The Photochemical Raction of 2-Alkoxy-1,4-naphthoquinones with Olefins. II. The Formation of Tetrahydropyran-ring Compounds[1)]

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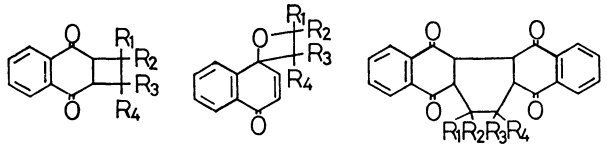
The photochemical reaction of 2-alkoxy-1,4-naphthoquinones with numerous types of olefins was investigated. The reaction was found to proceed smoothly in possible combinations of quinones and olefins to give photo-addition compounds in good yields. The structure of the addition compounds was determined to be **10** by their elemental analyses, mass, IR, PMR, and chemical reactions. The photo-addition reaction is characterized by the formation of a tetrahydropyran ring. This type of photo-addition reaction has not been previously known. The scope and limitations of the new photochemical reaction were described.

The photochemistry of quinones is one of the most attractive fields of study because quinones have been found to play an important role in nature. The irradiation of quinones with olefins produces addition compounds which are difficult to be prepared by any another method.[2)] Such a photochemical reaction of quinones has been found to provide a versatile synthetic route to form C–C and/or C–O bonds.[2)] The photochemistry of 1,4-naphthoquinone with olefins has been investigated by several workers,[3–5)] but systematic investigations in the field have been sparse.

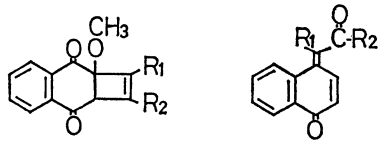
1,4-Naphthoquinone gives, in general, 1,4-naphthoquinhydrone in photochemical reactions with olefins which have active hydrogen atoms such as allylic hydrogen atoms. Olefins with no active hydrogen atoms give, on the other hand, addition compounds in photochemical reactions with 1,4-naphthoquinone, though the yields are relatively poor. The photo-addition compounds can be classified into three structural types: **1**, **2**, and **3**. The mechanism of the



1 **2** **3**

formation of **3** has been investigated in detail.[6)] The low yields of the photo-addition products and the complicated features in the photo-addition reaction of 1,4-naphthoquinone with olefins originate partly from hydrogen-atom abstraction from olefins due to the relatively higher positive oxidation potnetial of 1,4-naphthoquinone.[7,8)]

Since 2-alkoxy-1,4-naphthoquinones have lower positive oxidation potentials compared with that of 1,4-naphthoquinone itself,[7,8)] it seemed that it would be interesting to scrutinize the photochemical reactivities of the former to olefins. Although the photochemical reactions of 2-methoxy-1,4-naphthoquinone with some acetylenic compounds have been reported to yield



4 **5**

cyclobutene derivatives **4**, as well as their rearranged compounds **5**,[9–12)] no reaction mechanisms have been elucidated thus far.

In this work, the photochemical reactions of 2-alkoxy-1,4-naphthoquinones with olefins were examined, and it was found that the reactions proceed quite smoothly to give a novel type of photo-addition compound.

Results and Discussion

The 2-alkoxy-1,4-naphthoquinones examined here are 2-methoxy-, 2-ethoxy-, 2-isopropoxy-, and 2-allyloxy-1,4-naphthoquinone. The olefins selected in this work are 1-hexene, 1-heptene, 1-octene, cyclohexene, cyclooctene, 1,4-cyclooctadiene, bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.1]hept-2,5-diene, styrene, and indene. A benzene solution of a mixture of a 2-alkoxy-1,4-naphthoquinone and an olefin was subjected to photochemical reaction by irradiation with a high pressure Hg arc lamp at room temperature. Neither the precipitation of 2-alkoxy-1,4-naphthoquinhydrones nor any coloration was observed during the course of the reaction, even when olefins had active hydrogen atoms, such as 1-hexene. The reaction proceeded smoothly; this is one of the extremely different features of 2-alkoxy-1,4-naphthoquinones compared with 1,4-naphthoquinone. Photo-addition compounds were obtained in fairly good yields in every case examined here.

