

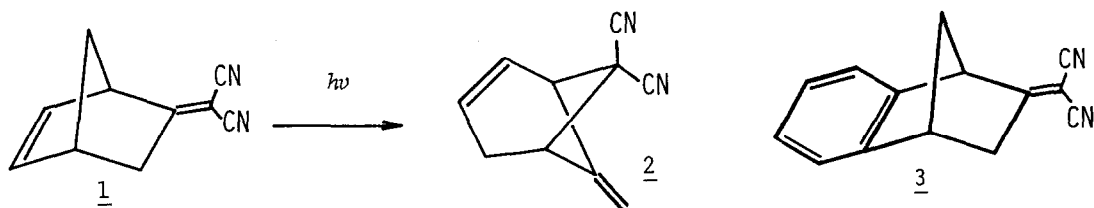
PHOTOREACTION OF 2-DICYANOMETHYLENE-1,2,3,4-TETRAHYDRO-1,4-METHANONAPHTHALENE¹

Tsutomu Kumagai, Takumi Nittono, Noriyuki Tanaka, and Toshio Mukai*

Department of Chemistry, Faculty of Science, Tohoku University
Sendai 980, Japan

Abstract: Upon irradiation, 2-dicyanomethylenebenzonorbornene 3 was converted into 1-dicyanomethylenebenzobicyclo[3.1.1]heptene 4. The reaction pathway is discussed with reference to the photoreaction of parent hydrocarbon.

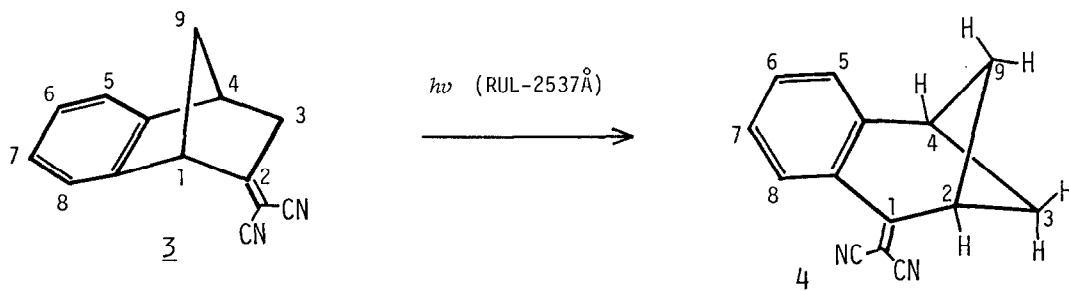
The interaction of two functionalities within an excited molecule has been of interest and extensively studied.² We have focused attention on the interaction of the dicyanomethylene group with a nonconjugated olefin in the photoreactions of norbornene and its related compounds possessing dicyanomethylene group as described in previous papers.^{1,3} For instance, the photoreaction of dicyanomethylenebicyclo[2.2.1]heptene 1 giving 6-methylenebicyclo[3.1.1]heptene 2 is best rationalized by the intermediacy of tricyclo[3.2.1.0^{1,3}]octene.¹ This result is in contrast to the reported photoreactions of 5-methylene- and 5-oxabicyclo[2.2.1]heptenes which lead to the tricyclo[3.2.0.0^{2,7}]heptane



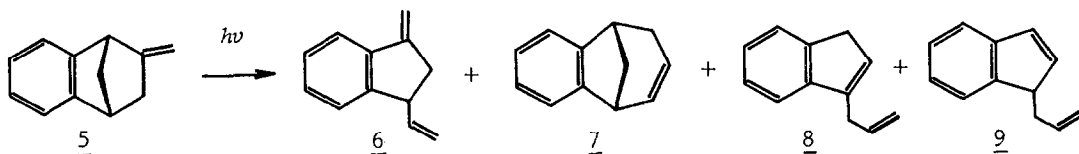
framework.⁴ In order to gain additional insight into the remarkable effect induced by cyano groups, we investigated the photoreaction of 2-dicyanomethylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (2-dicyanomethylenebenzonorbornene, 3⁵). In this paper the photochemical transformation to give benzobicyclo[3.1.1]heptene is described as new entry in the photochemistry of methylenebenzonorbornenes.⁶

