

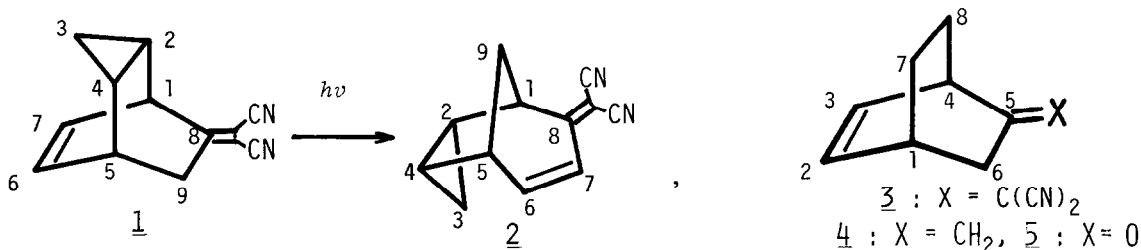
PHOTOCHEMICAL REACTION OF 5-DICYANOMETHYLENEBICYCLO[2.2.2]OCT-2-ENE
 AS A MODEL FOR A LIGHT-ENERGY CONVERSION AND STORAGE SYSTEM¹

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Abstract : Upon irradiation, 5-dicyanomethylenebicyclo[2.2.2]octene (3) gives a highly strained compound, 2,2-dicyanotricyclo[4.2.1.0^{1,3}]nonene (6) in good yield. Of additional interest is the observation that the starting material 3 can be quantitatively regenerated from the photo-product 6 with release of 28.8 kcal/mol.

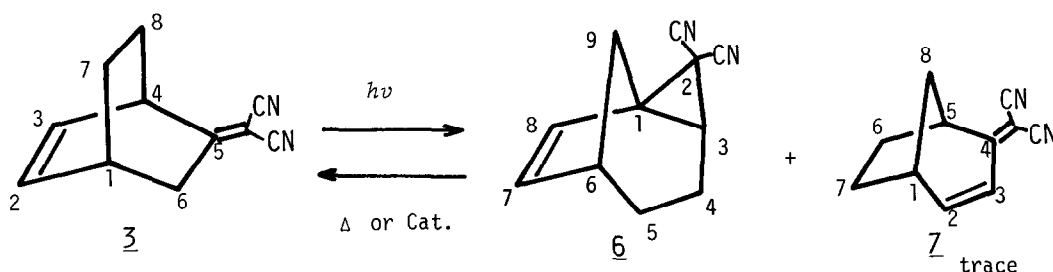
Previously, we reported the photoreaction of 8-dicyanomethylenetricyclo[3.2.2.0^{2,4}]nonene (1) to give 8-dicyanomethylenetricyclo[3.3.1.0^{2,4}]nonene (2).² The photochemical behavior of the structurally related bicyclo[2.2.2]octene derivative is described in this paper. In contrast



to the photoreaction of 1, we have observed that the photolysis of 3 affords the highly strained product 6 in excellent yield. Since the cyano group exhibits a significant effect on the photo-reactions of 1 and related compounds,^{2,3} the photochemistry of 3 is compared to those of the corresponding hydrocarbon 4 and β,γ -unsaturated ketone 5.⁴

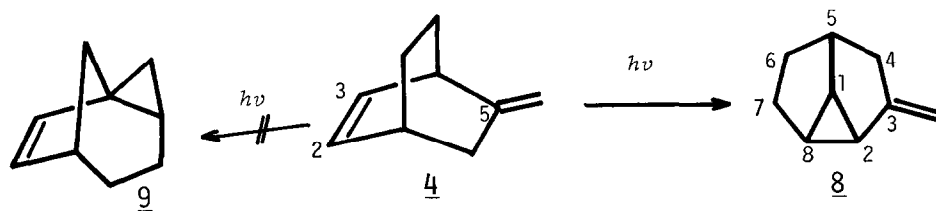
When a hexane solution of bicyclic dicyanodiene 3 (0.012 mol/l) was irradiated in a quartz vessel using RPR-2537Å lamps (35W), 2,2-dicyanotricyclo[4.2.1.0^{1,3}]non-7-ene (6)^{5,6}, mp 62-63°C, was obtained in 92 % yield. In addition, 4-dicyanomethylenetricyclo[3.2.1]oct-2-ene (7)⁷, which is related to the major product 2 in the photoreaction of 1,² was detected in a trace amount (0.1-0.8 %). The predominant photoproduct 6 shows the following spectral data : IR (KBr) 2960, 2230, 1480, 1235 cm⁻¹; ¹H NMR (in CC₄) δ 1.10 (H₃, d.d., J = 6.3, 6.0 Hz), 1.7-2.0 (4H, m.), 2.3-

-2.5 (2H, m.), 2.65 (H₆, m.), 6.22 (H₇, d.d., J = 5.9, 3.0 Hz), 6.33 (H₈, d., J = 5.9 Hz) ;
¹³C NMR (in CDCl₃) δ 12.69 (C₂, s.), 19.87 (C₄ or C₅, t.), 20.87 (C₅ or C₄, t.), 30.45 (C₃, d.),
 34.33 (C₆, d.), 37.73 (C₉, t.), 39.84 (C₁, s.), 111.81 (CN), 113.90 (CN), 132.73 (C₇, d.), 142.
 36 (C₈, d.) ; UV (in cyclohexane) λ_{max} = 217.1 nm (ε 4,460).