The yields of the photo-addition compounds are tabulated in Table 1.

The structures of the photo-addition compounds were determined by the following procedures. As a typical example, the photochemical reaction of 2-methoxy-1,4-naphthoquinone with styrene will be illustrated. After the usual work-up of the reaction mixture, white needles were obtained as the main reaction product in a 69% yield. Elemental analysis and molecular-weight determination by mass spectrometry revealed that the photo-addition compound was composed of one molecule of the 2-methoxy-1,4-naphthoquinone moiety and one molecule of the styrene moiety. The addition compound contained both a hydroxyl group and a carbonyl group, judging from an inspection of its infrared and electronic spectra. The PMR spectrum (Fig. 1) showed seven characteristic groups of lines. The PMR signals corresponding to H_c disappeared after the treatment of the chloroform solution with D_2O. The nuclear spin-spin interactions among H_a, H_b, H_d, and H_e were confirmed by the spin-decoupling technique.

Table 1. The yields of the photo-additon compounds obtained in the reaction of 2-alkoxy-1,4-naphthoquinones with olefins

2-Alkoxy-1,4-naphthoquinone	Olefin	Photo-addition compound	Yield[a] (%)	Mp (°C)
2-Methoxy-1,4-naphthoquinone	1-Hexene	**10 a**	25	—
2-Methoxy-1,4-naphthoquinone	1-Heptene	**10 b**	50	80.0—81.0
2-Methoxy-1,4-naphthoquinone	1-Octene	**10 c**	67	101.0—101.5
2-Methoxy-1,4-naphthoquinone	Cyclohexene	**10 d**	39	—
2-Methoxy-1,4-naphthoquinone	Cycloöctene	**10 e**	74	191.0—198.0
2-Methoxy-1,4-naphthoquinone	1,4-Cycloöctadiene	**10 f**	29	184.0—186.0
2-Methoxy-1,4-naphthoquinone	Bicyclo[2.2.1]hept-2-ene	**10 g**	50	214.0—217.0
2-Methoxy-1,4-naphthoquinone	Bicyclo[2.2.1]hept-2,5-diene	**10 h**	35	199.0—201.0
2-Methoxy-1,4-naphthoquinone	Styrene	**10 i**	69	164.0—164.5
2-Methoxy-1,4-naphthoquinone	Indene	**10 j**	73	225.0—227.0
2-Ethoxy-1,4-naphthoquinone	Styrene	**10 k**	60	168.0—169.0
2-Isopropoxy-1,4-naphthoquinone	Styrene	**10 l**	7.1	117.0—118.0
2-Allyloxy-1,4-naphthoquinone	Styrene	**10 m**	27	139.0—140.0

a) The yields were calculated on the basis of the starting quinones consumed.

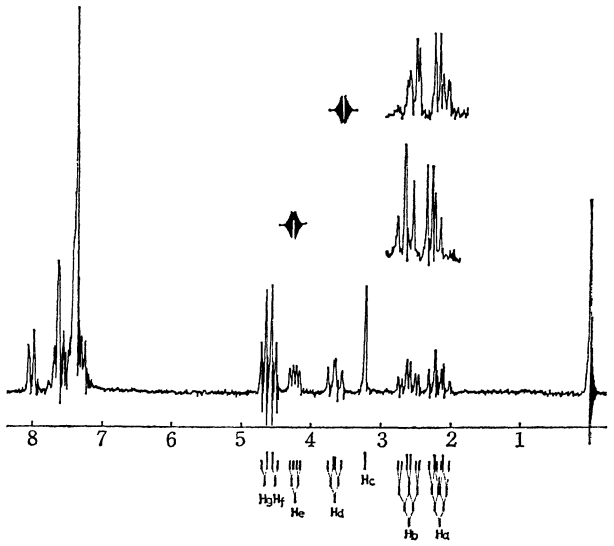
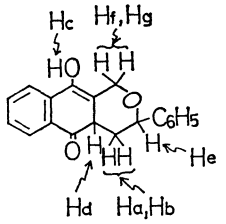


Fig. 1. PMR spectrum of the photo-addition compound.

