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PHOTOREACTION OF 9-DICYANOMETHYLENE-1,2,3,4-TETRAHYDRO-1,4-METHANONAPHTHALENE: THE 1,3-CARBON MIGRATIONS AND THE ETHYLENE EXTRUSION TO DICYANOISOBENZOFULVENE[1]

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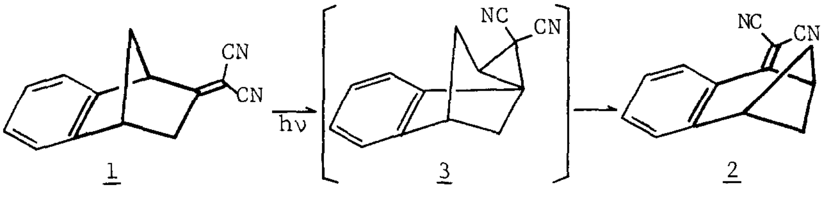
Summary: Irradiation of 9-dicyanomethylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene gave 3,3-dicyano-1,2,3,8b-tetrahydrocyclopent[a]indene and 2-dicyanomethylene-2H-indene.

The interaction between two π-functions in excited state has been of interest and much investigated.[2] Recently our attention has been given to the interaction induced by dicyanomethylene group in bicyclic system[3] where the photochemical behavior is influenced by the electron withdrawing ability and the stereochemical orientation. As described before, the photoreaction of 2-dicyanomethylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene 1 gave 1-dicyanomethylene-1,2,3,4-tetrahydro-2,4-methanonaphthalene 2 in good yield.[4] This result was explained most reasonably with the intermediacy of 6,7-benzotricyclo[3,2,1,$0^{1,3}$]octene 3 originated from the di-π-methane rearrangement. In order to obtain an information for the geometrical influence, we investigated the photoreaction of 9-dicyanomethylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene 4, a structural isomer of 1.



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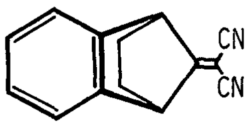

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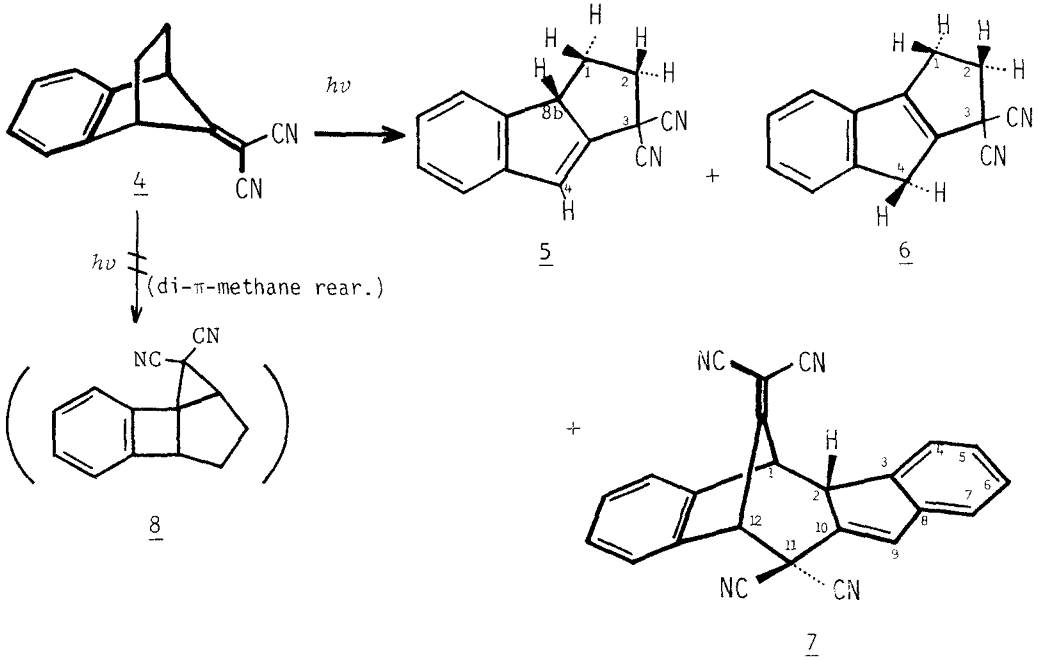
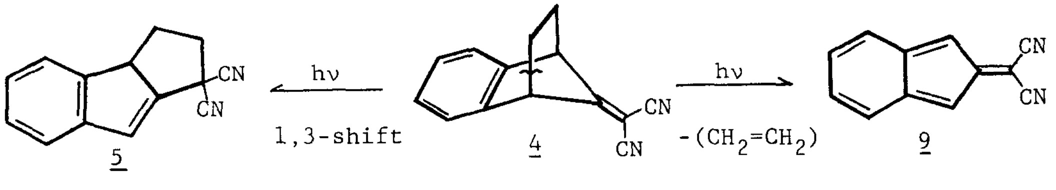
When a cyclohexane solution of 4^5 (1.8×10^{-3}M) was irradiated with RUL-2537Å lamps (105W) for 2 h, three product, 5, 6 and 7, were obtained in 7, 5, and 16 % yields along with 51 % of recovery. These photoproducts, which were separated by column chromatography on silica gel, are different from the structure 8 expected from di-π-methane rearrangement and show the following spectral



