The Photochemical Dimerization of 2-Acyl-1,4-quinones

Yo Miyagi,* Kazuhiro Maruyama,† Hideo Ishii, Sachie Mizuno, Masao Kakudo,††
Nobuo Tanaka,†† Yoshiki Matsuura,†† and Shigeharu Harada††
Faculty of Education, Kanazawa University, Kanazawa 920
†*Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606*
††*Institute for Protein Research, Osaka University, Suita, Osaka 565*

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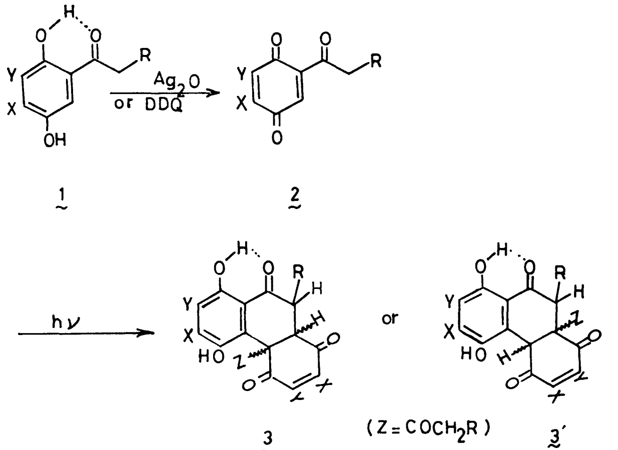
2-Acyl-1,4-benzoquinones and 2-acyl-1,4-naphthoquinones underwent a novel type of regiospecific and stereospecific cyclodimerization by photolysis. The reaction was general, being not affected by any variation in the substituents and solvents. The structure of the dimers was elucidated as 4aα-acyl-10β-alkyl-5,8-dihydroxy-4aα,10aα-dihydro-1,4,9(10*H*)-phenanthrenetriones and dibenzo[*b*,*h*]homologues (**8**). The structure of **8** suggests that the dimerization proceeds through *cis*-ring fusion, disposing two substituents of the dimer (an acyl and an alkyl group) to a *trans* configuration.

Many types of photochemical reactions have been reported for quinones and related compounds.[1] In the absence of other sustrates, 1,4-quinones undergo dimerization to give oxetanes and cyclobutanes. We wish to report here that acyl-1,4-quinones (**2**) suffer a novel and general type of dimerization upon irradiation.[2] For example, when a degassed solution of 2-butanoyl-1,4-benzoquinone (**2c**) in carbon tetrachloride was irradiated with a high-pressure mercury arc lamp in a Pyrex tube, a yellow solid product soon crystallized out, the yield of the product being up to 80% in 15 h. Elemental analysis and mass spectrometric data showed it to be a dimer of **2c**. When benzene was used as the solvent, none of the dimer crystallized out of the reaction solution, but the solution was deeply darkened because of the partial decomposition of the dimer formed. As is shown in Table 1, the reaction proceeded in the same fashion on acylquinones with a wide variety of substituents, and only a single compound was obtained in each case. The solutions of **2** gave no signs of affording such dimers after standing for a fairly long time without light at room temperature.

The isolation and purification of the dimers could not be performed under the same conditions since the dimers decomposed thermally or with a trace amount of water, sometimes even with moisture. Consequently, the yields of the purified dimers were of less constancy. This makes it hard to compare the each yields with others obtained under different conditions. However, there is a discernible tendency for the reaction to be considerably slower for acetylquinones **2** (R=H) than for the other acylquinones **2** (R≠H) (Table 1).

The Skeletal Structure of the Dimers. The structures of the dimers were determined by means of their ^{1}H NMR spectral data, which are listed in Table 2. They are all consistent either with **3** or **3′** (the usual double-resonance technique was used to determine the identity of protons causing ^{1}H-^{1}H couplings). The spectrum of a dimer of **2g** in CDCl$_3$ is exemplified, illustrated with the atoms denoted in Table 2.



