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# Photoisomerization Reactions of 8-Azatricyclo[3.2.1.$0^{2,4}$]oct-6-ene Derivatives Leading to Azabishomobenzene Derivatives

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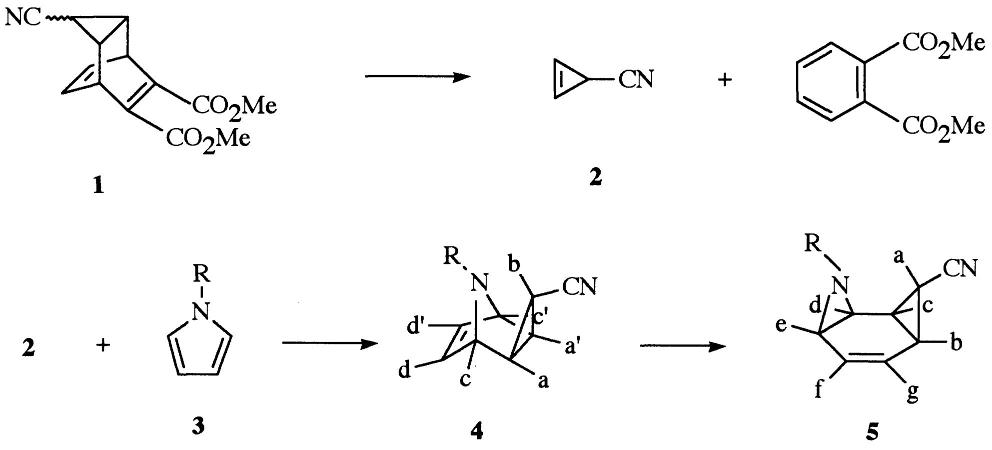
Irradiation of 8-azatricyclo[3.2.1.$0^{2,4}$]oct-6-enes in dry ether with a low pressure mercury lamp gave azabishomobenzenes through [$2\pi+2\sigma$]-type migration reactions between C–N bonds and olefin moieties.

Since the first introduction of the concept of homoaromaticity by Adams and Winstein it has been the subject of much interest to both experimentalists and theoreticians.[1,2] However the synthetic researches of homoaromatic compounds such as bis- and trishomobenzene derivatives have been rarely reported. The reason for this seems to be the tedious and difficult preparations of these compounds.[2]

Photoisomerization reactions of homoconjugated compounds such as 8-oxa- and 8-azabicyclo[2.2.1]hepta-2,5-dienes were known to afford oxepine and azepine derivatives through [$2\pi+2\pi$]-type cycloaddition reactions.[3] Similarly photoreactions of tricyclo-[3.2.1.$0^{2,4}$]oct-6-ene derivatives were reported to yield tetracyclo[$1.^{2,6}1.^{3,5}0.0.^{2,3}0^{5,6}$]-octane derivatives through [$2\pi+2\sigma$]-type reactions.[4]

The author investigated the photoreactions of 8-azatricyclo[3.2.1.$0^{2,4}$]oct-6-ene derivatives, which were analogous to the above bicyclo- and tricyclocompounds, to afford azabishomobenzene derivatives through [$2\pi+2\sigma$]-type migration reactions between C–N bond and olefin moieties. Here the results will be reported.

8-Azatricyclo[3.2.1.0$^{2,4}$]oct-6-ene derivatives (**4**) were prepared by addition reactions of 1-substituted pyrroles (**3**) with 3-cyanocyclopropene (**2**), which was generated *in situ* by Alder–Rickert cleavage of the adduct (**1**) of 7-cyano-1,3,5-cycloheptatriene and dimethyl acethylenedicarboxylate.[5] Irradiation of a solution of **4a** in dry ether with a high-pressure mercury lamp resulted in a quantitative recovery of **4a**. However the reaction using a low-pressure mercury lamp afforded an azabishomobenzene derivative (**5a**) in 36% yield. The analogous reactions using **4b**–**4d** gave the corresponding products (**5b**–**5d**) in 18, 11, and 20% yields, respectively. On the other hand, the reaction of **4e** afforded only a polymeric material. However, when the reaction was followed by NMR, the corresponding product (**5e**) was observed. Compound **5e** could not be isolated in a pure form, since it easily decomposed under the reaction conditions and during the purification process. The reaction of **4f** under the same reaction conditions did not afford any product, but **4f** was recovered quantitatively.



