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# PHOTOREACTIONS OF 8-METHYLENE- AND 8-DICYANOMETHYLENE-TRICYCLO[3.2.2.$0^{2,4}$]NON-6-ENE1)

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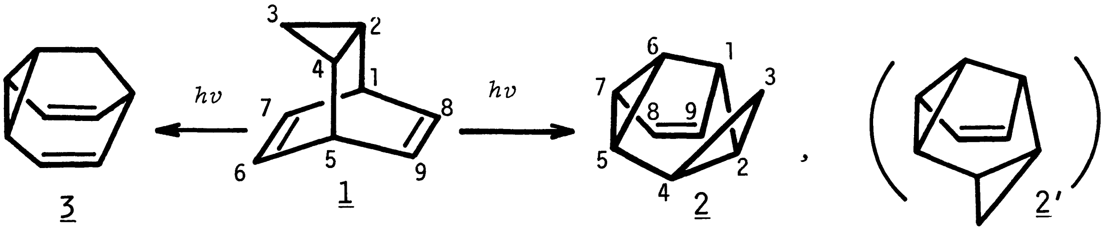
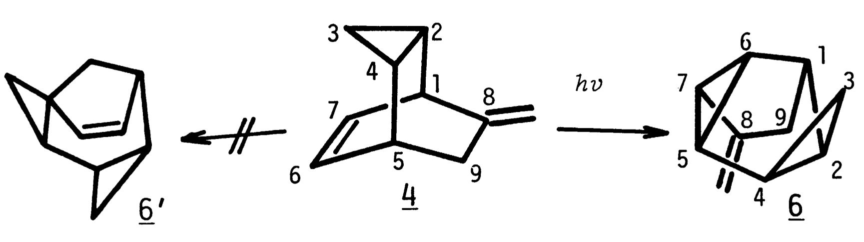
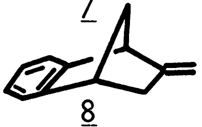
8-Methylenetricyclo[3.2.2.$0^{2,4}$]non-6-ene (4) gave 8-methylenetetracyclo-[4.3.0.$0^{2,4}$.$0^{5,7}$]nonane (6) on photolysis, whereas the dicyano-derivative (5) afforded two different-types of products, 8-dicyanomethylenetricyclo[3.3.1.$0^{2,4}$]-non-6-ene (9) and 9,9-dicycano-8-methylenetricyclo[3.2.2.$0^{2,4}$]non-6-ene (10).

In a previous paper, we reported the photoreaction of homobarrelene (1) giving homosemibullvalene (2) as the major product.2) This result stands in marked difference with the result reported by Daub and Schleyer3) who claimed that barbaralane (3) is the sole product. In addition to studying the photochemistry of 1, we have done a comparative study with 8-methylenetricyclo[3.2.2.$0^{2,4}$]non-6-ene (4) and its dicyano-derivative (5). Several structural features present in 4 and 5 led us to investigate their photochemistry. Since the 1,4-diene chromophores of 4 and 5 have a different geometry from that of 1, these compounds might be affected in the efficiencies of the photoreactions or show different photochemical behavior.4) With the dicyano-derivative (5), a charge-transfer interaction between the dicyano-substituted double bond and either the cyclopropane ring or the $C_6$-$C_7$ double bond is anticipated. The CT-interaction in 5 might influence the photochemical behavior.



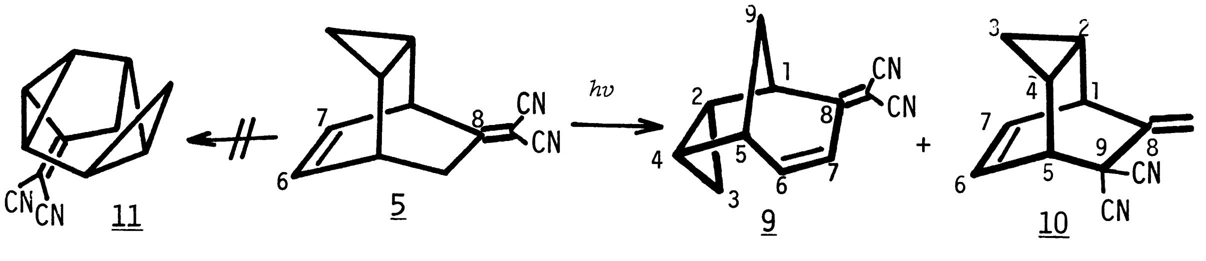
Compounds 4 5) and 5 6) were synthesized from the corresponding ketone by a Wittig reaction and a malononitrile condensation, respectively. The presence of any CT-interaction could not be determined in the absorption spectrum with certainty. When a 20 % acetone-benzene solution of 4 was irradiated with RUL-3000Å lamps using a quartz vessel, 8-methylenetetracyclo[4.3.0.$0^{2,4}$.$0^{5,7}$] nonane (6), a normal di-π-methane rearrangement product, was obtained in 41 % yield. Irradiation of 4 in benzene gave again 6 in slightly lower yield (36 %) at a slower rate. In contrast, the direct irradiation of 4 in a cyclohexane solution with RUL-2537Å lamps gave only 1.3 % yield of 6 even after the prolonged irradiation. Compound 6 was a sole photoproduct of 4, and the formation of 6', other possible di-π-methane rearrangement product, could not be observed. Quantum yield for the formation of 6 was determined to be 0.036 in acetone-sensitized condition.[8)] On the other hand,





