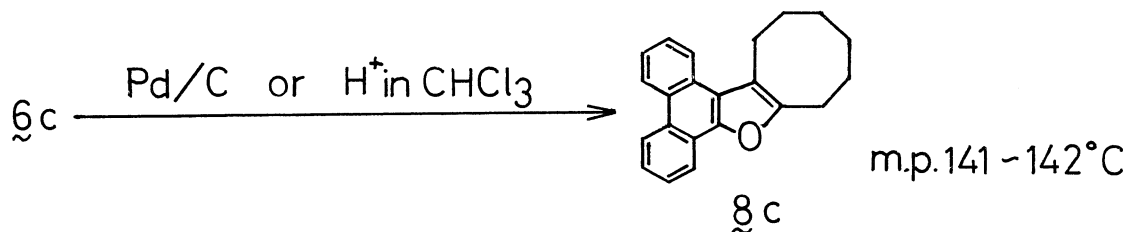


Products distributions of reactions are shown in Table 1. Yields were calculated on the basis of PQ consumed. Structures of isolated adducts were determined by means of IR, PMR, Mass., UV, and elemental analysis<sup>4)</sup>. Chemical reactions of products such as oxidation and thermal decomposition were also applied for the determination of structures. Major products in the reaction of 1a~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*<sup>2)</sup>, 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 1a~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→8c).

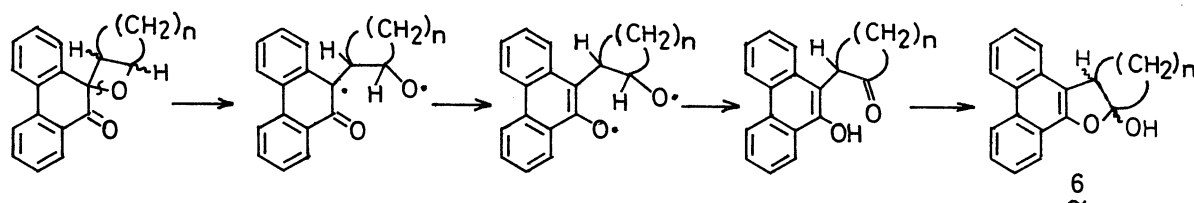
Table 1. Products of Photocycloadditions of PQ with Cyclic Olefins

Cyclic Olefins	Dihydro-1,4-dioxin(*)	Keto-oxetane	Others
<u>1a</u>	46%	-	<u>5a</u> :42%(mp 75-76°C), <u>6a</u> :2%(oil)
<u>1b</u>	54%	-	<u>5b</u> :23%(mp 90-93°C), <u>6b</u> :8%(mp 148-154°C)
<u>1c</u>	66%	-	<u>5c</u> : 6%(oil), <u>6c</u> :20%(mp 149-150°C)
<u>2</u>	-	75%(mp 152.5-153.5°C)	-

(\*) total yields of *cis*- and *trans*-isomers.



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*-isomer<sup>3)</sup>, 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*- and *trans*-Dihydro-1,4-dioxins

Cycloolefins	Isomers	Chemical Shifts of Bridge Head Protons	Relative Ratio	Physical Properties
<u>1a</u>	<i>cis</i> [ <u>3a</u> ]	4.08	85	oil
	<i>trans</i> [ <u>4a</u> ]	3.48	15	oil
<u>1b</u>	<i>cis</i> [ <u>3b</u> ]	4.25	69	oil
	<i>trans</i> [ <u>4b</u> ]	3.70	31	mp 189.5-193°C
<u>1c</u>	<i>cis</i> [ <u>3c</u> ]	4.41	70	mp 93.5-96°C
	<i>trans</i> [ <u>4c</u> ]	4.00	30	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, 1H) was coupled with  $H_b$  ( $\delta$ :2.47, doublet, 1H), but with neither of  $H_c$  or  $H_d$ . This excludes the configurations of other three possible isomers.
- W.D.Kumler, J. Am. Chem.Soc., 80 , 2533(1958)

J. Shigematsu, Y. Odaira, and S. Tsutsumi, *Tetrahedron Letters*, 1967, 55

There may be still two possible isomers (7(i) and 7(ii)) in *exo-cis* isomer.

It was not determined which of the isomers corresponds to the isolated one.

3) Y. L. Chow and J. C. Joseph, *Chem. Commun.*, 1968, 604

G. Pfundt and S. Farid, *Tetrahedron*, 22, 2237 (1966)

Recently, this is unambiguously confirmed by F. R. Jensen and R. A. Neese; *J. Am. Chem. Soc.*, 97, 4345 (1975)

4) Physical properties of representative photoadducts are followings;

[3c], mp 93.5-96°C, IR(KBr disc):  $\nu_{OH}$ ,  $\nu_{C=O}$  = none,  $\nu_{CH}$  = 2900, 3050  $\text{cm}^{-1}$ ,  $\nu_{C=C}$  = 1612, 1600  $\text{cm}^{-1}$ ; PMR( $\text{CCl}_4$ ):  $\delta$  = 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( $\text{CCl}_4$ ):  $\delta$  = 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(NaCl, liq. film):  $\nu_{OH}$  = 3470  $\text{cm}^{-1}$ ,  $\nu_{CH}$  = 3050, 3000, 2920, 2850  $\text{cm}^{-1}$ ,  $\nu_{C=O}$  = 1690  $\text{cm}^{-1}$ ,  $\nu_{C=C}$  = 1600  $\text{cm}^{-1}$ ; PMR( $\text{CCl}_4$ ):  $\delta$  = 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 [5c] 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):  $\nu_{OH}$  = 3400  $\text{cm}^{-1}$ ,  $\nu_{CH}$  = 2900, 3050  $\text{cm}^{-1}$ ,  $\nu_{C=O}$  = none,  $\nu_{C=C}$  = 1635, 1600  $\text{cm}^{-1}$ ; PMR( $\text{CDCl}_3$ ):  $\delta$  = 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):  $\nu_{OH}$  = none,  $\nu_{CH}$  = 3050, 2950, 2860  $\text{cm}^{-1}$ ,  $\nu_{C=O}$  = 1690  $\text{cm}^{-1}$ ,  $\nu_{C=C}$  = 1600  $\text{cm}^{-1}$ ; PMR( $\text{C}_6\text{D}_6$ ):  $\delta$  = 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):  $\nu_{OH}$  = none,  $\nu_{CH}$  = 3020, 2900, 2830  $\text{cm}^{-1}$ ,  $\nu_{C=O}$  = none,  $\nu_{C=C}$  = 1620, 1605, 1575  $\text{cm}^{-1}$ ; PMR( $\text{CCl}_4$ ):  $\delta$  = 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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