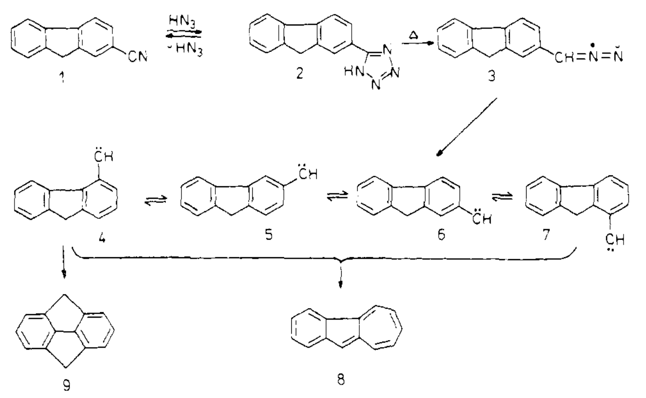
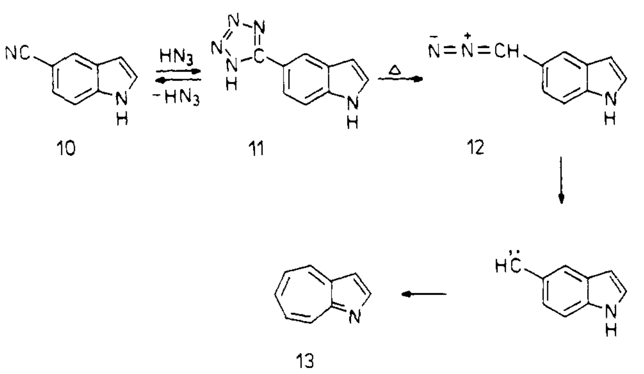
Scheme I



Scheme II



Evidence for the intermittant formation of 2-(diazomethyl)fluorene (**3**) was obtained by pyrolyzing **2** at 380 °C (10^{-4} torr) and condensing the product on a −196 °C KBr disk, thereby allowing the observation of a strong IR absorption at 2060 cm^{-1}. The formation of the products **8** and **9** is rationalized in terms of the equilibrating arylcarbenes **4–7**. Carbene **4** undergoes insertion into the peri C–H bond to give **9**. Ring expansion[1] of the carbenes **4–7** followed by a hydrogen shift gives **8**.

The preparative advantage of this synthesis of benz[*a*]azulene is readily seen when comparing with the 0.5% yield of the best current preparation from fluorene and ethyl diazoacetate.[8]

The usefulness of the tetrazole pyrolysis is further seen in our preparation of 1-azaazulene (**13**), an otherwise difficultly accessible and unstable compound previously prepared in a lengthy synthesis in low yield.[9] 5-Cyanoindole (**10**) was converted to the tetrazole **11** with HN_3.[10] Pyrolysis of **11** at 350 °C (10^{-4} torr) allowed the detection of 5-diazomethylindole (**12**; 2060 cm^{-1}). At 500 °C (10^{-1}–10^{-3} torr) 1-azaazulene[11] (**13**) was formed in 50% yield together with 30% of the product of cycloreversion, viz., 5-cyanoindole (**10**) (Scheme II). Thus, 1-azaazulene is readily available in a two-step synthesis from commercial **10**.

If the nascent carbene function is moved from the six-membered to the five-membered ring in compounds of the types **3** and **12**, the corresponding benzenoid hydrocarbons are formed in place of azulenes. Thus, we prepared the sodium salts of the tosylhydrazones of indene-2-carboxaldehyde, indole-3-carboxaldehyde, and fluorene-9-carboxaldehyde, which, on pyrolysis at 650 °C (10^{-3} torr) gave naphthalene, quinoline, and phenanthrene in isolated yields of 66%, 30%, and 50%, respectively.

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(7) 4,8-Dihydrocyclopenta[*d.e.f*]fluorene: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, *J* = 7 Hz, 2 H), 7.16 (t, *J* = 7 Hz, 4 H), 4.31 (s, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.3 (s), 127.8 (d, *J* = 158 Hz), 126.5 (s), 124.4 (d, *J* = 158 Hz), 44.1 (t, *J* = 133 Hz). This compound was identified by comparison with a sample prepared according to: Trost, B. M.; Kinson, P. L. *J. Am. Chem. Soc.* **1970**, *92*, 2591.

(8) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans 2* **1975**, 714.

(9) Nozoe, T.; Seto, S.; Matsumura, S.; Terasawa, T. *Chem. Ind. (London)* **1954**, *30*, 1356, 1357. Nishiwaki, T.; Abe, N. *Heterocycles* **1981**, *15*, 547.

(10) **11**: mp 245 °C dec; ^{1}H NMR (Me_2SO-d_6, 400 MHz) δ 11.50 (s, 1 H), 8.31 (s, 1 H), 7.81 (d, 1 H), 7.60 (d, 1 H), 7.48 (s, 1 H), 6.59 (s, 1 H), 6.5 (br, 1 H); mass spectrum, *m/z* 185.0773 (calcd for $C_9H_7N_5$, 185.0782); correct elemental analysis (C, H, N) was obtained.

(11) **13**: picrate mp 196–197 °C dec (lit.[9] 197–198 °C); UV (CH_3OH) λ 340, 330, 310, 260, 230 nm; ^{1}H NMR (CD_3OD, 400 MHz) δ 9.26 (d, *J* = 10 Hz, 1 H), 9.14 (d, *J* = 10 Hz, 1 H), 8.09 (d, *J* = 3 Hz, 1 H), 8.66 (t, *J* = 10 Hz, 1 H), 8.49 (t, *J* = 10 Hz, 1 H), 8.43 (t, *J* = 10 Hz, 1 H), 7.69 (d, *J* = 3 Hz, 1 H); mass spectrum, *m/z* 129 (M^+).

Additions and Corrections

Template Effects. 6. The Effect of Alkali Metal Ions on the Formation of Benzo-3*x*-crown-*x* Ethers over a Wide Range of Ring Sizes [*J. Am. Chem. Soc.* **1984**, *106*, 168]. LUIGI MANDOLINI* and BERNARDO MASCI*

Page 171: The corrected form of eq 3 is

$$k_{\mathrm{obsd}} = \frac{k_{\mathrm{i}} + k_{\mathrm{ip}}K_{\mathrm{ArO^-}}\gamma_{\pm}{}^2[\mathrm{M}^+] + k_{\mathrm{it}}K_{\mathrm{ArO^-}}K_{\mathrm{ArO^-M^+}}\gamma_{\pm}{}^2[\mathrm{M}^+]^2}{1 + K_{\mathrm{ArO^-}}\gamma_{\pm}{}^2[\mathrm{M}^+] + K_{\mathrm{ArO^-}}K_{\mathrm{ArO^-M^+}}\gamma_{\pm}{}^2[\mathrm{M}^+]^2} \quad (3)$$