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2-THIONIA- AND 2-AZONIA-AZULENES

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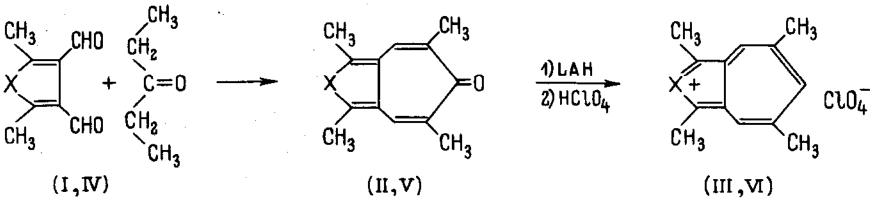
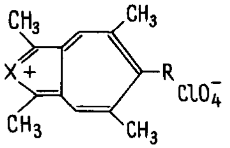
Condensation of 3,4-diformyl-2,5-dimethylthiophene (I) with diethylketone forms the tropone (II), which can readily be reduced with LAH to its carbinol. An ethereal solution of the latter with $HClO_4$ gives the perchlorate of the substituted 2-thioniaazulene (III) (1). Similarly, proceeding from the 3,4-diformyl-2,5-dimethylpyrrole (IV) (2) the substituted derivative of the 2-azonia-azulene has been obtained (3).



(I - III) X = S (IV - VI) X = C_6H_5N

By the action of organometallic compounds on the ketones (II,V) and subsequent treatment of the resulting carbinols in ethereal solution with perchloric acid, the corresponding 6-substituted 2-thionia-and 2-azonia-azulenes have been obtained.

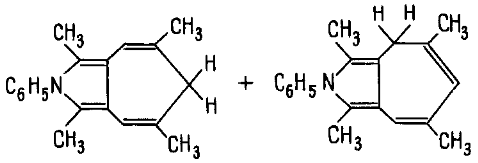


X = S, C_6H_5N

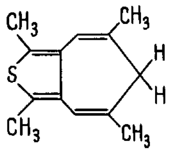
R = CH_3, C_6H_5, p - BrC_6H_4

The perchlorates are moderately soluble in organic solvents and can be crystallized from acetic acid. The sulphur derivatives are hydrolyzed by water. All the salts are deep blue. The location of the longwave band in the electronic spectrum (λ_{max} 660-710 mμ) depends very little on the nature of the heteroatom and the substituent at position 6.

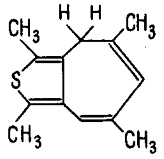
The conjugated hydroderivatives (VII) of the ion (VI) obtained by reduction of the latter with 1,3-dimethylbenzimidazoline (4) immediately reduces in acetonitrile solution both the cation (III) and tropylium, being oxidized to the ion (VI). This shows that the nitrogen-containing ion (VI) is less electrophilic than the corresponding isoelectronic analogue thioniaazulene (III) and tropylium.



(VII)



(VIII)



(IX)

On reducing an acetonitrile, nitromethane or methylenchloride solution 2-thioniaazulene perchlorate (III) with 1,3-dimethylbenzimidazoline, 1,3-dimethyl-2-phenylbenzimidazoline (5), 1,3-dimethyl-5-nitrobenzimidazoline (6), 1,2-dimethylindazoline (7), 1,2-dimethyl-3-phenylindazoline,* tropilidene and also with mixture (VII), the perchlorates of the corresponding nitrogen-containing ions and of tropylium ion are obtained along with a mixture of 6H-(VIII) and 4H-(IX) hydroderivatives in 1:5 ratio. Compounds (VIII) and (IX) are separated by chromatography of a petroleum ether solution on AL_2O_3 and identified by U.V. and PMR spectra. For compound (VIII):λ_{max} 242 mμ , log ε 4.53; PMR (in CCL_4)(δ in p.p.m.) 1.92 (5,7 CH_3), 230 (1,3 CH_3), 2.45 (6 CH_2), 6.09 (4,8 CH). For compound (IX):λ_{max} 296 mμ , log ε3.95, PMR 1.88 (5,7 CH_3), 2.24 (1,3 CH_3), 2.88 (4 CH_2), 5.46 (6 CH), 6.31 (4 CH). Quantitative analysis of the mixtures was carried out by U.V. spectrum. The composition of the mixture is the same, whatever the hydride donor. Consequently, the structure of the reaction complex does not influence the site of attack by the nucleophilic hydride-ion on compound (III).

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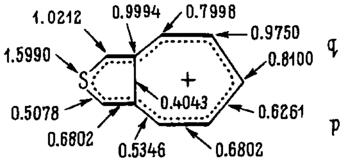
* Kindly given by M.Z. Girshovich.

On reducing a benzene suspension of perchlorate (III) with some of the above hydride donors, the ratio of the resulting compounds (VIII) and (IX) becomes 3:1. These compounds are also obtained in 1:1 ratio on reducing compound (III) in a powdered form with an acetonitrile solution of 1,3-dimethylbenzimidazoline. This suggests that the reactivity of the solvated and unsolvated tetramethyl-2-thioniaazulene is somewhat different.

On treating both the benzene suspension and acetonitrile solution of the 1,3,5,6,7-pentamethyl-2-thioniaazulene perchlorate with 1,3-dimethylbenzimidazoline, the 6H-and 4H-hydroderivatives have been obtained in a ratio of 1:1. Under the same conditions the 1,3,5,7-tetramethyl-6-phenyl-2-thioniaazulene perchlorate gives 1:3 ratio of the 6H-and 4H-hydroderivatives. Thus both the solvation and introduction of substituents into position 6 of the 1,3,5,7-tetramethyl-2-thioniaazulene produce an increase in the relative amounts of the corresponding 4H-hydroderivatives on attack by a hydride ion. Evidently, solvation of ion (III) results in blocking position 6 more than positions 4 and 8.

The reaction of the ethereal methyl magnesium iodide or phenyl magnesium bromide with a suspension of perchlorate (III) in ether results in the formation of a mixture of 6H-and 4H-substituted hydroderivatives in a ratio of 1:1 and 1:2 respectively.



$h_S = 1$

$h_{C_1} = 0.1$

$K_{C-S} = 0.6$

It appears from the above MO-calculation on 2-thioniaazulene ion, carried out by V.I. Minkin in Hückel approximation, that the electron density in positions 1 and 3 of the ion is relatively increased, and positions 4 (8) and 6 are most electrophilic. This comes to be in complete accordance with the experimental results on the action of nucleophilic reagents on 1,3,5,7-tetramethyl-2-thioniaazulene and its 6-substituted derivatives.

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