The 9-Azabarbaralane (9-Azatricyclo[3,3,1,$0^{2,8}$]nona-3,6-diene) System

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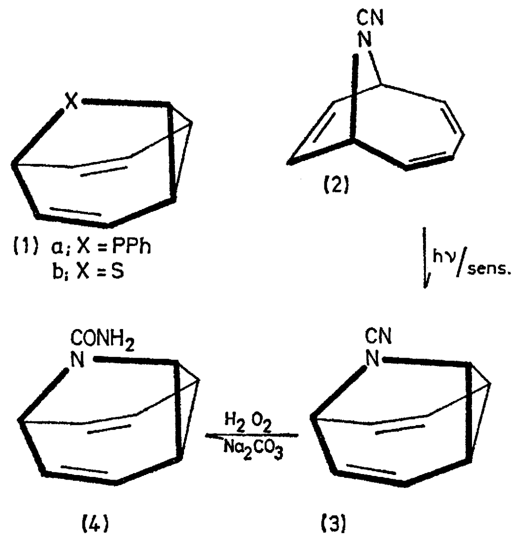
Summary A convenient, high-yield, photoinduced entry into the novel 9-azabarbaralane system is described.

Whereas 9-heterobarbaralanes incorporating second-row heteroatoms, *e.g.*, (**1a**)[1] and (**1b**),[2] are known, their first-row relatives have been unavailable. 9-Azabarbaralanes are of interest from a theoretical viewpoint[3] inasmuch as they allow for controlled variation of the electron density at the bridge, by proper choice of substitution, and hence for assessment of its effect on the stability of the potentially "aromatic" 6-electron transition state interconverting the two isoenergetic forms available to the barbaralane skeleton. We report a convenient photoinduced entry into the hitherto unknown 9-azabarbaralane skeleton.

The synthesis used was similar to those described earlier for the preparation of the second-row analogues (**1a**)[1] and (**1b**).[2] Specifically, Pyrex-filtered irradiation of a cold (*ca.* 0°), dilute, solution of (**2**)[4] in acetone (500 mg in 800 ml), in the presence of "Michler's" ketone, with a Hanovia 450-W lamp leads to a single product [air-sensitive white crystals, m.p. 78—80° (decomp.); ν (KBr) 2200 cm^{-1} (CN); λ_{max} (MeCN) < 200 nm; n.m.r. (60 MHz, CS_2) triplets centred at τ 4·18 (2H), 5·81 (4H), and 6·18 (2H)] in *ca.* 70% isolable yield after purification by low temperature (*ca.* $-15°$) column chromatography on alumina. The spectral information leads to the formulation of the photoproduct as *N*-cyano-9-azabarbaralane (**3**) in a state of rapid flux (n.m.r.). Moreover, exposure of (**3**) to basic 30% hydrogen peroxide leads to the corresponding urea (**4**) [m.p. 106—107°; ν_{max} (KBr) 1590, 1650 cm^{-1} (CO); λ_{max} (MeCN) < 200 nm; n.m.r. (60 MHz, $CDCl_3$) τ 4·15 (2H, t), 4·42 (2H, brs, exchangeable with D_2O), 5·48 (2H, t), and 5·82 (4H, t)] which, as in the case of (**3**), displays the characteristic n.m.r. pattern of a fluxional barbaralane.



As expected, the fluxional behaviour of (**3**) and (**4**) is temperature dependent by n.m.r. For example, in the case of the cyanamide (**3**) the n.m.r. resonances undergo considerable broadening, albeit with some retention of structure on cooling the solution to *ca.* −79° in CD_2Cl_2.† More strikingly, the n.m.r. spectrum of the corresponding urea (**4**), taken in $(CD_3)_2CO$,†‡ suffers complete loss of structure when cooled to −79°, the highest-field 4H signal undergoing partial separation with eventual coalescence at *ca.* −40°. Bearing in mind the substituent constants: $\sigma_p^-(CN) = +1{\cdot}00$ and $\sigma_p^-(CONH_2) = +0{\cdot}621$, and being aware of the preliminary nature of our findings§ and the need for additional work with other derivatives, we note that the differences observed in the variable-temperature n.m.r. spectra of (**3**) and (**4**) are indicative of increased stabilization of the 6-electron transition state, interconverting the two forms of 9-azabarbaralane, with decreased electron density at the bridge (atom 9).

We thank the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

(*Received, 13th August* 1973; *Com.* 1166.)

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† The choice of solvent was dictated by the solubility of the substrate and its ability to effect separation of the three key triplets.

‡ With added CD_3OD to effect exchange of the NH_2 protons and thus eliminate their complicating presence in the n.m.r. spectrum.

§ The major complication arises from our present inability to record the low-temperature n.m.r. spectra of (**3**) and (**4**) in the same solvent. However, it seems unlikely that the large differences in T_c between (**3**) (< −79°) and (**4**) (*ca.* −40°) are primarily due to the effect of solvent.

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