**a**: R = COPh,
**b**: R = COC$_6$H$_4$(*p*-OMe),
**c**: R = COC$_6$H$_4$(*p*-Me),
**d**: R = COC$_6$H$_4$(*p*-Cl),
**e**: R = Ph,
**f** : R = CO$_2$Me

Fig. 1.

The structural elucidation of 5 were accomplished on the basis of their spectral, especially NMR, properties.[6] The relation of the protons was determined by means of double resonace technique in $^1$H NMR specra. The coupling constant values (4.8 Hz) between the vicinal protons $H_a$ and $H_b$/$H_c$ on the cyclopropane moiety showed the *trans*-configuration of these protons.[7] The *syn*-configuration of the cyclopropane and the azirizine ring moieties was also confirmed by the coupling constant values (7.6 Hz) between $H_c$ and $H_d$. In the IR spectra the absorption of the cyano and the amido groups appeared at *ca.* 2240 and 1640 $cm^{-1}$, respectively. These facts supported the structures of 5 to be as shown in Fig. 1.

The above mentioned results showed that only the tricyclocompounds (**4a–e**) having aryl groups afforded the azabishomobenzene derivatives (5), suggesting that the reaction proceeded through the $\pi-\pi^*$ excited state on the aryl groups. In the UV spectra, **4a–e** having aryl groups possess the maximum absorptions, which could be assigned to $\pi-\pi^*$ transion at near 254 nm (**4a**; 221 nm (log $\varepsilon$, 4.10), **4b**; 254 (3.94), **4c**; 230 (3.97), **4e**; 240 (4.06)). Contray to this, the corresponding absorption of **4f** was very small. This fact supports the above consideration.

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4) H. Prinzbach, W. E. Berbach, M. Klaus, and G. V. Veh, *Chem. Ber.*, 101, 4066 (1968).

5) K. Saito, S. Isobe, K. Ito, S. Kagabu, and K. Takahashi, *Chem. Lett.*, **1989**, 1541; K. Saito, K. Ito, and K. Takahashi, *Heterocycles*, 29, 2135 (1989); 31, 1895 (1990). Physical data of new compounds: **4b**: Colorless oil. HRMS: m/z 250.1116. Calcd for $C_{16}H_{14}N_2O$: m/z 250.1106. MS m/z (rel intensity): 250 ($M^+$, 100), 234 (47), 215 (28). IR (oil): 2930, 2240, 1640 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 2.05 (d, 2H, $H_a$ and $H_{a'}$), 2.41 (s, 3H, Me), 2.52 (t, $H_b$), 4.84 (bs, $H_c$), 5.25 (bs, $H_{c'}$), 6.50 (bs, $H_d$), 6.80 (bs, $H_{d'}$), 7.20–7.40 (m, 4H, aromatic protons). Coupling constants in Hz; $J_{ab}$= $J_{a'b}$= 2.8 Hz. **4c**: Colorless oil. HRMS: m/z 266.1053. Calcd for $C_{16}H_{14}N_2O_2$: m/z 266.1054. MS m/z (rel intensity): 266 ($M^+$, 100), 200 (31), 148 (27). IR (oil): 2920, 2230, 1630 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 2.05 (d, 2H, $H_a$ and $H_{a'}$), 2.54 (t, $H_b$), 3.87 (s, 3H, Me), 4.86 (bs, $H_c$), 5.22 (bs, $H_{c'}$), 6.50 (bs, $H_d$), 6.80 (bs, $H_{d'}$), 6.90–7.50 (m, 4H, aromatic protons). Couping constants in Hz; $J_{ab}$= $J_{a'b}$= 2.8

Hz. **4d**: Colorless oil. HRMS: m/z 270.0573. Calcd for $C_{15}H_{11}N_2OCl$: m/z 270.0565. MS m/z (rel intensity): 270 ($M^+$, 11), 227 (100). IR (oil): 2240, 1630 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 2.07 (d, 2H, $H_a$ and $H_{a'}$), 2.48 (t, $H_b$), 4.68 (bs, $H_c$), 5.20 (bs, $H_{c'}$), 6.48 (bs, $H_d$), 6.82 (bs, $H_{d'}$), 7.42 (m, 4H, aromatic protons). Coupling constants in Hz; $J_{ab}$= $J_{a'b}$= 3.3 Hz.