Four methyl signals were observed. Two of them had coupling constants of 7.5 Hz; the triplet at 0.99 and the doublet at 1.29 were assigned to Me$_A$ and Me$_B$, respectively. Although the triplet suggests the existence of the COCH$_2$Me$_A$ group, the spectrum lacked a quartet normally expected for a methylene group. Instead, a lot of weak signals were observed at 2.1—2.6. This suggests that the COCH$_2$Me$_A$ group might be bound to an asymmetric carbon atom. The third methyl signal, arising at 1.99 as a doublet (J=1.5 Hz), may be ascribed to Me$_C$. The signal was split by coupling with H$_C$, which showed its signal at 6.77 as a quartet (J=1.5 Hz). The fourth methyl group, Me$_D$, and the aromatic

Table 1. Yields of the dimers 3

	a	b	c	d	e	f	g	h	i	j	k	l	m
R	H	Me	Et	*n*-Pr	*n*-Bu	H	Me	Me	H	Me	H	Me	Et
X	H	H	H	H	H	Me	Me	Cl	Br	Br	-(CH=CH)$_2$-		
Y	H	H	H	H	H	H	H	H	H	H			
Yield/%	60	40	80	15	44	40	20	40	0	10	0	30	25
Irradiation time/h	100	15	15	10	13	70	15	40	30	15	20	10	10
Solvent[a]	c	c	c	a	a	c	c	c	c	c	b	b	b

a) a, benzene–cyclohexane (1:4, v/v); b, benzene; c, carbon tetrachloride.

proton, H_D, showed their signals as singlets at 2.30 and 6.84, respectively. The double quartet at 2.81 may be due to H_B, which was coupled with Me_B (J=7.5 Hz) and H_A (J=3.5 Hz). The doublet at 3.84 (J=3.5 Hz) was assigned to H_A, which was coupled with H_B. A chelated and a non-chelated hydroxyl proton resonated at 12.28 and 6.10, respectively.

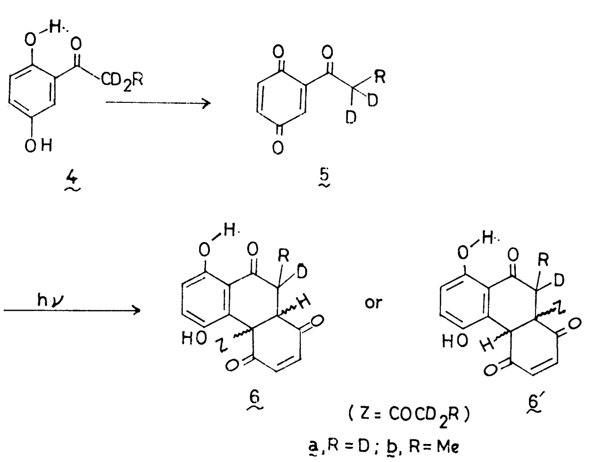
The other dimers showed similar spectra, but with partial variations dependent on their substituents.

i) The variation for R=H (the dimers of **2a** and **2f**). A set of signals of the ABX type was observed at about 3.0 (H_B and $H_{B'}$) and at about 4.1 (H_A). A singlet due to an acetyl group was observed at about 2.2.

ii) The variation for X=Y=H (the dimers of **2a**—**e**). Two AB quartets due to H_C and $H_{C'}$, and to H_D and $H_{D'}$, were observed at about 6.7 and about 7.1, respectively.

iii) The variation for X+Y=–(CH=CH)$_2$– (the dimers of **2l**—**m**). Two sets of four aromatic protons gave complex signals at 7.5—8.5.

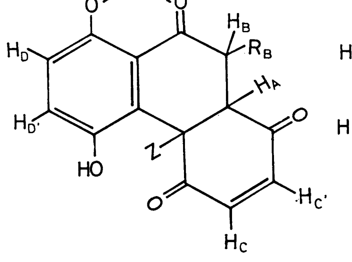
The above assignments were substantiated by the spectra of the dimers (**6a**—**b** or **6'a**—**b**) of the partially deuterated monomers (**5a**—**b**), which were prepared from **4a**—**b**. The signals due to H_B and $H_{B'}$ (dABq at 3.08) and $COCH_3$ (s at 2.23) of **3a** disappeared, and the signal of H_A became a singlet upon deuteration. The doublets due to Me_B (1.45) and H_A (4.08) and the triplet due to Me_A (0.96) of **3b** all became singlets in **6b**.



