Tetrahedron Letters No. 29, pp 2433 - 2436, 1975. Pergamon Press. Printed in Great Britain.

# PHOTOCHEMISTRY OF EPOXYQUINONES: PHOTOINDUCED CYCLOADDITION OF 2,3-EPOXY-1,4-NAPHTHOQUINONES WITH OLEFINS

Kazuhiro Maruyama, Seiichi Arakawa, and Tetsuo Oysuki
Department of Chemistry, Fuculty of Science,
Kyoto University, Kyoto 606, Japan

(Received in Japan 26 April 1975; received in UK for publication 3 June 1975)

We have reported the photochemical isomerization of 2-acetyl-3-methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone into a seven-membered lactone.[1] In the present paper, we wish to report on the striking difference of photochemical behavior of substituted 2,3-epoxy-1,4-naphthoquinones depending on their substituents in the reaction with olefins, especially with norbornene.

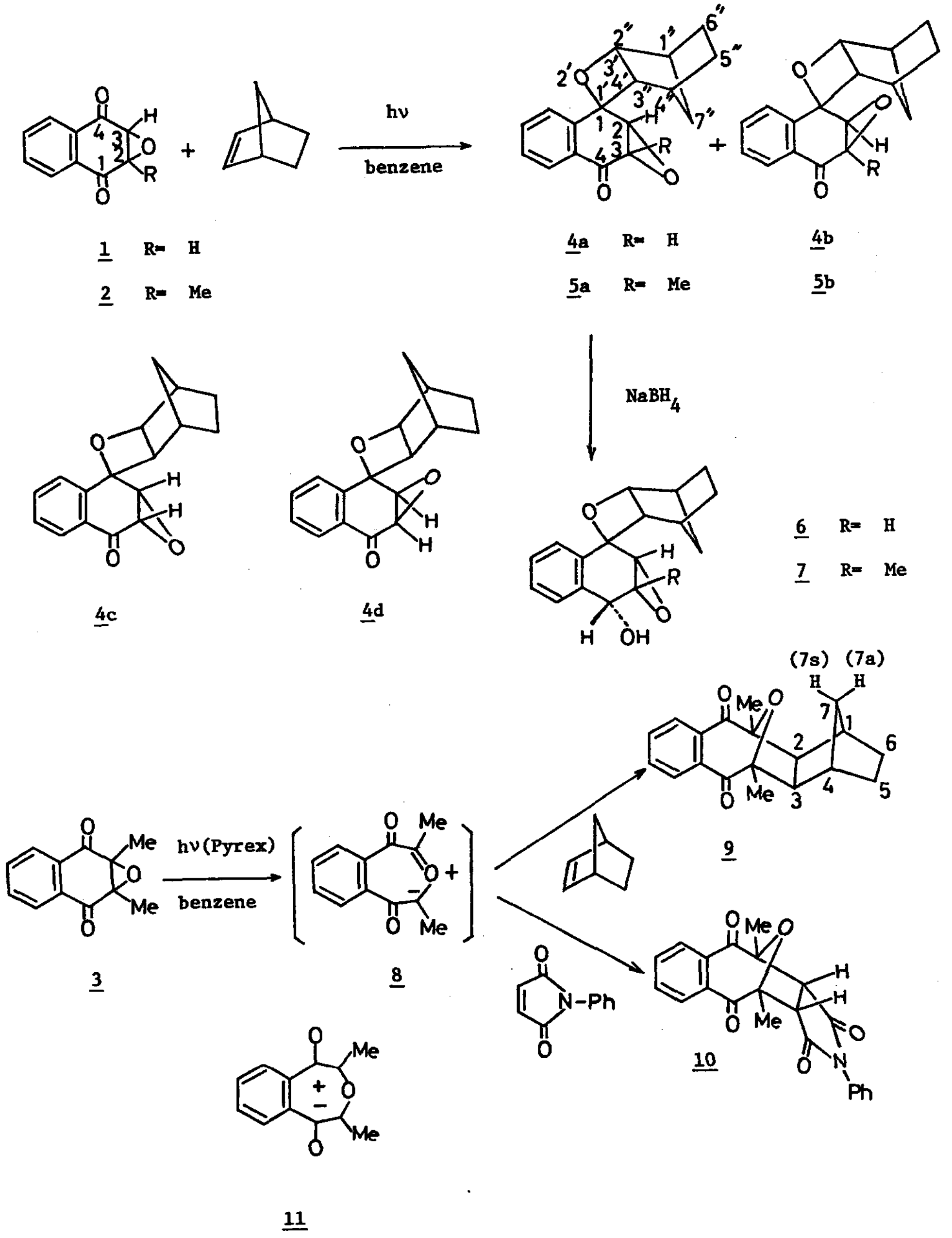
A solution of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone ( 0.06 M ) and norbornene ( 0.18 M ) in benzene was irradiated in a usual glass tube with a 300 W high pressure Hg-arc lamp for about 30 hr. The isolation of the products by preparative thin layer chromatography gave the mixture of two stereoisomeric oxetanes 4a and 4b ( yield 60 %, 4a : 4b = 1.4 : 1 estimated by PMR ). Two isomeric oxetanes could be separated by preparative thin layer chromatography and crystallized. 4a (35 %) ; colorless crystals; mp 158 °C; IR(KBr): 1690 $cm^{-1}$(C=O), 890 and 860 $cm^{-1}$(epoxide ring). PMR($CDCl_3$) $\delta$ 0.98(m, 2H, C-5" and C-6" $CH_2$-*endo*), 1.15(br d, 2H, C-5" and C-6" $CH_2$-*exo*), 1.28-1.80(m, 2H, C-7" $CH_2$), 2.27(d, 1H, C-4' CH, J= 5Hz), 2.46(m, 2H, C-1" and C-4" CH), 3.68 (d, 1H, C-3 CH, J= 4.5Hz), 4.36(d, 1H, C-2 CH, J= 4.5Hz), 4.96(d, 1H, C-3' CH, J=5 Hz), and 7.16-7.96(m, 4H, aromatic-H) ppm. Elemental analysis; found: C, 76.09; H, 6.04%, calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%. 4b (25%); colorless crystals; mp 181-182 °C; IR(KBr): 1689 $cm^{-1}$ (C=O), 880 and 850 $cm^{-1}$(epoxide ring). PMR($CDCl_3$) $\delta$ 0.90-1.30(m, 2H, C-5" and C-6" $CH_2$-*endo*), 1.50-1.80(m, 2H, C-5" and C-6" $CH_2$-*exo*), 1.56(br d, 1H, one proton at C-7" $CH_2$, J= 10Hz), 2.37 (br s, 1H, C-1" CH), 2.56(br d, 1H, another proton at C-7" $CH_2$, J=10Hz), 3.09(d, 1H, C-4' CH, J= 5Hz), 3.12(br s, 1H, C-4" CH), 3.73(d, 1H, C-3 CH, J= 4Hz), 4.36(d, 1H, C-2 CH, J= 4Hz), 4.92(d, 1H, C-3' CH, J= 5Hz), and 7.36-8.20(m, 4H, aromatic-H) ppm. Elemental analysis; found:

C, 76.05; H, 5.92%, calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%. The assignments of the PMR spectra were performed by means of the spin decoupling methods. The configurations of the *exo*-oxetanes 4a and 4b were determined on the basis of their PMR spectra. In the isomer 4b, the bridge head protons ( C-1" and C-4" ) are clearly in very different environments. It is the same situation as for the methylene bridge protons ( C-7" ), while in the isomer 4a bridge head protons have same chemical shifts. Such outstanding differences in their chemical shifts of methylene bridge protons and bridge head protons in 4b are explainable by considering the proximity of one methylene bridge proton and one bridge head proton to the oxygen atom of the epoxide ring in 4b. Under the consideration of molecular model, neither bridge head protons in 4a are affected by the oxygen atom of the epoxide ring. In addition to two isomers 4a and 4b, two other possible stereoisomers 4c and 4d may be formed. However, molecular models show that the methylene bridge in 4c and 4d is severely hindered by the fused aromatic ring and accordingly it is unlikely to result in these isomers. Furthermore, structure 4c and 4d are incompatible with the observed PMR spectra.

The photolysis of 2-methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone 2 with norbornene also gave the mixture of nearly equal amount of two stereoisomeric oxetanes 5a and 5b ( yield 86 % ). The configurations of 5a and 5b were assigned by comparing their PMR spectra with those of 4a and 4b. Since the epoxyquinone 2 is unsymmetrical, two carbonyl groups are of different property. In order to determine which carbonyl group was attacked by norbornene, the isomer 5a ( mp 200-201 °C ) was converted into the alcohol 7 by reduction with sodium borohydride.[2] If the C-1 carbonyl group of 2 was attacked by norbornene, the proton at C-2 of 7 would show a doublet, while the proton at C-2 of 7 would appear as a singlet if the C-4 carbonyl group of 2 was attacked by norbornene. Actually, the proton at C-2 of 7 ( mp 212-218 °C decomp. ) showed a singlet ( $\delta$ 3.90 ) and the selective addition of norbornene to the C-4 carbonyl group of 2 occurred.