Photoproduct 6, upon heating, isomerized to the starting diene 3 in quantitative yield.⁸ The half-life of 6 was measured to be 160 min at 75°C in a deuterated benzene solution. The back reaction was also achieved effectively and quantitatively when a hexane solution of 6 was treated with SiO₂, AgClO₄ or RhCl(PPh₃)₃ at room temperature. It is noticeable that this facile interconversion between 3 and 6 is a novel example of reversible di-π-methane rearrangement.⁹ The heat of reaction (ΔH) in this reverse process was determined to be 28.8 kcal/mol by differentially scanning calorimetry.¹⁰ Based on the reversibility and the high value of ΔH, this valence isomerization reaction may be regarded as a prospective model for a light-energy conversion and storage system.¹¹

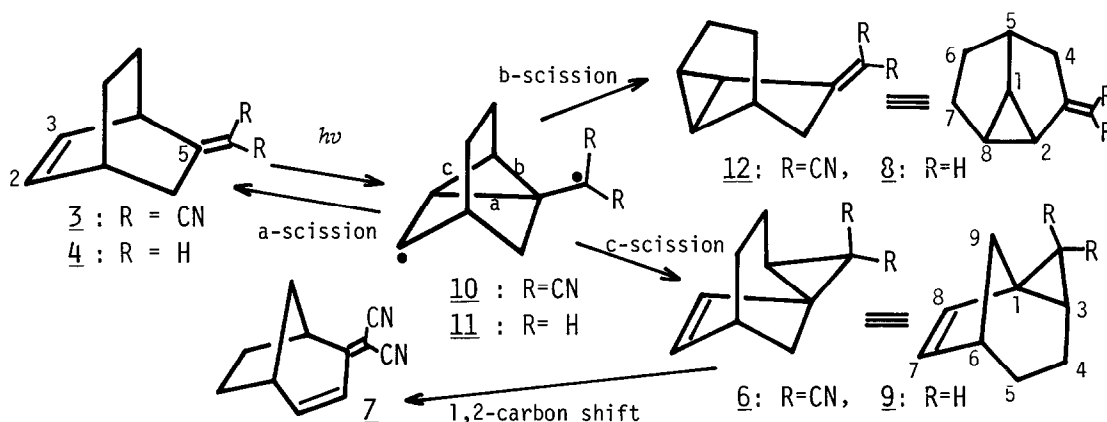
In sharp contrast, 5-methylenebicyclo[2.2.2]octene (4)¹² photoisomerized to 3-methylene-tricyclo[3.3.0.0^{2,8}]octane (8) without the formation of tricyclo[4.2.1.0^{1,3}]nonene (9).^{13,17}



It is also known that the corresponding bicycloketone 5 undergoes oxa-di-π-methane rearrangement leading to tricyclo[3.3.0.0^{2,8}]octanone from the triplet excited state.⁴

The photochemical transformations of these bicyclooctene derivatives are rationalized by

stepwise mechanisms involving diradical intermediates, 10 and 11, which are derived from di- π -methane interaction between the C₂-C₃ double bond and 5-methylene group. In intermediates 10 and 11, three types of bond scissions (a, b, and c) can be considered for the formations of two



kinds of rearranged skeletons in addition to the starting materials. It should be emphasized that the predominant photoproduct 6 contains higher strain energy than compound 12. These skeletons 6 and 9, have twisted three-membered rings in the tricyclic framework and the strain energy of this tricyclo[4.2.1.0^{1,3}]non-7-ene system is estimated to be 63 kcal/mol by MM-2 calculation.¹⁴ The less strained di- π -methane rearrangement product 12, however, is not detected in the photolysate of the dicyano derivative 3.¹⁵ On the other hand, the photolyses of hydrocarbon 4 afford the normal di- π -methane rearrangement skeleton 8 as a sole product.¹⁷

In the photoreactions of acyclic 1,4-dienes having electron deficient substituents such as the cyano group, Zimmerman has explained the observed regio-selectivity in terms of the small-K reaction.¹⁶ However, it seems unreasonable to adopt this explanation for the regio-selectivity observed in the photoreaction of 3 because of the high degree of strain associated with 6. The effect induced by the cyano-substituents is therefore intriguing and surprising.