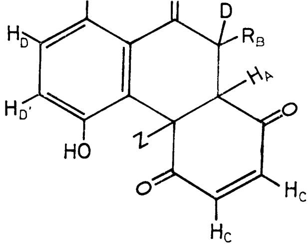
However, all the types of spectra illustrated above may be explained by the alternative structure, **3'**, *i.e.*, an orientational isomer of **3**, though **3** is more feasible for the following reason. The value of the ^{1}H-^{1}H coupling constant, which had been ascribed above to the H_A–C–C–H_B coupling of **3g**, was 3.5 Hz. The corresponding values of the other dimers were also in the range of 3.0—4.0 Hz. They are a little too large for the H–C–C–C–H couplings, which should be in **3'**. The ^{13}C NMR data of the dimer of **2h** was also either compatible with **3h** or **3'h**, shown with **3h** in Fig. 1. As was stated in a previous communication,[2] **3'** was excluded on the basis of chemical evidence by converting

Table 2. ^{1}H NMR data of the dimers **3** and **6**: δ/ppm

	Solv[a]	OH[b]	OH[c]	H_D and $H_{D'}$	H_C and $H_{C'}$	H_A	H_B (and $H_{B'}$)	R_B (R_B=H and $(CH_2)_nMe_B$ (n=0—3))	$COCH_2R_A$ (R_A=H and $(CH_2)_nMe_A$(n=0—3))
3a	A	12.30	9.28	7.18[d] (9 Hz)	6.76[d] (11 Hz)	4.09 (dd, 5 and 3 Hz)	3.08 (2H, dABq[e])	$R_B=H_{B'}$	2.23 (s, Ac): R_A=H
6a	A	12.59	8.91	7.30[d] (8.5 Hz)	6.88[d] (10 Hz)	4.15 (s)	$H_B=H_{B'}$ =D	$R_B=H_{B'}$=D	$CH_2R_A=CD_3$
3b	A	12.44	9.43	7.01[d] (9 Hz)	6.62[d] (10 Hz)	4.08 (d, 3.5 Hz)	unclear	1.46 (d, 7 Hz, Me_B): n=0	0.96 (t, 7 Hz, Me_A); $C\mathbf{H}_2$–Me_A, unclear
6b	A	12.30	9.09	6.98[d] (8.5 Hz)	6.59[d] (10 Hz)	4.09 (s)	H_B=D	1.45(s, Me_B): n=0	0.95 (s, Me_A); $CH_2R_A=CD_2Me_A$
3c	A	12.42	9.18	7.01[d] (9 Hz)	6.60[d] (10 Hz)	4.18 (d, 3.5 Hz)	unclear	1.01 (t, 7 Hz, Me_B); –$C\mathbf{H}_2Me_B$ and	0.80 (t, 7 Hz, Me_A); –$(C\mathbf{H}_2)_2Me_A$, unclear
	C	12.34	5.82	6.98[d] (8 Hz)	6.68[d] (10 Hz)	3.94 (d, 3.5 Hz)	unclear	0.94 (t, 7 Hz, Me_B); –$C\mathbf{H}_2Me_B$ and	0.78 (t, 7 Hz, Me_A); –$(C\mathbf{H}_2)_2Me_A$, unclear
3d	C	12.35	5.90	6.95[d] (9 Hz)	6.63[d] (10 Hz)	3.95 (d, 3.5 Hz)	unclear	0.91 (t, 6 Hz, Me_B); –$(C\mathbf{H}_2)_2Me_B$ and	0.82 (t, 7 Hz, Me_A); –$(C\mathbf{H}_2)_3Me_A$, unclear
3e	C	12.41	6.12	7.00[d] (9 Hz)	6.69[d] (10 Hz)	4.06 (d, 3.5 Hz)	unclear	0.90 (t, 6 Hz, Me_B); –$(C\mathbf{H}_2)_3Me_B$ and	0.83 (t, 6.5 Hz, Me_A); –$(C\mathbf{H}_2)_4Me_A$, unclear



3a-e
(Z=COCH$_2$R$_A$)

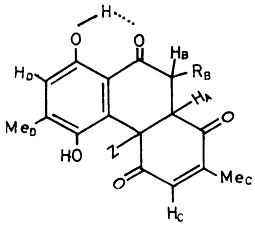


6 (Z=COCD$_2$R$_A$)
a, R=D; b, R=Me

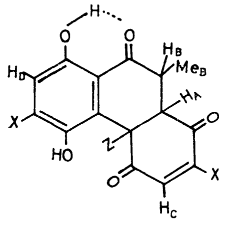
Table 2. (Continued)

