CHEMISTRY LETTERS, pp.135-138, 1972. Published by the Chemical Society of Japan

STRUCTURE OF PHOTO-ADDUCT BETWEEN 1,2-NAPHTHOQUINONE AND XANTHENE

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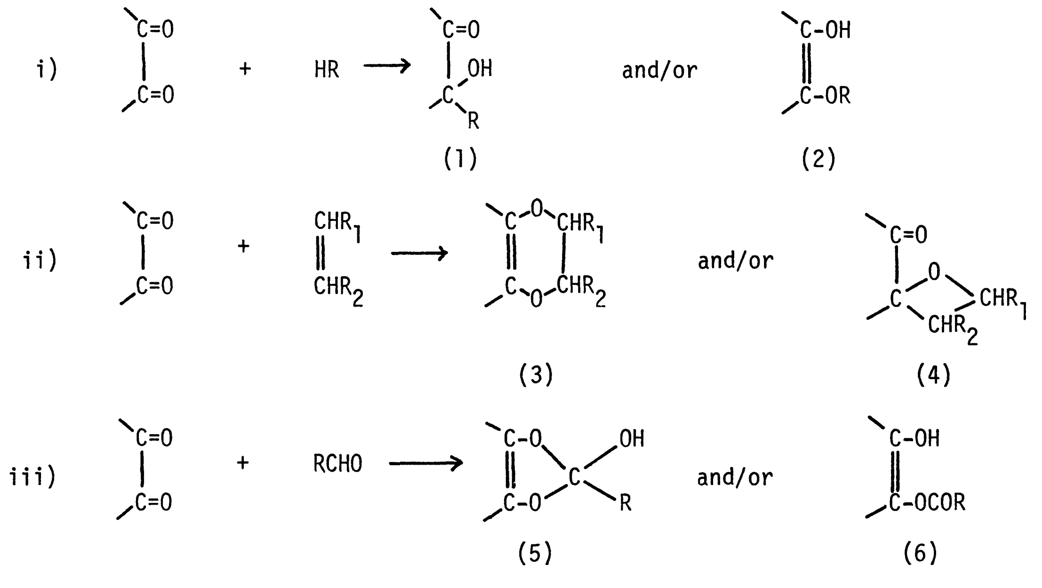
Photochemical reaction between 1,2-naphthoquinone and xanthene was studied. By a smooth reaction photo-adduct is produced as white needles after irradiation for several hours. Structure of the photo-adduct was determined as (7) through the investigation by PMR, IR, Mass, and elemental analysis. The photo-adduct between the o-quinone and the hydrogen donor having such a type of structure have never been reported so far. This reaction was examined from the dynamical point of view using CIDNP technique and the results substantiated further the structure (7).

Photochemical reactions of o-quinones with alkylaromatics,[1,2,3] alkenes,[4] and aldehydes[5] to give photo-adducts have been investigated by the several research groups. The structural types of the photo-adducts reported can be classified as the followings;



Especially, photochemical reactions of halogen substituted 1,2-naphthoquinone with alkenes and aldehydes have been widely examined to get the photo-adducts of types (3), (5), and (6) by A.Schönberg and his co-workers. However, we shall report on another type of photo-adduct produced by the reaction of 1,2-naphthoquinone with xanthene.

Equimolar 1,2-naphthoquinone and xanthene dissolved in benzene was irradiated in a usual glass tube by 400 W high-pressure Hg-arc lamp through 10 cm thick of water layer at 0-5°C. Photo-adduct (yield ~50%) precipitated as white needles after irradiation for five hours, was separated and recrystallized from benzene-petrol ether, mp. 121-123 °C (decomp.). The photo-adduct is stable in the air at room temperature, but in chloroform or more polar solvent it decomposes gradually to give 1,2-naphthoquinone, its quinhydrone, 9,9'-bixanthyl and some tarry matters. For the elucidation of the structure the photo-adduct was subjected to the following examinations;

a) Elemental analysis: Found : C, 81.31 ; H, 4.81 %.

