PRODUCTS AND MODES OF PHOTOCYCLOADDITION OF 9,10-PHENANTHRAQUINONE WITH CYCLIC OLEFINS

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Photocycloaddition of 9,10-phenanthraquinone(PQ) and cyclic olefins; cyclohexene(la), cycloheptene(lb), cis-cyclooctene(lc), and bicyclo[2.2.1]hept-2-ene(la) was investigated. It was found that the product distributions and the modes of photocycloaddition were profoundly dependent on the structure of cyclic olefins.

Although extensive studies 1) on photocycloaddition of PQ with olefins have revealed that dihydro-1,4-dioxin and keto-oxetane derivatives are obtained in general in the reactions, controlling factors over the modes of photoadditions; e.g. structure of adducts or configurations around added centre, are remained to be clarified. In this investigation photochemical reactions of PQ with cyclic olefins described above were examined, and other two types of products (5 and 6) unidentified so far were isolated. Furthermore, the configurations of cycloadducts were determined by examination of their PMR spectra. Reactions run fairly smoothly and the quantum yields of olefin consumption were of the order of one tenth or higher. Reactions can be summarized as the followings:

P.Q. + H (CH₂)_n
$$\xrightarrow{h\nu}$$
 CGH₆ CH₂)_n + \xrightarrow{h} CGH₂)_n + \xrightarrow{h} Cis trans $\frac{1}{3}$ a~c $\frac{4}{3}$ a~c

P.Q. +
$$\frac{h\nu}{2}$$
 $\frac{h\nu}{C_6H_6}$ $\frac{h\nu}{C_6H$

Products distributions of reactions are shown in Table 1. Yields were calculated on the basis of PQ consumed. Structures of isolated adducts were determined by means of IR, PMR, Mass., UV, and elemental analysis 4). Chemical reactions of products such as oxidation and thermal decomposition were also applied for the determination of structures. Major products in the reaction of la~c were dihydro-1,4-dioxins, but not in the reaction with 2; instead keto-oxetane derivative 7 was found in high yield(>75%) accompanying with too small amount of other products to isolate. Adduct 7, of which configuration is $exo-cis^2$, is less stable than dihydro-1,4-dioxins, and decomposes gradually on Florisil or silica gel to give rise again PQ and 2 or some resinous matter at room temperature. Adducts 6a~c derived from la~c are of unusual, but their yields are relatively high. They are easily transformed to 8 by treating with Pd/C or proton in polar solvent in nearly quantitative yield (for example, $6c \rightarrow 8c$).

Table 1. Products of Photocycloadditions of PQ with Cyclic Olefins

Cyclic Olefins Dihydro-1,4- Keto-oxetane Others
dioxin(*)

1a 46% - 5a:42%(mp 75-76°C), 6a:2%(oil)

1b 54% - 5b:23%(mp 90-93°C), 6b:8%(mp 148-154°C)

1c 66% - 5c: 6%(oil), 6c:20%(mp 149-150°C)

2 - 75%(mp 152.5-153.5°C)
(*) total yields of cis- and trans-isomers.

$$gc ext{Pd/C or } H^{\dagger}in CHCl_3 ext{ } m.p. 141 - 142°C$$

This is indicative of the presence of active hydrogen atom in the molecule, and its spectral data and elemental analysis are all compatible with structure 6. Product 6 may be derived out of the keto-oxetane type adduct of PQ and olefin through thermal and/or photochemical decomposition as shown in the following reaction;

Since it is established that the PMR signal of bridge head protons of the trans-fused bicyclic compound appears in the higher magnetic field than that of the cis-isomer³⁾, relative amounts of cis- and trans-dihydro-1,4-dioxins(3:4) could be determined by means of PMR spectroscopy. The results are summarized in Table 2.