When 2-deuteriomethoxy-1,4-naphthoquinone was subjected to the same photochemical reaction, the PMR signals corresponding to H_f, and H_g (Fig. 1) of the photo-addition compound disappeared. On the other hand, the PMR signals corresponding to H_d disappeared completely when 2-methoxy-3-deuterio-1,4-naphthoquinone was used in the reaction. These results indicate that the protons, denoted by H_d, H_f, and H_g, of the photo-addition compound originated from the 2-methoxy-1,4-naphthoquinone moiety. From



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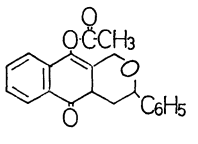
these results, the structure **6** could be proposed as the most probable one for the addition compound. In order to ascertain the structure **6**, the addition compound was submitted to the following chemical reactions. Upon treatment with acetyl chloride, an acetylated product was obtained. This acetylated product was confirmed to be **7** by its IR, PMR, and mass analyses. The Clemmensen reduction of the photo-addition compound gave a mixture of the two compounds. Their structures were assigned to **8** and **9**



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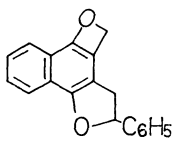

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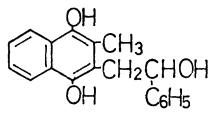

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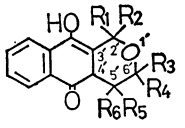
respectively on the basis of an inspection of their IR, PMR, and mass spectra. A similar reaction was reported by the Clemmensen reduction of eleutherins.[13]

Taking these results into account, the structure of the photo-addition compound should be the structure **6**.

The photo-addition compound is characterized by containing a tetrahydropyran ring. A similar type of photochemical reaction was found to proceed in all the 2-alkoxy-1,4-naphthoquinones examined here with a variety of olefins. The structures of the photo-addition compounds obtained here are concluded to have a tetrahydropyran ring and to be **10** on the basis of analyses of their mass, IR, and PMR spectra and their elemental analyses.

The photo-addition reaction could be initiated by the excitation of 2-alkoxy-1,4-naphthoquinones by irradiation, and the addition reaction may proceed *via* radical intermediates to give compounds characterized by containing a tetrahydropyran ring.

To give **10**, the 1,4-naphthoquinone moiety of 2-alkoxy-1,4-naphthoquinones should migrate from the oxygen atom to the α-carbon atom of the alkoxy group during the course of the photochemical reaction; the diradical should then add to olefins to give a final product. Two different routes seem to be plausible



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	R_1	R_2	R_3	R_4	R_5	R_6
10a	H-	H-	n-C_4H_9-	H-	H-	H-
b	H-	H-	n-C_5H_{11}-	H-	H-	H-
c	H-	H-	n-C_6H_{13}-	H-	H-	H-
d	H-	H-	H-	$-(CH_2)_4-$		H-
e	H-	H-	H-	$-(CH_2)_6-$		H-
f	H-	H-	H-	$-(CH_2)_2CH{=}CH(CH_2)_2-$		H-
g	H-	H-	H-	$-CH<^{CH_2}_{(CH_2)_2}>CH-$		H-
h	H-	H-	H-	$-CH<^{CH_2}_{CH=CH}>CH-$		H-
i	H-	H-	C_6H_5-	H-	H-	H-
j	H-	H-	H-	$-CH_2$ 		H-
k	H-	CH_3-	C_6H_5-	H-	H-	H-
l	CH_3-	CH_3-	C_6H_5-	H-	H-	H-
m	H-	CH_2=CH-	C_6H_5-	H-	H-	H-

for the migration.

When the migration proceeds *via* Route (i), the scrambling of the hyrdogen atom at Position Three in the starting quinones should be observed. However, this is not the case, as was determined by the reaction of deuterium-labelled quinone derivatives. That is, the PMR signal corresponding to H_d in the photo-addition compound (see **6**) disappeared completely when 2-methoxy-3-deuterio-1,4-naphthoquinone was used as the starting quinone. From this fact only Route (ii) remains as a possible route for the migration of the 1,4-naphthoquinone moiety.

