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SYNTHESIS AND REACTIONS OF 5-AZIDOTROPOLONES (1)

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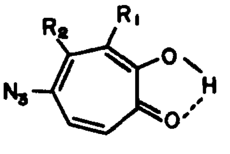
A number of interesting properties of organic azides are known (3), and recently Hobson and Malpass have reported the synthesis and thermolysis of 2-azidotropone (4). In this paper, we wish to report the synthesis and properties of 5-azidotropolones including the synthesis of triazolyl derivatives of tropolones and azulenes.

5-Azidotropolones (Ia - g) were prepared from the diazotized 5-aminotropolones and sodium azide in good yield as shown in Table I (5). With the exception of the 4-isopropyl and 4-methyl derivatives, the obtained azidotropolones are stable at room temperature and show strong absorption bands between 2110 - 2150 cm^{-1} due to the azide group (6). The UV spectra of the azido tropolones are analogous to those of the tropolones (7,8) ----- e.g.



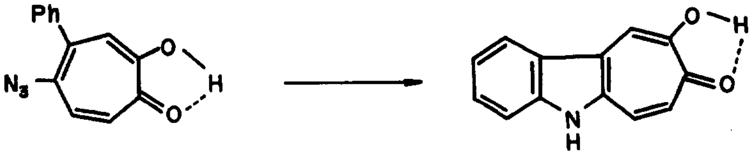
(Ia - g)

TABLE I

Compound	R_1	R_2	mp°C(dec.)	Yield %
(Ia)	H	H	140	88
(Ib)	Br	H	117	85
(Ic)	Me	H	100	65
(Id)	Ph	H	115	62
(Ie)	H	Ph	122	50
(If)	H	Me	133	
(Ig)	H	i-Pr	109	

Ia: λ_{max}^{MeOH} mμ (log ε); 233 (4.19), 242 (4.20), 355 (3.99) and 426 (3.48). The azido-tropolones decompose with evolution of nitrogen at their melting points, but afforded stable sodium salts and copper complexes (both of which do not decompose until 300°C). Catalytic reduction of Ia over palladized charcoal afforded 5-aminotropolone in good yield. Bromination of Ia and Ib in acetic acid gave the same 3,7-dibromo compound, mp 119° (dec.), and bromination of Ic, Id and Ie also afforded the corresponding 7-bromo derivatives. Ia gave a methyl ether (IIa), mp 110° (dec.), a tosylate (IIb), mp 126° (dec.) and an acetate, mp 119° (dec.).

The thermal decomposition of Ia and IIa in boiling ethylene glycol yielded 5-aminotropolone (45%) and its methyl ether (27%), respectively, accompanied by some unidentified acidic substances. On the other hand, the thermolysis of Ie afforded yellow acidic substance (III), mp 241°, in 50% yield with some unidentified substances. III shows a positive ferric chloride test and a UV spectrum analogous to that of indolo[2,3-d]tropone (9). Furthermore, III gave a diacetate, mp 203°, and a methyl ether, mp 267° (its acetate, mp 207°, IR 1690 cm^{-1}). The IR spectra of III and the three derivatives mentioned above showed absorption between 1480 - 1690 cm^{-1} due to the stretching vibrations of a conjugated carbonyl group and double bonds of the tropolone nuclei analogous to that of other troponoid compounds (10). Therefore, III must be an indolo[3,2-d]tropolone.

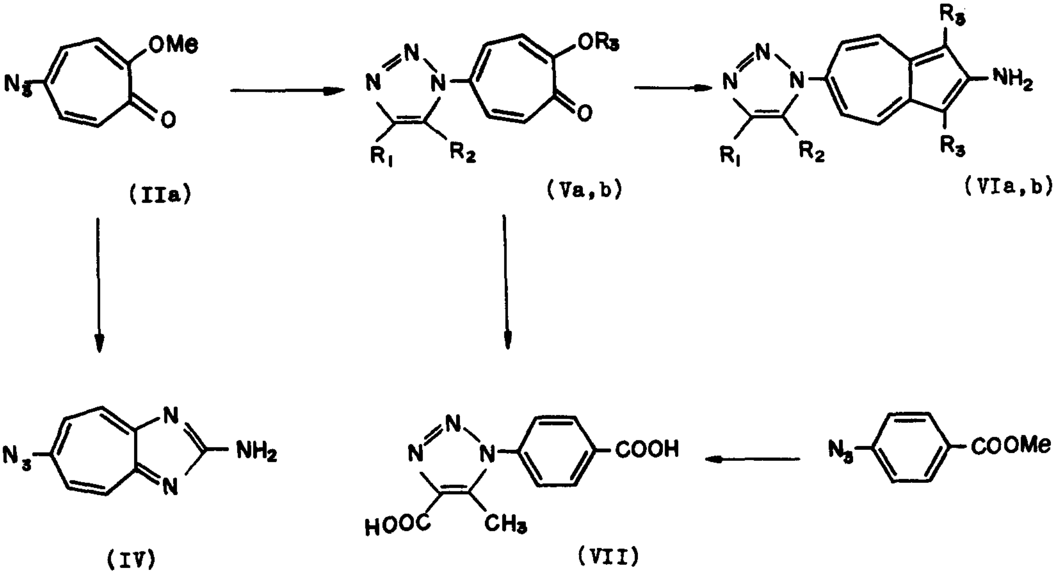


(Ie) (III)

