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Photochemical Reaction of 2,3-Dihydro-2,3-methano-1,4-naphthoquinone Derivatives. Three Different Types of Reaction

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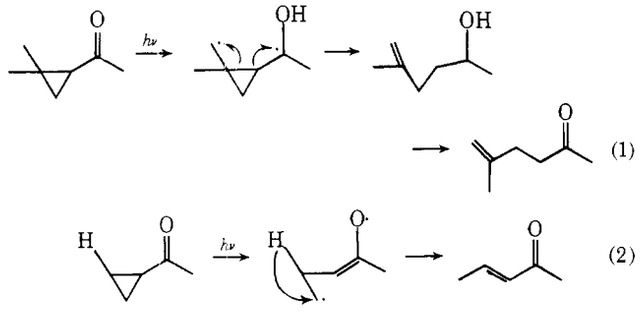
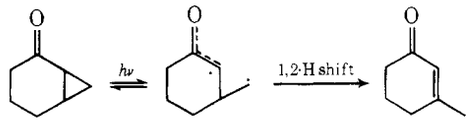
Photochemical reactions of 2,3-dihydro-2,3-methano-1,4-naphthoquinone derivatives in the presence or absence of a hydrogen donor were investigated. The modes of the photochemically induced reactions are dependent on the substituents on the cyclopropane ring, and the reactions can be classified as three different types: isomerization, hydrogen abstraction, and degradation.

The photochemistry of conjugated cyclopropyl ketones has been studied by W. G. Dauben et al. systematically.[1] Photoisomerization of the conjugated cyclopropyl ketones can occur via at least two different mechanistic sequences. The first is the well-known type II reaction (eq 1).[1] The second, found when the δ hydrogen is absent or its abstraction by the carbonyl oxygen atom is sterically impossible, is the cleavage of the bond of the cyclopropane ring adjacent to the carbonyl group. This reaction is accompanied with subsequent 1,2-hydrogen migration (eq 2).

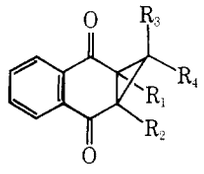


In the bicyclo[4.1.0]heptan-2-one series,[2] the two adjacent cyclopropyl bonds are in a different geometry with respect to the carbonyl group, and in these cases the C_1–C_7 bond cleaves to give cyclohexenones (eq 3). The irradiation of bicyclo[4.1.0]heptan-2-ones in 2-propanol gives cyclohexanones, resulting from the rupture of the outer bond.



(3)

In the present study, eight methanonaphthoquinones(**1a–h**) were prepared, and their photochemical behaviors were examined in both the presence and absence of xanthene, known as a highly reactive hydrogen donor.



1a	$R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
b	$R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
c	$R_1 = R_2 = R_3 = R_4 = H$
d	$R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
e	$R_1 = R_2 = COOEt$; $R_3 = R_4 = H$
f	$R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = Ph$
g	$R_1 = CH_3$; $R_2 = H$; $R_3 = R_4 = Ph$
h	$R_1 = CH_3$; $R_2 = H$; R_3,R_4 = fluorenyl

Results and Discussion

Photoisomerization of 2,3-Diethoxycarbonyl-2,3-dihydro-2,3-methano-1,4-naphthoquinone (1e). A solution of **1e** was irradiated under deaerated conditions in a Pyrex

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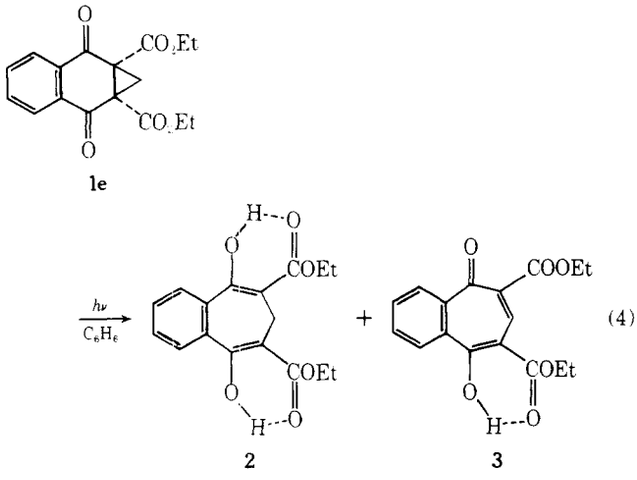
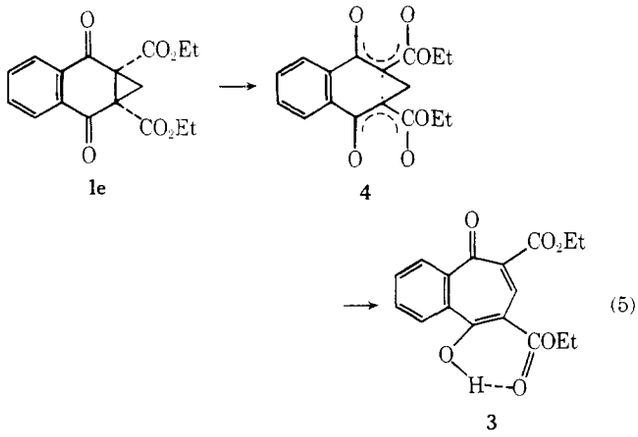
vessel for 12 h with light from a high-pressure Hg-arc lamp at room temperature. After workup, separation by column chromatography gave the two major photoproducts **2** and **3** in yields of 24 and 42%, respectively (eq 4). The structure of



