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PHOTOREACTIONS OF 2,3-DIAZATETRACYCLO[5.3.1.$0^{4,11}$.$0^{6,8}$]UNDECA-2,9-DIENES ; THE RETRO-1,3-DIPOLAR CYCLOADDITIONS AND THE NITROGEN EXTRUSION REACTIONS[1)]

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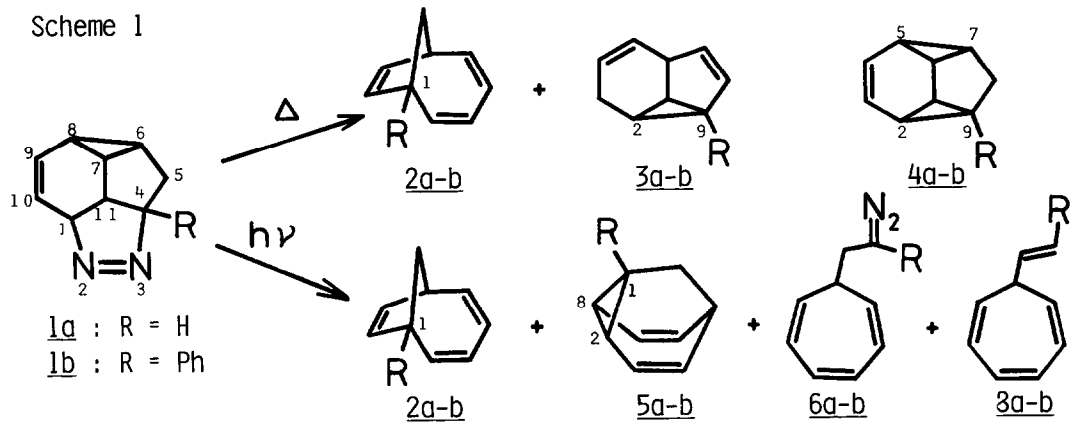
Summary : The photochemical reactions of tetracyclic azo compounds (1a-b) giving 5a-b and 8a-b *via* diazoethane derivatives (6a-b) were investigated in addition to the nitrogen extrusion reactions leading to tetracyclo[4.3.0.$0^{2,9}$.$0^{5,7}$]nonenes (4a-b).

The thermal and photochemical nitrogen extrusion reactions of cyclic azo compounds have been extensively studied as the most prospective methods for transient unstable species.[2)] For the purpose of preparation of tetracyclo[4.3.0.$0^{2,9}$.$0^{5,7}$]nonene[3)], the thermal and photochemical reactions of titled cyclic azo compounds (1a-b) were investigated. As will be reported separatedly,[4)] the thermolyses of 1a-b gave bicyclo[4.2.1]nonatrienes (2a-b) and tricyclo[4.3.0.$0^{2,9}$]nonadienes (3a-b). When the irradiations of 1a-b were carried out under various conditions, the tetracyclic hydrocarbons (4a-b) could not be detected directly but the formations of 2a-b, barbaralanes (5a-b) and diazoethane derivative (6b) were observed. These results are so different from the thermal behaviors of 1a-b that outline of the study is presented in this paper.

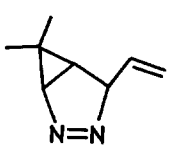
The cyclic azo compounds (1a-b) were synthesized by Bamford-Stevens reactions of 7-cycloheptatrienyl-acetaldehyde (7a) and -acetophenone (7b).[5)] When a solution of 1a in cyclohexane was irradiated with RUL-3500Å lamps, 2a (81 %), 5a (5 %) and 7-vinylcycloheptatriene (8a,trace) were obtained.[6)] A solution of 1b turned pink temporarily under similar condition. When the color was disappeared, the formations of 2b (71 %), 5b (9 %) and 7-styrylcycloheptatriene (8b, 3 %) were observed in the photolysate.[7)] The transient species with pink color was independently prepared when the Bamford-Stevens reaction of 7b was carefully performed under argon atmosphere at 50°. The solvent free diazo-1-phenyl-2-(7-cycloheptatrienyl)ethane (6b)[8)] shows a dark purple color : IR (oil) 2030 cm^{-1}; UV (cyclohexane) λ_{max}= 287.5 nm (ε 13,800), 512.1 nm (ε 20.6); ^{1}H-NMR (CCl_4) δ 2.19(1H, m), 2.75(2H, d, J = 8.5 Hz), 5.26(2H, d.d, J = 9.5, 3.5 Hz), 6.16(2H, m), 6.59(2H, m), 6.7-7.0(2H, m), 7.1-7.3(3H, m). The maximum yield