	Solv[a]	OH[b]	OH[c]	H_D	H_C	H_A	H_B (and $H_{B'}$)	Me_D	Me_C	R_B (R_B=H and $(CH_2)_nMe_B$ (n=0—1))	$COCH_2R_A$ (R_A=H and $(CH_2)_nMe_A$ (n=0—1))
3f	A	12.81	8.03	6.81 (1H, s)	6.75 (1H, q, 1.5 Hz)	3.99 (dd, 5 and 4 Hz)	3.00 (2H, dABq[f])	2.14 (s)	1.81 (d, 1.5 Hz)	R_B=$H_{B'}$	2.34 (s, Ac): } R_A=H
	C	12.20	—	6.88 (1H, s)	6.83 (1H, q, 1.5 Hz)	3.76 (dd, 8.5 and 5 Hz)	2.95 (2H, dABq[g])	2.13 (s)	2.01 (d, 1.5 Hz)		2.35 (s, Ac):
3g	A	12.41	7.84	6.76 (1H, s)	6.60 (1H, q, 1.5 Hz)	4.08 (d, 3 Hz)	2.82 (1H, dq, 7 and 3 Hz)	2.30 (s)	1.74 (d, 1.5 Hz)	1.43 (d, 7 Hz, Me_B)	0.94 (t, 7 Hz, Me_A); CH_2Me_A, unclear
	C	12.28	6.10	6.84 (1H, s)	6.77 (1H, q, 1.5 Hz)	3.84 (d, 3.5 Hz)	2.81 (1H, dq, 8 and 3.5 Hz)	2.30 (s)	1.99 (d, 1.5 Hz)	1.29 (d, 7.5 Hz, Me_B)	0.99 (t, 7.5 Hz, Me_A); CH_2Me_A, unclear
3h	C	12.54	5.78	7.15 (1H, s)	7.08 (1H, s)	4.10 (d, 3.5 Hz)	2.92 (1H, m)	—	—	1.52 (d, 7 Hz, Me_B)	1.06 (t, 7 Hz, Me_A); CH_2Me_A, nuclear
3j	A	12.44	8.64	7.42 (1H, s)	7.29 (1H, s)	4.19 (d, 3.5 Hz)	3.06 (1H, dq, 6 and 3.5 Hz)	—	—	1.48 (d, 6 Hz, Me_B)	0.98 (t, 7 Hz, Me_A); CH_2Me_A, unclear
3l	C	14.18	6.40	7.6—8.4 (8H, m)		4.11 (d, 4 Hz)	3.01 (1H, dq, 7 and 4 Hz)	—	—	1.30 (d, 7 Hz, Me_B)	1.02 (t, 7 Hz, Me_A); CH_2Me_A, unclear
3m	C	14.19	6.60	7.6—8.5 (8H, m)		4.16 (d, 3.5 Hz)	2.78 (1H, m)	—	—	0.92(t, 7 Hz,Me_B); CH_2Me_B and	0.77 (t, 7 Hz, Me_A); $(CH_2)_2Me_A$, unclear

a) A, CD_3COCD_3; C, $CDCl_3$. b) Chelated (1H). c) Non-chelated (1H). d) 2H, ABq. e) Analyzed as AMX: 2.90 (H_B, $J_{A,B}$=5 Hz), 3.26 ($H_{B'}$, $J_{A,B'}$=3 Hz); $J_{B,B'}$=18 Hz. f) Analyzed as AMX: 2.84 (H_B, $J_{A,B}$=5 Hz), 3.16 ($H_{B'}$, $J_{A,B'}$=4 Hz); $J_{B,B'}$=18.5 Hz. g) Analyzed as AMX: 2.81 (H_B, $J_{A,B}$=5 Hz), 3.09 ($H_{B'}$, $J_{A,B'}$=8.5 Hz); $J_{B,B'}$=18.5 Hz.

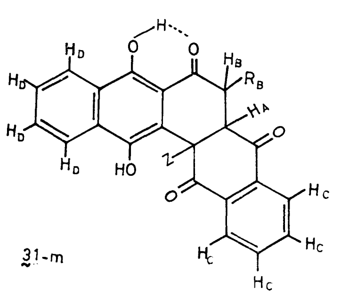


3 f-g



3 h and j

(Z= $COCH_2R_A$)



3l-m

a dimer to a phenanthrenequinone derivative. Finally, **3** was confirmed by X-ray analysis.

The Stereochemistry of the Dimers. The structures of the dimers, including their stereochemistry, were unequinvocally resolved by X-ray structure analysis. It was carried out for the monoacetyl derivative of

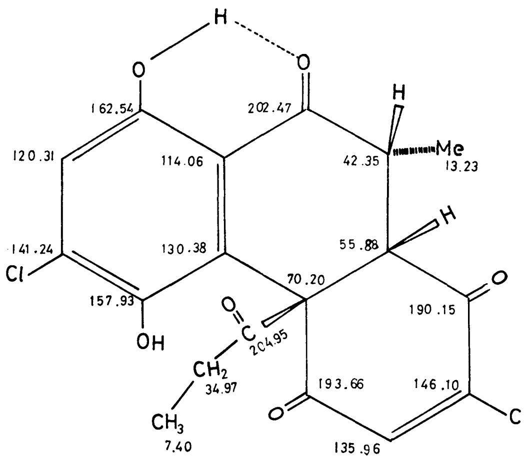


Fig. 1. Carbon chemical shifts of **3h** in $CDCl_3$(δ/ppm).