1e **2** **3** (4)

the first was identified as 6,8-diethoxycarbonyl-7*H*-5,9-dihydroxybenzocycloheptene (**2**) by comparison of its melting point and IR and NMR spectra with those of an authentic sample.[3] The second photoproduct was assigned as 6,8-diethoxycarbonyl-9-hydroxybenzocycloheptene-5-one (**3**) by comparison of its melting point IR and NMR spectra with those of an authentic sample.[3] In the presence of xanthene in a benzene solution, a higher yield (45%) of **2** was obtained upon irradiation of **1e**, but no appreciable change in the yield of **3** (42%) was noted. The result indicates that product **2** is the reduction product formed by intermolecular hydrogen abstraction; the photoexcited species of **1e** abstracts hydrogen atoms from another molecule of **1e** when a hydrogen donor such as xanthene is absent from the reacting solution. The mechanism for intermolecular hydrogen atom abstraction by methanonaphthoquinones, including **1e**, will be discussed in detail below.

For the formation of photoproduct **3**, the mechanism shown in eq 5 is highly probable. The initial photoexcitation of **1e** is

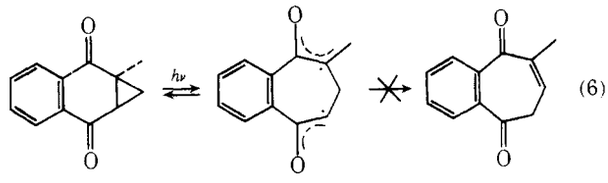


1e **4** **3** (5)

followed by the opening of the inner cyclopropane bond to form biradical **4**. Through subsequent 1,4-hydrogen atom migration, photoisomerization product **3** may be formed.

The present results are quite interesting when compared with the photoisomerization of bicyclo[4.1.0]heptan-2-ones, in which the outer cyclopropane bond cleaves. The preferred rupture of the inner bond of **1e** is probably due to the fact that the developing biradical **4** could be stabilized by the delocalization of the two unpaired electrons over the two separated ethoxycarbonyl groups and the two carbonyl groups. The inner dipole–dipole repulsive force due to the ethoxycarbonyl groups could also be responsible for the easier C_2–C_3 bond cleavage.

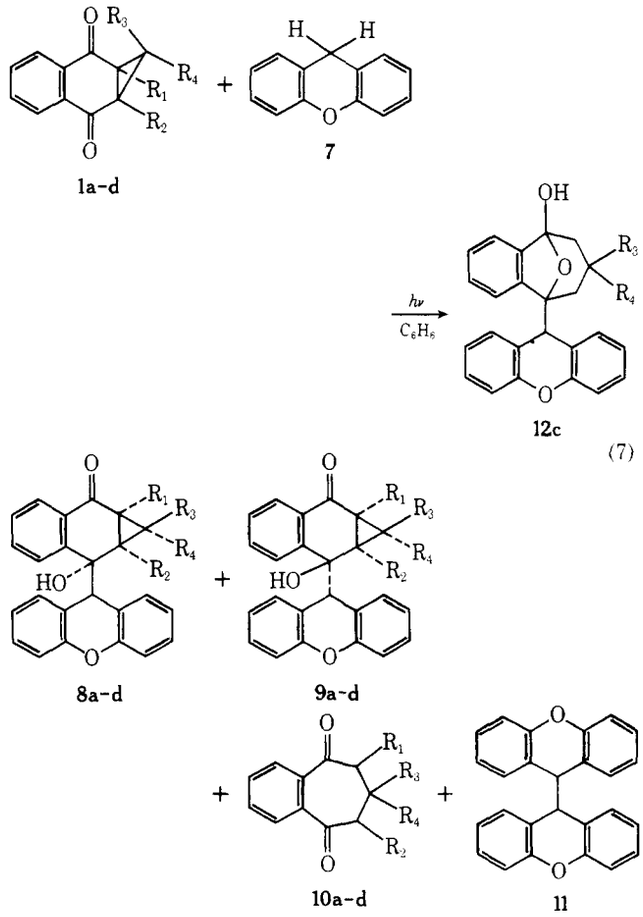
On the contrary, irradiation of the other methanonaphthoquinones (**1a–d** and **1f–g**) in benzene under comparable conditions gave none of the photoproducts corresponding to **2** and **3**. The extreme reluctance of these methanonaphthoquinones to photoisomerize is dramatic. As for methanonaphthoquinone **1a**, for example, biradical **5**, if it once was formed, would not be as stable as biradical **4**. **5** may simply undergo ring closure to give the starting material (eq 6).



1a **5** **6** (6)

Photoreduction of Alkyl-Substituted 2,3-Dihydro-2,3-methano-1,4-naphthoquinones (1a–d). We previously published a note on the photochemical reactions of **1a–b**.[4] Products and the cause of the reactions were briefly discussed in it. Further details and extensions of the reaction will be given below.