Calcd. for $C_{23}H_{16}O_3$: C, 81.16 ; H, 4.74 %.

b) Oxidation by potassium permanganate in acetone-water solution: Phthalic acid (mp. 190-190.5 °C) and xanthone (mp. 173 °C) was isolated from the reaction mixture.

c) Mass spectrometry: m/e = 340 (M^+), 159 $[(\text{naphthoquinone} + H)\ \text{rest}]^+$, 181 $[(\text{xanthene} - H)\ \text{rest}]^+$

These results described above indicate one to one combination of 1,2-naphthoquinone and xanthene rest in the molecule of the photo-adduct.

d) IR spectrum (Fig.1): Two characteristic strong absorptions corresponding to the existence of carbonyl group($\nu_{C=O}$ = 1640 cm^{-1}) and hydroxyl group hydrogen-bonded intramolecularly(ν_{OH} = 3375 cm^{-1})

e) PMR spectrum (Fig.2): Five characteristic groups of lines in the regions of τ: 2.05-4.50(aromatic-H), 4.24 (H_c:doublet), 5.46(H_b:doublet), 6.07(H_a:quartet), 8.45($H_{hydroxyl}$: broad singlet).

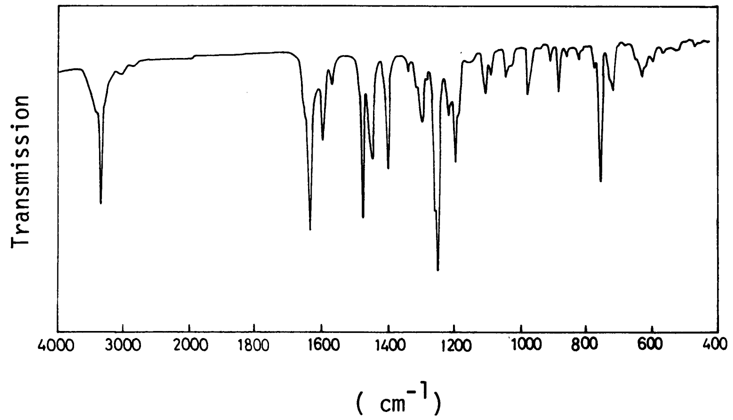
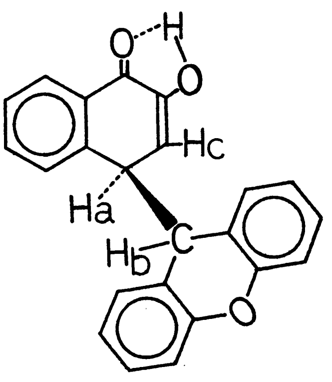


Fig.1 IR Spectrum of Photo-adduct



The corresponding protons are indicated in parenthesis [see Structure (7)]. H_a coupled with H_b(J=3.8 Hz) and H_c(J=4.5 Hz) respectively. This was confirmed by the spin decoupling technique. The signal at τ: 5.46 could not be observed with the photo-adduct which was obtained by the reaction of 1,2-naphthoquinone with xanthene-9-d_2 , and at the same time the signal at τ: 6.07 changed to doublet. The rather broad signal at τ:8.45 was assigned to the hydroxyl proton. This was confirmed by adding one drop of deuterium oxide into the sample (the signal disappeared). In the examination of this photochemical reaction by CIDNP technique[6), we could recognize the strongly polarized PMR signals only at τ:5.46(doublet, enhanced absorption) and τ:6.07(quartet, enhanced emission)(see Fig.3). This phenomenon indicates that the protons which show the polarized PMR signals are situated at the nearest neighbour to the coupling center of 1,2-naphthoquinone and xanthene rest. The signal at τ: 4.24 was assigned to H_c comparing with those of 4-cyano-1,2-naphthoquinone and 4-cyano-1,2-dihydroxynaphthalene.