6) Physical data of 5 were as follows: **5a**: Colorless oil. HRMS: m/z 236.0948. Calcd for $C_{15}H_{12}N_2O$: m/z 236.0949. MS m/z (rel intensity): 236 ($M^+$ 41), 207 (18), 133 (39), 105 (100). IR (oil): 2930, 2240, 1640 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 1.02 (dd, $H_a$), 2.30 (ddd, $H_b$), 2.46 (ddd, $H_c$), 4.67 (dd, $H_d$), 5.04 (dd, $H_e$), 5.97 (dd, $H_f$), 6.75 (dd, $H_g$), 7.40–8.00 (m, 5H, aromatic protons). Coupling constants in Hz; $J_{ab}$= 4.8, $J_{ac}$= 4.8, $J_{bc}$= 8.8, $J_{bg}$=4.8, $J_{cd}$= 7.6, $J_{de}$= 9.2, $J_{ef}$= 4.8, $J_{fg}$= 10.8. $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.9, 21.9, 26.3, 58.9, 74.0, 121.5, 127.8, 128.4, 128.6, 130.3, 131.2, 131.9. **5b**: Colorless oil. HRMS: m/z 250.1098. Calcd for $C_{16}H_{14}N_2O$: m/z 250.1105. MS m/z (rel intensity): 250 ($M^+$, 100), 204 (71), 148 (76). IR (oil): 2920, 2240, 1630 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 1.02 (dd, $H_a$), 2.28 (ddd, $H_b$), 2.42 (s, 3H, Me), 2.45 (ddd, $H_c$), 4.65 (dd, $H_d$), 5.03 (dd, $H_e$), 5.98 (dd, $H_f$), 6.25 (dd, $H_g$), 7.20–7.90 (m, 4H, aromatic protons). Coupling constants in Hz; $J_{ab}$= 4.8, $J_{ac}$= 4.8, $J_{bc}$= 8.8, $J_{bg}$= 4.8, $J_{cd}$= 7.0, $J_{de}$= 9.8, $J_{ef}$= 5.3, $J_{fg}$= 10.0. $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.9, 21.6, 22.0, 26.4, 58.9, 73.7, 121.7, 127.9, 128.3, 129.1, 129.2, 130.2. **5c**: Colorless oil. HRMS: m/z 266.1056. Calcd for $C_{16}H_{14}N_2O_2$: m/z 266.1055. MS m/z (rel intensity): 266 ($M^+$, 40), 148 (44), 135 (100). IR (oil): 2950, 2240, 1640 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 1.02 (dd, $H_a$), 2.28 (ddd, $H_b$), 2.45 (ddd, $H_c$), 3.87 (s, 3H, Me), 4.63 (dd, $H_d$), 5.00 (dd, $H_e$), 5.96 (dd, $H_f$), 6.44 (dd, $H_g$), 6.90–7.95 (m, 4H, aromatic protons). Coupling constants in Hz; $J_{ab}$= 4.8, $J_{ac}$= 4.8, $J_{bc}$= 8.8, $J_{bg}$= 4.8, $J_{cd}$= 6.6, $J_{de}$= 9.6, $J_{ef}$= 4.8, $J_{fg}$= 9.6. $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.9, 22.0, 26.3, 55.5, 58.4, 74.1, 113.8, 113.9, 121.5, 129.9, 130.4, 130.5. **5d**: Colorless oil. HRMS: m/z 270.0589. Calcd for $C_{15}H_{11}N_2OCl$: m/z 270.0559. MS m/z (rel intensity): 270 ($M^+$, 7), 141 (41), 139 (100), 111 (35). IR (oil): 2240, 1640 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 1.00 (dd, $H_a$), 2.31 (ddd, $H_b$), 2.46 (ddd, $H_c$), 4.66 (dd, $H_d$), 5.05 (dd, $H_e$), 5.95 (dd, $H_f$), 6.45 (dd, $H_g$), 7.30–8.00 (m, 4H, aromatic protons). Coupling constants in Hz; $J_{ab}$= 4.6, $J_{ac}$=5.3, $J_{bc}$= 8.5, $J_{bg}$= 4.9, $J_{cd}$= 6.7, $J_{de}$= 9.4, $J_{ef}$= 4.9, $J_{fg}$= 10.7. $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.9, 26.3, 29.7, 59.0, 74.1, 121.5, 128.8, 128.9, 129.3, 129.7, 130.3.

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