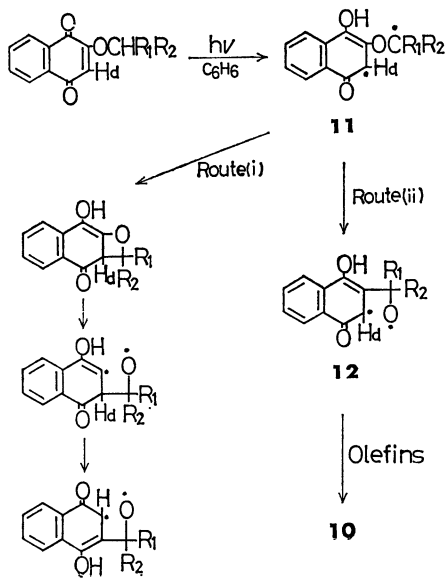


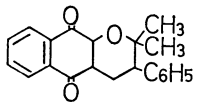
Table 2. Yield dependencies of the photo-addition products on 2-alkoxy groups

R_1, R_2 of the alkoxy groups		Yield of the product **10**[a]	
H	H	**10 i**	69 %
H	CH_3	**10 k**	60 %
CH_3	CH_3	**10 l**	7.1%

a) The yields were calculated on the basis of the starting quinones consumed.

On the other hand, when three quinones with different alkoxy groups were submitted to photochemical reactions with styrene under the same conditions, the yields of similar types of photo-addition compounds vary with the structures of the alkoxy groups. The results obtained are summarized in Table 2. Taking into account the stability of the diradical **11**, the trend of the yields for the photo-addition compounds (**10 i**, **10 k**, and **10 l**) is explicable. The most stable diradical having one of the two radical centers on the tertiary carbon atom (**11**, R_1, R_2=CH_3); an intremediate derived from the reaction of 2-isopropoxy-1,4-naphthoquinone shows the least tendency to yield **10 l**. In this case, another type of photo-addition compound **13** was obtained as the main reaction product; this is the compound produced by the simple addition of **11** to styrene.

In the absence of olefins, compound **14** was isolated as a photochemical reaction product of 2-methoxy-1,4-naphthoquinone. The formation of **14** is feasible *via* the generation of a free radical **11** (R_1,R_2=H), the subsequent 1,2-migration of the 1,4-naphthoquinone



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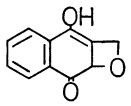

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moiety to **12**, and the final ring closure. All of the results described above confirm the intermediacy of the free radical **11**, and the subsequent 1,2-migration process.

Tetrasubstituted olefins, such as 2,3-dimethylbut-2-ene and tetraphenylethylene, however, give no photo-addition products, but only compound **14** in the photochemical reaction with 2-methoxy-1,4-naphthoquinone. This is presumably because of their sterical requirements.

Experimental

Starting Materials. *2-Methoxy-1,4-naphthoquinone*:[14] 2-Hydroxy-1,4-naphthoquinone (5.0 g), methanol (80 ml), and concd. sulfuric acid (1.2 ml) were heated under reflux for 5 hr. 2-Methoxy-1,4-naphthoquinone precipitated as yellow needles was isolated by a usual work-up and was recrystallized from ethanol (4.0 g); mp 178.0—180.5 °C. Found: C, 70.48; H, 4.25%. Calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.29%. IR(KBr disk); 1680, 1650 cm^{-1} (C=O). UV max($CHCl_3$); 274 nm (log ε=4.22), 355 nm (log ε=3.54).

PMR(CCl_4); δ: 3.88 (3H, singlet), 6.02 (1H, singlet, 7.56—8.08 ppm (4H, multiplet).

2-Ethoxy-1,4-naphthoquinone:[15] By treating 2-hydroxy-1,4-naphthoquinone (2.5 g) with ethanol (30 ml) in the presence of concd. sulfuric acid (1.0 ml) for 8 hr, 2-ethoxy-1,4-naphthoquinone was obtained as yellow needles (1.5 g); mp 118.0—119.0 °C. IR(KBr disk); 1680, 1640 cm^{-1} (C=O). PMR(CCl_4); δ: 1.56 (3H, triplet, J=7.0 Hz), 4.08 (2H, quartet, J=7.0 Hz), 6.02 (1H, singlet), 7.60—8.10 ppm (4H, multiplet).