a value of 0.119 was obtained for the formation of 2 on the photolysis of homobarrelene (1). Compared with the photorearrangement of homobarrelene, the lower quantum efficiency for 6 can be attributed the free-rotor effect induced by the $C_8$-exo-double bond of 4. It is also of interest to compare the photoreaction of 4 with those of 5-methylenenorbornene (7) and its benzo-analogue (8).[9,10)] These structurally related compounds are reported to give the products by the direct irradiation more effectively, where 7 gives the normal di-π-methane rearrangement product and 8 isomerizes to the highly strained system like 6'. In contrast to these results, it is noteworthy that the sensitization by excited acetone or benzene is effective for the photoreaction of 4.

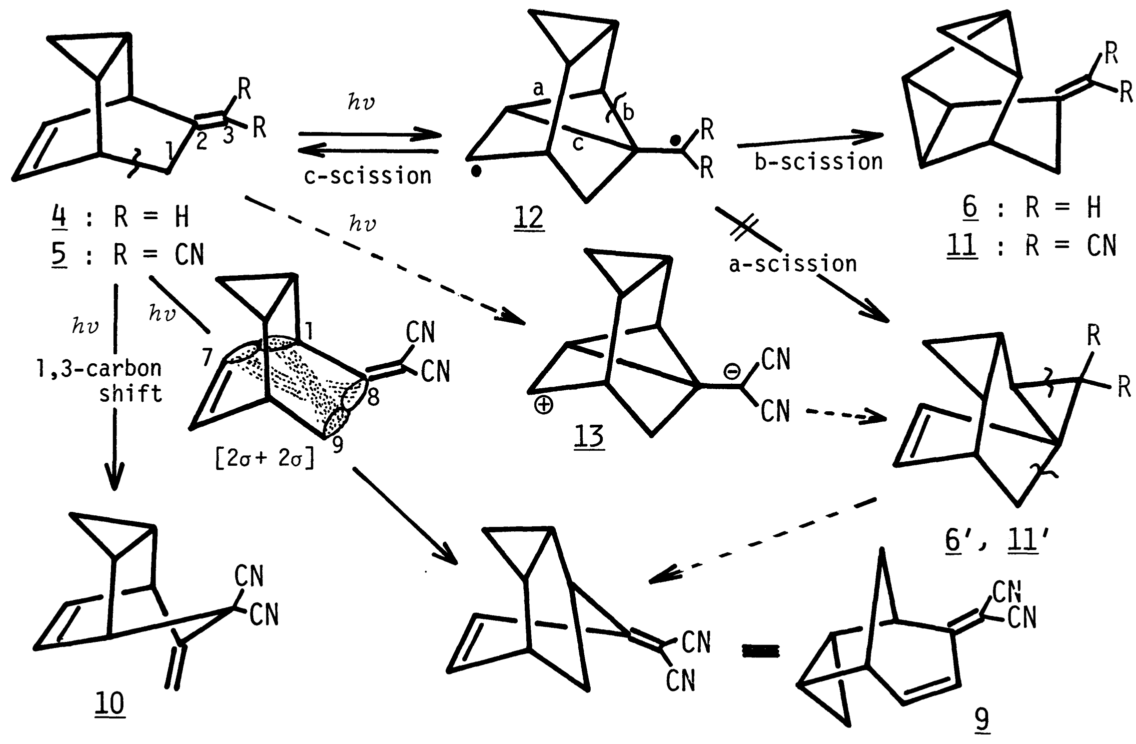
The irradiation of the dicyano derivative (5) brought about a dramatic change in the photochemistry. When 5 was irradiated under triplet-sensitized conditions, the expected product(11) was not formed. Contrary, the direct irradiation resulted in the formation of 9[11)] and 10.[12)]



They were isolated in 69 % and 5 % yield, respectively, after the irradiation of 5 in hexane. In a acetonitrile solution, the yield of 9 was decreased to 37 % and a significant increase of 10 (18 %) was accompanied upon the irradiation.

