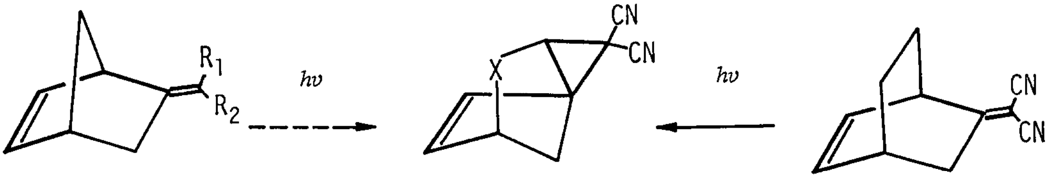
Tetrahedron Letters,Vol.26,No.47,pp 5771-5774,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

PHOTOREACTION OF 5-DICYANOMETHYLENEBICYCLO[2.2.1]HEPT-2-ENE[1]

Tsutomu Kumagai, Hisashi Honda, and Toshio Mukai*
Department of Chemistry, Faculty of Science, Tohoku University
Aramaki, Sendai 980, Japan

Abstract: Irradiation of 5-dicyanomethylenebicyclo[2.2.1]hept-2-ene induces new types of photoreactions, i.e., unprecedented skeletal rearrangement leading to 7,7-dicyano-6-methylenebicyclo[3.1.1]hept-2-ene, and novel 1,3-carbon shifts to bicyclo[3.2.0]- and bicyclo[4.1.0]heptene.

5-Methylenebicyclo[2.2.1]hept-2-enes (methylenenorbornenes) are classified as a typical bicyclic di-π-methane system which is expected to give tricyclic vinylcyclopropane derivatives under irradiation. The photorearrangements of 5-methylene- (1), 5-ethylidene- (1a), and 5-benzylidenebicyclo[2.2.1]hept-2-ene (1b) leading to tricyclo[3.2.0.0^{2,7}]heptane framework are reported by Hammond[2] and Goldschmidt[3], but the photoreaction of methylenenorbornene possessing electron withdrawing group has been still unknown. Recently, we reported the unexpected formation of constrained compound (3c) on the irradiation of 5-dicyanomethylenebicyclo[2.2.2]oct-2-ene (2c).[4] As an intriguing example of structure-photoreactivity relationship of these bicyclic 1,4-dienes involving dicyanomethylene group, we describe new skeletal rearrangements of 5-dicyanomethylenebicyclo[2.2.1]hept-2-ene (1c) in this paper.

