupling (J=2 cps) with H-8 (τ 3.19); while the right-hand member of the H-5 doublet is obscured by the H-4 singlet at 4.17. The sharp singlet at 2.92 is assigned to H-10. At higher fields (not shown in Figure 3), the spectra of both III and IV show a singlet at *ca.* 7.7 and a doublet at *ca.* 8.9, which are assigned to the ring methyl and isopropyl methyls, respectively. Integration of both spectra gives results consistent with the above assignments.

Apparently two molecules of benzonitrile are incorporated in the formation of the tricyclic structure IV from V, but the exact mechanism of this unusual cyclization remains to be investigated.

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