When a hexane solution of 3 was irradiated in a quartz vessel using RUL-

2537Å lamps (120W) for 70 h, a photoisomer (mp 172-174°C) was obtained in 83 % yield as a single product. This photoproduct shows the following spectral data: Mass m/e 206 (M^+ , base); IR(KBr) 2220, 1548, 780, 755 cm^{-1} ; ^1H NMR(CDCl_3) 2.18($\text{H}_{3\text{syn}}, \text{H}_{9\text{syn}}$), 2.90($\text{H}_{3\text{anti}}, \text{H}_{9\text{anti}}$), 3.33(H_4), 4.08(H_2), 7.28(H_5), 7.43(H_6 or H_7), 7.52(H_7 or H_6), 8.74(H_8); ^{13}C NMR(CDCl_3) 40.9(C_4), 43.8(C_3 and C_9), 44.6(C_2), 75.0($\text{C}(\text{CN})_2$), 113.6(CN), 114.2(CN), 125.7($\text{C}_{8\text{a}}$), 126.4, 127.5, 128.0 ($\text{C}_5, \text{C}_6, \text{C}_7$), 134.1(C_8), 150.7($\text{C}_{4\text{a}}$), 174.6(C_1); UV $\lambda_{\text{max}} = 230.4$ (ϵ 6400), 300.0 (15900), 312.0 (17400), 328.6 (13500), 343.5 (12400) nm in cyclohexane. In the ^{13}C NMR spectrum two carbon atoms at C_3 - and C_9 -position show the same chemical shift value at 43.8 ppm. The four protons of C_3 - and C_9 -position are also observed as two signals at 2.18 and 2.90 ppm being in a reflection of the symmetrical structure.⁷ The high field signals are assigned to the outer protons ($\text{H}_{3\text{syn}}$ and $\text{H}_{9\text{syn}}$) and the low field signals to the inner protons ($\text{H}_{3\text{anti}}$ and $\text{H}_{9\text{anti}}$) in accordance with the magnetic anisotropy effect of a puckered cyclobutane ring.⁸ The coupling constants were determined by double resonance technique as follows: $J_{2,4} = 5.7$, $J_{2,3\text{anti}} = J_{2,9\text{anti}} = 5.7$, $J_{4,3\text{anti}} = J_{4,9\text{anti}} = 5.6$, $J_{3\text{syn},9\text{anti}} = J_{3\text{anti},9\text{syn}} = 0.1$, $J_{3\text{syn},3\text{anti}} = J_{9\text{syn},9\text{anti}} = 9.5$, $J_{3\text{syn},9\text{syn}} = 8.4$, $J_{5,6} = J_{6,7} = J_{7,8} = 7.6$, $J_{5,7} = J_{6,8} = 1.7$ Hz. The lack of coupling of the outer protons with the bridgehead protons is consistent with a consideration of a molecular model. As a consequence, the structure of this novel photoproduct was determined to be 1-dicyanomethylene-1,2,3,4-tetrahydro-2,4-methanonaphthalene (4-dicyanomethylene-2,3-benzobicyclo[3.1.1]heptene 4).

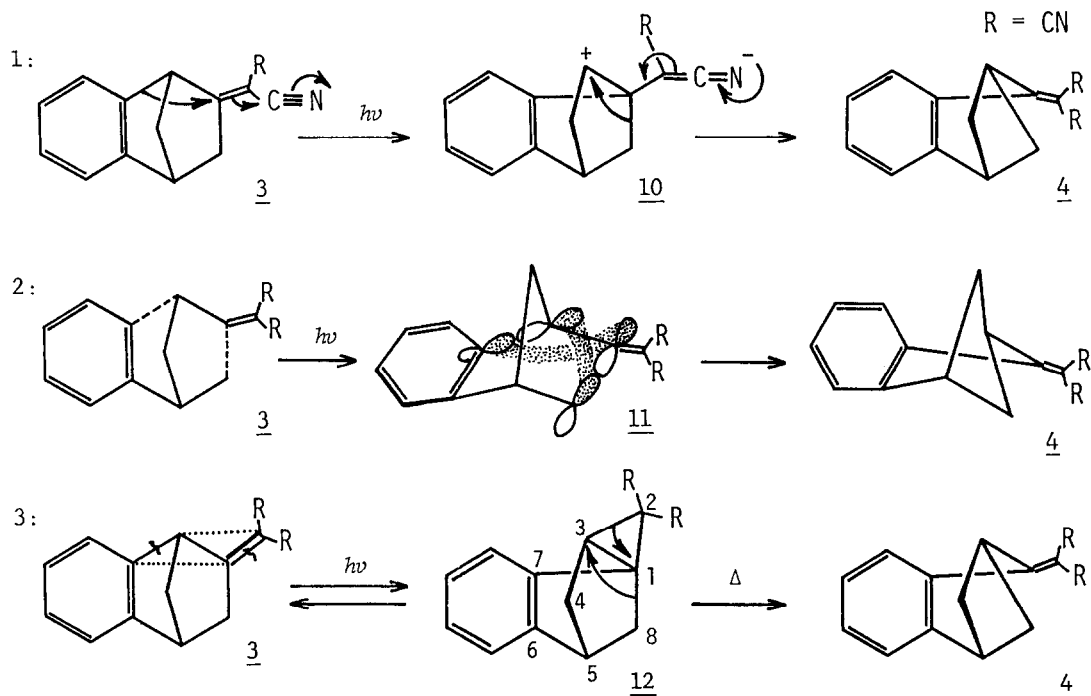


The formation of a benzobicyclo[3.1.1]heptene framework is noticeable as a hitherto unknown photoreaction in the benzonorbornene series where indane, benzobicyclo[3.2.1]octadiene, and indene derivatives 6-9 are known as isolable



