A Convenient Synthesis of Benzo[*b*]-1-azaazulene Derivatives

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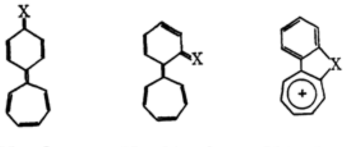
It has been reported that the hydride abstraction of *p*-tropylphenol, followed by the base treatment, furnished a deep-colored dye named *p*-benzoquinonetropide (Ia).[1] The hydride abstraction of *p*-tropylanilines also afforded immonium ions (Ib).[1b,2]

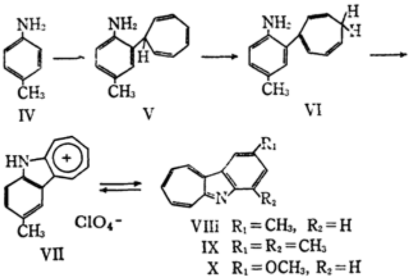


Ia X=O IIa X=O IIIa X=O
Ib $X=\overset{+}{N}R_2$ IIb X=NH IIIb X=NH

On the other hand, the similar treatment of *o*-tropylphenol did not yield *o*-benzoquinonetropide (IIa), but the tricyclic tropylium cation (IIIa).[1d,3] These results led us to investigate the hydride abstraction of *o*-tropylanilines to see if the reaction would give either *o*-benzoquinonetropidimine (IIb) or the tricyclic compound (IIIb). The results will be reported in this communication.

The tropylation of *p*-toluidine (IV) with ethoxytropilidene in ethanol in the presence of hydrochloric acid afforded oily 2-(7-tropyl)-*p*-toluidine (V).[*1]

The distillation of V under reduced pressure easily triggered the thermal isomerization of the tropyl group[4] to give mainly 2-(3-tropyl)-*p*-toluidine (VI), bp 143°C/1.8 mmHg; *N*-acetyl derivative, mp 113—114°C. The treatment of VI with 2.3 molar equivalents of triphenylmethyl perchlorate in methylene chloride yielded a tropylium perchlorate (VII), mp 260°C (decomp.), in a 62.6% yield. The use of a smaller amount of the reagent in the above reaction diminished the yield of the compound VII. The basification of VII with sodium hydrogencarbonate yielded violet crystals (VIII), mp 120—120.5°C, in a quantitative yield; these crystals were readily reversed to VII with perchloric acid.



The spectroscopic properties of the compound (VIII) as well as the results of the elemental analyses support the idea that the compound is not a *o*-benzoquinonetropidimine derivative, but 2-methylbenzo[*b*]-1-azaazulene: UV (Table 1); similar to that of benzo[*b*]-1-azaazulene, NMR (in $CDCl_3$); methyl protons at 2.58 ppm and aromatic protons (8H) between 7.5—8.7 ppm, mass spectrum; parent ion peak (base peak) at 193.

Although benzo[*b*]-1-azaazulenes have already been synthesized by several methods, the present method is the simplest and most convenient.

2,4-Dimethylbenzo[*b*]-1-azaazulene (IX), deep violet crystals, mp 100—101°C, and 2-methoxybenzo[*b*]-1-azaazulene (X), deep violet plates, mp 132.5—133°C, were synthesized by a similar method starting from 2,4-dimethylaniline and *p*-anisidine respectively. The ultraviolet and visible absorption maxima of these azaazulenes are shown in Table 1.

TABLE 1. ABSORPTION MAXIMA OF THREE BENZO[*b*]-1-AZAAZULENES

Compound	λ_{max}^{MeOH} mμ (log ε)
VIII	230^{sh}(4.50), 290^{sh}(4.57), 313(4.70), 360^{sh}(4.10), 490(2.64)
IX	238(4.27), 291.5(4.39), 318.5(4.48), 360^{sh}(3.76), 520(2.60)
X	228(4.40), 314(4.65), 324(4.64), 363(3.89), 550(2.66)

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2) J. J. Looker, *J. Org. Chem.*, **30**, 4180 (1965).

3) T. Nozoe and K. Takahashi, This Bulletin, **40**, 1480 (1967).

[*1] All the compounds were characterized by their IR and NMR spectra.

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