Table 2. Relative Amounts of $cis ents$ and $trans ents$ -Dihydro-1,4-dioxins				
Cycloolefins		Chemical Schifts of Bridge Head Protons	Relative Ratio	Physical Properties
la	cis [3a] trans [4a]	4.08	85	oil
~		3.48	15	oil
lb	cis [3b]	4.25	69	oil
∼	trans [4b]	3.70	31	mp 189.5-193°C
1c	cis [3c]	4.41	7 0	mp 93.5-96°C
~	trans [4c]	4.00	3 0	oil

References

- 1) For example, A.Schönberg, "Preparative Organic Photochemistry", Springer-Verlag, New York, (1968), p.119
- 2) It was confirmed that $H_a(\delta:4.90, doublet, lH)$ was coupled with $H_b(\delta:2.47, doublet, lH)$, but with neither of H_c or H_d . This excludes the configurations of other three possible isomers.

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- 3) Y.L.Chow and J.C.Joseph, Chem. Commun., 1968, 604
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 Recently, this is unambiguously confirmed by F.R.Jensen and R.A.Neese; J. Am.
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- 4) Physical properties of representative photoadducts are followings; [3c], mp 93.5-96°C, IR(KBr disc): v_{OH} , $v_{C=0}$ = none, v_{CH} =2900,3050 cm⁻¹, $v_{C=C}$ =1612, 1600 cm⁻¹; PMR(CC1_A): δ =1.4-2.3(m,12H), 4.41(bd.2H), 7.46(m,4H), 8.10(m, 2H), 8.50(m,2H). [4c], oil, IR(KBr disc): quite similar to [3c]; PMR(CCl₄): δ = 1.4-2.3(m,12H), 4.00(m, 2H), 7.46(m, 4H), 8.10(m,2H), 8.50(m,2H). [5c]. oil, IR(NaC1, liq.film): v_{OH} =3470 cm⁻¹, v_{CH} =3050, 3000, 2920, 2850 cm⁻¹, $v_{C=0}$ =1690 cm^{-1} , $v_{C=C}=1600 cm^{-1}$; PMR(CC1₄): $\delta=1.0-2.9(m, 11H)$, 4.06(bs., 1H), 5.39(m, 2H), 7.1-7.9(m, 8H). In the photochemical reactions of PQ with aralkyl benzenes such as diphenylmethane or xanthene, this type of photoadducts is of major. The comparisons of spectral data of $\begin{bmatrix} 5c \end{bmatrix}$ with those of photoadducts obtained from the reaction of PQ and aralkyl benzenes are enable us to conclude the structure of [5c]. [6c], mp 149-150°C, IR(KBr disc): v_{OH} =3400 cm⁻¹, v_{CH} =2900, 3050 cm⁻¹, $v_{C=0}$ =none, $v_{C=C}$ =1635, 1600 cm⁻¹; PMR(CDC1₃): δ =1.1-2.0(m,10H), 2.1-2.7(m, 2H), 3.02(s. 1H), 3.26(m,1H), 7.54(m, 5H), 8.10(m, 1H), 8.68(m, 2H). [7], mp 152.5-153.5°C, IR(KBr disc): v_{OH} =none, v_{CH} =3050,2950,2860 cm⁻¹, $v_{C=0}$ =1690 cm⁻¹, $v_{C=C}$ =1600 cm⁻¹; PMR(C₆D₆): δ =0.2-1.5(m,5H), 1.63(d. 1H), 2.30(m,1H) 2.47(d,1H), 2.66(m, 1H), 4.90(d. 1H), 6.9-8.1(m, 8H). [8c], mp 141-142°C, IR (KBr disc): v_{OH} =none, v_{CH} =3020,2900,2830 cm⁻¹, $v_{C=0}$ =none, $v_{C=C}$ =1620,1605,1575 cm⁻¹; PMR(CC1_A): δ =1.2-2.1(m, 8H), 3.00(two coupled t, 4H), 7.50(m, 4H), 8.22 $(m, 2H), 8.61(m, 2H); M^{+}: 300.$

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