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Transannular Photocycloaddition in 2,5-(trans-4-Octeno)hydroquinones. Striking Difference in Reactivity due to Relative Orientation of the Two Reacting Functions

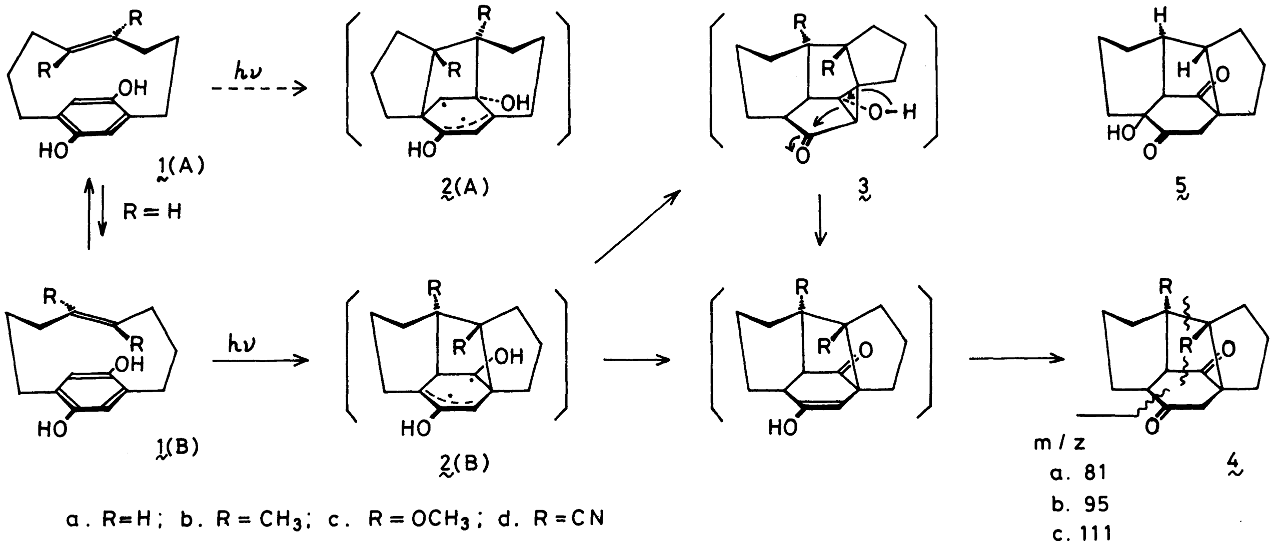
Masaru MIYAKE, Takashi TSUJI,* and Shinya NISHIDA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

2,5-(trans-4-Octeno)hydroquinones with pseudo-gauche (B) configuration undergo transannular photocycloaddition with ease ultimately to give diketones whereas those with pseudo-eclipse (A) configuration are much less reactive. The difference in the reactivity may be interpreted in terms of frontier MO control.

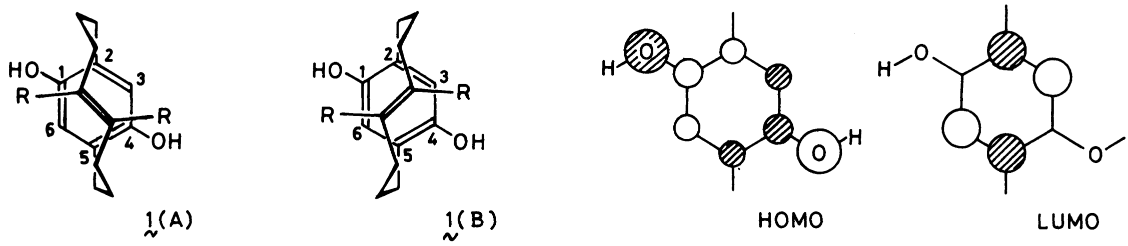
Despite extensive studies on the photocycloaddition reactions of aromatic systems with olefins,$^{1)}$ to the best of our knowledge, this type of photoreaction involving hydroquinone is not known. In this letter we report that 2,5-(trans-4-octeno)hydroquinones (**1**)$^{2)}$ undergo transannular photocycloaddition and that their reactivities critically depend on both the electronic property of the double bond in the bridge and its orientation with respect to the hydroquinone ring. Thus, **1** with the pseudo-gauche (B) configuration underwent efficient transannular photocycloaddition ultimately to give **4**, while **1** with the pseudo-eclipse (A) configuration were much less reactive. The present results reveal a potential, if not essential, photochemical reactivity of hydroquinone toward alkenes and also provide information concerning the mechanistic aspect of photocycloaddition of arenes with alkenes.