products under similar photolysis conditions.⁹ This unprecedented photoreaction, which can be classified as a 1,2-carbon migration of dicyanomethylene group, might be explained by the three different pathways, i.e., an ionic reac-

tion path (mechanism-1), a concerted $[2\sigma+2\sigma]$ process (mechanism-2), and a two step reaction involving a di- π -methane rearrangement (mechanism-3).



Among them, the ionic intermediate 10 can be eliminated from the reaction pathway because of the inconsistency with solvent effect, i.e., the yield of 4 diminished to 16 % and the quantum yield for 4 is also decreased to 0.0016 in acetonitrile, while the value of 0.0023 is observed in cyclohexane. The concerted reorganization (mechanism-2) is attractive for this new photorearrangement, but the difference induced by dicyano-substitution seems to be difficult to explain. Therefore, we wish to propose the two step mechanism via 6,7-benzotricyclo[3.2.1.0^{1,3}]octene 12 (mechanism-3). The discrepancy between the photoreactions of 3 and 5 should be attributable to the cyano-substitution on the cyclopropane ring of intermediate that makes the $\text{C}_1\text{-C}_3$ bond strong as a good π -acceptor.¹⁰ The $\text{C}_1\text{-C}_3$ bond fission is consequently inhibited and the cleavage of $\text{C}_2\text{-C}_3$ bond leads instead to the formation of 4. The highly strained intermediate 12 seems to regenerate the starting material competitively. This would account for the low quantum efficiency. In addition, when 6 was irradiated at 65°C, the reaction efficiency was enhanced by a factor of 1.5 suggesting that the following rearrangement of 12 to 4 is thermal process.

It is known that the charge-transfer interaction from exo-double bond to a condensed benzene ring plays an important role in the photochemistry of methylenebenzonorbornenes.¹¹ Introduction of a cyano group on the exo-double bond is expected to induce the electronic interaction in a reverse direction. It is

worthy of note that the dicyanomethylene derivative 3 gives rise to the di- π -methane rearrangement to 12 in an ordinary course. This result suggests that polar interactions do not predominantly control the photoreaction of methylenebenzonorbornenes. On the other hand, the chemical property of the initial photoproduct 12 is directly affected by cyano groups to induce the selective formation of benzobicyclo[3.1.1]heptene.¹² The photo-induced rearrangement of 3 leading to 4 is considered to be a useful procedure for the preparation of this molecular frame. Further work is in progress with the related systems.

References and Notes

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5. Compound 3: colorless needles, mp 73.5-75°C; IR(KBr) 2235, 1620 cm^{-1} ; ^1H NMR(CDCl_3) 2.00($\text{H}_{9\text{anti}}$), 2.26($\text{H}_{9\text{syn}}$), 2.45 ($\text{H}_{3\text{endo}}$), 2.88($\text{H}_{3\text{exo}}$), 3.68 (H_4), 4.40 (H_1), 7.0-7.4(H_{5-8}), $J_{1,3\text{syn}} = 1.9$, $J_{1,3\text{anti}} = 1.6$, $J_{3\text{exo},3\text{endo}} = 17.7$, $J_{3\text{exo},4} = 3.5$, $J_{3\text{endo},9\text{syn}} = 3.6$, $J_{4,9\text{syn}} = 3.8$, $J_{4,9\text{anti}} = 1.6$, $J_{9\text{exo},9\text{endo}} = 9.8$ Hz; ^{13}C NMR(CDCl_3) 40.6(C_9), 43.1(C_4), 51.9(C_3), 54.0(C_1), 80.3 ($=\text{C}(\text{CN})_2$), 111.7(CN), 121.9, 123.0, 127.4, 128.1 (C_{5-8}), 139.6($\text{C}_{8\text{a}}$), 147.1 ($\text{C}_{5\text{a}}$), 187.8(C_2); UV $\lambda_{\text{max}} = 232.2$ (ϵ 12400), 243.6 (11500), 262.2 (8000), 283.7 (4600) nm in cyclohexane, $\lambda_{\text{max}} = 234.0$ (13300), 260 (sh, 7900), 285 (sh, 4400) nm in CH_3CN .
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12. Photolysis of 2-cyanomethylenebenzonorbornenes gave a mixture of 12:1 ratio of indane and benzobicyclo[3.2.1]octadiene derivatives where no benzobicyclo[3.1.1]heptene was detected at all. This result shows that the dicyano-substitution is necessary for the selective breakness of C_2-C_3 bond.

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