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Distinctive Photochemical Behavior of Rotationally Isomeric 2,5-(trans-4-Octeno)-p-benzoquinones

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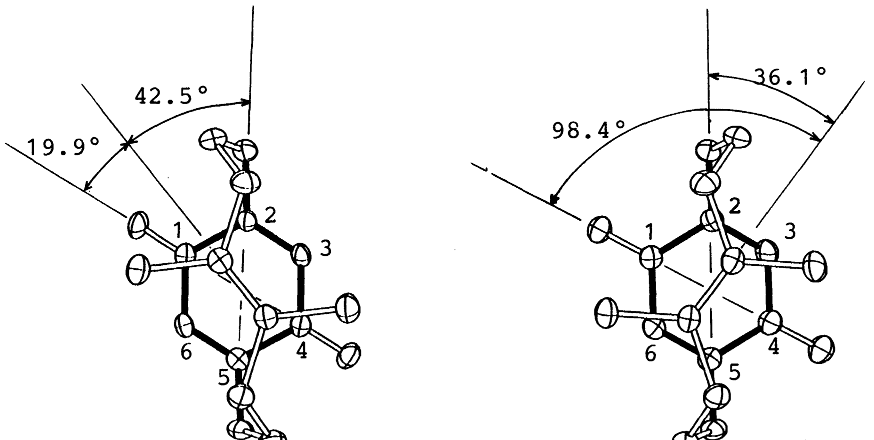
Rotational isomers of 2,5-(trans-4-octeno)-p-benzoquinones, (**1**-A) and (**1**-B), behave distinctively in the photoreaction. The double bond in the side chain of **1**-A cycloadds to the C(2) and C(5) of the quinone moiety, whereas **1**-B is reluctant to do so. The results are interpreted in terms of frontier orbital interactions.

The study of interactions between functional groups held in a rigid, geometrically well-defined structure provides valuable informations undisturbed by complication arising from conformational uncertainty. In 2,5-(trans-4-octeno)-p-benzoquinones (**1**),[1)] a quinone ring and a double bond are disposed face-to-face with specific orientations as shown in Fig. 1. When both the olefinic carbons in the bridge are substituted, interconversion between the conformers, **1**-A and **1**-B, is sterically inhibited and the rotational isomers can be separated from each other.[2)] This unique structural feature of **1** makes it possible to study interaction between the two unsaturated moieties held in those specific arrangements. In the present letter, we report that the rotational isomers of dimethyl[3)] and dicyano[1)] derivatives, **1**c-A and -B, and, **1**d-A and -B, exhibit distinctive behavior in their photochemical reactions. The observed effect of the specific orientation on the reactivity may be rationalized in terms of frontier orbital interactions and will provide an insight into stereochemical requirements for reactants in a cycloaddition reaction.