Scheme 1



(46 %) of the diazoethane derivative (6b) was obtained along with 2b (35 %), 5b (3 %) and 8b (0.5 %) by the irradiation of 1b using a monochromic light of 345 nm.[9] And the independently synthesized 6b afforded 2b, 5b and 8b upon the prolonged irradiation. Although the corresponding diazoethane derivative (6a) could not be detected by the irradiation of 1a, the formations of 5a and 8a suggest the similar photochemical transformation leading to 6a.[10]

The fact that the nitrogen-extruded, primary products (4a-b) were not detected on the photolyses even at -50°~ -78°C reflects the severely strained structure of tetracyclo[4.3.0.$0^{2,9}$.$0^{5,7}$]nonene. The formations of the diazoethane derivatives (6a-b) are of interest, because cyclic azo compounds are known to extrude the nitrogen molecule on electronic excitation.[11] This is an unusual example of retero-1,3-dipolar cycloaddition reaction that only one precedent was reported by Schneider on the irradiation of 9.[12] This unusual transformation of 1 leading to 6 was brought by the simultaneous C_1-N_2 and C_4-C_{11} bond scissions of the 2,3-diazatetracyclo[5.3.1.$0^{4,11}$.$0^{6,8}$]undecadiene system. The phenyl group of 6b is effective for the direct detection of the diazoalkane because of the low reactivety under the reaction conditions.



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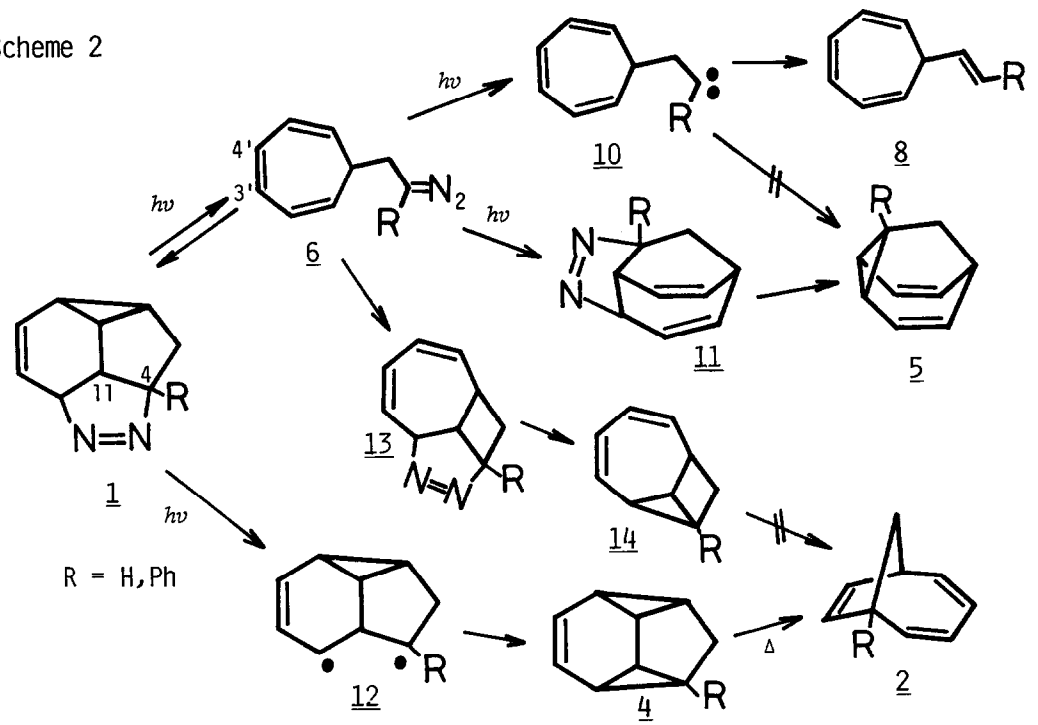
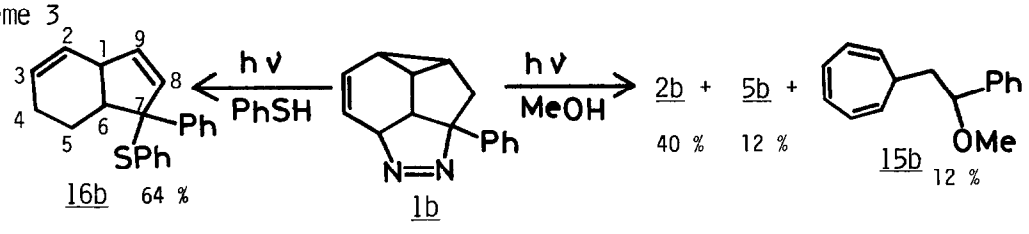
The reaction pathways leading to 2, 5 and 8 are summarized in Scheme 2. The carbene 10 would be a reasonable precursor for barbaralane 5 and cycloheptatriene 8. However, it was demonstrated by a quenching experiment for 10 using MeOH that barbaralane did not originate from the carbene but from the alternative precursor 11, i.e., the intramolecular 1,3-dipolar adduct of the diazoalkane 6. Namely, when 1b was irradiated in MeOH, the methanol adduct 15b[13] was obtained in 12 % yield in addition to 2b (40 %) and 5b (12 %). This experimental result indicates that the formation of cycloheptatriene 8b *via* the carbene intermediate 10 was quenched by the insertion to MeOH giving 15b. On the other hand, the formation of barbaralane 5b