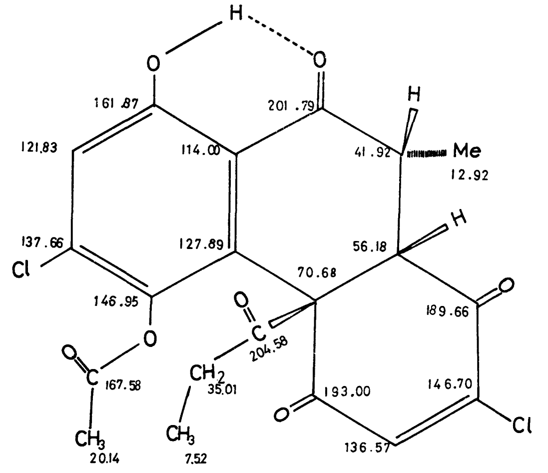


Fig. 2. Carbon chemical shifts of **7** in $CDCl_3$ (δ/ppm).

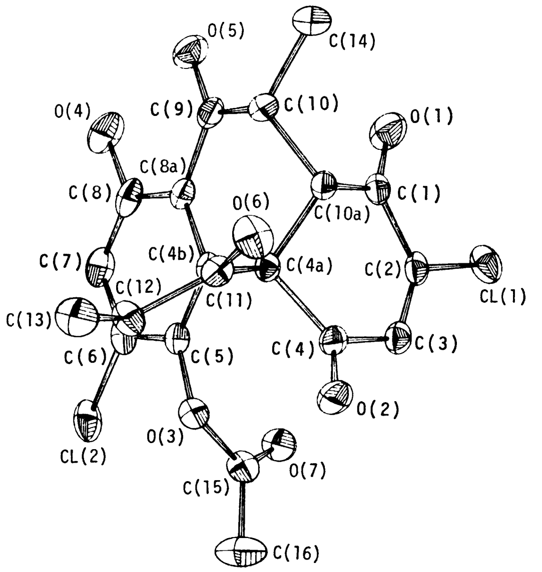
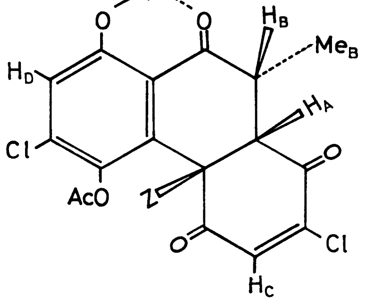


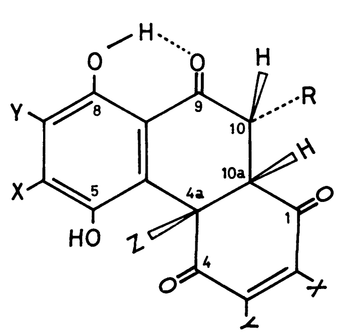
Fig. 3. Perspective view of **7**.

the dimer of **2h** because the dimer itself gave no satisfactory single crystals. The monoacetyl derivative was prepared by treating the dimer with Ac_2O-*p*-TsOH; it showed a ^1H NMR spectrum quite similar to that of the parent dimer (Table 2). Its ^{13}C NMR spectrum was also similar to that of the dimer (Fig. 2).

Figure 3 presents a stereoscopic view of one molecule. Here, the acetyl derivative has the structure and complete stereochemistry shown in **7**. Accordingly, those of the dimers should be shown as **8**, confirming **3** as the sketletal structure. The *cis* disposition of the hydrogen atom at C_{10a} and the acyl group at C_{4a} indicates that the condensation proceeds through a *cis* addition. The disposition of the hydrogen atoms at C_{10} and C_{10a} was also clarified as *cis*.



7 ($Z=COCH_2Me_A$)



8 ($Z=COCH_2R$) 4aα-Acyl-10β-alkyl-5,8-dihydroxy-4aα,10aα-dihydro-1,4,9(10*H*)-phenanthrenetrione.