Respective solutions of **1a–d** in benzene are photostable when they are irradiated by light from a 300-W high-pressure Hg-arc lamp. However, in the presence of xanthene (**7**), they reacted fairly fast to afford **8a–d**, **9a–d**, and **10a–d** as the main products together with 9,9′-bixanthenyl (**11**). These results are summarized in eq 7 and Table I.



1a-d **7** **12c** (7)

8a-d **9a-d** **10a-d** **11**

The photoproducts **8a** and **9a**, for example, result from the addition of xanthene to C_4-carbonyl group, and they are configurational isomers of each other. The basis for structural assignment of **8a**, **9a**, and **10a** was described in the previous

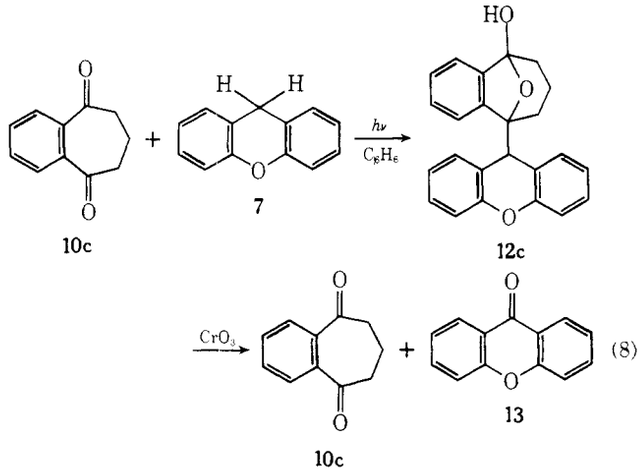
Table I. Yields of Products in the Photochemical Reactions of Methanonaphthoquinones 1a–d with Xanthene[a]

Methanonaphthoquinones	Irradiation time, h	Isolated yields,[b] % 8a–d	9a–d	10a–d	12c
1a	6	35	21	19	c
b	18	45	14	Trace	c
c	4	20	8	30	14
d	6	29	10	15	c

[a] The solution of methanonaphthoquinones and 2 equiv of xanthene was irradiated in benzene using a 300-W high-pressure Hg-Arc lamp. [b] Yield was based on the amounts of methanonaphthoquinones used. [c] Not determined.

paper.[4] Similarly, the structures of **8b–d, 9b–d,** and **10b–d** were determined on the basis of their IR, NMR, and mass spectral data. Elemental analyses of these compounds were all compatible with their structures. Chromic acid oxidation and sodium borohydride reduction were used as the major weapons for the structural differentiation between two configurational isomers (**8** and **9**).

The structure of **12c** was assigned on the basis of the following: IR spectrum showed the absence of a carbonyl group and the presence of a hydroxyl group (3400 cm^{-1}) and ether bonding (1000 cm^{-1}); chromic acid oxidation gave **10c** and xanthone; **12c** was formed on irradiation of a benzene solution of **10c** and xanthene (**7**) (eq 8).



(8)

Furthermore, the rate of disappearance of methanonaphthoquinones **1a–d** in the presence of xanthene was measured in order to estimate the relative reactivities of **1a–d.** The results are summarized in Table II. It is noticeable that the reactivity of **1b** was extremely low compared with that of other methanonaphthoquinones. The reason for the low reactivity is probably due to the two carbonyl groups on C_1 and C_4 being hindered sterically by two methyl groups. Such a steric effect of methyl groups explains the photochemical behavior of **1a,** i.e., the exclusive addition of xanthene moiety to the sterically less-hindered C_4-carbonyl group. On the same basis, the low reactivity of **1f** will be explainable; **1f** was recovered unchanged even after irradiation for 80 h in the presence of xanthene.

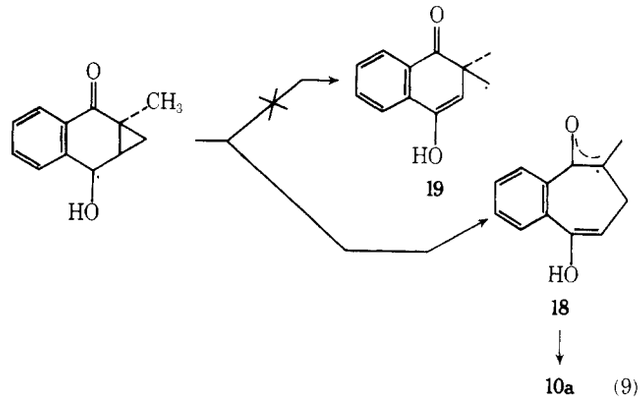
As was described in the previous paper,[4] ^1H CIDNP examination of the reactions revealed that **8a** and **9a** are recombination products via an initial triplet radical pair. Considering that the methine proton on C_3 of **1a** showed an emission polarized signal, we concluded that the starting material, **1a,** was reproduced again as the escape product from the triplet radical pair (**16**).[5]

Table II. Relative Reactivities of Methanonaphthoquinones 1a–d[a]

Methanonaphthoquinones	Recovery, %	Conversion %
1a	31	69
b	95	5
c	58	42
d	67	33

[a] Irradiation of a benzene solution of methanonaphthoquinone (5×10^{-4} M) and xanthene (1×10^{-3} M) was carried out under deaerated conditions for 1.5 h (20 mL of benzene used).