2-Isopropoxy-1,4-naphthoquinone:[16] 2-Hydroxy-1,4-naphthoquinone (1.0 g), isopropyl alcohol (20 ml), and the boron trifluoride ether complex (3.0 ml) were heated at 70 °C for 7 hr. After cooling, 2-isopropoxy-1,4-naphthoquinone precipitated was collected by filtration, washed with an aqueous solution of sodium hydrogencarbonate until the filtrate was colorless, and then washed once with isopropyl alcohol (0.7 g); mp 111.5—112.0 °C. IR(KBr disk); 1680, 1660 cm^{-1} (C=O). PMR(CCl_4); δ: 1.44(6H, doublet. J=6.0 Hz), 4.56(1H, septet, J=6.0 Hz), 6.00(1H, singlet), 7.58—8.10 ppm (4H, multiplet).

2-Allyloxy-1,4-naphthoquinone:[16] 2-Hydroxy-1,4-naphthoquinone (1.0 g), allyl alcohol (20 ml), and the boron trifluoride ether complex (3.0 ml) were heated at 70 °C for 5 hr. After cooling, water (80 ml) was added to the reaction mixture. 2-Allyloxy-1,4-naphthoquinone precipitated was collected by filtration, washed with an aqueous solution of sodium hydrogencarbonate until the filtrate was colorless, and then recrystallized from ligroin as yellow needles (0.45 g); mp 98.0—100.0 °C. IR(KBr disk); 1680, 1650 cm^{-1} (C=O). PMR(CCl_4); δ: 4.60(2H, broad doublet, J=4.0 Hz), 5.52 (2H, multiplet), 6.00(1H, multiplet), 6.16(1H, singlet), 7.64—8.20 ppm (4H, multiplet).

Olefins: All the olefins used here were commercially available and were purified by distillation before use.

General Procedures. 2-Alkoxy-1,4-naphthoquinone (1 mmol) and olefin (2 mmol) were dissolved in benzene (20 ml) and irradiated in a glass tube by means of a high pressure Hg arc lamp (300 W) through a 5-cm thick water layer. After the 2-alkoxy-1,4-naphthoquinone had been consumed completely, the benzene was distilled off under reduced pressure. Then the reaction mixture was purified by chromatography on silica gel and then further purified by recrystallization from an appropriate solvent.

Identification of the Photo-addition Compound: *6'-n-Butyltetrahydropyrano*[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10a**); yellow oil (yield, 25%). Mass; m/e=272(M^+). IR(liq. film); 3480 (OH), 2920, 2840 (CH), 1680 cm^{-1} (C=O). PMR (CCl_4); δ: 0.96 (3H, CH_3, broad triplet), 1.40 (6H, aliphatic protons, broad multiplet), 1.64—1.90(2H, C-5' CH_2, multiplet), 2.84(1H, C-6' CH, multiplet), 3.28(1H, C-4' CH, triplet, J=10.0 Hz), 3.80 (1H, OH, singlet), 4.34, 4.56(2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 7.24—7.92 ppm (4H, aromatic protons, multiplet).

6'-n-Pentyltetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10b**); white needles from *n*-hexane (yield, 50%); mp 80.0—81.0 °C. Mass; m/e=286(M^+). Found: C, 75.78; H, 8.05%. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74%. IR(KBr disk); 3360 (OH), 2920, 2840 (CH), 1670 cm^{-1} (C=O). PMR(CCl_4); δ: 0.92 (3H, CH_3, broad triplet), 1.36 (8H, aliphatic protons, broad multiplet), 1.64—1.90 (2H, C-5' CH_2, multiplet), 2.92 (1H, C-6' CH, multiplet), 3.28 (1H, C-4' CH, triplet, J=10.0 Hz), 3.92 (1H, OH, singlet), 4.34, 4.56 (2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 7.22—7.96 ppm (4H, aromatic protons, multiplet).