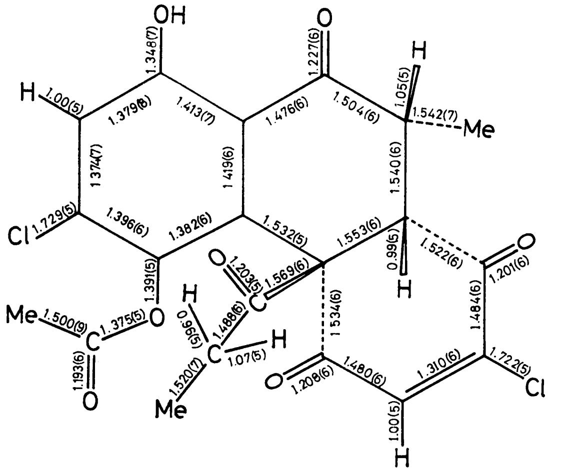
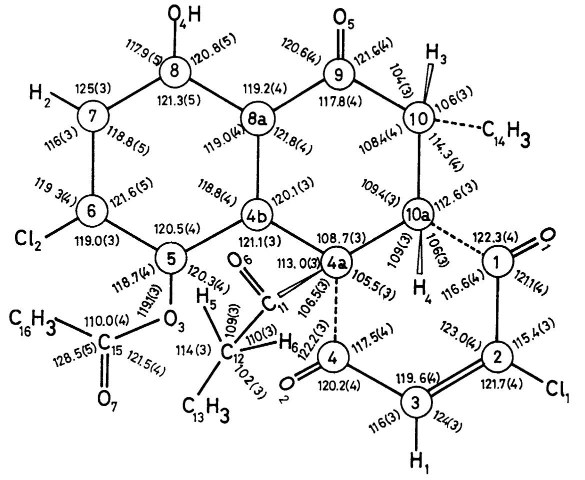


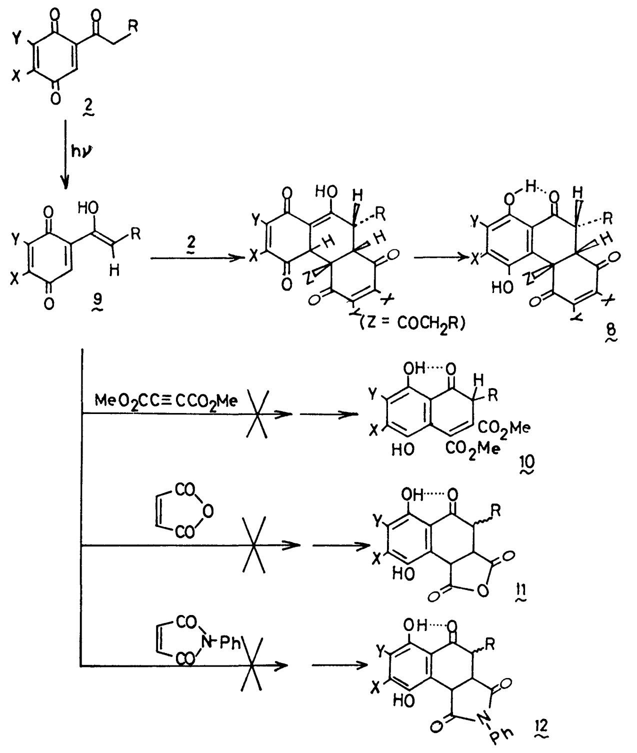
Fig. 4. Bond lengths of **7** (l/Å).



∠C(4)-C(4a)-C(4b), 114.2(3); ∠C(10a)-C(4a)-C(11), 108.5(3); ∠C(9)-C(10)-C(14), 114.4(4); ∠C(10a)-C(10)-H(3), 109(3); ∠C(10)-C(10a)-H(4), 109(3); ∠C(1)-C(10a)-C(4a), 109.6(3); ∠O(6)-C(11)-C(4a), 118.0(4); ∠O(6)-C(11)-C(12), 123.7(4); ∠C(4a)-C(11)-C(12), 118.3(3); ∠C(11)-C(12)-C(12)-C(13), 113.7(4); ∠H(5)-C(12)-H(6), 108(4).

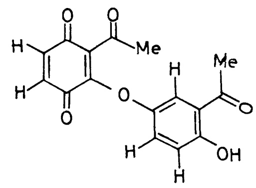
Fig. 5. Numbering of atoms and bond angles (ϕ/°) of **7**.