data: Product 5, colorless leaves, mp 76-77.5°C; Mass m/e 206 (M^+, 39%), 178 (28), 151(10), 128(base); IR(KBr) 2240, 1450, 745, 725 cm^{-1}; ^1H NMR($CDCl_3$) 1.25($H_{1\text{-}anti}$), 1.41($H_{1\text{-}syn}$), 3.16($H_{2\text{-}anti}$), 3.17($H_{2\text{-}syn}$), 3.96(H_{8b}), 6.96(H_4), 7.1-7.5(H_{5-8}), $J_{1\text{-}syn,1\text{-}anti}$= 11.4, $J_{1\text{-}syn,2\text{-}syn}$= 5.3, $J_{1\text{-}syn,2\text{-}anti}$= 4.0, $J_{1\text{-}anti,2\text{-}anti}$= 9.7, $J_{1\text{-}anti,2\text{-}syn}$= 9.0, $J_{1\text{-}anti,8b}$= 8.0, $J_{4,8b}$= 2.0 Hz; ^{13}C NMR($CDCl_3$) 25.50(C_1), 29.99($C(CN)_2$), 47.39(C_2), 54.55(C_{8b}), 114.85(CN), 115.47(CN), 122.97, 124.13, 126.61, 127.85, 129.91 (C_{4-8}), 144.79, 144.85, 148.25 ($C_{3a,4a,8a}$); UV λmax= 221(11600), 227(14300), 267(8850) nm in cyclohexane. Product 6: colorless needles, mp 139-139.5°C; Mass m/e 206 (M^+, 87%), 178(35), 151(9), 128(base); IR(KBr) 2240, 1455, 755, 700 cm^{-1}; ^1H NMR($CDCl_3$) 2.91(H_1), 3.24(H_2), 3.37(H_4), 7.1-7.7(H_{5-8}), $J_{1,2}$= 6.0 Hz; ^{13}C NMR($CDCl_3$) 28.39(C_1), 34.00($C(CN)_2$), 35.62(C_4), 43.77(C_2), 114.60(CN), 118.66, 124.88, 125.86, 127.09 (C_{5-8}), 136.03, 138.95, 146.80, 157.62 ($C_{3a,4a,8a,8b}$); UV λmax= 212(11300), 218(11000), 225(8330), 258(6000) nm in cyclohexane. Product 7[6]: colorless prisms, mp 260-263°C; Mass 356(M^+,27%), 178(base), 149(26), 129(29), 115(14); IR(KBr) 3000, 2240, 1640, 1460, 755, 735, 710 cm^{-1}; ^1H NMR($CDCl_3$) 3.97(H_2), 4.76(H_1), 4.86(H_{12}), 6.46(H_4), 6.73(H_9), 6.9-7.7(8H), $J_{1,2}$= 3.3, $J_{2,9}$= 1.0, $J_{2,4}$= 1.0, $J_{4,5}$= 6.8 Hz; UV λmax= 240 (sh, 14300), 286 (sh, 5650), 310 (sh, 3410) nm in acetonitrile. The products 5 and 6 exhibit no dicyanomethylene function. The ^1H NMR spectrum of 5 shows the characteristic olefinic and methine protons at 3.96 and 6.96 ppm indicating the structure of 3,3-dicyano-1,2,3,8b-tetrahydrocyclopent[a]indene which was produced by the 1,3-carbon shift of ethano bridge. The product 6 was explained to be derived by the subsequent 1,3-hydrogen migration of 5. On the other hand, the major product 7 shows a molecular formula of $C_{24}H_{12}N_4$ and the spectral data similar to those of dimer of 2-isopropylideneisoindene.[8]