6'-n-Hexyltetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10c**); white needles from *n*-hexane (yield, 67%); mp 101.0—101.5 °C. Mass; m/e=300(M^+). Found: C, 76.21; H, 8.32%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%. IR(KBr disk); 3320 (OH), 2920, 2840 (CH), 1680 cm^{-1} (C=O). PMR(CCl_4); δ: 0.92 (3H, CH_3, broad triplet), 1.36 (10H, aliphatic protons, broad multiplet), 1.64—1.90 (2H, C-5' CH_2, multiplet), 2.92 (1H, C-6' CH, multiplet), 3.30 (1H, C-4' CH, triplet, J=10.0 Hz), 3.50 (1H, OH, singlet), 4.38, 4.58 (2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 7.28—7.96 ppm (4H, aromatic protons, multiplet).

5',6'-Tetramethylenetetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10d**); yellow oil (yield, 39%). Mass; m/e=270(M^+). IR(liq. film); 3350 (OH), 2920, 2840 (CH), 1660 cm^{-1} (C=O). PMR($CDCl_3$); δ: 0.80—3.25 (10H, aliphatic protons, multiplet), 3.42 (1H, C-4' CH, doublet, J=8.0 Hz), 4.48, 4.64 (2H, C-2' CH_2, AB-quartet, J=6.0 4.80 (1H, OH, singlet), 7.24—8.10 ppm (4H, aromatic protons, multiplet).

5',6'-Hexamethylenetetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10e**); white crystals (yield, 74%); mp 191.0—198.0 °C (decomp.). Mass; m/e=298(M^+). IR(KBr disk); 3360 (OH), 2920, 2840 (CH), 1660 cm^{-1} (C=O). PMR($CDCl_3$); δ: 0.90—3.00 (14H, aliphatic protons, multiplet), 3.04 (1H, C-4' CH, doublet, J=8.0 Hz), 4.52, 4.64 (2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 4.72 (1H, OH, singlet), 7.36—8.12 ppm (4H, aromatic protons, multiplet).

5',6'-3''-Hexenylenetetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10f**); white crystals (yield, 29%); mp 184.0—186.0 °C (decomp.). Mass; m/e=296(M^+). IR(KBr disk); 3320 (OH), 3000, 2910, 2840 (CH), 1670 cm^{-1} (C=O). PMR($CDCl_3$); δ: 1.00—2.80 (11H, aliphatic protons and OH, multiplet), 3.16 (1H, C-4' CH, doublet, J=10.0 Hz), 4.68 (2H, C-2' CH_2, broad singlet), 5.52 (2H, C-5'' and C-6'' CH's, broad doublet), 7.28—7.96 ppm (4H, aromatic protons, multiplet).

Bicyclo[*2.2.1*]*heptano*[*2'',3''*-e]*tetrahydropyrano*[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10g**); white crystals from chloroform (yield, 50%); mp 214.0—217.0 °C. Mass; m/e=282 (M^+). Found: C, 76.49; H, 6.63%. Calcd for $C_{18}H_{18}O_3$: C, 75.56; H, 6.44%. IR(KBr disk); 3420 (OH), 2960, 2930, 2880 (CH), 1670 cm^{-1} (C=O). PMR($CDCl_3$); δ: 1.04—2.16 (7H, aliphatic protons, multiplet), 2.42 (2H, aliphatic protons, multiplet), 2.82 (1H, OH, singlet), 2.90 (2H, aliphatic protons, multiplet), 4.56, 4.72 (2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 7.24—7.92 ppm (4H, aromatic protons, multiplet).

Bicyclo[*2.2.1*]*hept-5''-eno*[*2'',3''*-e]*tetrahydropyrano*[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10h**); white crystals from chloroform (yield 35%); mp 199.0—201.0 °C. IR(KBr disk); 3380 (OH), 2960, 2880 (CH), 1665 cm^{-1} (C=O). PMR($CDCl_3$); δ: 1.22—2.00 (3H, aliphatic protons, multiplet), 2.60 (1H, OH, singlet), 2.76 (2H, aliphatic protons, multiplet), 3.06 (2H, aliphatic protons, multiplet), 4.64, 4.78 (2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 6.04 (2H, C-5'' and C-6'' CH's, multiplet), 7.24—7.96 ppm (4H, aromatic protons, multiplet).