Scheme 2



could not be quenched at all. Accordingly, the intramolecular 1,3-dipolar cycloadduct (11) of 6 using the $C_{3'}$-$C_{4'}$ double bond is proposed as a most plausible precursor for 5 even though it could not be detected. In addition, the fact that the S-H inserted product (16b)[15] was

Scheme 3



isolated in 64 % yield by the photoreaction of 1b in PhSH confirms the formation path of bicyclo[4.2.1]nonatriene (2) that 1 gives 1,3-diradical 12 followed by recombination and retro Diels-Alder reaction. An alternative route was already ruled out by our previous study including the syntheses of some derivatives of 14.[16]

The photochemical behaviors of the tetracyclic azo compounds (1a-b) giving diazoethane derivatives (6a-b) and tetracyclo[4.3.0.$0^{2,9}$.$0^{5,7}$]nonene (4a-b) are interesting in comparison with the thermal reactions. Further studies are in progress for the full elucidation.

References and Notes

1. Organic Photochemistry 57. Part 56: T. Kumagai, M. Ichikawa, and T. Mukai, Chem. Lett., 1981.
2. W. Adam and O.D. Lucchi, Angew. Chem. Int. Ed. Engl., 19, 762 (1980); H.E. Zimmerman, R.J. Boettcher, N.E. Buehler, G.E. Keck, and M.G. Steinmetz, J. Am. Chem. Soc., 98, 7680 (1976); B.M. Trost and R.M. Cory, ibid., 93, 5573 (1971); N.J. Turro, C.A. Renner, W.H. Waddell, and T.J. Katz, ibid., 98, 4320 (1976).
3. H. Tsuruta, T. Kumagai, and T. Mukai, J. Syn. Org. Chem. Jpn., 32, 496 (1974) and references therein; R.C. De Selems , J. Am. Chem. Soc., 96, 1967 (1974).
4. Thermal reactions of 1a-b will be reported in a separated paper.
5. Compound 1a : colorless needles, mp 48.0-48.5°C; UV(cyclohexane) λ_{max}= 341.5 nm (ε 212). Compound 1b : colorless needles, mp 72.0-72.5°C; UV(cyclohexane) λ_{max}= 334.2 nm (ε 177).
6. Products 2a, 5a and 8a were synthesized independently; 2a and 5a; H. Tsuruta, K. Kurabayashi, and T. Mukai, Tetrahedron Lett., 3775 (1967), 8a; H. Tsuruta, T. Kumagai, T. Mukai, Chem. Lett., 981 (1972).