For the photochemical reaction of methanonaphthoquinone **1a** with xanthene, the mechanism shown in Scheme I may be postulated. The photochemical reaction of **1b–d** with xanthene is recognized on the same line. Isomerization of ketyl radical **17** to possible alternative **19** seems to be excluded because the derivative of the latter could not be found in the reaction mixture (eq 9).

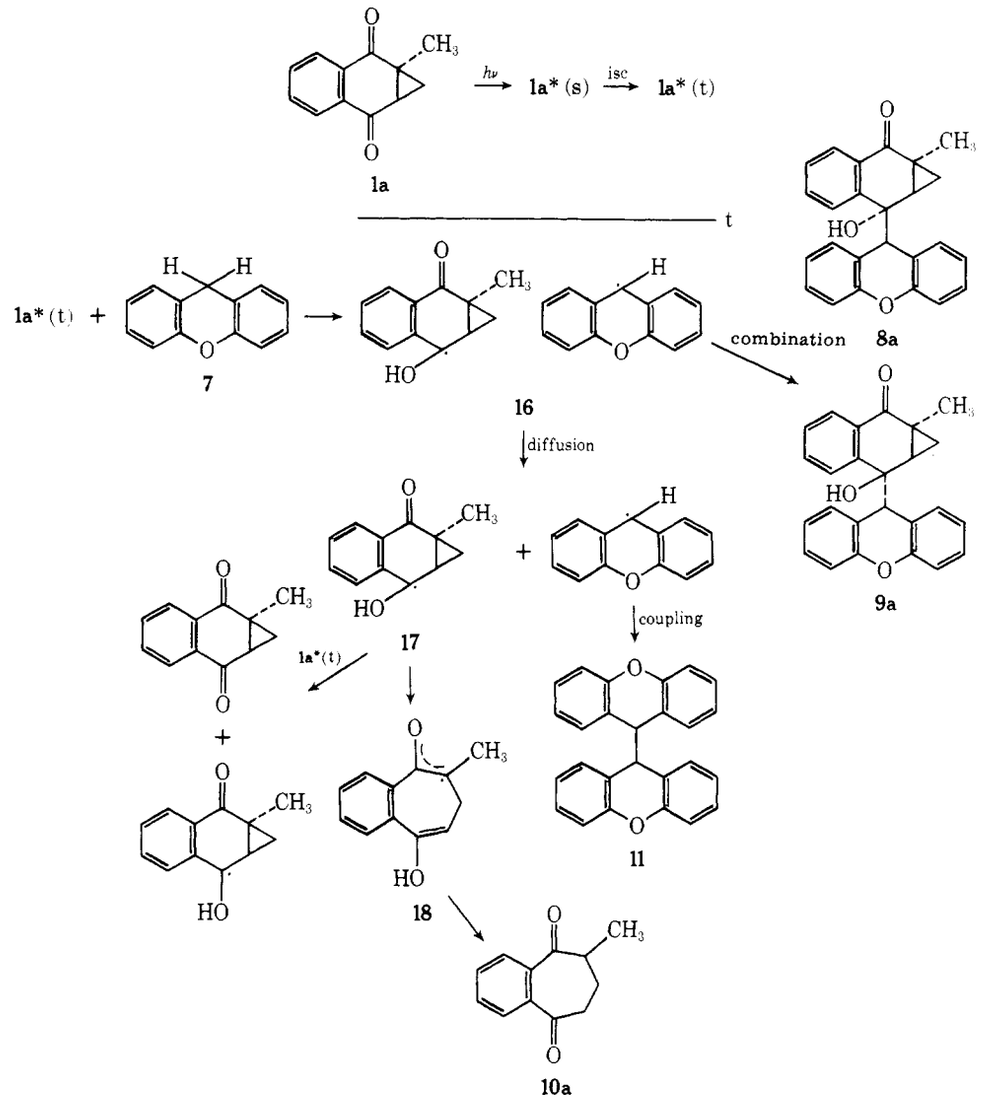


(9)

