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Isolation and Photolysis of 2,3-Bis(diphenylmethylene)-5,6-diazaspiro[3.4]octa-5,7-dien-1-ones

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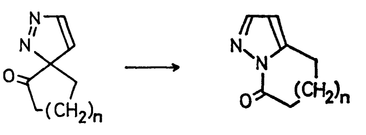
Synopsis. Pyrazole given in the title was prepared by the reaction of 2-diazo-3,4-bis(diphenylmethylene)cyclobutanone with acetylenes. Photolysis of the pyrazole afforded 1,2-dihydro-3*H*-benzo[*a*]cyclobuta[*c*]cycloheptan-1-one.

All attempts to isolate 3-acyl-3*H*-pyrazole (**1**) have been unsuccessful because of its easy isomerization to *N*-substituted pyrazole (**2**).[1–3] We report the isolation of the title pyrazole (**4**) and its photochemical conversion into 1,2-dihydro-3*H*-benzo[*a*]cyclobuta[*c*]cycloheptan-1-one (**8**).



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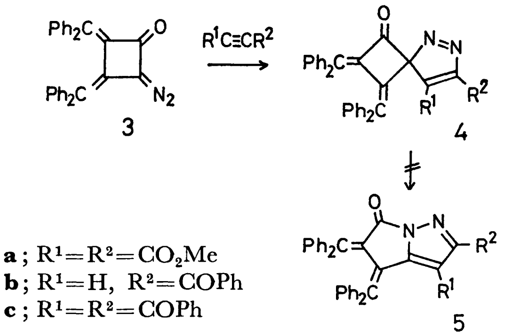
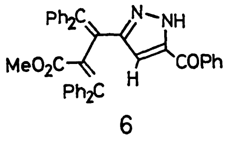
Treatment of 2-diazo-3,4-bis(diphenylmethylene)-cyclobutanone (**3**) with dimethyl acetylenedicarboxylate, benzoylacetylene, and dibenzoylacetylene afforded 7,8-bis(methoxycarbonyl)- (**4a**, 78%), 7-benzoyl- (**4b**, 82%), and 7,8-dibenzoyl-2,3-bis(diphenylmethylene)-5,6-diazaspiro[3.4]octa-5,7-dien-1-one (**4c**, 80%), respectively. The formation of 3*H*-pyrazole by 1,3-dipolar cycloaddition of diazo ketone to acetylene is well established.[1,4,5] The structure of **4b** was characterized by the following experiment. Treatment of **4b** with $ZnCl_2$ in MeOH afforded 3-(1-diphenylmethylene-2-methoxycarbonyl-3,3-diphenyl-2-propenyl)-5-benzoyl pyrazole (**6**, 90%).



a; $R^1=R^2=CO_2Me$
b; $R^1=H$, $R^2=COPh$
c; $R^1=R^2=COPh$

Scheme 1.



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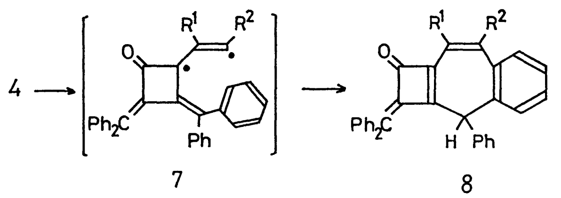
Frank-Neumann and Buchecker[2] reported that the easy thermal conversion of **1** into **2** is due to the stability of **2** bearing heteroaromatic pyrazole ring. However, no analogous thermal conversion of **4** into **5** took place even in boiling xylene. The contrast would be due to destabilization of **5** which may not be planar because of ring strain and/or steric repulsion between the two diphenylmethylene groups. This is supported by examination of molecular models.

In contrast to the photochemical conversion of 3*H*-pyrazole into cyclopropane,[6,7] photolysis of **4a**—**c** afforded 8,9-bis(methoxycarbonyl)- (**8a**), 8-benzoyl- (**8b**), and 8,9-dibenzoyl-3-phenyl-2-diphenylmethylene-1,2-dihydro-3*H*-benzo[*a*]cyclobuta[*c*]cycloheptan-1-one (**8c**), respectively, in quantitative yields. The reaction sequence can be formulated by successive cyclization and hydrogen migration of the initially formed biradical intermediate (**7**),[8,9] as shown in Scheme 2.



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Scheme 2.

Experimental

All the melting points are uncorrected. Photolysis was carried out at room temperature under N_2, using light from a 100-W high-pressure mercury lamp (Riko Kagaku Sangyo Co.) The IR, UV, and NMR were measured in KBr disk, $CHCl_3$, and $CDCl_3$, respectively. The mass spectra were obtained with an ionization energy of 75 eV.

Cycloaddition of 3 to Acetylenes. A solution of **3**[10] (3 mmol) and an equimolar amount of the acetylenes in benzene (50 ml) was kept at 0 °C for 1 day. Crude crystals remaining after evaporation of the solvent were recrystallized from AcOEt to give cycloadduct as red prisms.