7. Product 2b: IR(oil) 3055,3020,2955,1600,1490cm^{-1} ; NMR(CCl_4) δ 1.72(1H,d,J= 11.5Hz), 1.85 (1H,d.d,J=11.5, 6.5Hz), 3.22(1H,m), 5.12(1H,d.d,J=5.5, 2.4Hz), 5.40(1H,d,J=5.5Hz), 5.8-6.4(4H,m), 7.2-7.5(5H,m); UV(cyclohexane) λ_{max}=268.4 nm (ε 4,090), 259.3 nm (ε 4,410). Product 5b: IR(oil) 3045,2940,2855,1620,1600,1495,1445 cm^{-1}; NMR(CCl_4) δ 1.31(2H,d,J=3.0 Hz), 2.40-2.90(3H,m), 5.4-6.0(4H,m), 7.1-7.6(5H,m); UV(cyclohexane) λ_{max}= 230 nm (ε 8,740, sh.). Products 2b, 5b and 8b were isolated by column chromatography on SiO_2. Styrylcycloheptatriene (8b) was synthesized by Grignard reaction of 7-methoxycycloheptatriene.
8. Compound 6b is stable at room temperature in a degassed solution but labile under light and with air.
9. Hitachi MPF-4 Fluorescence Spectrometer was used as a source of the monochromic light.
10. It is known that bicyclo[4.2.1]nonatrienes isomerize to barbaralanes on irradiation; H. Tsuruta, T. Kumagai, and T. Mukai, Chem. Lett., 933 (1973) and references therein. However, the photoisomerizations of 2a-b giving 5a-b are completely ruled out under these reaction conditions.
11. H. Meier and K.-P. Zeller, Angew. Chem. Int. Ed. Engl., 16, 835 (1977); P.S. Engel, Chem. Rev., 80, 99 (1980) and references therein.
12. M. Schneider and B. Csacsko, Angew. Chem. Int. Ed. Engl., 16, 867 (1977).
13. Product 15b : IR(oil) 3075,3045,2945,1604,1495,1451,1395,1149 cm^{-1}; NMR(CCl_4) δ 1.6-2.2 (3H,m), 3.10(3H,s), 4.17(1H,d.d,J=7.4, 5.4Hz), 5.13(2H,d.d,J=9.0, 6.0Hz), 6.04(2H,m), 6.50(2H,t,J=3.0Hz) 7.1-7.4(5H,m).
14. H.F. Schaefer, Acc. Chem. Res., 12, 288 (1979).
15. Product 16b : IR(oil) 3060,3030,2945,1602,1586,1495,1480,1447,1440 cm^{-1}; NMR($CDCl_3$) δ 2.19(H_{5a},d.d.d.d), 2.44(H_{4a},d.d.d.d), 2.59(H_{5b},d), 2.80(H_{4b},d.d.d.d), 3.12(H_6,d.d.d.d), 3.99(H_1,d.d.d.d.d.d), 5.48(H_3,d.d.d.d), 5.60(H_2,d.d.d.d), 5.81(H_9,d.d.d.d), 6.00(H_8,d), 7.1-7.6(Ph), $J_{1,2}$=5.0, $J_{1,3}$=1.0, $J_{1,5a}$=1.0, $J_{1,6}$=4.0, $J_{2,3}$=12.8, $J_{2,4a}$=1.2, $J_{2,4b}$=2.4, $J_{2,6}$=1.2, $J_{3,4a}$=5.4, $J_{3,4b}$=2.4, $J_{4a,4b}$=18.8, $J_{4a,5a}$=2.4, $J_{5a,5b}$=12.4, $J_{5a,6}$=8.4, $J_{6,9}$= 2.4, $J_{8,9}$=5.5, $J_{1,4a}$=1.2. $J_{1,4b}$=2.4 Hz
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