4-Azabicyclo[5,2,0]nona-2,5,8-triene and Derivatives

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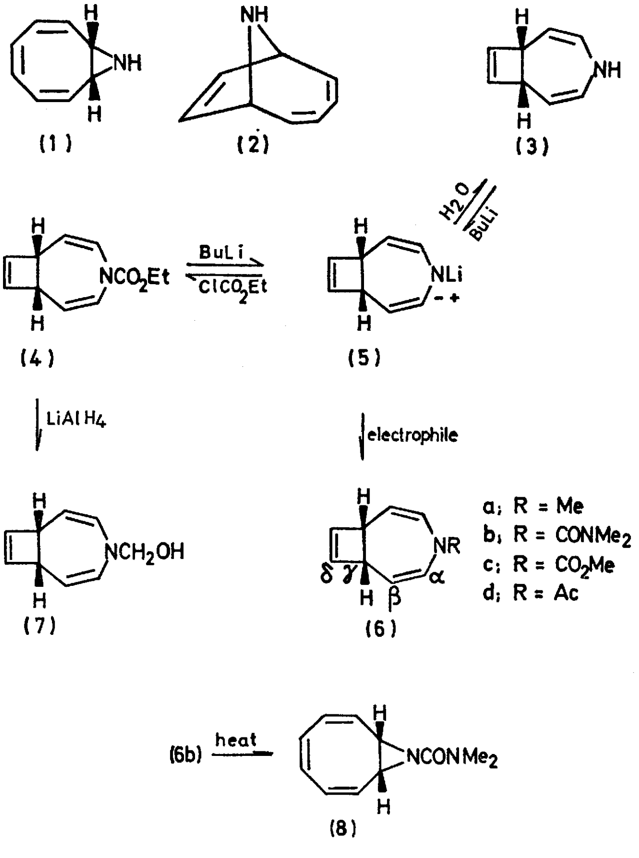
Summary The synthesis of 4-azabicyclo[5,2,0]nona-2,5,8-triene and its conversion into various derivatives are described.

Previously we have described the synthesis of the C_8H_8NH bicyclic compounds (**1**)[1] and (**2**)[2], and now report the preparation of another compound (**3**). Besides its significance as a valence tautomer of 1*H*-azonine,[3] this substance is readily convertible into various *N*-substituted derivatives which constitute ideal n.m.r. models for quantitatively assessing the effect of *N*-substitution on the electron density at C_α and C_β of (**6**).

Compound (**3**) [air-sensitive clear oil; ν_{N-H} (neat) 3310 cm^{-1}, λ_{max} (n-hexane)† 264·5 nm (ϵ 1580), 219 (2330); *m/e* 119 (P^+ 45%); τ (60MHz, CCl_4) 3·81 (2H, s, H_δ), 4·20 (2H, dd, *J* 9·5, 6·0 Hz, H_α), 5·43 (2H, dd, *J* 9·5, 4·5 Hz, H_β), 6·25 (2H, d, H_γ)] was prepared by degradation of its urethane (**4**)[4] on treatment with either n-butyl-lithium or potassium t-butoxide in tetrahydrofuran. While (**3**) is surprisingly inert to $ClCO_2Et$, its lithio salt, prepared either from (**4**) or on reaction of (**3**) with Bu^nLi, readily yields (**4**) (n.m.r.) when treated with this reagent and derivatives (**6a**),‡ (**6b**)‡ (m.p. 45—45·5°), (**6c**) (n.m.r.),[5] and (**6d**) (n.m.r.)[1] when exposed to MeI, $ClCONMe_2$, $ClCO_2Me$, and ClCOMe, respectively. In contrast, exposure of (**4**) to $LiAlH_4$ affords the amino-alcohol (**7**),‡ m.p. 53·5—54·5°.

In theory, the influence of the NR function in (**6**) should be primarily inductive on the α site and mesomeric on the β position. In full substantiation of this prediction, the n.m.r. chemical shifts of the α protons show good linear correlation with the σ_m substituent constants (Figure, A) while those of the β hydrogens correlate well with the corresponding σ_p^- terms (Figure, B).§ Also, as judged by



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† Band intensities are necessarily approximate owing to serious difficulties encountered in handling this substance which readily resinifies when neat.

‡ This substance displays consistent n.m.r., i.r., u.v., and m.s. characteristics.

§ The use of the chemical shifts of H_β and H_α extracted from the n.m.r. spectra of (**6b**) and (**7**) allows one to estimate $\sigma_p^- = +\ 0{\cdot}55$ and $\sigma_m = +\ 0{\cdot}22$ for $CONMe_2$, and $\sigma_p^- = +\ 0{\cdot}12$ and $\sigma_m = +\ 0{\cdot}03$ for CH_2OH.

the n.m.r. criterion the substituent effect in (**6**) does not appear to extend to the γ and δ positions of the molecule, the protons associated with these sites resonating uniformly at *ca.* τ 6·3 and 3·8, respectively. Nonetheless, the widely different rates at which compounds (**3**) ($t_{\frac{1}{2}}$ *ca.* 60 h, decomp.), (**6c**) ($t_{\frac{1}{2}}$ *ca.* 17 h),[5] and (**6d**) ($t_{\frac{1}{2}}$ *ca.* 80 min)[6] undergo irreversible thermal rearrangement at 76° are suggestive of progressive cross-link weakening with decreased availability of the nitrogen lone pair for participation into the system.

Finally, we note that the urea (**6b**) is thermally labile, rapidly rearranging ($k = 9·97 \pm 1·17 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger}$ = 25·4 kcal mol^{-1} at 56·3°) to (**8**) when warmed in C_6D_6. The mechanistic implications of this conversion, which is the exact reverse of the [6,1,0] → [5,2,0] process observed in the case of (**4**),[4] (**6c**),[5] and (**6d**),[1] are under examination.

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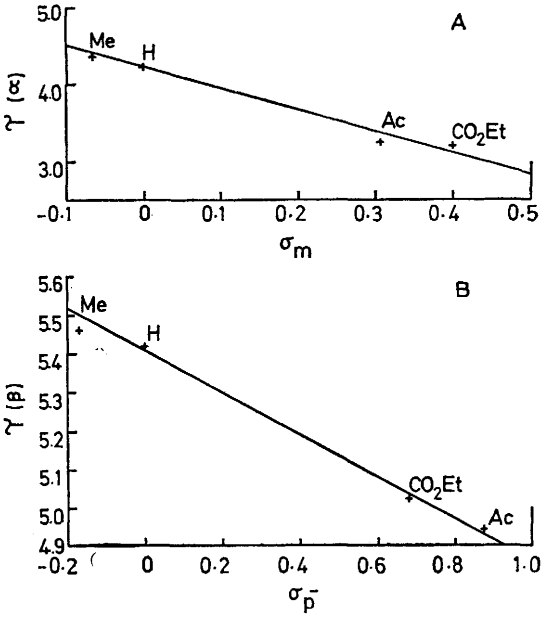

FIGURE. *Plot of* ^{1}H *n.m.r. chemical shifts of* (**6**) vs. σ *constants of substituent* R. [*All determinations were made with* ca. 0·75M-*molar solutions of* (**6**) *in* CCl_4.]

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