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Synthesis and Properties of 3-Substituted 8H-3-Azaheptalen-8-ones

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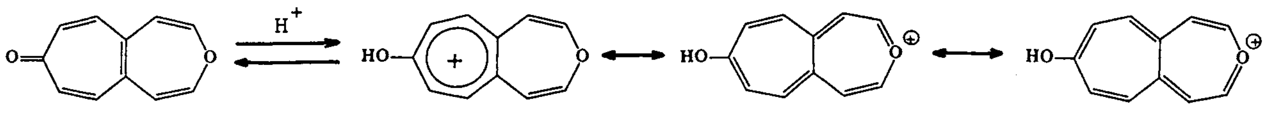
3-Substituted 8H-3-azaheptalen-8-ones were synthsized in good yields by photoirradiation of corresponding 7-substituted 7-azanorbornadienes fused with tropone in ethanol with a 450-W Hg lamp through pyrex filter.

We have been interested in heteropines condensed with a non-benzenoid aromatic system. Recently we communicated the first synthesis of the oxepine having such fused conjugated system, 8H-3-oxaheptalen-8-one (1). For its protonated form 2, it was observed that 3-oxoniaheptalen-8-ol forms, 2' and 2", exhibiting intramolecular electron transfer, contribute to 2 to some extent.$^{1)}$ Extensive studies on 1H-azepines have shown that they exist in boat-shaped conformations$^{2a)}$ and behave chemically as cyclic olefins.$^{2b)}$ Here we now report the synthesis of azepines fused with seven-membered aromatics, 3-substituted 8H-3-azaheptalen-8-ones 4.



1 2 2' 2"

1-Substituted 1H-azepines have been synthesized by irradiation of 7-azanorbornadienes followed by thermal rearrangement of labile 3-azaquadricyclanes formed intermediately.$^{3)}$ We have applied this building sequence to the synthesis of 4. The starting materials for this route, 7-substituted 7-azanorbornadienes 3 fused with tropone, were prepared by the cycloaddition reactions of 4,5-dehydrotropone with the corresponding pyrrols. Treatment of 1-amino-1H-cycloheptatriazol-6-one with lead tetraacetate in dichloromethane in the presence of the pyrrol gave the addition products 3 (3a; 33%, 3b; 26%, 3c; 19%).

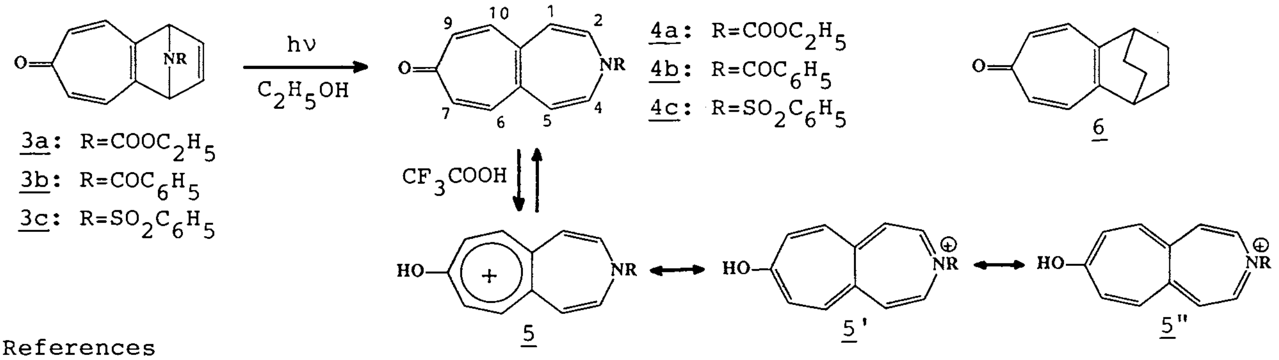
Irradiation of 3 with a 450-W Hg lamp in ethanol (1-2 mmol/L) through pyrex filter followed by careful workup under nitrogen gave 3-substituted 8H-3-azaheptalen-8-ones 4 (4a; 60 - 80%, 4b; 65%, 4c; 52%).

The ^{13}C NMR as well as the ^{1}H NMR spectra of 4 confirm their structures.$^{4)}$ The vicinal proton coupling constants of 4 [$J_{1,2}=J_{4,5}=8.4$ Hz for 4a; 8.5 Hz for 4b; 7.8 Hz for 4c (in $CDCl_3$), 8.6 Hz for 4b (in CD_3CN) and $J_{6,7}=J_{9,10}=12.8$ Hz for

4b (in CD_3CN)] are comparable to the corresponding coupling constants of 1H-azepine (7.97 Hz)',[5a)] cycloheptatriene (8.58 Hz),[5b)] and a 4,5-dialkyltropone 6 (12.0 Hz),[6)] respectively. These data reveal that the azepine rings of 4a, 4b, and 4c exist in boat-shaped conformations whereas the tropone moieties remain almost planar geometry.

Protonation of 4 with CF_3COOH afforded 3-substituted 8-hydroxy-8H-3-aza-heptalenium ions 5 [e. g. 5a: ^1H NMR (60 MHz, CF_3COOH) δ 1.40 (t, J=7.0 Hz, CH_3), 4.47 (q, J=7.0 Hz, CH_2), 5.60 Hz (d, J=9.3 Hz, H-1,5), 6.45 (d, J=9.3 Hz, H-2,4), 7.72 (s-like, H-6,7,9,10)]. Downfield chemical shifts ($\Delta\delta$=0.92 ppm for 5a and $\Delta\delta$=1.18 ppm for 5b) of the troponoid protons in the ^1H NMR spectra of 5 compared with those of 4 are moderately smaller than the corresponding values (1.29 - 1.47 ppm) observed for the dialkyltropone 6 and its protonated species but somewhat larger than those (0.67 - 0.80 ppm) observed for 1 and 2.[1)] These data suggest that 3-azoniaheptalen-8-ol forms, 5' and 5", do not contribute to 5 so significantly as 2' and 2" do to 2 owing to the electron-withdrawing N-substituents.

4a, 4b, and 4c exhibit UV spectra [e. g. 4a: (CH_3OH) λ_{max} nm (log ε) 237 (4.31), 274 sh (3.96), 354 (3.57)] similar to that of 1, since their molecular geometries are analogous to that of 1.[1)]



3a: $R=COOC_2H_5$
3b: $R=COC_6H_5$
3c: $R=SO_2C_6H_5$

4a: $R=COOC_2H_5$
4b: $R=COC_6H_5$
4c: $R=SO_2C_6H_5$

6

5 5' 5"

References

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4) 4a: ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.44 (CH_3), 63.07 (CH_2), 121.36 (C-1,5), 136.73 (C-2,4), 139.39, 140.21 (C-6,10,7,9), 142.67 (C-5a,10a), 152.58 (CO of ester), 186.08 (C-8); ^1H NMR (60 MHz, $CDCl_3$) δ 1.32 (t, J=7.0 Hz, CH_3), 4.28 (q, J=7.0 Hz, CH_2), 5.54 (d, J=8.4 Hz, H-1,5), 6.25 (d, J=8.4 Hz, H-2,4), 6.80 (s-like, troponoid H).

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