The Photoreactions of 2,3-Dicyanobarrelene[1]

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The direct irradiation of 2,3-dicyanobarrelene (II) provided 1,2-dicyanocyclooctatetraene (III). On the other hand, the acetone-sensitized photoreaction of II afforded semibullvalene derivatives (IV and V). Investigations of their NMR spectra clarified that IV completely degenerates, whereas V inclines to the favorable form of the valence isomers.

It is well known that the activation energy of the Cope rearrangement of the I system is very low.[2–9] Recently, Hoffmann and Stohrer thoretically considered the substituent effects on such valence isomerizations and proposed a general rule for the prediction of the favorable isomers.[10] However, the substituted derivatives possessing the I skeletone are not numerous, so the adequacy of the rule has not been proved sufficiently. Therefore, it seemed that it would be interesting to synthesize new derivatives of this system and to study their properties from the viewpoint of the substituent effects on the valence isomerizations. This study will be concerted with the photoreactions of 2,3-dicyanobarrelene (II),[11] which is expected to give cyano-substituted semibullvalenes suitable for the study of the valence isomerizations.

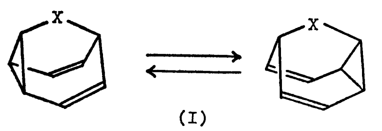

Fig. 1.

When a solution of II in *n*-hexane containing 10% of acetone was irradiated with a medium-pressure mercury lamp (Rayonet 300 nm) through a Pyrex filter, 1,2-dicyanocyclooctatetraene (III) was obtained in an almost quantitative yield. On the other hand, the irradiation of an acetone solution of II afforded 1,5-dicyanosemibullvalene (IV) and 3,4-dicyanosemibullvalene (V) in 4 and 56% yields respectively, in addition to 20% of III. As is well known in the photoreactions of barrelenes,[12] the formation of semibullvalene derivatives (IV and V) may be ascribed to the acetone-sensitized reaction of II, although the cyclooctatetraene derivative (III) was also formed. It was also confirmed that IV and V are the primary photoproducts from II, because III did not afford IV and V upon irradiation under the same conditions.

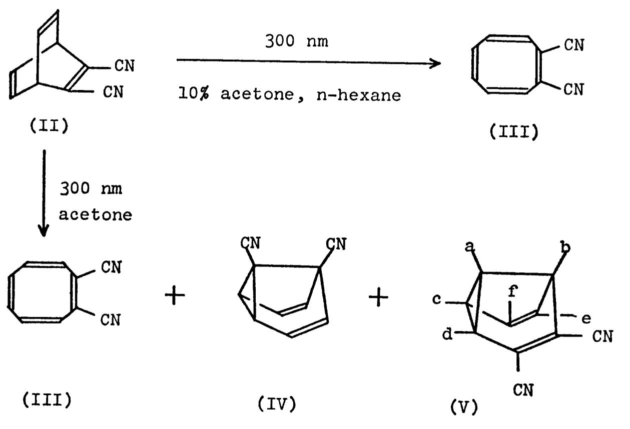

Fig. 2.

All the products, III, IV, and V, have the same molecular formula, $C_{10}H_6N_2$, and thier mass spectra exhibit the same molecular ion peak ($M^+=154$). The structures of the products were based on their spectral properties, shown below.

NMR (100 MHz, δ ppm): for III (in acetone-d_6), 6.2 (broad singlet 4H), 7.12 (broad singlet 2H); for IV (in $CDCl_3$), 4.78 (narrow multiplet 4H), 5.48 (narrow multiplet 2H); for V (in acetone-d_6), 3.45 (multiplet H_a), 3.72 (multiplet H_b), 4.32 (multiplet H_c), 4.55 (multiplet H_d), 5.26 (multiplet H_e), and 5.73 (multiplet H_f). Coupling constants in Hz; $J_{ab}=6.5$, $J_{ac}=4.0$, $J_{ad}=3.0$, $J_{be}=3.5$, $J_{cd}=3.0$, $J_{ce}=0.5$, $J_{cf}=3.5$, and $J_{ef}=4.0$.

UV (in methanol) nm (log ε): for III, 233 (4.31), 303 (2.79); for IV, 310 (2.31); for V, 310 (2.32).

IR (KBr): for III, 2226 cm^{-1}; for IV, 2240 cm^{-1}; for V, 2220 cm^{-1}.

The NMR spectrum of IV is very similar to that of 1,5-bis(trifluoromethyl)semibullvalene.[9] The NMR spectrum of V is very complex, but the above data could be obtained using the double- and triple-resonance techniques.

The reaction mechanism for the formation of III can reasonably explained *via* a $2\pi+2\pi$-type intermediate (VI) which is derived from the singlet excited state.[12] The formation of IV and V may be *via* a biradical intermediate (VII), which is an intermediate

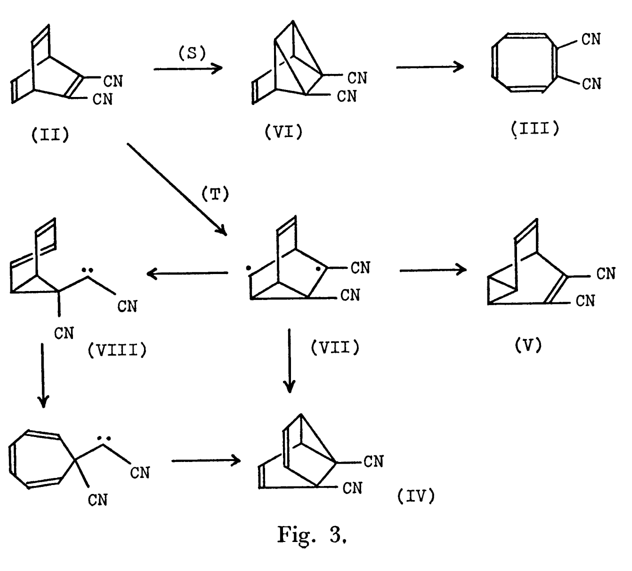

Fig. 3.