It was proved by control experiments that both photoproducts, 9 and 10, independently originated from the starting material, respectively. The formation of the major product (9) might suggest a novel photorearrangement involving the σ-bonds, because the $C_6$-$C_7$ double bond and 8-dicyanomethylene group of 5 seem to be kept as the $C_6$-$C_7$ double bond and 8-dicyanomethylene group in the molecular structure of 9. The formation of the minor product (10) is derived from a 1,3-carbon shift that has been sometimes observed in the photoreactions of dicyano-vinyl compounds.[13)]

Scheme 1



Plausible reaction pathways for 6, 9 and 10 are summarized in Scheme 1. Triplet-sensitized excitation of 4 gives diradical intermediate 12, in which cleavage of the b-bond occurs with great facility giving rise to the more stable product 6. On the other hand, the formation of 6', which induced from the a-scission, was inhibited by the molecular strain. In the photoreaction of the dicyano-derivative (5), no generation of the normal di-π-methane rearrangement product (11) supports that 12 is not suitable as the common intermediate for the photoreactions of 4 and 5.14) Instead of 11, the formations of 9 and 10 were observed on photolysis of 5. Especially, the photorearrangement of 5 leading to the tricyclic compound 9 is noteworthy. The product 9 might originate from 11' which is an alternative, constrained di-π-methane rearrangement product of 5. However, the formation of the precursor 11' has a disadvantage for its molecular strain. Even if 11' was derived from the different intermediate such as polar species 13, it seems to be incompatible with the phenomenon that the yield of 9 was depressed in acetonitrile solution. Now, a concerted [2σ + 2σ] process between the $C_1$-$C_7$ bond and the $C_8$-$C_9$ bond is proposed as another plausible route for the formation of 9, although there is no precedent for such transformation. The sharp contrast in the photochemical behaviors between 4 and 5 represents a noticeable polar effect in the photochemistry of cyclic 1,4-dienes and a new photochemical transformation leading to 9 has been uncovered.