Treatment of IIa with aliphatic amines such as ethylamine and diethylamine in alcohol afforded 5-azido-2-ethylaminotropone, mp 43°, and 5-azido-2-diethylaminotropone (an oil), respectively. With guanidine hydrochloride and sodium ethoxide, IIa gave 2-amino-6-azido-1,3-diazaazulene (or in its tautomeric form) (IV) which gradually decomposed above 120°.

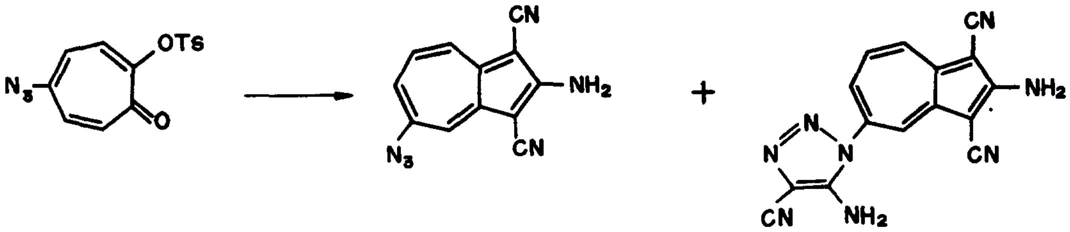
The reaction of Ia with three equivalents of malononitrile and a small amount of triethylamine afforded 5-(5-amino-4-cyano-1,2,3-triazol-1-yl)-tropolone (Va: R_1 = CN, R_2 = NH_2, R_3 = H), mp 285° (dec.): λ_{max}^{MeOH} mμ (log ε) 227 (4.41), 246 (4.20), 346 (3.88) and 405 (sh). The methyl ether of 5-(4-ethoxycarbonyl-5-methyl-1,2,3-triazol-1-yl)tropolone (Vb: R_1 = COOEt, R_2 = R_3 = Me), mp 185°, was obtained by the reaction of IIa with two mole equivalents of ethyl acetoacetate, and other corresponding triazolyltropolone methyl ethers were also obtained by the same method with other active methylene compounds such as acetylacetone, ethyl benzoylacetate, etc. (50 - 90 % yields).

The reaction of IIa with four mole equivalents of ethyl cyanoacetate and malononitrile gave diethyl 2-amino-6-(5-amino-4-ethoxycarbonyl-1,2,3-triazol-1-yl)azulene-1,3-dicarboxylate (VIa: R_1 = COOEt, R_2 = NH_2, R_3 = COOEt), mp 240° (45%), and 2-amino-6-(5-amino-4-cyano-1,2,3-triazol-1-yl)-1,3-dicyanoazulene (VIb: R_1 = R_3 = CN, R_2 = NH_2), mp 280° (dec., 77 %), respectively (11,12).



Recently, the direction of 1,3-dipolar addition of phenylazides has been clarified (13). Treatment of Vb with sodium methoxide in boiling methanol (14), followed by alkaline hydrolysis, afforded a dicarboxylic acid (VII), mp 235°. On the other hand, the reaction of methyl p-azidobenzoate (15) and ethyl acetoacetate gave ethyl 5-methyl-1-(p-methoxycarbonylphenyl)-1,2,3-triazole-4-carboxylate, mp 175°; hydrolysis of the obtained triazole afforded the free dicarboxylic acid which was identical with VII. Therefore, the structure of Vb is established and hence those of the other triazolytropolone methyl ethers. The methyl ether of Va and malononitrile afforded VIb. Thus, the direction of addition of active methylene compounds to I is confirmed and is the same with its methyl ether.

Two kinds of azulene derivatives (VIIIa), mp 290° (dec.), and (VIIIb), mp 300° (dec.), were obtained by the reaction of the tosylate (IIb) with malononitrile. They are 2-amino-5-azido-1,3-dicyanoazulene and 2-amino-(5-amino-4-cyano-1,2,3-triazol-1-yl)-1,3-dicyanoazulene, respectively, formed by abnormal condensation reaction as in the case of other reactions of tropolone tosylates (12).



(IIb) (VIIIa) (VIIIb)

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5 All new compounds obtained in this paper gave UV and IR spectra, as well as elemental analysis, in agreement with the assigned structures.

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