Mechanistic Consideration. The following mechanism may be the most plausible. In many cases, the Diels-Alder reaction resulted in the preferential formation of a certain one of the possible orientational and stereochemical isomers. Photochemically formed enols have been known to undergo the Diels-Alder reaction with dienophiles.[3] If the above mechanism indeed holds, the condensation of the enol, **9**, with the other kinds of dienophiles should proceed. However, the expected products, **10**, **11**, or **12**, were not obtained and the dimer **8** was still the only isolable product when the



reaction was carried out in the presence of twice as many moles of maleic anhydride, *N*-phenylmaleimide, or dimethyl acetylenedicarboxylate.

In contrast to the above dimerization, the other type of dimer, **13**, was obtained by the irradiation of degassed solutions of **2a**—**c** in the presence of Rose Bengal.[4] The mechanisms of the above two dimerizations are now under investigation.



13

Experimental

2-Acylhydroquinones (1). **1a**—**j** were prepared from hydroquinones and carboxylic acids by known methods.[5-7] **1k**—**m** were photochemically prepared from 1,4-naphthoquinone and aldehydes by a known method.[8] All the new compounds gave satisfactory results in elemental analyses and

Table 3. Physical data of 2-acyl-1,4-quinones (**2**)

	X	Y	R	Mp/°C	Found (%) (Calcd (%))			Molecular formula	^{1}H NMR: δ (CDCl$_3$)		Method of prepn.	Yield %
					C	H	X		Aliphatic	Aromatic		
a	H	H	H	62.5— 65.5	Known compound[a)]				2.57 (3H, s, Ac)	6.94 (2H, d[d)]) 7.10 (1H, d[d)])	A	90
b	H	H	Me	36—37	65.89 (65.85	5.04 4.91)	—	$C_9H_8O_3$	1.14 (3H, t, 7 Hz, Me) 2.88 (2H, q, 7 Hz, CH_2)	6.70 (2H, d[d)]) 6.88 (1H, d[d)])	A	80
c	H	H	Et	39— 40.5	67.47 (67.40	5.63 5.66)	—	$C_{10}H_{10}O_3$	0.98 (3H, t, 7 Hz, Me) 1.70 (2H, sex, 7 Hz, CH_2) 2.85 (2H, t, 7 Hz, $COCH_2$)	6.88 (2H, d[d)]) 7.02 (1H, s)	A	80
d	H	H	*n*-Pr	37.5— 39	68.98 (68.73	6.21 6.29)	—	$C_{11}H_{12}O_3$	0.93 (3H, t, 7 Hz, Me) 1.2—1.7 (4H, m, $(CH_2)_2$) 2.87 (2H, t, 7 Hz, $COCH_2$)	6.81 (2H, d[d)]) 6.93 (1H, d[d)])	C	65
e	H	H	*n*-Bu	50.5— 52	69.58 (69.88	6.95 6.84)	—	$C_{12}H_{14}O_3$	0.86 (3H, t, 7 Hz, Me) 1.2—1.6 (6H, m, $(CH_2)_3$) 2.70 (2H, t, 7 Hz, $COCH_2$)	6.60 (2H, d[d)]) 6.74 (1H, d[d)])	C	60
f	Me	H	H	78—80	65.90 (65.85	5.07 4.91)	—	$C_9H_8O_3$	2.10 (3H, d, 1.5 Hz, Me) 2.56 (3H, s, Ac)	6.64 (1H, q, 1.5 Hz) 7.00 (1H, s)	A	90
g	Me	H	Me	40—41	67.32 (67.40	5.59 5.66)	—	$C_{10}H_{10}O_3$	1.15 (3H, t, 7 Hz, Me) 2.10 (3H, d, 1.5 Hz, Me) 2.90 (2H, q, 7 Hz, CH_2)	6.62 (1H, q, 1.5 Hz) 6.92 (1H, s)	A	80
h	Cl	H	Me	51—54	54.70 (54.41	3.41 3.53	18.00 17.88)	$C_9H_7O_3Cl$	1.17 (3H, t, 7 Hz, Me) 2.91 (2H, q, 7 Hz, CH_2)	7.01 (1H, s) 7.10 (1H, s)	B	80
i	Br	H	H	93—96	42.74 (42.90	2.38 2.18	34.87 34.92)	$C_8H_5O_3Br$	2.57 (3H, s, Ac)	7.17 (1H, s) 7.30 (1H, s)	B	70
j	Br	H	Me	56—58	——— b ———			$C_9H_7O_3Br$	1.15 (3H, t, 7 Hz, Me) 2.87 (2H, q, 7 Hz, CH_2)	7.14 (1H, s) 7.33 (1H, s)	B	50
k	-(CH=CH)$_2$-		H	83.5— 84	Known compound[c)]				2.50 (3H, s, Ac)	6.92 (1H, d[d)]) 7.5—7.6 (2H, m) 7.8—7.9 (2H, m)	A	90
l			Me	78.5— 80	72.59 (72.89	4.98 4.71)	—	$C_{13}H_{10}O_3$	1.18 (3H, t, 6 Hz, Me) 2.96 (2H, q, 6 Hz, CH_2)	7.10 (1H, s) 7.8—7.9 (2H, m) 8.1—8.2 (2H, m)	A	80
m			Et	58—59	73.49 (73.67	5.37 5.30)	—	$C_{14}H_{12}O_3$	0.97 (3H, t, 7 Hz, Me) 1.68 (2H, sex, 7 Hz, CH_2) 2.87 (2H, t, 7 Hz, $COCH_2$)	7.06 (1H, s) 7.8—7.9 (2H, m) 8.1—8.2 (2H, m)	A	80