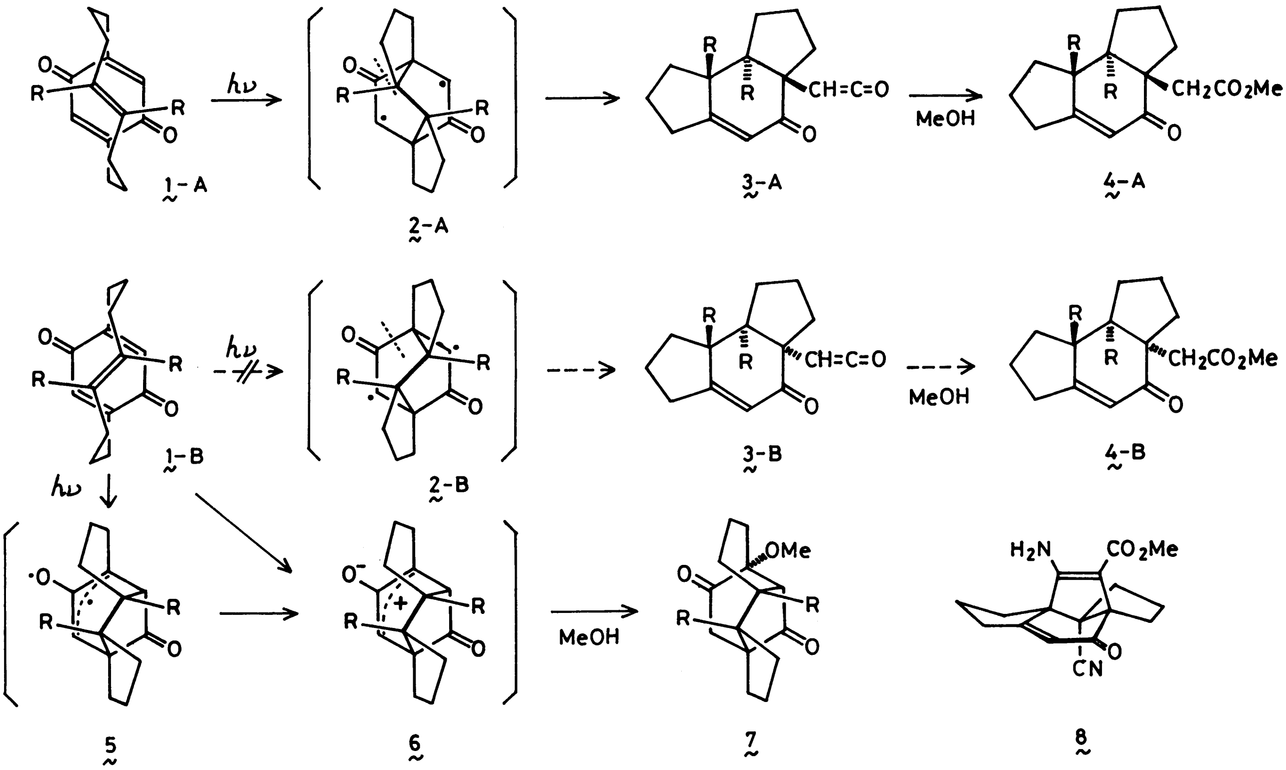


1c-A **1**c-B

Fig. 1. Structures of **1**c-A and **1**c-B viewed down along the approximate C_2 axis.

The phototransformations of 1c-A and 1d-A proceeded in the same manner as previously reported for 1a and 1b.2,4) Thus, upon irradiation of 1c-A in THF-methanol with a UV lamp ($>$330 nm), a single product was isolated in 62% yield (Φ = 0.080) and it was characterized as (4c-A).5) The dicyano derivative, 1d-A, behaved similarly except for the formation of (8) besides 4d-A (Φ = 0.21, 90% yield, 4d-A/8 = 0.50). These methanol adducts, 4d-A and 8, would be derived from a common precursor as discussed below.6) In marked contrast, 1c-B and 1d-B failed to produce any product related to 4. Namely, upon irradiation in methanol, 1c-B yielded a different methanol adduct (7c) in 90% yield (Φ = 0.070) while 1d-B afforded a mixture of 7d (5%) and the corresponding hydroquinone (9d) (47%), (Φ = 0.20). Thus it is clear that the distinctive behavior observed here is due to the specific orientation of the two reacting moieties and that the substituents on the double bond play a minor role in these photochemical transformations.

With regard to spin multiplicity of the reactive species in the photoreaction of 1c-A, it was observed that the addition of Michler's ketone led to the formation of 9c instead of 4c-A. Moreover, the addition of anthracene as a triplet quencher did not affect the rate of production of 4c-A.7) Accordingly, 4c-A would probably be derived via the singlet excited state of 1c-A. The transformation of 1-A to 4-A and 8 can be rationalized by the transannular addition of the double bond to the quinone ring followed by the ring cleavage to a ketene (3-A), which ultimately reacts with methanol to give 4-A (Scheme 1).4) In the reaction of 1d-A, the ketene moiety in 3d-A is fixed in a proximate position to one of the



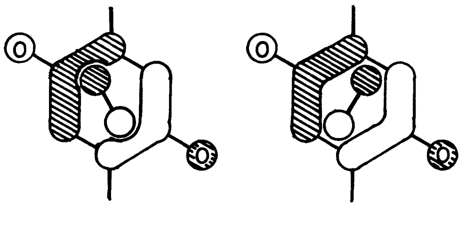
a, R = H/H; b, R = H/Me; c, R = Me/Me; d, R = CN/CN

Scheme 1.

cyano groups and hence rare cyclization might take place to give **8**. On the other hand, the transformation of **1**-B to **7** suggests the generation of zwitterionic intermediates (**6**) similar to those postulated for the thermal reactions of **1**a and **1**b.8) Control experiments, however, demonstrated beyond doubt that the present reactions were induced photochemically.

As described above, the transannular cycloaddition of the double bond in the bridge to the C(2) and C(5) of the quinone ring took place only in the **1**-A conformers. The reason for the failure of **1**-B to give **4**-B is of great interest. No particular steric hindrance for the transformation of **1**-B to **3**-B is revealed by the examination of molecular models. One may argue that the phototransannular reaction of **1**-B to give **4**-B might be overshadowed by the more facile reactions leading to **7** and **9**. However, this also appears not to be the case because, firstly, the quantum yield for the disappearance of **1**-A was nearly equal to that of **1**-B and hence the pathways to **7** and **9** are not particularly favored. Secondly, **1**-B was in fact found to be intrinsically reluctant to give **3**-B. The irradiation of fine dispersion of crystalline **1**c-A or **1**d-A in a KBr disk led to rapid development of a strong IR band at 2110 cm^{-1}, characteristic of a ketene. In contrast, **1**c-B and **1**d-B are photochemically fairly stable in the solid state or in CCl$_4$ and, even after prolonged irradiation in KBr, only a very weak absorption, if any, was observed around 2100 cm^{-1}. Evidently, there is an essential difference in photoreactivity between **1**-A and **1**-B.