The minor 7 was shown to be a secondary product derived from 6, i.e., the prolonged irradiation of the major 6 did result in the formation of 7 albeit in a rather low efficiency. Although we earlier had proposed a [2 σ +2 σ] process for the photoreaction of 1 giving 2, more recent studies have indicated that a primary product similar to 6 is formed with subsequent transformation leading to 2.² Additional studies on photochemistry of these systems are in progress.

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References and Notes

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5. Compound 3: colorless prisms, mp 59-60°C; IR (KBr) 3050, 2980, 2880, 2230, 1589, 713 cm⁻¹; ¹H NMR (in CDCl₃) δ 1.4-1.8(4H, m.), 2.38(1H, m.), 2.66(1H, m.), 3.04(1H, m.), 3.92(1H, m.), 6.18(1H, d.d.d., J = 7.5, 6.8, 1.5 Hz), 6.55(1H, d.d.d., J = 7.5, 6.8, 1.3 Hz); UV (in cyclohexane) λ_{max} = 243.1 nm (ε 11,930), (in CH₃CN) λ_{max} = 245.1 nm (ε 11,900).
6. All new compounds gave satisfactory elemental analyses and Mass spectra.
7. Product 7: colorless needles, mp 59-61°C; IR (KBr) 2970, 2870, 2220, 1596, 1551 cm⁻¹; ¹H NMR (in CDCl₃) δ 1.3-2.5(6H, m.), 2.95(1H, m.), 3.59(1H, m.), 6.50(1H, d.d., J = 9.5, 1.7 Hz), 7.03(1H, d.d.d., J = 9.5, 6.8, 1.5 Hz); UV (in cyclohexane) λ_{max} = 290.2 nm (ε 20,640): 7 was independently synthesized from bicyclo[3.2.1]oct-3-en-2-one. R.L. Cargill, A.M. Foster, J. J. Good, and F.K. Davis, *J. Org. Chem.*, **38**, 3829 (1973).
8. Product 6 is a potential precursor of both 7 and 3. The C₂-C₃ and C₁-C₉ scissions in 6 and subsequent recombination between C₃ and C₉ are expected to give 7 (1,2-shift of C₉ carbon). On the other hand, the C₂-C₃ and C₁-C₈ scissions lead to the regeneration of starting diene 3 (1,2-shift of C₈-carbon, reverse di-π-methane rearrangement).
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10. The value (ΔH) was determined by Rigaku Thermoflex (DSC) on solid sample at 70-120°C.
11. A high quantum efficiency (φ = 0.19) was also obtained for the formation of 6 upon irradiation of 3 in cyclohexane at 25°C with 254 nm light using potassium ferrioxalate actinometry.
12. Compound 4: colorless oil, bp 77°C (83 mmHg); IR (oil) 3060, 2950, 2915, 2875, 1650, 867, 690 cm⁻¹; ¹H NMR (in CDCl₃) δ 1.3-1.7(4H, m.), 2.08(1H, d.d.d., J = 16.5, 3.2, 1.7 Hz), 2.27(1H, d.d.d., J = 16.5, 2.7, 1.7 Hz), 2.64(1H, m.), 3.00(1H, m.), 4.56(1H, q., J = 1.7 Hz), 4.75(1H, m.), 6.23(1H, d.d.d., J = 9.3, 4.7, 1.5 Hz), 6.29(1H, d.d.d., J = 9.3, 3.8, 1.5 Hz); UV (in cyclohexane) λ 220 nm (ε 1,070), 240 nm (ε 2.0).
13. Product 8 was isolated by preparative GLC (SE-30 20% on Chromosorb-P, 3/8 in x 5 m, 90°): IR (oil) 3080, 3050, 3035, 2950, 2910, 2870, 2830, 1650, 860 cm⁻¹; ¹H NMR (in CCl₄) δ 1.3-2.1(7H, m.), 2.28(1H, t.d., J = 6.2, 4.5 Hz), 2.41-2.76(2H, m.), 4.88(2H, m.): Compound 8 was independently synthesized by Wittig reaction of the corresponding ketone.⁴
14. E. Ohsawa (Hokkaido University), private communication.
15. Under sensitized irradiation of 3 by acetone, the formation of 6 and 7 were also observed in 67 and 9 % yields in addition to the starting material. Compound 12 could not be detected in the photolysate at all.
16. H.E. Zimmerman, D. Armesto, M.G. Amezuza, T.P. Gannett, and R.P. Johnson, *J. Am. Chem. Soc.*, **101**, 6367 (1979) and references therein.
17. The maximum yield for the formation of 8 was 27 and 3 % under acetone-sensitized and direct irradiation, respectively. No product originated from 9 could be detected.

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