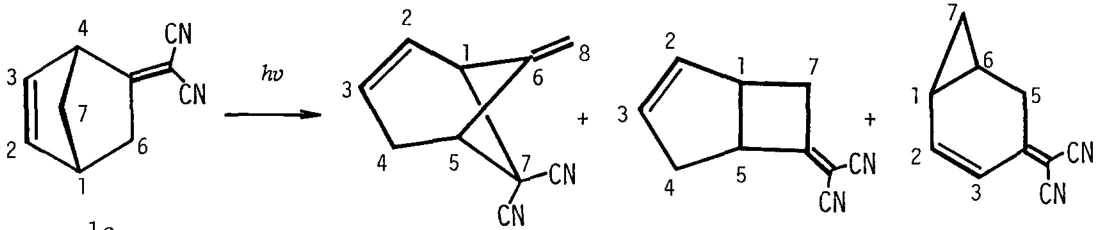


1,1a,1b: R_1,R_2= H,Me,Ph
1c : $R_1 = R_2$= CN

3c : X= $(CH_2)_2$
4c : X= CH_2

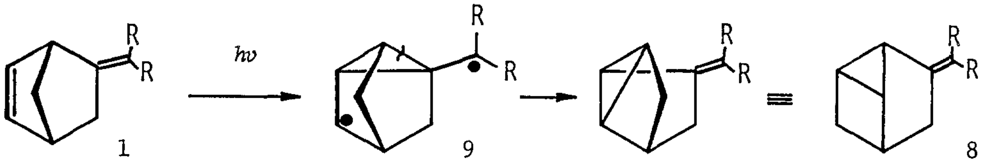
2c

Dicyanomethylene derivative 1c of norbornenone is synthesized from the ketone by Knoevenagel condensation and shows new absorption at 260-280 nm region originated from the interaction of 5-dicyanomethylene group with C_2-C_3 double bond.[5] When a hexane solution of 1c (5 x 10^{-3}mol/dm^3) was irradiated in a quartz vessel using RUL-2537Å lamps (120W) for 4 h, three products, 5, 6, and 7, were produced in 25 %, 27 %, and 18 % yield with the recovery of 12 %. The photoproducts were separated by column chromatography on silica gel and characterized to be bicyclo[3.1.1]heptene, bicyclo[3.2.0]heptene, and bicyclo-[4.1.0]heptene derivatives based on the following physical data : Product 5 : colorless plates, mp 85-85.5°C; IR(KBr) 2240, 1865, 1677, 922 cm^{-1}; NMR($CDCl_3$) 2.60(H_4), 2.74($H_{4'}$), 3.9-4.1(H_1, H_5), 5.48(H_8), 5.59($H_{8'}$), 5.91(H_3), 6.23(H_2), $J_{1,2}$= 1.0. $J_{1,3}$= 0.8, $J_{1,4}$= 2.0, $J_{1,8}$= 2.2, $J_{1,8'}$= 2.2, $J_{2,3}$= 5.8, $J_{2,4}$= $J_{2,4'}$= 2.2, $J_{3,4}$= $J_{3,4'}$= 2.2, $J_{3,5}$= 0.8, $J_{4,4'}$= 17.4, $J_{4,5}$= 2.2, $J_{4',5}$= 7.0, $J_{5,8}$= $J_{5,8'}$= 2.2, $J_{8,8'}$= 3.0 Hz; UV end absorption, ε = 290 at 220 nm in cyclohexane. Product 6: colorless oil; IR(oil) 2230, 1631, 715 cm^{-1}; NMR($CDCl_3$) 2.7-2.9(H_4, $H_{4'}$), 2.87(H_7), 3.36($H_{7'}$), 3.61(H_1), 3.94(H_5), 5.85-5.95(H_2, H_3), $J_{1,5}$= 8.1, $J_{1,7}$= 3.2, $J_{1,7'}$= 8.5, $J_{5,7}$= 4.2, $J_{5,7'}$= 1.6, $J_{7,7'}$= 19.2 Hz; UV λmax= 236.1 (ε 10000) nm in cyclohexane. Product 7: light yellow oil; IR(oil) 2220, 1598, 1570 cm^{-1}; NMR($CDCl_3$) 0.17(H_{7syn}), 1.45 (H_{7anti}), 1.6-1.9(H_1, H_6), 2.91(H_5), 3.42($H_{5'}$), 6.49(H_3), 7.12(H_2), $J_{1,2}$= 2.9, $J_{1,5}$= 2.8, $J_{1,5'}$= 0.5, $J_{1,7syn}$= 4.2, $J_{1,7anti}$= 6.7, $J_{2,3}$= 9.9, $J_{2,6}$= 2.9, $J_{2,5}$= 0.3, $J_{5,5'}$= 19.5, $J_{5,6}$= 2.8, $J_{6,7syn}$= 5.3, $J_{6,7anti}$= 9.3, $J_{7syn,7anti}$= 3.5 Hz; UV λmax= 314.5 (ε 12700) nm in cyclohexane. The novel photoproduct 5 can be characterized as 7,7-dicyano-6-methylenebicyclo[3.1.1]hept-2-ene possessing α-pinene structure from the spectral data.[6] Product 6 shows an analogous NMR pattern to the ketene-cyclopentadiene adduct synthesized independently,[7] and product 7 shows characteristic pattern due to cyclopropane protons.



