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# A NEW AND SIMPLE SYNTHESIS OF 1,2-DIAZAAZULENE

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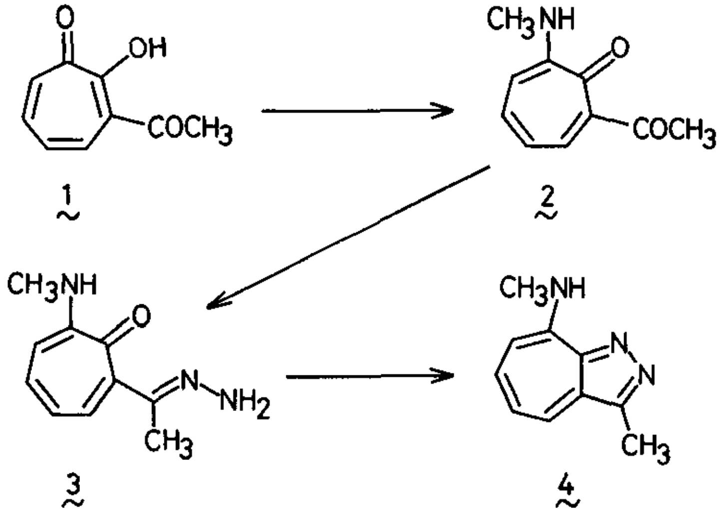
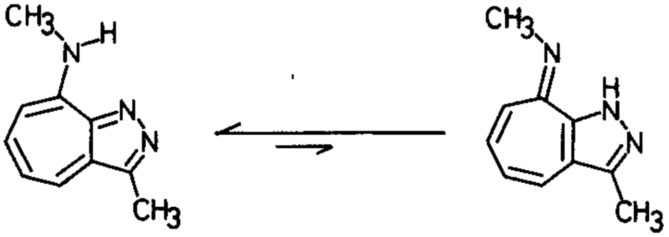
Abstract —— 3-Methyl-8-methylamino-1,2-diazaazulene was synthesized in 24% yield from 3-acetyltropolone *via* 2-acetyl-7-methylaminotropone and its hydrazone.

1,2-Diazaazulene is of interest for their relationship with 1,3-diazaazulenes. However, little is known about the chemistry of 1,2-diazaazulene derivatives, except for two reports by Matsumoto[1] and by Treibs.[2] These communications gave no details of their preparation and properties.

Recently, we found that 3-acetyltropolone (1) reacted with amines at room temperature to afford regioselectively 2-acetyl-7-(substituted amino)tropones.[3] 2-Acetyl-7-methylaminotropone (2) was readily available from the reaction of 1 with methylamine in 90% yield. In this commnication, we wish to describe a new and convenient synthesis of 1,2-diazaazulene from 3-acetyltropolone (1).



A mixture of 2-acetyl-7-methylaminotropone (2) and hydrazine hydrate in methanol was refluxed for 2 h to afford 2-acetyl-7-methylaminotropone hydrazone (3) (66%): mp 133-135°C; Ir ($CHCl_3$) 3320 and 1595 $cm^{-1}$; Nmr ($CDCl_3$) $\delta$ 2.09 (3H, s, $CH_3$), 3.00 (3H, d, J = 6.0 Hz, $N-CH_3$), 5.25 (2H, br, $NH_2$), and 6.3-7.7 (5H, m, NH + tropone). Found: C, 62.81; H, 6.77; N, 22.14%. Calcd for $C_{10}H_{13}N_3O$: C, 62.80; H, 6.85; N, 21.98%.
A solution of 3 in acetic acid was heated on a water bath for 1 h. After the removal of the solvent, the residue was chromatographed on a Wakogel B-10 plate to give 3-methyl-8-methylamino-1,2-diazaazulene (4) (40%): mp 174-176°C; Ir ($CHCl_3$) 3320, 1620, and 1580 $cm^{-1}$; Uv ($CH_3OH$) 233 (log $\varepsilon$ 4.21), 255 (4.33), 309 (3.87), 366 (3.58), and 437 nm (3.67); Nmr ($CDCl_3$) $\delta$ 2.73 (3H, s. $C-CH_3$), 3.36 (3H, s, $N-CH_3$), 6.6-7.1 (2H, m), 7.55 (1H, br, NH), and 7.5-8.1 (2H, m). Found: C, 69.25; H, 6.27; N, 24.14%. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26%. The overall yield of the 1,2-diazaazulene (4) from 1 was 24%.



A

B

Although the compound (4) has two tautomeric forms such as A and B, it seems that the structure A is reasonable from the following spectral data. The Uv spectrum of 4 is shown in Fig. 1 together with those of 3-methyl-1,8-dihydrocycloheptapyrazol-8-one (5) and its hydrazone (6),[4] which are corresponding to the tautomeric form (B). The absorption maxima of 4 are almost consistent with Treibs' data[2] and were observed at fairly longer wavelengths than those of 5 and 6. Furthermore, the absorption bands in visible region showed a shift towards long wavelength region in comparison with those of 1,3-diazaazulene.[5,6] In Nmr spectrum of 4, the signals in the seven-membered ring protons were observed at lower magnetic field than those of the compounds (5 and 6). The values of chemical shifts are comparable to the values in 1,3-diazaazulenes.[7]
Studies on reactions of the 1,2-diazaazulene (4) are now in progress.

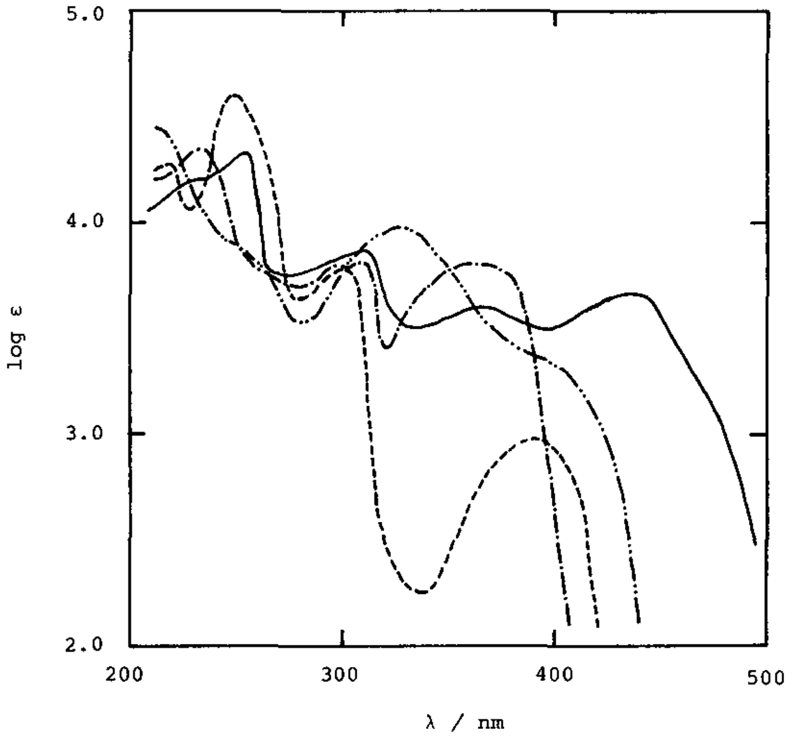


Fig. 1. Uv and Visible Spectra

—— 4, —·— 5, —··— 6,
---- 1,3-Diazaazulene

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