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in di-π-methane rearrangements.[12] However, a path *via* a carbene intermediate (VIII) can not be eliminated for the formation of IV. The difference between the yields of IV and V can reasonably be explained by the stabilization ascribed to the formation of the double bond conjugated with two cyano groups.

Hoffmann and Stohrer pointed out that the symmetrically substituted semibullvalenes (possessing the same substituents at the positions which are symmetric with regard to the C_{2v}-axis or the mirror plane through C_3, C_7, and the center of the C_1–C_5 bond), should exist as degenerated valence isomers, except for an irrational compound (1,5-difluoro-2,4,6,8-tetracyanosemibullvalene).[10] That the NMR spectrum of IV shows two narrow multiplets with an area ratio of 2 : 1 implies that IV exists as a degenerated valence isomer; this fact coincides well with the prediction of Hoffmann *et al.*

According to the study of Hoffmann *et al.*,[10] the activation energies of the valence isomerizations of the symmetrically substituted semibullvalenes are sensitive toward substituents. In the case of the 1,5-dicyano derivative (IV), the activation energy may be expected to be considerably large and to be fixed more easily than those of other symmetric derivatives, bacause the stabilization effect of the cyano group operates more effectively on the reactant than on the transition state of the isomerization. From the above point of view, a low-temperature NMR study of IV was made, but the degenerated isomerization still occurs at low temperatures such as −100 °C, and no change was observed in the NMR spectrum.

3,4-Dicyanosemibullvalene (V) is likely to be fixed in the structure shown in Fig. 2. Hoffmann[13] and Günther[14] have proposed that an electron-withdrawing group attached to the C_1-position of a cyclopropane ring strengthens the C_2–C_3 bond and, instead, weakens the C_1–C_2 and C_1–C_3 bonds, whereas the electron-donating groups have the opposite effects. According to their proposition, when the substituent, R, in the structures in Fig. 4 are electron-withdrawing groups such as the cyano group, the C_2–C_8 bond of the structure (IX) weakens and, consequently, another valence isomer (X) should predominate. This is the case in our results. On the contrary, though, Liu and Krespan[9] have reported that 2,3-bis(trifluolomethyl)-semibullvalene, which has electron-withdrawing substituents at the same positions as V, is fixed in another structure, IX. Although this result seems to conflict with the above proposition, it can be reasonably explained as follows. The steric repulsion between the two trifluoromethyl groups which are located on a common plane in the X structure cause the shift of the isomerization to the IX structure, in which these two groups are in a twisted position. When the substituents are small, like the cyano group, the electronic effect dominates, whereas when the substituents become large, as the trifluoromethyl group, the steric effects seem to be predominant.

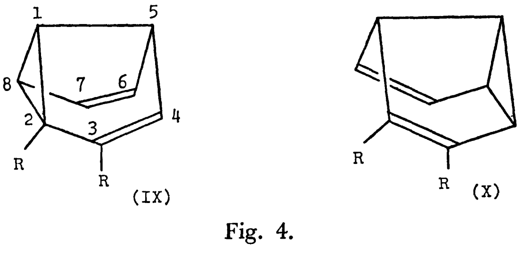

Fig. 4.

Experimental[15]

Direct Irradiation of 2,3-Dicyanobarrelene (II). A *n*-hexane solution of II containing 10% of acetone (100 mg/100 ml) was irradiated in a Pyrex vessel by means of a medium pressure mercury lamp (Rayonet 300 nm) for 2.5 hr. The subsequent evaporation of the solvent afforded a yellow crystalline product of III in a quantitative yield. III was recrystallized from methanol; mp 112 °C. Found: C, 77.72; H, 4.16; N, 18.35%. Calcd for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17%.

Acetone-sensitized Irradiation of 2,3-Dicyanobarrelene (II). An acetone solution of II (100 mg/100 ml) was irradiated in a Pyrex vessel by means of a medium pressure mercury lamp (Rayonet 300 nm) for 2.5 hr. After the subsequent removal of the solvent, an oily product (80 mg) was isolated by thin-layer chromatography (on silica gel, with benzene as the solvent). The NMR spectrum showed that this oil contained only III, IV, and V in a ratio of 25, 5, and 70; thus, the yields of III, IV, and V were calculated as 20, 4, and 56%, respectively. The distillation of this oil (85 °C, 0.02 mm/Hg) afforded an oily product, V. When the residue was separated by column chromatography using alumina, III was eluted with petroleum ether-benzene (3 : 7), and IV, with benzene. The recrystallization of IV from methanol afforded crystals with mp of 116 °C. Anal. for IV. Found: C, 77.94; H, 3.94; N, 18.17%. Calcd for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17%. Anal. for V. Found: C, 77.64; H, 3.90; N, 17.88%. Calcd for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17%.

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15) All mp and bp were uncorrected. NMR spectra were measured by Varian-HA-100 spectrometer, and referred to TMS as an internal standard.