1c 5 6 7

The photoreaction of 1c giving 5-7 is sharply contrasted with those of 5-methylenebicyclo[2.2.1]heptenes (1 and 1a-b) and norbornenones.[8] The normal di-π-methane rearrangement of this system is presupposed to give tricylo-



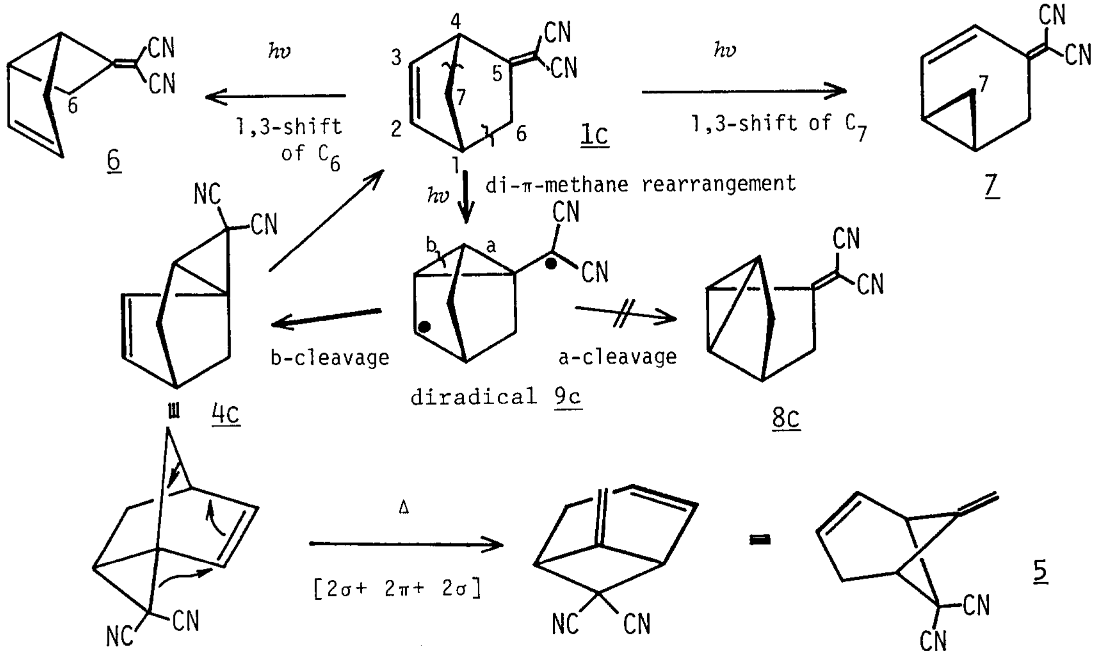
1 9 8

$[3.2.0.0^{2,7}]$heptane framework (8) via diradical intermediate. It is worthy of note that the unprecedented photorearrangement was observed by an introduction of cyano substituents. Controlled experiments showed that the three types of photoproducts were produced by independent pathways, respectively. The photoreaction of 1c leading to the products 6 and 7 are classified as 1,3-carbon shifts of the C_6- and the C_7-carbon, where the formation of 6 is little affected in polar media but the yield of 7 is decreased to 2 % in an acetonitrile solution.[9] The quantum yields determined in cyclohexane and acetonitrile are summarized in Table 1. The quantum efficiency for the formation of α-pinene derivative 5 is 0.034 in cyclohexane and the value is also decreased to 0.003 in acetonitrile indicating that the polar interaction in the excited molecule 1c does not contribute for the formation of 5 at all.

Table 1 Quantum yields for the photoreaction of 1c (25°C, 254nm).

Solvent	Formation of 5	Formation of 6	Formation of 7
Cyclohexane	0.034	0.043	0.016
Acetonitrile	0.003	0.035	0.002

Now, we wish to propose the reaction mechanism via tricyclic vinylcyclopropane 4c for the formation of 5 (Scheme-1). The structure of 4c can be related to the product 3c isolated by the irradiation of the corresponding bicyclo[2.2.2]octene 2c.[4] This compound 4c, which is produced by di-π-methane rearrangement, is much more constrained compared with tricyclo[$4.2.1.0^{1,3}$]-nonene 3c and the strain release results in the formation of α-pinene derivative 5.