4a: 78%; mp 158—159 °C. IR: 1765, 1740 cm^{-1}; λ_{max}: 335 (22600), 415 nm (ε, 5000); NMR: δ=7.7—6.5 (m, 20H), 3.90 (s, 3H), 3.39 (s, 3H); MS: *m/e* (rel intensity) 566 (M^+, 32), 507 (M^+-CO_2Me, 56), 479 (100). Found: C, 76.15; H, 4.78; N, 4.92%. Calcd for $C_{36}H_{26}O_5N_2$: C, 76.31; H, 4.63; N, 4.94%.

4b: 82%; mp 147—148 °C. IR: 1750, 1640 cm^{-1}; λ_{max}: 325 (25800), 427 nm (ε, 5500); NMR: δ=8.5—8.2 (m, 2H), 7.4—6.5 (m, 23H), 6.06 (s, 1H); MS: *m/e* (rel intensity) 554 (M^+, 25), 449 (M^+-PhCO, 10), 105 ($PhCO^+$, 100). Found: C, 84.30; H, 4.98; N, 5.13%. Calcd for $C_{39}H_{26}O_2N_2$: C, 84.45; H, 4.73; N, 5.05%.

4c: 80%; mp 124—125 °C. IR: 1755, 1660 cm^{-1}; λ_{max}: 320 (26000), 432 nm (ε, 5000); NMR: δ=8.3—6.4 (m); MS:

m/e (rel intensity) 658 (M^+, 22), 553 (M^+-PhCO, 6), 105 ($PhCO^+$, 100). Found: C, 83.64; H, 4.72; N, 4.38%. Calcd for $C_{46}H_{30}O_3N_2$: C, 83.87; H, 4.59; N, 4.25%.

Formation of 6. A mixture of **4b** (555 mg, 1 mmol), $ZnCl_2$ (150 mg, 1.1 mmol), and MeOH (20 ml) was stirred at room temperature for 15 min. The reaction mixture was decomposed with dil HCl, and then extracted with benzene. Crude crystals remaining after evaporation of the solvent were recrystallized from MeCN to give **6** as pale yellow needles; 510 mg (90%); mp 176—177 °C. IR: 3350, 1715 cm^{-1}; λ_{max}: 252 (29800), 290 (22300), 335 nm sh (ε, 11000); NMR: δ=9.05 (br s, 1H), 7.9—6.7 (m, 25H), 6.43 (s, 1H),[11] 3.35 (s, 3H). Found: C, 81.62; H, 5.12%. Calcd for $C_{40}H_{30}O_3N_2$: C, 81.88; H, 5.15%.

Photolysis of 4. A solution of **4a** (1.13 g, 2 mmol) in MeOH (150 ml) was irradiated for 30 min. Crude crystals remaining after evaporation of the solvent were recrystallized from CH_2Cl_2–MeOH to give **8a** as colorless prisms in a quantitative yield; mp 273—273.5°C. IR: 1785, 1750, 1730 cm^{-1}; λ_{max}: 320 (14500), 343 nm (ε, 16600); NMR: δ= 7.7—6.4 (m, 19H), 5.10 (s, 1H), 3.80 (s, 3H), 3.08 (s, 3H); MS: *m/e* 538 (M^+). Found: C, 80.12; H, 4.86%. Calcd for $C_{36}H_{26}O_5$: C, 80.28; H, 4.87%.

Similar photolysis of **4b** and **4c** afforded **8b** and **8c**, respectively, in quantitative yields.

8b: Colorless prisms: mp 268—270 °C. IR: 1780, 1660 cm^{-1}; λ_{max}: 245 (25200), 329 nm (ε, 17200); NMR: δ=8.3—8.1 (m, 2H), 7.7—6.7 (m, 22H), 6.17 (s, 1H), 5.10 (s, 1H). Found: C, 88.76; H, 4.69%. Calcd for $C_{39}H_{26}O_2$: C, 88.95; H, 4.98%.

8c: Colorless prisms: mp 257—258 °C. IR: 1780, 1660 cm^{-1}; λ_{max}: 258 (30000), 330 nm (ε, 21600); NMR: δ=8.3—6.6 (m, 29H), 5.19 (s, 1H); MS: *m/e* 630 (M^+). Found: C, 87.37; H, 4.76%. Calcd for $C_{46}H_{30}O_3$: C, 87.59; H, 4.79%.

References

1) M. Franck-Neumann and C. Dietrich-Buchecker, *Tetrahedron Lett.*, **1976**, 2069.

2) M. Franck-Neumann and C. Buchecker, *Angew. Chem. Int. Ed. Engl.*, **12**, 240 (1973).

3) M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, **1972**, 937.

4) G. L. Closs and W. A. Boell, *Angew. Chem.*, **75**, 640 (1963).

5) A. C. Day and M. C. Whiting, *J. Chem. Soc., C*, **1966**, 1719.

6) C. Dietrich-Buchecker and M. Franck-Newmann, *Tetrahedron*, **33**, 751 (1977).

7) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y. (1971), p. 23.

8) G. Baum, R. Bernard, and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5307 (1967).

9) G. L. Closs and L. R. Kaplan, *J. Am. Chem. Soc.*, **91**, 2168 (1969).

10) K. Ueda, M. Igaki, and F. Toda, *Bull. Chem. Soc. Jpn.*, **49**, 3173 (1976).

11) The signal can be assigned to the C-4 proton of pyrazole nucleus on the basis of the study by Tensmeyer and Ainsworth: L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966).