The X-ray structural analysis of **1**c-A and **1**c-B was performed to confirm their geometrical structures.9) Pertinent torsional angles, i.e. those between the double bond in the bridge and the C(1)-C(4) and C(2)-C(5) lines, with respect to an approximate two-fold symmetry axis passing through the centers of the quinone ring and the double bond in the bridge are indicated in Fig. 1. Distances between the C(2) of the quinone ring and the proximate unsaturated carbon in the bridge in **1**c-A and **1**c-B are 3.13 and 3.10 Å, respectively. Thus, the geometry of **1**c-B appears to be rather somewhat more favorable than that of **1**c-A for the transannular addition of the double bond in the bridge to the C(2) and C(5) of the quinone ring. Therefore, the lack of reactivity in **1**-B to give **3**-B will not be attributable to a steric effect. In photochemical reaction involving (n, π^*) excited state, LUMO-'LUMO'10) interaction plays a dominant role in bond-making process.11) Since the LUMO of p-benzoquinone is in a shape as depicted in Fig. 2,12) it is easily realized that the bond-forming process in the excited **1**-A to give **2**-A would be promoted by the favorable orbital interaction. In the isomer **1**-B, however, the stabilizing orbital interaction would be largely precluded owing to near orthogonality between the LUMO and 'LUMO', and the structure would have to be deformed to make those orbitals interact effectively for the transannular addition. This poor stabilizing frontier orbital interaction along the reaction coordinate leading to **2**-B would certainly deprive **1**-B of photochemical reactivity to give **3**-B almost completely.



1-A **1**-B

Fig. 2. LUMOs in **1**-A and **1**-B.

In the photolysis of **1**-B, the zwitterionic intermediates **6** might be generated via the vibrationally hot ground state or via electron demotion in the initially formed, excited biradical intermediates (5).$^{13,14)}$ In the case of 1d-B, photoreduction to 9 might become predominant as a result of the retardation of competing transannular reaction to give 6d. The thermal reactivity of 1d-B giving 7d is indeed substantially lower than that of 1c-B affording 7c. Ready photoreduction of p-benzoquinones to the corresponding hydroquinones in alcoholic solvents is well precedented.$^{15)}$

References

1) Y. Hienuki, T. Tsuji, and S. Nishida, Tetrahedron Lett., 22, 863 (1981).
2) When at least one of the olefinic carbons is unsubstituted as in 1a and 1b, rapid interconversion between 1-A and 1-B can take place and an equilibrium is set up at ambient temperature.
3) The dimethyl derivatives, 1c-A and -B, were prepared in the same manner as reported for 1d-A and -B.$^{1)}$
4) T. Tsuji, Y. Hienuki, M. Miyake, and S. Nishida, J. Chem. Soc., Chem. Commun., 1985, 471.
5) All new compounds gave satisfactory elemental analysis and, spectroscopic and mass spectral data were consistent with their structures. Quantum yields are for the disappearance of starting materials.
6) The product ratio, 4d-A/8, was 2.4 when 1d-A was photolyzed in THF-methanol (2:1) and 7.1 when the photolysate in benzene was treated with methanol. These ratios reflect kinetic product distributions.
7) The lowest triplet energy (E_T) of 1c-A was estimated to be 52 kcal/mol from the phosphorescence spectrum. The E_T of anthracene and Michler's ketone have been reported to be 42 and 62 kcal/mol, respectively.
8) Y. Hienuki, T. Tsuji, and S. Nishida, Tetrahedron Lett., 22, 867 (1981).
9) Crystal data. 1c-A: monoclinic, space group $p2_1/c$, a=6.850(2), b=24.083(9), c=8.610(2) Å, ß=109.98(2)°, Z=4, D_c=1.216 g/cm^3. 1c-B: triclinic, space group P$\bar{1}$, a=8.849(2), b=12.193(5), c=6.820(2) Å, α=106.57(3), ß=111.18(2), γ=81.59(3)°, Z=2, D_c=1.235 g/cm^3.
10) 'LUMO' denotes what was the LUMO of photochemically excited component when it was in its ground state.
11) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," Wiley, London (1976), p. 208.
12) M. D. Rozeboom, I.-M. Tegmo-Larsson, and K. N. Houk, J. Org. Chem., 46, 2338 (1981).
13) For the generation of zwitterions by electron demotion in closely related biradical intermediates, see, K. Schaffner and M. Demuth, "Rearrangements in Ground and Excited States, 3," ed by P. de Mayo, Academic Press, New York (1980), p. 281.
14) The addition of double bond in the bridge to the C(2) and C(6) of quinone ring in 1-A is sterically inhibited.
15) H. J. Hageman, "Methoden der Organischen Chemie (Houben-Weyl)," ed by E. Müller, Georg Thieme, Stuttgart (1975), Band IV/5b, p. 941.

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