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Synthesis of 1-azaazulene and benz[a]azulene by carbene rearrangement

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JUNE 1984

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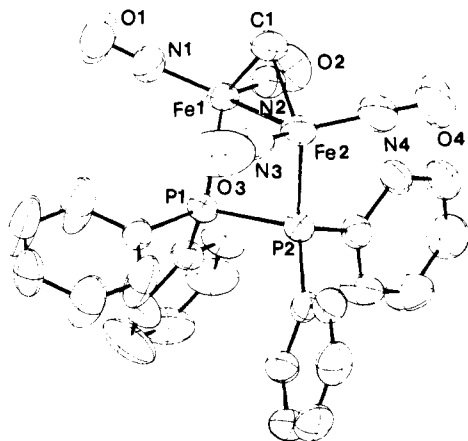


Figure 2. ORTEP drawing of 6.

ically,⁶ can also be obtained by reduction of **1** with LiAlH_4 or $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ in THF. By way of contrast, treatment of **1** with 1 equiv of LiEt_3BH in THF at ca. -24°C results in the formation of a red-brown solution of $\text{Li}^+\textbf{3}$. The air-sensitive but thermally stable (at ambient temperatures) monoanion **3**⁷ contains a bridging NO, a bridging PPh_2 supported by an Fe-Fe bond,^{1a} and a terminal PPh_2H , with the PH hydrogen originating from the reducing agent (**1** and LiEt_3BD yield $\text{Li}^+\textbf{3-d}_1$).

When a THF solution of $\text{Li}^+\textbf{3}$ was treated with 1 equiv of *n*-BuLi at -78°C , immediate reaction occurred as evidenced by color change to bright red. The deprotonated binuclear species is provisionally assigned structure **4**.⁸ It is thermally unstable and at ca. -70°C in solution readily isomerizes to **2**.

Solutions of $(\text{Li}^+)_2\textbf{4}$ and $\text{Li}^+\textbf{3}$ represent convenient entries to the novel isomeric complexes **5** and **6**. Thus, the former rapidly reacts with CH_2I_2 at -78°C to yield **5**, which was isolated (ca. 20%) at 25°C as a red, air-stable solid.⁹ Reaction of $\text{Li}^+\textbf{3}$ with CH_2I_2 commences at ca. -63°C to afford **6**, which was isolated (35%) at 25°C , along with **5** (<5%), as a deep red, moderately air-stable solid. Both **5** and **6** were characterized by X-ray crystallography, and their molecular structures are shown in Figures 1 and 2, respectively. Since **5** was not detected when the latter reaction was monitored by ^{31}P NMR spectroscopy, its formation must have occurred during workup. Indeed, **6** undergoes unprecedented isomerization to **5** on heating in THF solution. This conversion is complete within 20 h at 55°C , with **1** also being produced.

Whereas the formation of **5** from **4** and CH_2I_2 is not unexpected, that of **6** from **3** and CH_2I_2 invites comment. The former likely proceeds by interaction of the CH_2I_2 or CH_2I_2 -derived carbon with the terminal PPh_2 group, followed by rapid completion of the $\mu\text{-CH}_2\text{PPh}_2$ bridge. Since the first step of such a sequence is blocked for the reaction of CH_2I_2 with **3**, initial interaction of the carbon probably occurs with $\text{Fe}_{(1)}$. The formation of $\text{Fe}_{(1)}(\mu\text{-CH}_2)\text{Fe}_{(2)}$ may then continue by dissociation of PPh_2H and oxidative addition of $\text{Fe}_{(1)}\text{CH}_2\text{I}$ to $\text{Fe}_{(2)}$. Several pathways to the $\text{Fe}_{(1)}(\mu\text{-Ph}_2\text{PPPPh}_2)\text{Fe}_{(2)}$ bridge in **6** may be proposed; the formation of $\mu\text{-Ph}_2\text{PPPPh}_2$ is unusual since reactions of P_2R_4 with metal carbonyls and nitrosyls commonly afford phosphido-bridged binuclear complexes.¹⁰

(6) Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001. No spectroscopic data were reported for **2**, however.