On the other hand, irradiation ( using pyrex vessel, >290 nm ) of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone 3 in the presence of norbornene gave no oxetanes but another type of a 1 : 1 adduct 9 (45 %), together with two minor 1 : 1 adducts.[3] 9 ; colorless crystals; mp 131.5-133 °C; IR(KBr): 1760 $cm^{-1}$(C=O). PMR($CDCl_3$) $\delta$ 0.91(br d, 1H, C-7 $CH_2$-*anti*), 1.17(s, 6H, $CH_3$), 1.50-1.64(m, 4H, ethylene bridge protons), 1.53(br d, 1H, C-7 $CH_2$-*syn*), 2.32 (s, 2H, two methine protons), 2.38(br s, 2H, bridge head protons), and 7.4-8.0(m, 4H, aromatic-H) ppm. UV($CHCl_3$) $\lambda_{max}$(log $\varepsilon$) 239, 277, and 285 nm(3.70, 3.46, and 3.45). Mass *m/e* 296 ( $M^+$ ).

## SCHEME 1


hν
benzene
1 R= H
2 R= Me
4a R= H
5a R= Me
4b
5b
NaBH$_4$
4c
4d
6 R= H
7 R= Me
hν(Pyrex)
benzene
3
8
(7s) (7a)
9
10
11

Elemental analysis; found: C, 76.79; H, 6.73%, calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80%. The configuration of 9 was assigned on the basis of the PMR spectrum of 9. That is, the proximity of the oxygen bridge to the *syn* methylene bridge proton (7s) caused the proton (7s) deshielding ( at $\delta$ 1.53 ) and the proton (7a) shielding ( at $\delta$ 0.91 ).[4] These data suggested the symmetrical structure 9 and its *exo,exo*-configuration.

The 1 : 1 adduct 9 seemed to suggest the intermediary formation of the carbonyl ylide 8 or its mesoionic form 11. This is supported by the photolysis of 3 with N-phenylmaleimide to get a 1 : 1 adduct 10 in relatively good yield (60 %). 10 ; colorless needles; mp 291-292 °C; IR(KBr): 1770 and 1700 $cm^{-1}$(C=O). PMR($CD_3SOCD_3$) $\delta$ 1.54(s, 6H, $CH_3$), 3.93(s, 2H, two methine protons of the imide moiety), and 7.3-8.0(m, 9H, aromatic-H) ppm. Mass *m/e* 375 ( $M^+$ ). Elemental analysis; found: C, 70.48; H, 4.35; N, 3.53%, calcd for $C_{22}H_{17}O_5N$: C, 70.39; H, 4.57; N, 3.73%. In this case, the symmetrical adduct 10 has an *endo*-configuration,[5] since only one isomer has been produced. 2,3-Diphenyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone[6] and 2,3-diethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone[7] also showed the same behaviors as that of the 2,3-dimethyl derivative.

## REFERENCES AND NOTES

1. K. Maruyama and S. Arakawa, Chemistry Lett., 719 (1974).
2. A. Rashid and G. Read, J. Chem. Soc. (C), 2053 (1969).
3. Two minor 1 : 1 adducts were resulted from the photolysis of the adduct 9 which was formed initially. The irradiation of 9 in a quarz vessel gave smoothly these adducts. The structural analyses of these adducts are in progress.
4. M. P. Cava and F. M. Sheel, J. Org. Chem., 32, 1304 (1967).
5. J. W. Lown and K. Matsumoto, Can. J. Chem., 49, 3443 (1971).
6. 2,3-Diphenyl-1,4-naphthoquinone was prepared by the method of Beringer *et al.*.
   F. M. Beringer, S. A. Galton, and H. J. Huang, Tetrahedron, 19, 809 (1963); F. M. Beringer and S. A. Galton, J. Org. Chem., 28, 3250 (1963).
   The photolysis of 2,3-diphenyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone with norbornadiene and N-phenylmaleimide was already reported, but it was reexamined by us.
   H. Kato, K. Yamaguchi, and H. Tezuka, Chemistry Lett., 1089 (1974).
7. N. Jacobsen and K. Torssell, Ann. Chem., 763, 135 (1972).