Irradiation of a methanolic solution of the unsubstituted derivative (**1a**) with a high pressure mercury lamp through Pyrex led to the rapid consumption of **1a** and the formation of a single major product, **4a** (71% yield).$^{3)}$ Photolysis of **1a** in ether also provided **4a** in a somewhat better yield (92%). The structural assignment for the product was made on the basis of spectroscopic property. Notable features in its spectra are an AX quartet ($J = 17$ Hz) in the ^{1}H-NMR, two carbonyl stretching bands in the IR, and an $m/z = 81$ fragment as the base peak in the MS,$^{4)}$ which are all consistent with the structure of **4a**. Close correspondence in the spectral characteristics between **4a** and **5** which we previously obtained$^{5)}$ was particularly informative for the characterization of **4a**. The educt (**1a**) is a mixture of principally two conformers, **1a**(A) and **1a**(B), which rapidly interconvert at ambient temperature and the equilibrium is displaced in favor of **1a**(A).$^{5)}$ The structure of **4a** indicates that the photochemical transformation of **1a** selectively took place in the less populated conformer **1a**(B), which in turn suggests that the (B) conformer should be substantially more photoreactive than the (A) conformer.$^{6)}$ This was confirmed by examining the reactivity of the isomeric pairs (A) and (B) of substituted derivatives, **1b** and **1c**, respectively. These isomers are separable from each other since the substituents on the olefinic carbons sterically inhibit the interconversion.2) Thus, irradiation of 1b(B) and 1c(B) in methanol afforded 4b (≈100%) and 4c (79%),7) respectively, with the efficiency comparable to that of the production of 4a. In contrast, the isomers with the (A) configuration, namely 1b(A) and 1c(A), were photochemically much less reactive. More than ten times longer irradiation time was required for their consumption under the same photolysis conditions and the reaction was found to be much less clean. The only products isolated from the photolysates were 4b (18%) and 4c (14%), respectively, and the residue was a complex mixture of many minor components and resinous material. No characterizable product which would be derived from 1(A) was obtained. In contrast to 1a-1c, both dicyano derivatives, 1d(A) and 1d(B), were relatively photochemically inert and prolonged irradiation of their methanolic solutions only led to the production of intractable complex mixtures.

The formation of 4 from 1 would proceed via the transannular cycloaddition of the double bond in the bridge to the C-2 and C-6 of the hydroquinone ring and subsequent hydrogen migration-ketonization in the resultant 2(B) as depicted in Scheme 1. Ring-closure to 3 might precede the formation of 4.1) What is striking is the effect of relative stereochemical arrangement of the two reacting moieties in 1 on the photochemical reactivity. Top views of the presumed orientations of the double bond in the bridge with respect to the hydroquinone ring in 1(A) and 1(B) are shown in Fig. 1.8) Apparently the photocycloaddition of the double bond to the C-1 and C-5 of the hydroquinone in 1(A) to give 2(A) is much less efficient than the reaction in 1(B) to give 2(B). It should be noted that these processes would be irreversible.9) Therefore, a possibility that efficient reversion of 2(A) to the precursor might deprive 1(A) of apparent photochemical reactivity may be ruled out. A theoretical model for cycloadditions of excited aromatics to alkenes has been presented by Houk on the basis of frontier molecular orbital (FMO) method.10) Although general applicability of this model to rationalization of regio- and



Scheme 1.

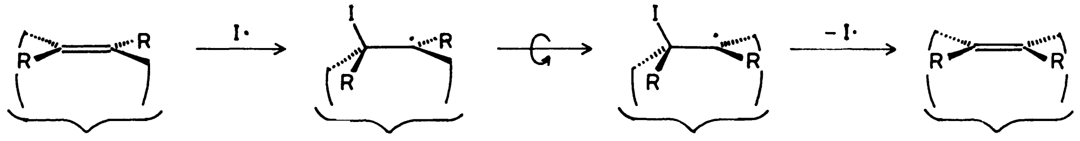


1(A) 1(B) HOMO LUMO

Fig. 1. Presumed configurations of 1(A) and 1(B), and FMOs of 2,5-dimethylhydroquinone (HMO).

stereo-selectivities in those reactions has recently been questioned,11) the present results seem to be best explained in terms of FMO control. The shapes of FMOs of hydroquinone (Fig. 1) unequivocally indicate that bonding 'HOMO'-HOMO and 'LUMO'-LUMO interactions12) between the excited hydroquinone and the olefinic double bond would develop in the (B) configuration along the reaction co-ordinate leading to 2(B), whereas the FMO interactions in the (A) configuration would remain ineffective unless the molecule was severely distorted. The poor FMO interactions in the excited 1(A) would presumably be responsible for the diminished photochemical reactivity.13)

The relatively low photochemical reactivity of the dicyano derivatives might arise from the efficient intramolecular electron transfer (ET) followed by the energy-wasting back ET in their electronically excited states. In fact, differing from the other derivatives, these compounds exhibit pronounced intramolecular charge transfer bands in 330-400 nm region in their electronic spectra.2) The formation of 4b and 4c from 1b(A) and 1c(A), respectively, would most probably result from the preceding isomerization of these (A) isomers to the corresponding (B) isomers. The mechanism of the isomerization, however, is an open question. Stepwise isomerization initiated by an impurity or reversible transannular bond formation (Scheme 2) should yield the isomer with the cis double bond. However, the corresponding cis isomer was not detected during the irradiation of 1. Rapid, reverse cis to trans isomerization might make the detection of the cis isomers difficult.



