BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2647—2648 (1976)

Photochemical Reduction of 2,3-Dihydro-2,3-methano-1,4-naphthoquinones with Xanthene

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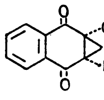
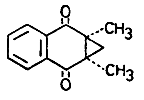
(Received April 14, 1976)

Synopsis. Photochemical reduction of 2,3-dihydro-2-methyl-2,3-methano-1,4-naphthoquinone (**1a**) and 2,3-dihydro-2,3-dimethyl-2,3-methano-1,4-naphthoquinone (**1b**) with xanthene was investigated. 6,7,8,9-Tetrahydrobenzocycloheptene-5,9-dione derivatives and stereochemical isomers of the so-called "1,2-adducts" of xanthene to carbonyl groups were isolated as the reaction products. CIDNP technique was applied for the examination of the course of the reactions.

The titled compounds have two vicinal carbonyl groups connected with cyclopropane ring in the molecule, and their photochemical behavior is quite interesting compared with those of 1,4-naphthoquinone and of 1,4-naphthoquinone 2,3-epoxide. Their relative photochemical reactivities for hydrogen abstraction from xanthene are in the following order: 2-methyl-1,4-naphthoquinone > 2,3-dihydro-2-methyl-2,3-methano-1,4-naphthoquinone > 1,4-naphthoquinone 2,3-epoxide.[1)] In this work photochemical reaction of **1a** and **1b** with xanthene was investigated in detail.



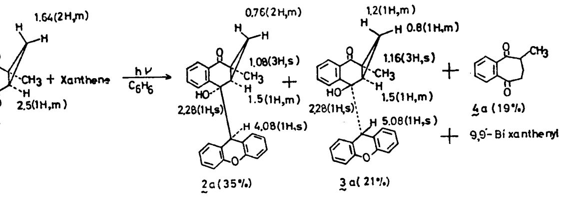
(**1a**)



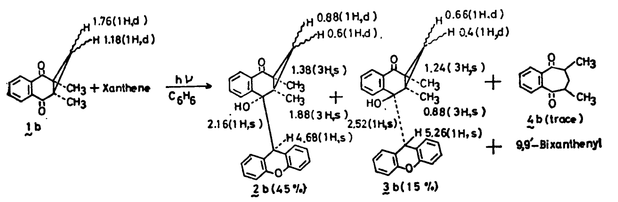
(**1b**)

Experimental

Irradiation of a benzene solution of **1a-b** and xanthene (1 : 2, M/M) for six hours at a room temperature gave four major products in the respective yields given in the following schemes. The yields of products are mean values of several runs. The products, **2a**; mp 145—146 °C, IR (KBr); $\nu_{C=O}=1670$, $\nu_{OH}=3400$ cm^{-1}, and **3a**; mp 216—218 °C, IR (KBr); $\nu_{C=O}=1655$, $\nu_{OH}=3400$ cm^{-1}, are both 1: 1 adduct of **1a** and xanthene[2)], and are in the relation of configurational isomers each other, which are confirmed by elemental analysis and spectroscopy along with the chromic acid oxidation of them to give rise to the same products; *i.e.*, **1a** and xanthone. Reduction product (mp 162—164 °C) of **2a** with sodium borohydride revealed that the attaching position of xanthene moiety was at C_4, because the hydrogen atom thus introduced (bonded to C_1) coupled with no other protons. Reduction of **3a** under identical condition afforded the corresponding secondary alcohol (mp 170—172 °C), which led to the same conclusion.



Scheme 1.



Scheme 2.

Assignment of the configuration of **2a** and **3a** rests on their PMR spectra. Outstanding differences of **2a** and **3a** in their PMR spectra are, at first, the chemical shifts of benzene ring protons; in **2a**, ring protons spread into the region of δ: 5.6—7.5 ppm, but in **3a** into δ: 6.8—8.0 ppm (for comparing, in **1a**, in the region of δ: 7.5—8.0 ppm), which is indicative that in **2a**, there are magnetically stronger interactions among three benzene rings than those in **3a**[3)]. The other supports for the configutation of **2a** and **3a** are the followings. The methylene protons (*endo*- and *exo*-H) of **2a** give a coincided multiplet, centred at δ: 0.76 (2H) ppm, and the methine proton of xanthenyl moiety appears at δ: 4.08 (1H, s) ppm. On the contrary, in **3a** the methylene protons appear as two separated multiplets, δ: 1.2 (*endo*-H, 1H, m) and δ: 0.80 (*exo*-H, 1H, m) ppm and the methine proton of xanthenyl moiety gives a singlet at δ: 5.08 (1H, s) ppm. The *endo*- and *exo*-H were assigned by referring the works reported[4a,4b)], *i.e.*, in **2a**, coupling constants of protons in cyclopropane moiety are J_{trans}: 5.5 Hz, J_{cis}: 7.5 Hz, J_{gem}: 5.5 Hz, and those in **3a** are J_{trans}: 6.3 Hz, J_{cis}: 8.4 Hz J_{gem}: 5.6 Hz.