(7) $\text{Li}^+\textbf{3}$: IR (THF) $\nu_{\text{N=O}}$ 1704 m, 1660 s, $\nu_{\text{N-O}}$ 1420 w-m cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, 25°C) δ 164.6 (d), 43.4 (d, $J_{\text{PP}} = 19.6$ Hz), temperature invariant to -73°C ; ^{31}P NMR (THF, 25°C) δ 164.6 (s, br), 43.4 (d, br, $J_{\text{PH}} = 338$ Hz); $\text{Li}^+\textbf{3-d}_1$: $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, 25°C) δ 164.0 (d), 42.2 (dt, $J_{\text{PP}} = 20$, $J_{\text{PD}} = 50$ Hz). $\text{Na}^+\textbf{3}$ and $\text{K}^+\textbf{3}$ (from **1** and appropriate MBEt_3H): IR (THF) $\nu_{\text{N=O}}$ 1435 w-m cm^{-1} .

(8) $(\text{Li}^+)_2\textbf{4}$: $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, -78°C) δ 159.6 (d), 20.5 (d, $J_{\text{PP}} = 50$ Hz); similar ^{31}P NMR (THF, -78°C), i.e., no one-bond P-H coupling for signal at δ 20.5.

(9) In contrast, $(\text{Li}^+)_2\textbf{2}$ and CH_2I_2 at -78°C followed by warming to 25°C afford 80-90% **1**, but no detectable **5**.

(10) (a) Hieber, W.; Kummer, R. *Z. Anorg. Allg. Chem.* **1966**, *344*, 292. (b) Hayter, R. G.; Williams, L. F. *Inorg. Chem.* **1964**, *3*, 717.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-7911882), Ministero Pubblica Istruzione (Rome), and NATO (through Grant 068.81).

Registry No. **1**, 14917-04-5; $(\text{Na}^+)_2\textbf{2}$, 89958-70-3; $\text{Li}^+\textbf{3}$, 89958-71-4; $(\text{Li}^+)_2\textbf{4}$, 89958-72-5; **5**, 89958-73-6; **6**, 89958-74-7.

Supplementary Material Available: Crystal data, final positional and thermal parameters, selected bond lengths and bond angles, and spectroscopic data for **5** and **6** (9 pages). Ordering information is given on any current masthead page.

Synthesis of 1-Azaazulene and Benz[a]azulene by Carbene Rearrangement

Curt Wentrup* and Jürgen Becker

Department of Chemistry, Philipps-Universität Marburg, Lahnberge, D-3550 Marburg, West Germany

Received February 21, 1984

The ring expansion of arylcarbenes to cycloheptatrienyldenes/cycloheptatetraenes has been the subject of numerous mechanistic investigations,¹ but this reaction has found little use in the synthesis of seven-membered ring compounds. In fact, the equilibrating tolylcarbenes are trapped by methyl groups in the form of benzocyclobutene and styrene,^{1,2} but no corresponding intramolecular trapping products of the methylcycloheptatrienyldenes/methylcycloheptatetraenes have been reported. We now find that it is indeed possible to trap these seven-membered ring intermediates and to put the reaction to synthetic use in the preparation of azulene derivatives.

The initial experiments were not very encouraging: flash vacuum pyrolysis of the sodium salt of fluorene-2-carboxaldehyde tosylhydrazone³ at 400°C (10^{-3} torr) gave a 1.5% yield of benz[a]azulene (**8**) together with a 2.0% yield of 4,8-dihydrocyclopenta[*d.e.f*]fluorene (**9**).⁴

Much better results were obtained with a different carbene precursor, 5-(2-fluorenyl)tetrazole (**2**), obtained by addition of HN_3 to the nitrile **1**.⁵ The pyrolysis of **2** (1 g) at 420°C (10^{-1} - 10^{-3} torr) gave a 44% yield of benz[a]azulene (**8**) together with 4% of **9** (Scheme I). As is typical of tetrazoles, a cycloreversion to 2-cyanofluorene (**1**), isolated in 33% yield, also occurred. The products were separated by preparative gas chromatography (SE 30, 135°C) and identified by spectral comparison with authentic samples.^{6,7}

(1) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173. Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; p 109. Wentrup, C. "Reactive Molecules"; Wiley: New York, 1984.

(2) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739.