6'-Phenyltetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10i≡6**); white needles from benzene (yield, 69%); mp 164.0—164.5 °C. Mass; m/e=292(M^+). Found: C, 78.03; H, 5.45%. Calcd for $C_{19}H_{16}O_3$: C, 78.08; H, 5.52%. IR(KBr disk); 3250 (OH), 2940 (CH), 1675 cm^{-1} (C=O). UV max ($CHCl_3$); 290 nm (log ε=3.48). PMR($CDCl_3$); δ: 2.16 (1H, C-5' CH, multiplet), 2.58 (1H, C-5' CH, multiplet), 3.22 (1H, OH, singlet), 3.62 (1H, C-4' CH, double doublet, J=8.0, 12.0 Hz), 4.18 (1H, C-6' CH, double doublet, J=6.0, 10.0 Hz), 4.56, 4.64 (2H, C-2' CH_2, AB-quartet, J=6.0 Hz), 7.24—8.10 ppm (9H, aromatic protons, multiplet).

Indeno[2″,3″-e]tetrahydropyrano[c-*2,3*]-*hydroxy-4-oxo-3,4-dihydronaphthalene* (**10j**); white needles from benzene-petroleum ether (yield, 73%); mp 225.0—227.0 °C (decomp.). Mass; *m/e*=304 (M^+). Found: C, 79.22; H, 5.28%. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30%. IR(KBr disk); 3320 (OH), 2920 (CH), 1675 cm^{-1} (C=O). PMR($CDCl_3$); δ: 2.04 (1H, OH, singlet), 2.64 (1H, C-5′ CH, multiplet), 3.04 (2H, C-1″ CH_2, double doublet, J=6.0, 10.0 Hz), 3.19 (1H, C-2′ CH_2, AB-quartet, J=6.0 Hz), 7.10—8.00 ppm (8H, aromatic protons, multiplet).

2′-Methyl-6′-phenyltetrahydropyrano[c-*2,3*]-1-*hydroxy-4-oxo-3,4-dihydronaphthalene* (**10k**); white needles from benzene (yield, 60%); mp 168.0—169.0 °C. Found: C, 78.73; H, 5.73%, Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%. IR(KBr disk); 3280 (OH), 2980 (CH), 1680 cm^{-1} (C=O). PMR($CDCl_3$); δ: 1.16 (3H, CH_3, doublet, J=6.0 Hz), 2.16 (1H, C-5′ CH, multiplet), 2.58 (1H, C-5′ CH, multiplet), 2.94 (1H, OH, singlet), 3.62 (1H, C-4′ CH, double doublet, J=8.0, 12.0 Hz), 4.18 (1H, C-6′ CH, double doublet, J=6.0, 10.0 Hz), 4.70 (1H, C-2′ CH, quartet, J=6.0 Hz), 7.22—8.10 ppm (9H, aromatic protons, multiplet).

2′,2′-Dimethyl-6′-phenyltetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10l**); white needles from benzene (yield, 7.1%); mp 117.0—118.0 °C. Mass; *m/e*=320(M^+). Found: C, 78.55; H, 6.22%. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29%. IR(KBr disk); 3320 (OH), 2990, 2920 (CH), 1680 cm^{-1} (C=O). PMR($CDCl_3$); δ: 0.92 (3H, CH_3, singlet), 1.46 (3H, CH_3, singlet), 2.16(1H, C-5′ CH, multiplet), 2.58 (1H, C-5′ CH, multiplet), 2.92 (1H, OH, singlet), 3.62 (1H, C-4′ CH, double doublet, J=8.0, 12.0 Hz), 4.18 (1H, C-6′ CH, double doublet, J=6.0, 10.0 Hz), 7.20—8.16 ppm (9H, aromatic protons, multiplet).

6′-Phenyl-2′-vinyltetrahydropyrano[c-*2,3*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**10m**); white needles from benzene (yield, 27%); mp 139.0—140.0 °C. Mass; *m/e*=318(M^+). IR(KBr disk); 3280 (OH), 3060, 3020, 2880 (CH), 1680 cm^{-1} (C=O). PMR($CDCl_3$); δ: 2.16(1H, C-5′ CH, multiplet), 2.58(1H, C-5′ CH, multiplet), 3.00(1H, OH, singlet), 3.80(1H, C-4′ CH, double doublet, J=8.0, 12.0 Hz), 4.12(1H, C-6′, CH, double doublet, J=6.0, 10.0 Hz), 5.04—6.16(4H, vinyl protons and C-2′, CH, multiplet), 7.22—8.18(9H, aromatic protons, multiplet).