Such a situation is essentially same for configurational isomers, **2b** and **3b**, but in these cases the methylene protons of **2b** and **3b** appear as two separated doublets (their *endo*- or *exo*-configurations are remained to be decided). Chemical shifts of representative protons are described in Scheme-1 and Scheme 2.

The structure of the third product, **4a** (mp 30 °C), was determined by comparison with the authentic sample prepared by Zn-CH_3COOH reduction of **1a**[5)]. The other product in the

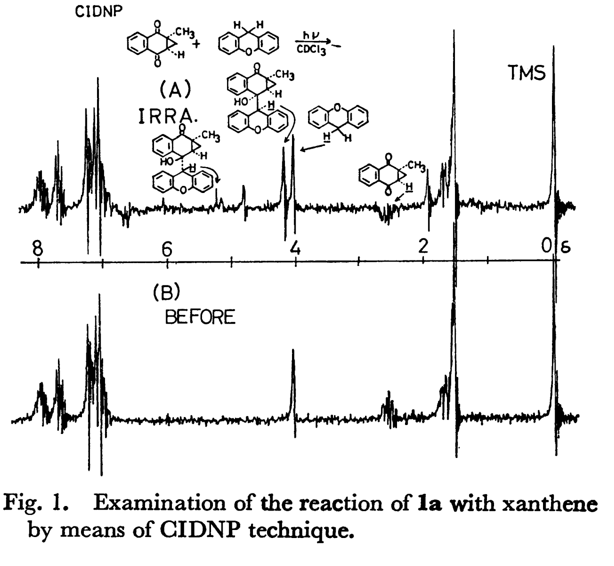
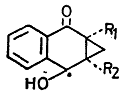


Fig. 1. Examination of the reaction of **1a** with xanthene by means of CIDNP technique.

reaction of **1a** and xanthene was 9,9′-bixanthenyl, which was identified by comparison (mixed melting point, chromatographic, spectroscopic, and chemical behaviors) with authentic sample.

The structure of **4b** (mp 97—98 °C), produced in trace, was determined by comparison with the authentic sample, which was prepared by reduction of **1b.**

Examination of the reaction by means of CIDNP revealed some insight of the reaction course. Methine proton of xanthenyl moiety of 1,2-adducts showed absorption polarization (see Fig. 1). The phenomenon leads to the conclusion that 1,2-adduct of **1a** (or **1b**) and xanthene is mostly produced via direct recombination of the original triplet radical pair composed of **5** and xanthenyl radical[6].



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5a : $R_1=CH_3$, $R_2=H$
5b : $R_1=CH_3$, $R_2=CH_3$

Emission polarization of methine proton of methano-naphthoquinone moiety is another remark indicating the re-production of **1a** from **5a**.

References

1) The relative reactivity was estimated by following the remained amount of xanthene in the reacting mixture after one hour reaction at a room temperature (carbonyl compound: xanthene=0.075/0.15, M/M).

2) Elemental analyses of **2a**, **3a**, **2b**, and **3b** and integrations of their PMR signals reveal that these products are composed of 1: 1 ratio of **1a** or **1b** with xanthene.

3) From the inspection of the molecular models the assignments of the structures are straightforward.

4) a) W. Rundel and P. Kastner, *Justus Liebigs Ann. Chem.*, **737**. 87 (1970); b) J. Heller, A. Yogev and A. S. Dreiding, *Helv. Chim. Acta*, **55**, 1003 (1972).

5) T. Asano, S. Imai, K. Okawa and T. Hanafusa, *Nippon Kagaku Zasshi*, **92**, 532 (1971).

6) K. Maruyama, T. Otsuki, and Y. Naruta, *Bull. Chem. Soc. Jpn.*, **49**, 791 (1976) and references cited therein.