Scheme 1

It is noteworthy that the excited molecule of 4 undergoes the 1,3-carbon migration giving 5 as well as the ethylene extrusion reaction to isobenzofulvene 9 (Scheme 1). This experimental result is remarkably different from that of the structural isomer 1 and makes an entry of new photoreaction of bicyclic allyl benzenes.[2] Although the ethylene extrusion reaction of 9-alkylidene-tetrahydro-1,4-methanonaphthalenes is known in the flash vacuum pyrolysis,[9] the photo-induced extrusion in this system is hitherto unknown. Furthermore, the formation of 9 is a milestone in fulvene chemistry because attempts to prepare such derivatives possessing electron withdrawing group had been unsuccessful. The evidence of dicyanoisobenzofulvene (9) was also available from the low temperature photolysis of 4 at 77K (Fig. 1) where the 2-methyltetrahydrofuran matrix (0.6 mmol/l) was irradiated with 254 nm light. The irradiated matrix showed a red purple color where the observed absorption maxima at 528, 539, 561, and 575 nm were assigned to dicyanoisobenzofulvene.[10] When the matrix was melted at elevated temperature, the coloration was immediately disappeared to

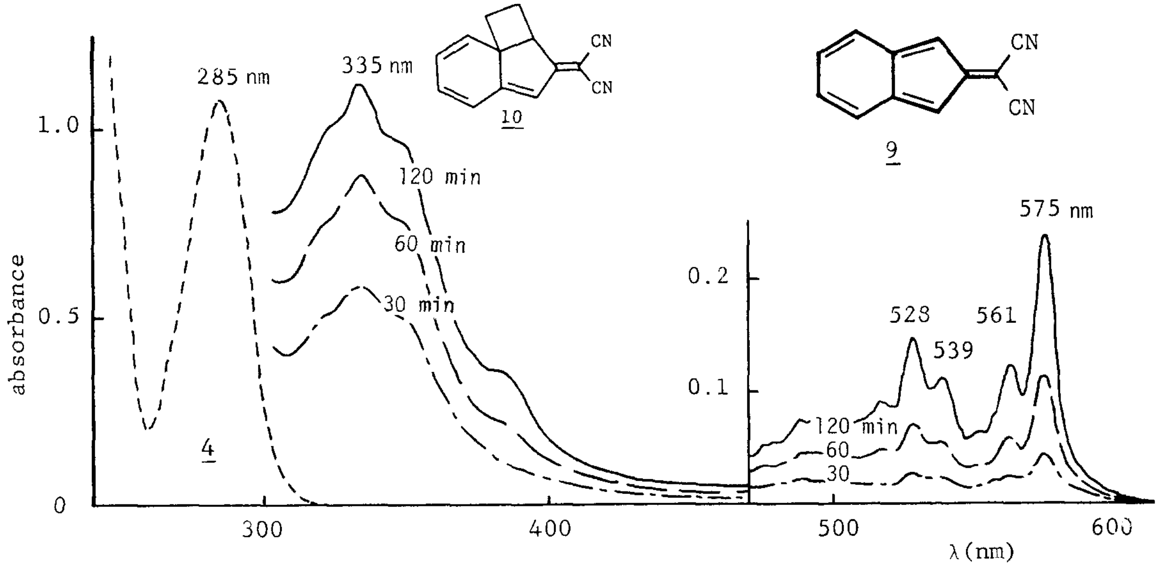


Fig. 1 Irradiations of 4 in 2-Methyltetrahydrofuran at 77K (RUL-2537Å).

give the dimer 7 where the formations of 5 and 6 were suppressed in a trace amount. Under this condition, the observed absorption at 335 nm is tentatively assigned to the precursor of 9 5-dicyanomethylentricyclo[5.4.0.0^{1,4}]undeca-6,8,10-triene (10).

In this case, 1,3-migration of the C_1 carbon takes place in two different ways to give 5 and 10 instead of the di-π-methane rearrangement to 8. The remarkable difference of the photochemical behaviors between 1 and 4 is attributed to the geometrical reason and/or the highly constrained structure of 8. Further study is in progress in order to gain insights into the characteristic photochemical behavior of this kind of dicyanomethylene compounds.

References and Notes

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5. Compound 4 was prepared from diphenylfulvene-benzyne adduct by three steps, mp 104-105°C; IR(KBr) 2215, 1640, 764 cm^{-1}; ^{1}H NMR($CDCl_3$) 1.4-1.7(H_{2-syn}, H_{3-syn}), 2.0-2.3(H_{2-anti},H_{3-anti}), 4.09(H_1,H_4), 7.22(H_{5-8}); ^{13}C NMR($CDCl_3$) 25.49(C_2,C_3), 47.35(C_1,C_4), 77.21($C(CN)_2$), 110.90(CN), 121.39, 128.28 (C_{5-8}), 141.53(C_{4a},C_{8a}), 190.78(C_9); UV λmax= 219 (18800) and 283 (5930) nm in cyclohexane.
6. The irradiations of 4 in the presence of dienophile such as dimethyl maleate did not influenced the formation of 7 in contrast to the facile quenching of dimethyl- and diphenylisobenzofulvenes.[7]
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