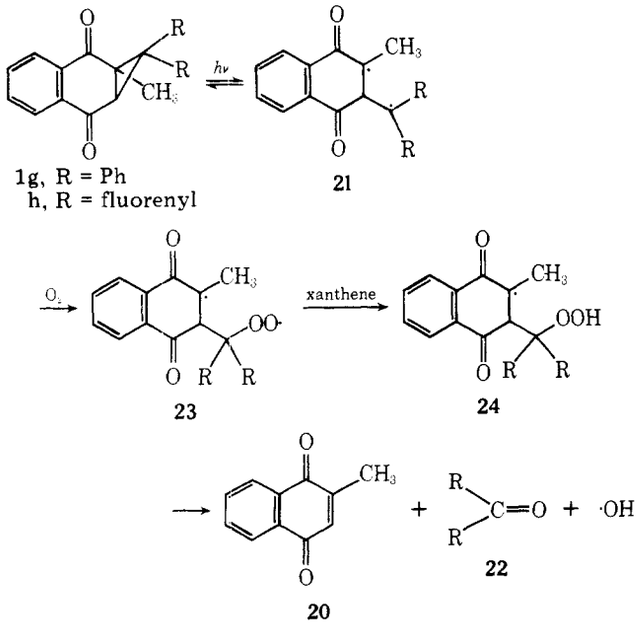
Photodecomposition of Aryl-Substituted 2,3-Dihydro-2,3-methano-1,4-naphthoquinones (1g and 1h). Whereas **1f** is quite stable upon irradiation as described above, under aerated conditions a benzene solution of **1g** or **1h** degradated fairly fast in the presence of xanthene. On the other hand, when under complete deaerated conditions a benzene solution of **1g** or **1h** irradiated in the presence or absence of xanthene in a Pyrex vessel using a 300-W high-pressure Hg-arc lamp showed no reaction even after prolonged exposure (50 h). Thus, 7,7-diaryl-substituted 2,3-dihydro-2,3-methano-1,4-naphthoquinones, **1g–h,** are photostable even in the presence of a good hydrogen donor, contrary to the reaction of **1a–d.** However, oxygen dissolved in the solution brought about a drastic change in the feature of the reactions. As described above, under the aerated conditions, **1g** and xanthene dissolved in benzene reacted fairly fast upon irradiation and disappeared completely after exposure for 40 h, giving 2-methyl-1,4-naphthoquinone (**20,** 49%), benzophenone (**22g,** 32%), and 9,9′-bixanthenyl. The other products were composed of intractable brown materials. Dissolved oxygen in solution has a similar effect on the reaction of **1h.** The result was comparable to that of **1g,** yielding 2-methyl-1,4-naphthoquinone (67%), fluorenone (45%), and 9,9′-bixanthenyl.

At first sight, the mechanism involving the formation of diarylcarbene might be postulated for this type of photochemical reaction. In fact, such a mechanism has already been proposed for the gas-phase photolysis of benzylcyclopropane.[6] However, the route via carbene as a reactive intermediate was ruled out for our reactions by the following experimental data. Irradiation of a benzene solution of **1g** or **1h** in the absence of xanthene afforded no photoproduct. In addition, when a so-

Scheme I



Scheme II



lution of **1g** and xanthene in benzene/methanol was irradiated, no photoproduct resulting from the insertion of diphenylcarbene into methanol was isolated.[7] The above results are likely to suggest that photodegradation of **1g** or **1h** under aerated conditions did not proceed via diarylcarbene but via diradical **21**, which is probably soon stabilized to **1g** or **1h**. The lifetime of diradical **21** will be elongated by the presence of substituents, aryls and methyl, at radical centers in an appreciable degree.[7] It is reasonable to consider that diradical **21** can uptake an oxygen molecule but not abstract a hydrogen atom from xanthene. Thus, the reaction of **1g** and **1h** under aerated conditions will be tentatively formularized as shown in Scheme II.

Experimental Section

Infrared spectra were recorded on a JASCO IR-G spectrometer using a KBr disk or a liquid film. ^{1}H NMR spectra were obtained on a JEOL PS-100 MHz instrument with Me_4Si as internal standard in a suitable solvent. Ultraviolet spectra were recorded on a Shimadzu UV-200 spectrometer. Mass spectra were taken on a Hitachi M-52 mass spectrometer. All melting points were taken on a Yanagimoto micro-melting-point apparatus and are uncorrected.

1. **Preparation of 2,3-Dihydro-2,3-methano-1,4-naphthoquinones (1a–h).** The methanonaphthoquinones used were prepared by denitrogenation of the corresponding indazoles.[8] The indazoles were synthesized from appropriate diazo compounds and 1,4-naphthoquinone derivatives. Methanonaphthoquinones **1c** and **1e**, however, were prepared as described by G. L. Buchanan.[3,9] If not otherwise stated, denitrogenation of indazoles was performed by treating them with 72% perchloric acid. Physical constants and spectral data of the prepared 2,3-dihydro-2,3-methano-1,4-naphthoquinones, **1a–h**, are tabulated in Table III. The UV absorption spectrum of **1a** in cyclohexane exhibited three characteristic bands at 245.5 (log ϵ 3.84), 293.5 (3.24), and 331 nm (2.4). The other methanonaphthoquinones showed similar bands to those of **1a**.