Scheme-1. Reaction pathways of 5-dicyanomethylenebicyclo[2.2.1]hept-2-ene (1c)

In order to gain an additional information for this two-step mechanism, dicyanomethylenenorbornene 1c was irradiated in methylcyclohexane at 82°C and -80°C. Although the formations of 6 and 7 were not affected, the quntum yield for 5 was changed to 0.044 at 82°C and to 0.014 at -80°C. This temperature dependency refers to the intermediacy of 4c suggesting the intervention of thermal process, i.e., α-pinene 5 originates from the six electron reorganization of 4c. Attempts to detect the intermediate, 2,2-dicyanotricyclo[3.2.1.0^{1,3}]-octene (4c), at low temperature were unsuccessful in this stage.

The dicyano-substitution of methylenenorbornene suppresses the normal di-π-methane rearrangement leading to 8c and gives different photoproducts, 5, 6, and 7. These new photorearrangements were initially considered to be introduced by the charge transfer interaction, but the remarkable solvent effect supports that no polar interaction is effectively operated for these photochemical processes.[10] Further study is currently in progress to gain insight to the effect of cyano group and clarify the reaction mechanism.[11]

References and Notes

1. Organic Photochemistry 72. Part 71: Y. Yamashita, H. Yaegashi, and T. Mukai, Tetrahedron Lett., in press.
2. R.G. Weiss and G.S. Hammond, J. Am. Chem. Soc., 100, 1172 (1978).
3. Z. Goldschmidt and M. Shefi. J. Org. Chem., 44, 1604 (1979).
4. T. Kumagai, K. Murakami, H. Hotta, and T. Mukai, Tetrahedron Lett., 23, 4705 (1982).
5. Compound 1c: colorless oil, bp 83-86°C/0.05mmHg; IR(oil) 3060, 2995, 2220, 1615 cm^{-1}; ^{1}H NMR($CDCl_3$) 1.70(H_{7anti}, d), 2.0(H_{7syn}, d d t), 2.34(H_{6endo}, d d), 2.68(H_{6exo}, d d), 3.27(H_1, m), 3.93(H_4, d d), 6.06(H_3, d d d), 6.55 (H_2, d d); ^{13}C NMR($CDCl_3$) 38.8(C_7), 42.0(C_1), 51.6(C_6), 52.4(C_4), 79.3(C_8), 111.7(CN), 112.1(CN), 130.4(C_3), 143.1(C_2), 189.4(C_5) ; UV λmax = 235.9 (13400) and 265 (sh, 5700) nm in cyclohexane, λmax = 237.6 (15000) and 275 (sh, 3500) nm in acetonitrile.
6. The 9:2 mixture of 1c and 6,6-dicyano-5-methylenebicyclo[2.2.1]hept-2-ene was obtained by heating of compound 5 at 120°C for 5 h.
7. B.T. Brooks and G. Wilbert, J. Am. Chem. Soc., 63, 870 (1941).
8. K.N. Houk, Chem. Rev., 76, 1 (1976) and references cited therein.
9. The 1,3-carbon shift of C_7 looks like concerted process and that of C_6 might occur as a radical reaction.
10. The CT-interaction of dicyanomethylene group of 1c with the C_2-C_3 double bond is consider to accelerate the decay or decomposition process. A.B.B. Ferreira and K. Salisbury, J. Chem. Soc. Perkin II, 995 (1978).
11. This photoreaction leading to 4c is an example of small K controlled di-π-methane rearrangement but attempts to produce 8c under triplet sensitized conditions are unsuccessful. H.E. Zimmerman, D. Armesto, M.G. Amezua, T.P. Gannett, and R.P. Johnson, J. Am. Chem. Soc., 101, 6367 (1978).

(Received in Japan 13 August 1985)