6′,6′-Dimethyl-5′-phenyltetrahydropyrano[b-*2,3*]-*1,4-dioxo-1,2,3,4-tetrahydronaphthalene* (**13**); white needles (yield, 41%); mp 91.0—92.0 °C. Mass; *m/e*=320(M^+). Found: C, 79.07; H, 5.85%. Calcd for $C_{21}H_{20}O_3$: C, 78.75; H, 6.25%. IR(KBr disk); 2970(CH), 1690, 1680 cm^{-1}(C=O). PMR (CCl_4); δ: 0.68(3H, CH_3, doublet, J=6.0 Hz), 0.90(3H, CH_3 doublet, J=6.0 Hz), 2.14(1H, C-4′ CH, multiplet), 2.83(1H, C-4′ CH, multiplet), 3.60—4.00(3H, C-2′, C-3′ and C-5′ CH's, multiplet), 7.24 (5H, aromatic protons, singlet), 7.60—8.24 ppm(4H, aromatic protons, multiplet).

Oxetano[b-*3,2*]-*1-hydroxy-4-oxo-3,4-dihydronaphthalene* (**14**); white crystals (yield, 9%); mp 213.0—218.0 °C (decomp.). Mass; *m/e*=188(M^+). IR(KBr disk); 3450(OH), 1685 cm^{-1} (C=O). PMR(CCl_3); δ: 3.20(1H, CH, singlet), 4.80, 5.28 (2H, CH_2, AB-quartet, J=6.0 Hz), 5.30(1H, OH, singlet), 7.40—8.24 ppm (4H, aromatic protons, multiplet).

Acetylation of a Photo-addition Compound. A photo-addition compound (**6**) (50 mg) was treated with acetyl chloride (2.5 ml) in 1,2-dichloroethane (10 ml) at room tempreature. After having been stirred for 8 hr, the solution was poured onto crashed ice and extracted with chloroform. The chloroform layer was then separated and dried on anhydrous sodium sulfate, and then the reaction mixture was purified by thin layer chromatography on silica gel. An acetylated product (**7**) was isolated as yellowish crystals; mp 160.0—164.0 °C. Mass; *m/e*=334(M^+). IR(KBr disk); 2920 (CH), 1735, 1680 cm^{-1} (C=O). PMR($CDCl_3$); δ: 1.96(3H, $COCH_3$, singlet), 2.50—3.10(2H, C-5′ CH_2, multiplet), 3.60—4.40(2H, C-4′ and C-6′ CH's, multiplet), 4.54, 4.78(2H, C-2′ CH_2, AB-quartet, J=10.0 Hz), 6.90—8.24 ppm (9H, aromatic protons, multiplet).

Clemmensen Reduction of Photo-addition Compound. A photo-addition compound (**6**) (500 mg), toluene (5 ml), amalgamated zinc (10 g), and concd. hydrochloric acid (12 ml) were heated for 8 hr. Two reaction products, **8** and **9**, were then isolated from the reaction mixture using thin layer chromatography on silica gel. The physical properties were as follows; product **8**; white needles; mp 137.0—139.0 °C (decomp.). Mass; *m/e*=274 (M^+). Found: C, 83.06; H, 5.35%. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15%. IR(KBr disk); no absorption signals due to OH or C=O. PMR ($CDCl_3$); δ: 3.14 (2H, CH_2, multiplet), 4.82 (1H, CH, double doublet, J=4.0, 10.0 Hz), 5.44 (2H, CH_2, AB-quartet, J=15.0 Hz), 7.14—7.90 ppm (9H, aromatic protons, multiplet). product **9**; colorless oil. Mass; *m/e*= 276 (M^+–18 (H_2O)). IR(liq. film); 3580, 3400 cm^{-1} (OH). PMR(CCl_4); δ: 2.56 (3H, CH_3, singlet), 3.18 (2H, CH_2, doublet, J=6.0 Hz), 4.82 (1H, CH, triplet, J=6.0 Hz), 7.10—8.00 (9H, aromatic protons, multiplet).

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