Table III. Physical Constants of 2,3-Dihydro-2,3-methano-1,4-naphthoquinones

Compound	Registry no.	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H	*m/e* (M^+)	^{1}H NMR, ppm
1a	16650-34-3	68–69	77.38	5.41	77.41	5.40	186	1.50 (s, 3 H), 1.58 (m, 2 H), 2.50 (d ofd, 1 H), 7.5–8.0 (m, 4 H)
b	36225-17-9	80–81	77.96	6.04	77.95	6.03	200	1.40 (AB q, 2 H), 1.80 (s, 6 H), 7.60–8.0 (m, 4 H)
c	29200-97-3	68–69	76.71	4.68	76.70	4.73	172	1.42–1.90 (m, 2 H), 2.60–2.8 (m, 2 H), 7.6–8.1 (m, 4 H)
d	64044-71-9	59–61	77.96	6.04	78.00	6.02	200	1.30 (d, 3 H), 1.50 (s, 3 H), 2.0 (m, 1 H), 2.30 (d, 1 H), 7.60–8.10 (m, 4 H)
e	64044-72-0	118–119	69.83	5.51	69.81	5.55	292	2.50 (AB q, 2 H), 3.20 (t, 6 H), 4.28 (q, 4 H), 7.7–8.2 (m, 4 H)
f	64044-73-1	132–134	84.99	4.59	85.02	4.55	307	1.25 (s, 3 H), 3.12 (AB q, 1 H), 7.2–7.4 (m, 5 H), 7.6–8.2 (m, 4 H)
g	13599-29-6	216–218	85.18	5.36	85.16	5.34	172 (M^+ − 166	1.40 (s, 3 H), 3.30 (s, 1 H), 6.8–8.0 (m, 14 H)
h[10]	64070-49-1	219–220	85.69	4.79	85.70	4.71	172 (M^+ − 164)	1.82 (s, 3 H), 3.55 (s, 1 H), 6.2–8.4(m, 12 H)

2. Isomerization of 2,3-Diethoxycarbonyl-2,3-dihydro-2,3-methano-1,4-naphthoquinone (1e). A solution of **1e** (500 mg) in benzene was irradiated in a Pyrex vessel by light from a 300-W high-pressure Hg-arc lamp for 12 h at room temperature. Isolation of the photoproducts by column chromatography on silica gel gave 6,8-diethoxycarbonyl-7*H*-5,9-dihydroxybenzocycloheptene (**2**, 48 mg, 24%) and 6,8-diethoxycarbonyl-9-hydroxybenzocycloheptene-5-one (**3**, 86 mg, 46%) together with the recovered starting material **1e** (297 mg). The structures of photoproducts **2** and **3** were determined by comparison with the corresponding authentic samples.[9]

6,8-Diethoxycarbonyl-7*H*-5,9-dihydroxybenzocycloheptene (**2**): colorless needles from ethanol; mp 86–87 °C; IR (KBr) 2900 (H-bonding OH), 1620, 1250, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.4 (t, 6 H, ethyl CH_3), 3.00 (broad s, 2 H, CH_2), 4.34 (q, 4 H, ethyl CH_2), 7.64 (m, 2 H, aromatic H), 12.5 (s, 2 H, bonding OH).

6,8-Diethoxycarbonyl-9-hydroxybenzocyclohepten-5-one (**3**): pale yellow needles from ethanol; mp 76–76.5 °C; IR (KBr) 2900 (H-bonding OH), 1710 (C=O), 1650 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.36 (t, 3 H, ethyl CH_3), 4.32 (q, 4 H, ethyl CH_2), 7.76 (m, 2 H, aromatic H), 7.92 (m, 1 H, aromatic H), 8.36 (m, 1 H, aromatic H), 8.44 (s, 1 H, CH), 14.8 (s, 1 H, H-bonding OH).

3. Photoreduction of Alkyl-substituted 2,3-Dihydro-2,3-methano-1,4-naphthoquinones (1a–d). General Procedure. With some exceptions where it is noted, irradiations were conducted in a Pyrex vessel using a 300-W high-pressure Hg-arc lamp through a 5-cm thick water layer at room temperature. During irradiation, the reacting mixture was monitored by thin layer chromatography. Evaporation of solvent gave semisolids which were crystallized on the addition of methanol. Filtration of the semisolid and recrystallization from benzene/methanol gave 9,9′-bixanthenyl as colorless needles: mp 212–213 °C; IR (KBr) 1480, 1450, 1250, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.2 (s, 2 H, CH), 6.6–7.4 (m, 16 H, aromatic H). 9,9′-Bixanthenyl was obtained in all cases for the reactions examined and isolated as the first eluent on column chromatography of the products.

Photoreduction of 1a,b with Xanthene. The structures and spectral data of photoreduction products of **1a** and **1b** with xanthene were described already in a previous paper.[4,5]

Photoreduction of 1c with Xanthene. Irradiation of a solution of **1c** (200 mg) and xanthene (400 mg) in benzene (30 mL) gave *cis*-4-xanthenyl-2,3-methano-3,4-dihydro-4-hydroxynaphthalene-1(2*H*)-one (**8c**, 70 mg, 20%), *trans*-4-xanthenyl-2,3-methano-3,4-dihydro-4-hydroxynaphthalene-1(2*H*)-one (**9c**, 28 mg, 8%), 6,7,8,9-tetrahydrobenzocycloheptene-5,9-dione (**10c**, 52 mg, 30%), and 9-xanthenyl-5,9-epoxy-6,7,8,9-tetrahydrobenzocycloheptene-5-ol (**12c**, 49 mg, 14−) together with recovered starting material **1c** (25.1 mg).

Photoproduct **8c:** colorless needles from benzene/hexane; mp 157–158 °C; IR (KBr) 3400 (OH), 1650 (C=O), 1480, 1430, 1240, 750 cm^{-1}; ^{1}H NMR $CDCl_3$) δ 0.64 (m, 1 H, CH_2), 1.00 (m, 1 H, CH_2), 1.90 (m, 2 H, CH), 2.4 (s, 1 H, OH), 4.24 (s, 1 H, CH), 6.2–7.68 (m, 12 H, aromatic H); MS *m/e* 172 (M^+ − 181), 181, 182. Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.12; H, 5.30.