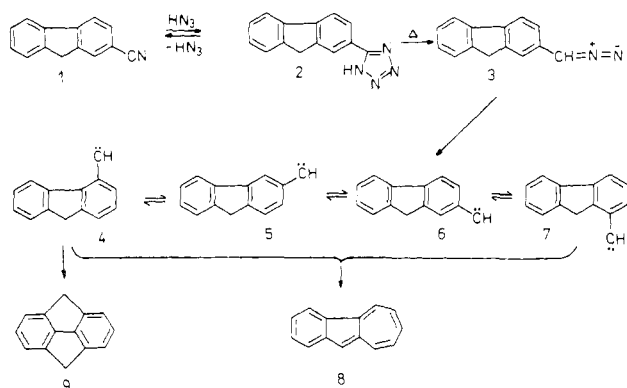
(3) Fluorene-2-carboxaldehyde tosylhydrazone: mp 190 - 192°C ; correct elemental analysis (C, H, N) was obtained. The sodium salt was prepared with NaH in ethanol-ether 1:1 (25°C , 1 h), filtered under N_2 , and dried at 50°C (10^{-2} torr) for 8 h.

(4) Alder (Alder, R. W. University of Bristol, UK, private communication) has independently observed the formation in low yield of benz[a]azulene on pyrolysis of the sodium salt of fluorene-2-carboxaldehyde tosylhydrazone. The presence of **9** was assumed but not ascertained.

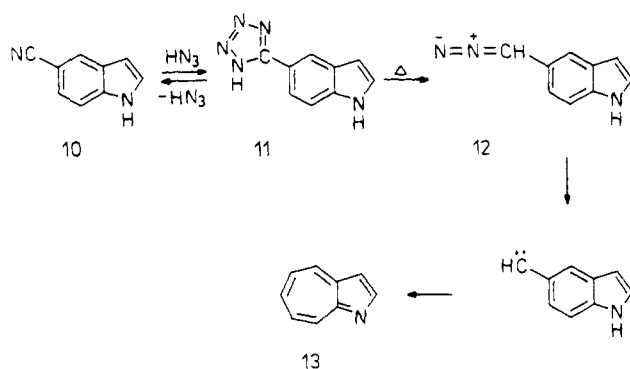
(5) **2** was obtained in 67% yield from **1** with $\text{NaN}_3/\text{NH}_4\text{Cl}$ in DMF at 120°C for 12 days: mp (dec) 252°C ; ^1H NMR ($\text{Me}_2\text{SO}-d_6$, 400 MHz) δ 8.26 (s, 1 H), 8.13 (d, 1 H), 8.08 (d, 1 H), 8.00 (d, 1 H), 7.64 (d, 1 H), 7.45 (t, 1 H), 7.39 (t, 1 H), 4.05 (s, 2 H), 3.5 (br, 1 H); mass spectrum m/z 234.0891 (calcd for $\text{C}_{14}\text{H}_{10}\text{N}_4$, 234.0905); correct elemental analysis (C, H, N) was obtained.

(6) Benz[a]azulene: ^1H NMR (CDCl_3 , 400 MHz, integral 1 H in each instance) δ 8.40 (d, $J = 8$ Hz), 8.32 (d, $J = 8.3$ Hz), 7.97 (d, $J = 10.9$ Hz), 7.89 (t of d, $J = 1$ and 8 Hz), 7.70 (ddd, $J = 1$, 7, and 8 Hz), 7.50 (ddd, $J = 1$, 7, and 8 Hz), 7.35 (s), 7.21 (tdd, $J \leq 0.7$, 8.3, and 10.6 Hz), 7.05 (tdd, $J \leq 0.7$, 8.3, and 10.6 Hz), 6.86 (ddd, $J \leq 0.7$, 8.3, and 10.9 Hz); ^{13}C NMR (CDCl_3 , 25 MHz) δ 142.5, 140.6, 139.2, 135.9, 134.6, 131.9, 128.5, 127.9, 125.4, 123.7, 121.8, 120.8, 120.3, 116.1. This compound was identified by comparison with a sample prepared according to Alder and Whittaker.⁸

Scheme I



Scheme II



Evidence for the intermittent formation of 2-(diazomethyl)fluorene (3) was obtained by pyrolyzing 2 at 380 °C (10^{-4} torr)

(7) 4,8-Dihydrocyclopenta[*d,e,f*]fluorene: ^1H 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.

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 expansion¹ 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-azaazulene¹¹ (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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(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; ^1H NMR ($\text{Me}_2\text{SO}-d_6$, 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 $\text{C}_9\text{H}_7\text{N}_5$, 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; ^1H 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-3x-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

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