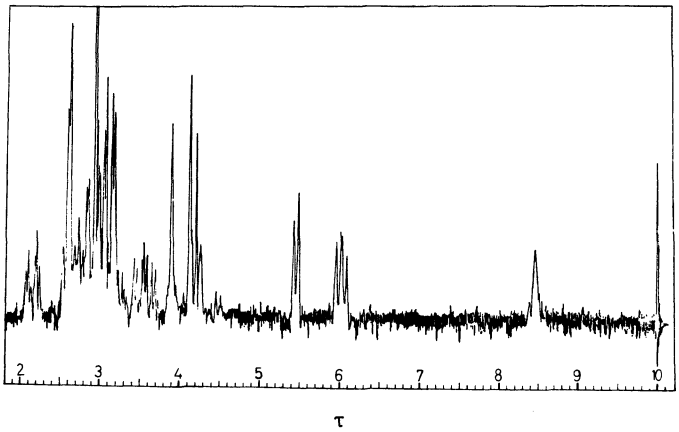


Fig.2 PMR Spectrum of Photo-adduct

Thus, considering the results explained above none of the photo-adducts having the structural type (1) - (6) consists with the experimental data, and only the structure (7) can be accepted as the most plausible one.

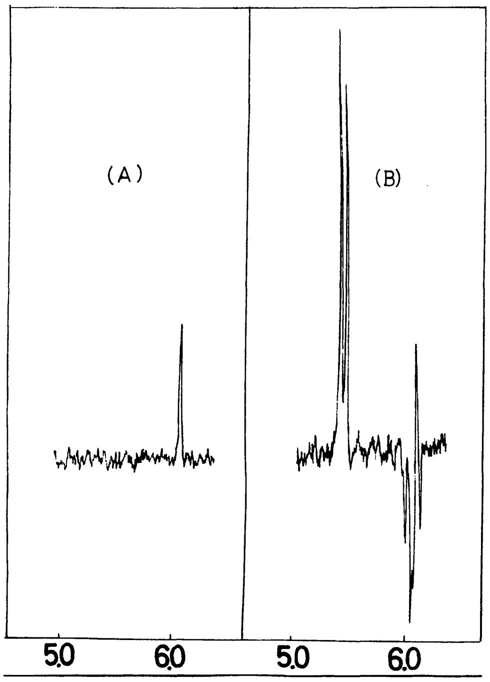


Fig.3

Fig.3 Polarized PMR Spectrum

(A): Non-polarized PMR signal observed before photo-irradiation. The signal at τ: 6.08 is due to the methylene proton of xanthene.

(B): Polarized PMR signals observed during the course of the photochemical reaction of 1,2-naphthoquinone with xanthene.

(solvent: benzene), room temperature

References

1) H. Klinger, Chem. Ber., 19, 1862 (1886).

2) M. B. Rubin, J. Org. Chem., 28, 1949 (1963).
M. B. Rubin and P. Zwitkowits, ibid., 29, 2362 (1964).

3) K. Maruyama, K. Ono, and J. Osugi, Bull. Chem. Soc. Japan, 42, 3357 (1969).
K. Maruyama, K. Ono, and J. Osugi, ibid., in press.

4) A. Schönberg, N. Latif, P. Moubasher, and A. Sina, J. Chem. Soc., 1951, 1364.

5) A. Schönberg, W. I. Awad, and G. A. Mousa, J. Amer. Chem. Soc., 77, 3850 (1955).
A. Mustafa, A. H. E. Harash, A. K. E. Mansour, and S. M. A. E. Omran, ibid., 78, 4306 (1956).

6) K. Maruyama, H. Shindo, and T. Maruyama, Bull. Chem. Soc. Japan, 44, 585 (1971).
K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, ibid., 44, 2756 (1971).
K. Maruyama and T. Otsuki, ibid., 44, 2885 (1971).

(Received December 10, 1971)