Photoproduct **9c:** colorless needles from benzene/hexane; mp 206–208.5 °C; IR (KBr) 3400 (OH), 1650 (C=O), 1470, 1240, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (m, 2 H, CH_2), 1.6–2.0 (m, 2 H, CH), 2.6 (s, 1 H, CH), 6.7–8.3 (m, 12 H, aromatic H); MS *m/e* 172 (M^+ − 181), 181, 182. Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.55; H, 5.02.

Photoproduct **12c:** colorless needles from benzene/hexane; mp 203–205 °C; IR (KBr) 3320 (OH), 1470, 1450, 1250, 1000, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.4–2.0 (m, 6 H), 3.32 (s, 1 H, OH), 4.52 (s, 1 H, CH), 6.9–7.5 (m, 12 H, aromatic H); MS *m/e* 356 (M^+), 185 (M^+ − 181), 182, 181.

The structure of **10c** was identified by comparison with an authentic sample obtained by Zn–CH_3COOH reduction of **1c.** Photoproduct **10c:** colorless needles from hexane; mp 39–40 °C; IR (KBr) 1685 (C=O), 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.92–2.29 (m, 2 H, CH_2), 2.80 (t, 4 H, CH_2), 7.4–7.72 (m, 4 H, aromatic H).

Photoreduction of 1d with Xanthene. Irradiation of a solution of **1d** (200 mg) and xanthene (400 mg) in benzene (30 mL) gave cis-2,9-dimethyl-4-xanthenyl-2,3-methano-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one (**8d,** 98.6 mg, 29%), *trans*-2,9-dimethyl-4-xanthenyl-2,3-methano-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one (**9d,** 34.1 mg, 10%), and 6,7-dimethyl-6,7,8,9-tetrahydrobenzocycloheptene-5,9-dione (**10d,** 25.5 mg, 15%) together with recovered starting material **1d** (30.2 mg).

Photoproduct **8d:** colorless needles from benzene/hexane; mp 188–189 °C; IR (KBr) 3320 (OH), 1650 (C=O), 1475, 1450, 1245, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91–1.16 (m, 1 H, *endo*-H), 1.00 (s, 3 H, *exo*-CH_3), 1.10 (s, 3 H, CH_3), 1.28 (d, 1 H, CH), 2.22 (s, 1 H, OH), 4.16 (s, 1 H, CH), 5.8–7.7 (m, 12 H, aromatic H); MS *m/e* 201 (M^+ − 181), 182, 181. Anal. calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.44; H, 5.68.

Photoproduct **9d:** colorless needles from benzene/hexane; mp 220–222 °C; IR (KBr) 3480 (OH), 1650 (C=O), 1475, 1450, 1245, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.44 (m, 1 H, *endo*-H), 0.8 (d, 3 H, *exo*-CH_3), 1.16 (s, 3 H, CH_3), 1.24 (d, 1 H, CH), 2.2 (s, 1 H, OH), 5.16 (s, 1 H, CH), 6.7–8.1 (m, aromatic H); MS *m/e* 201 (M^+ − 181), 182, 181. Anal. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.68; H, 5.69.

The assignment of **10d** was made by comparison with an authentic sample prepared by Zn–CH_3COOH reduction of **1d.** Photoproduct **10d:** oil; IR (liquid film) 1695 (C=O), 1590 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.04 (d, 3 H, CH_3), 1.16 (d, 3 H, CH_3), 2.2–3.3 (m, 4 H), 7.48–7.80 (m, 4 H, aromatic H).

Oxidation of 12c with Chromic Acid. Oxidation of photoproduct **12c** (52 mg) with chromic acid (300 mg) under the same conditions used for that of **8a** gave 6,7,8,9-tetrahydrobenzocycloheptene-5,9-dione (**10c**) (12 mg, 50%) and xanthone (15 mg, 52%).

4. Photodegradation of Aryl-Substituted 2,3-Dihydro-2,3-methano-1,4-naphthoquinones (1f–h). Reaction of 1f with Xanthene. Irradiation of a solution of **1f** (100 mg) and xanthene (200 mg) in benzene (20 mL) for 80 h gave no photoproduct, and the starting material was recovered quantitatively. Even under deaerated conditions the feature of the reaction was quite similar.

Reaction of 1g with Xanthene. Under deaerated conditions, a solution of **1g** (480 mg) and xanthene (800 mg) in benzene (60 mL) was irradiated for 50–60 h in a Pyrex vessel. After the solvent was removed, we recovered only a mixture composed of **1g** and xanthene. However, under aerated conditions, irradiation of a solution of **1g** (480 mg) and xanthene (800 mg) in benzene (60 mL) for 40 h by light from

a 300-W high-pressure Hg-arc lamp gave reaction products. After removal of the solvent, isolation of the residue by column chromatography on silica gel gave 2-methyl-1,4-naphthoquinone (**20**, 85 mg, 49%) and benzophenone (**22g**, 62 ng 32%) together with 9,9′-bixanthenyl.

