

## Novel Heteroaromatic Compounds Related to Acepleiadylene\*

By A. R. J. ARTHUR, P. FLOWERDAY, and M. J. PERKINS

(*Department of Chemistry, King's College, London, W.C.2.*)

THE non-alternant aromatic hydrocarbon acepleiadylene\* (I) has been the subject of considerable theoretical interest. We now report the prepara-

tion of triazines (II) and (III). These are related to acepleiadylene in the same fashion as 1- and 2-methylbenzotriazoles are related to naphthalene.

\* Some confusion has arisen over nomenclature in the acepleiadylene series. Compound (I), synthesised by Boekelheide and Vick (*J. Amer. Chem. Soc.*, 1956, **78**, 653) is commonly referred to by this name; however Cava and Schlesinger (*Tetrahedron*, 1965, **21**, 3051) have argued that the corresponding benzo-derivative, recently obtained by them, should be termed acepleiadylene.

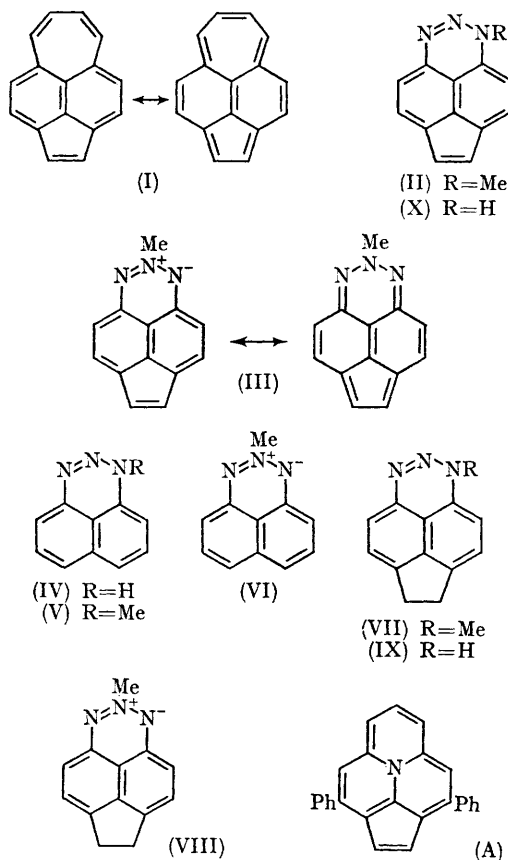
They constitute the first examples of acepleiadylene analogues in which the 7-membered carbocyclic ring has been replaced by a 6-membered heterocyclic ring.<sup>†</sup>

By analogy with the preparation of the red (V) and blue (VI) monomethyl derivatives of the naphthotriazine (IV), reported recently,<sup>1</sup> it has been found that diazotisation of 5,6-diaminoacenaphthene (prepared by Richter's method<sup>2</sup>) in acetic acid, followed by methylation of the crude product with dimethyl sulphate, also yields a red compound (m.p. 108–109°) and a blue compound (m.p. 167–168°), identified as (VII) and (VIII) respectively.<sup>‡</sup>

Both (VII) and (VIII) were cleanly dehydrogenated by *o*-chloranil (tetrachloro-*o*-benzoquinone) in benzene to give the two new aromatic compounds (II) (yellow, m.p. 114–115°) and (III) (red, m.p. 178–179°) in good yield.<sup>§</sup> The aromaticity of (II) and (III) is revealed by the generally low  $\tau$ -values of both the methyl and the ring protons.<sup>\*\*</sup> Typically the protons on the 5-membered ring of (II) give a highly perturbed AB-quartet centred at  $\tau$  2.09; in (III) they give a two-proton singlet at  $\tau$  1.83. In (I) the corresponding resonance is at  $\tau$  1.85, whereas in acenaphthylene it occurs at much higher field ( $\tau$  2.82). In the same way, the methyl resonances of compounds (II) and (III) are shifted downfield by more than 1 p.p.m. relative to those of compounds (VII) and (VIII), respectively. There are also similarities between the electronic spectra of (I), (II), and (III), just as there are between those of naphthalene and the methylbenzotriazoles.

The acenaphthene and acenaphthylene analogues of (IV) have not yet been obtained pure. However, the crude triazine (IX) on oxidation with *o*-chloranil, gives a yellow product to which structure (X) has been tentatively assigned as, on methylation, it furnishes red and yellow derivatives

chromatographically indistinguishable from (II) and (III).



(Received, February 8th, 1967; Com. 123.)

<sup>†</sup> An unsuccessful attempt to synthesise the related system with a thiapyran ring has been reported by Anderson (*Diss. Abs.*, 1961, **21**, 2105). On the other hand, the suggested azaphenalene precursor (A), prepared by Gibson and Leaver (*Chem. Comm.*, 1965, 11) might constitute a true  $\pi$ -electron analogue of acepleiadylene.

<sup>‡</sup> New compounds gave satisfactory elemental analyses, and exhibited spectra consistent with the assigned structures. Catalytic hydrogenation of both (III) and (VIII) gave 5,6-diaminoacenaphthene; hydrogenation of (II) and (VII) gave *N*-methyl-5,6-diaminoacenaphthene.

<sup>§</sup> This oxidation procedure is also the method of choice for the synthesis of compound (I) from its 1,2-dihydro-derivative ("acepleiadiene").

<sup>\*\*</sup> N.m.r. spectra were recorded on deuteriochloroform solutions, employing tetramethylsilane as an internal standard.

<sup>1</sup> M. J. Perkins, *J. Chem. Soc.*, 1964, 3005.

<sup>2</sup> R. J. Richter, *J. Org. Chem.*, 1956, **21**, 619.