Scheme 2.

References

1) D. Bryce-Smith, Tetrahedron, 32, 1309 (1976); 33, 2459 (1977); A. Gilbert, "Photochemistry," ed by D. Bryce-Smith, The Chemical Society, London (1970-1986), Vols. 1-17; Pure Appl. Chem., 52, 2669 (1980); J. Mattay, J. Photochem., 37, 167 (1987) and references cited therein.

2) Y. Hienuki, T. Tsuji, and S. Nishida, Tetrahedron Lett., 22, 863 (1981).

3) NMR (CDCl$_3$, 500 MHz); δ 1.08(ddd, J = 6, 11, and 13 Hz, 1H), 1.19-1.26(m, 1H), 1.31-1.43(m, 2H), 1.47-1.53(m, 2H), 1.63-1.72(m, 2H), 1.75-1.82(m, 2H), 1.83-1.91(m, 1H), 2.20(dt, J = 2 and 8 Hz, 1H), 2.25(ddd, J = 3, 6, and 12 Hz, 1H), 2.41 (dq, J = 13 and 3 Hz, 1H), 2.52(t, J = 5 Hz, 1H), 2.67-2.72(m, 1H), 2.72(d, J = 17 Hz, 1H), 2.85(d, J = 17 Hz, 1H): IR (KBr); 1752, 1712 cm^{-1}: MS (rel intensity); m/z 218(M$^+$, 65), 190(17), 147(21), 131(22), 109(56), 81(100): HRMS, Calcd for C$_{14}$H$_{18}$O$_2$ 218.1306; Found 218.1304.

4) The base peak would result from the fragmentation shown in Scheme 1. Base peaks in the MS spectra of 4b and 4c were also observed at m/z expected for the analogous fragmentation.

5) Y. Hienuki, T. Tsuji, and S. Nishida, Tetrahedron Lett., 22, 867 (1981).

6) The electronic absorption spectrum of 1b(A) is almost superimposable to that of 1b(B).

7) 4b. NMR (CDCl$_3$, 500 MHz); δ 1.00(s, 3H), 1.03(s, 3H), 1.15-1.24(m, 2H), 1.34-1.43(m, 2H), 1.43-1.65(m, 6H), 2.13(d, J = 4 Hz, 1H), 2.29-2.34(m, 1H), 2.49 (dt, J = 14 and 9 Hz, 1H), 2.58(dd, J = 5 and 6 Hz, 1H), 2.66(d, J = 19 Hz, 1H), 2.78(d, J = 19 Hz, 1H): IR (KBr); 1748, 1708 cm^{-1}: MS (rel intensity); m/z 246 (M$^+$, 5), 218(16), 123(12), 95(100). Found: C, 77.94; H, 9.03%. Calcd for C$_{16}$H$_{22}$O$_2$: C, 78.01; H, 9.00%.

4c. NMR (CDCl$_3$, 500 MHz); δ 1.15(ddd, J = 7, 9, 13 Hz, 1H), 1.19-1.27(m, 1H), 1.35-1.44(m, 1H), 1.58-1.77(m, 3H), 1.82-1.98(m, 3H), 2.20(ddd, J = 4, 6, and 12 Hz, 1H), 2.24(ddd, J = 4, 6, and 12 Hz, 1H), 2.41(ddt, J = 14, 4, and 2 Hz, 1H), 2.60(dd, J = 2 and 17 Hz, 1H), 2.68(d, J = 6 Hz, 1H), 2.82-2.85(m, 1H), 2.84(d, J = 17 Hz, 1H), 3.15(s, 3H), 3.32(s, 3H): IR (KBr); 1754, 1716 cm^{-1}: MS (rel intensity); m/z 278(M$^+$, 0.6), 250(15), 111(100), 79(33), 53(20): HRMS, Calcd for C$_{16}$H$_{22}$O$_4$ 278.1518; Found 278.1491.

8) M. Miyake, T. Tsuji, A. Furusaki, and S. Nishida, Chem. Lett., 1988, 47.

9) Biradicals which would be generated as intermediates in the photocycloaddition of cyclopentene to xylenes do not revert to the educts (D. E. Reedich and R. S. Sheridan, J. Am. Chem. Soc., 107, 3360 (1985)).

10) K. N. Houk, Pure Appl. Chem., 54, 1633 (1982).

11) J. Mattay, Tetrahedron, 41, 2405 (1985).

12) 'HOMO' and 'LUMO' denote what were the HOMO and LUMO of the hydroquinone moiety in the ground state, respectively, before the excitation took place.

13) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," Wiley, London (1976), p. 208.

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