Photoproduct **20:** yellow needles from ethanol; mp 107 °C; IR (KBr) 1650 (C=O), 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (d, 3 H, CH_3), 6.84 (d, 1 H, CH), 7.64–7.84 (m, 2 H, aromatic H), 7.96–8.16 (m, 2 H, aromatic H).

Photoproduct **22 g:** colorless crystals; mp 49–50 °C, confirmed by mixture-melting-point method compared with an authentic sample.

Reaction of 1h with Xanthene. Under completely deaerated conditions, irradiation of a mixture of **1h** and xanthene dissolved in benzene gave no photoproduct. However, under aerated conditions, irradiation of **1h** (200 mg) and xanthene (400 mg) dissolved in benzene (30 ml) for 40 h gave 2-methyl-1,4-naphthoquinone (**20**, 63 mg, 67%) and fluorenone (**22h**, 4 mg, 45%). Photoproduct **22n** was assigned to fluorenone by comparing with an authentic sample.

Registry No.—**2**, 64044-74-2; **3**, 64044-75-3; **8c**, 64044-76-4; **8d**, 64044-77-5; **9c**, 64069-99-4; **9d**, 64070-00-4; **10c**, 54034-10-5; **10d**, 64044-78-6; **12c**, 64044-79-7; **20**, 58-27-5; **22g**, 119-61-9; 9,9′-bixanthenyl, 4381-14-0; xanthene, 92-83-1.

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Pericyclic Synthesis and Exploratory Photochemistry of Potentially Direct Progenitors of the Unrestricted Hetero[11]annulene System

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The procedure of α-pyrone C_4H_4 homologation was applied to the synthesis of the heterotricycles shown in **5, 6, 9,** and **18,** which were judged to be useful, potentially direct, synthetic precursors for the construction of "unrestricted" hetero[11]annulenes. Compounds **6, 9,** and **18** readily fragment under the influence of heat or light to produce benzene and the corresponding five-membered heterocycle. On the other hand, exploratory photochemical work with **5** has revealed the system's propensity to undergo dimerization on sensitized illumination and multidirectional bond relocation, to **20** and **21** and **22,** on direct irradiation.

The tactical use of pericyclic transformations offers a unique means of gaining entry into potentially labile unrestricted[1] π-excessive frames such as the hetero[9]-,[2] hetero[13]-,[2b,3] and hetero[17]annulenes.[3] One notable common characteristic of these monocyclic substances is that they were all prepared by synthetic procedures utilizing cyclooctatetraene as the basic synthon and are thus associated with a $(4n + 1)$-membered periphery containing a total of $(4n + 2)$ π electrons. In other words, the pericyclic synthetic schemes developed here[2] and elsewhere[3] are strictly designed for the construction of potentially aromatic heterocycles. In theory, extension of this useful procedure to the preparation of potentially antiaromatic π-excessive heterocycles, i.e., molecules incorporating a $(4n - 1)$-membered periphery and a total of $4n$ π electrons, may be realized simply by changing the basic hydrocarbon building unit from cyclooctatetraene to benzene. We have examined the practical aspects of such a modification to the original synthetic design and wish to present in this report a description of our experiences in this connection, relating to the construction of a variety of potentially direct synthetic progenitors of the unrestricted hetero[11]annulene system.

Multicyclic Valence Tautomers of the Aza[11]annulene System

Since N-substituted azepines are known to undergo thermal cycloaddition[4-6] with a variety of reactive dienes yielding symmetrically bridged 1:1 adducts of general structure **1,** our initial attempts in this project concentrated on the possible application of the α-pyrone-induced C_4H_4 homologation procedure we previously devised[7,8] for converting an aza[9]annulene (azonine) to the 13-membered counterpart. All effort along these lines, however, was effectively frustrated by the failure of the azepine **2**[9] to react with α-pyrone (**3**) on prolonged contact and over a wide temperature range (70–110 °C). Our failure to effect cycloadditive coupling between **2** and **3** was not entirely unexpected insofar as the homologation process as initially designed calls for cycloadditive trapping of a skeletally uncomfortable trans double bond, i.e., a reactive functionality not present in **2.** Therefore, it became necessary to utilize in the basic homologation scheme a C_6H_6NR synthon with more reactive double bonds than are present in **2.** With this in mind we directed our attention to the readily available [3.2.0] photoisomer of **2,** shown as **4**[10] in Scheme I. This molecule does indeed react with a benzene solution of **3** at 65 °C to produce a mixture of cycloadducts (A, Scheme I) in ca. 62% yield. A, in turn, readily extrudes CO_2 upon heating at 140–145 °C in vacuo (ca. 0.05 mm) to yield a thermolysate consisting of the three nonvolatiles **5** (^1H NMR, IR, UV, MS), **6** (^1H NMR, IR, UV, MS), and **7** (^1H NMR, IR) in a molar ratio of 1:1.2:1.8 (60% yield). The assignment of anti stereochemistry to **5** follows from the small value of $J_{8,9}$ (2 Hz) which is more consistently accommodated by the dihedral angle estimated (Dreiding models) for a trans H–H disposition (~100°) than

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