## References

1) Organic Photochemistry 56. Part 55: T. Kumagai, K. Shimizu, H. Tsuruta, and T. Mukai, Tetrahedron Lett., 22, 4965 (1981).
2) T. Kumagai and T. Mukai, Chem. Lett., 1975, 1197.
3) J. Daub and P.v.R. Schleyer, Angew. Chem. Int. Ed. Engl., 7, 468 (1968).
4) H.E. Zimmerman and G.A. Epling, J. Am. Chem. Soc., 94, 8749 (1972); H. Morrison, Acc. Chem. Res., 12, 383 (1979).
5) Compound 4 : colorless oil; Mass m/e 132($M^+$), 91(base); IR(oil) 3050, 1665, 881 $cm^{-1}$; NMR($CCl_4$) δ 0-0.2(2H,m), 0.9-1.4(2H,m), 1.92($H_{9a}$,sp.d), 2.30($H_{9b}$,sp.d), 2.80($H_5$,m), 3.10($H_1$,m), 4.63(1H, m,$C=CH_2$), 4.73(1H,m,$C=CH_2$), 5.73(2H,m); UV(cyclohexane) λ 220 nm (ε 1,330), 254 nm (ε 11).
6) Compound 5 : colorless powder, mp 80-81°C; Mass m/e 182($M^+$), 39(base); IR(KBr) 3080, 2235, 1584 $cm^{-1}$; NMR($CDCl_3$) δ 0.3-0.5(2H,m), 0.9-1.4(2H,m), 2.38($H_{9a}$,d.d), 2.75($H_{9b}$,d.d), 3.20($H_5$,m), 4.15 ($H_1$,m), 5.76($H_7$,m), 6.13($H_6$,m); UV(cyclohexane) $\lambda_{max}$= 243.0 nm (ε 12,480).
7) Product 6 : colorless oil; Mass m/e 132($M^+$), 42(base); IR(oil) 3080, 1650, 867 $cm^{-1}$; NMR($CCl_4$) δ 0.15($H_{3b}$,t.d), 0.39($H_{3a}$,d.d.d), 0.77($H_4$,d.d.d), 1.35($H_2$,t.d), 1.7-1.9(3H,m), 2.2-2.3(1H,m), 2.65-2.95(2H,m), 5.02(2H,m), $J_{2,3a}$= 6.4, $J_{2,3b}$= 3.2, $J_{2,4}$= 6.4, $J_{3a,3b}$= 4.2, $J_{3a,4}$= 6.8, $J_{3b,4}$= 4.2 Hz.; UV(cyclohexane) λ 223 nm (sh.ε 1,780).
8) Quantum Yields were measured using 280 nm monochromic light in acetone-cyclohexane solution.
9) R.G. Weiss and G.S. Hammond, J. Am. Chem. Soc., 100, 1172 (1978).
10) F. Scully, J. Grutzner, and H. Morrison, J. Am. Chem. Soc., 95, 5100 (1973); H. Morrison and T. Nylund, J.C.S. Chem. Comm., 785 (1976); F. Scully, T. Nylund, F. Palensky, and H. Morrison, J. Am. Chem. Soc., 100, 7352 (1978); T. Nylund and H. Morrison, ibid., 100, 7364 (1978).
11) Product 9 : colorless oil; Mass m/e 182($M^+$), 41(base); IR(oil) 3045, 2220, 1590, 1549 $cm^{-1}$; NMR($CDCl_3$) δ 0.63($H_{3a}$,d.d.d), 0.87($H_{3b}$,t.d.d), 1.90($H_{9a}$,m), 2.0($H_4$,m), 2.1($H_2$,m), 2.27($H_{9b}$,d.t.d), 3.10($H_5$,m), 3.60($H_1$,m), 6.57($H_6$,d.d.d), 6.82($H_7$,d.d.d), $J_{1,7}$= 1.2, $J_{1,9a}$= 3.5, $J_{1,9b}$= 4.8, $J_{2,3a}$= 3.5, $J_{2,3b}$= 8.2, $J_{3a,3b}$= 6.6, $J_{3a,4}$= 3.4, $J_{3b,4}$= 8.2, $J_{3b,9b}$= 2.2, $J_{5,6}$= 6.7, $J_{5,7}$= 1.0, $J_{5,9a}$= 3.5, $J_{5,9b}$= 4.8, $J_{6,7}$= 9.6, $J_{9a,9b}$= 10.2 Hz.; UV(cyclohexane) $\lambda_{max}$= 291.0 nm (ε 15,400)
12) Product 10 : colorless needles, mp 89.0-90.5°C; Mass m/e 182($M^+$), 91(base); IR(KBr) 3055, 2240, 919 $cm^{-1}$; NMR($CDCl_3$) δ 0.32($H_{3a}$,d.t), 0.53($H_{3b}$,t.d), 1.26($H_2$,m), 1.50($H_4$,m), 3.48($H_1$,m), 3.61 ($H_5$,m), 5.41(1H,m,$C=CH_2$), 5.49(1H,d,J=1.0Hz,$C=CH_2$), 5.91($H_6$,d.d), 6.15($H_7$,d.d), $J_{1,2}$= 4.5, $J_{1,7}$ = 6.5, $J_{2,3a}$= 3.7, $J_{2,3b}$= 7.2, $J_{2,4}$= 7.0, $J_{3a,3b}$= 6.0, $J_{3a,4}$= 3.7, $J_{3b,4}$= 7.2, $J_{4,5}$= 3.6, $J_{5,6}$= 6.6, $J_{6,7}$= 8.0 Hz.; UV(cyclohexane) λ 250 nm (ε 63).
13) R.C. Cookson, V.N. Gogte, J. Hudec, and N.A. Mirza, Tetrahedron lett., 3955 (1965); R.F.C. Brown, R.C. Cookson, and J. Hudec, Tetrahedron, 24, 3955 (1968); R.C. Cookson, J. Hudec, and M. Sharma, J.C.S. Chem. Comm., 107, 108 (1971); R.C. Cookson and J.E. Kemp, ibid., 398 (1971).
14) H.E. Zimmerman, D. Armesto, M.G. Amezua, T.P. Gannett, and R.P. Johnson, J. Am. Chem. Soc., 101, 6367 (1979).

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