a) Ref. 12. b) Satisfactory results were not obtained because of the hygroscopic character of the sample. c) Ref. 9. d) Slightly splitting.

the expected values of *m/e* for the molecular peaks in the mass spectroscopy. The melting points of **1a**—**m** were: **a**, 200—202 °C, lit, 201—203 °C,[6] 204 °C;[7] **b**, 97—99 °C, lit, 96 °C;[7] **c**, 91 °C;[7] **d**, 61—62.5 °C; **e**, 82—83 °C; **f**, 149—150 °C, lit, 141 °C;[7] **g**, 110—116 °C; **h**, 127—129 °C; **i**, 144—156 °C; **j**, 121—123 °C; **k**, 215—216 °C, lit, 210—211 °C,[9] 206 °C,[10] and 216—217 °C;[11] **l**, 187—189 °C;[8] **m**, 151—153 °C.

*2-(Acetyl-*d$_3$*)hydroquinone (4a) and 2-(Propanoyl-2-*d$_2$*)hydroquinone (4b).* A solution of **3a** or **3b** (1 g) in dioxane (30 ml) and a solution of NaOH (1 equiv) in D$_2$O (3 ml) were successively syringed into a flask equipped with a rubber-serum cap and purged with nitrogen. The solution immediately turned reddish yellow. After stirring for 0.5 h, deuteriochloric acid (1.5 equiv) was added (the color of the solution thereupon turned back yellow). The solution was concentrated to yellow crystals, which were subsequently recrystallized from aqueous acetone to give **4a** or **4b**, respectively; mp: **4a**, 200—202 °C; **4b**, 96—98 °C. They showed no ^{1}H NMR signals due to methyl or methylene protons adjacent to a carbonyl group and the expected values of *m/e* for the molecular peaks in the mass spectroscopy.

2-Acyl-1,4-benzoquinones (2). These substances were prepared by one of the following methods. The yields were usually high, but showed less constancy. Their physical data are tabulated in Table 3.

Method A: This was originally described by Kloetzel *et al.*[12] A solution of **1** (1 g) in benzene (20 ml; for **1a**—**c**, **f**, and **g**) or diethyl ether (100 ml; for **1k**—**m**) was stirred with silver oxide (3 g) and magnesium sulfate (1.5 g) for 0.5 h. The powder was then filtered off and washed with diethyl ether under a slightly reduced pressure to prevent moisture from being condensed on the filtrate. The residue obtained by the concentration of the filtrate was submitted to sublimation under a vacuum to give **2a**—**j**. **2k**—**m** were purified by recrystallization from ligroin.

The partially deuterated monomers (**5a**—**b**) were prepared from **4a**—**b**. **5a**—**b** were not subjected to elemental analysis, but they gave satisfactory results in the mass and ^{1}H NMR spectroscopies.

Method B: When **1h** and **1i** were oxidized by Method A, many unsublimable solids remained. The use of DDQ was successful for oxidation. A solution of the calculated amount of DDQ in acetonitrile (20 ml) was added to a stirred solution of **1h** or **1i** (1 g) in acetonitrile (20 ml). Immediately the solution became deeply colored, and a colorless powder soon began to precipitate. After *ca.* 15 min the solution turned yellow and precipitation had ended. After filtration, the filtrate was concentrated to a residue, which was submitted to sublimation under a vacuum to give **2h**—**i**.

Method C: **2d** and **2e** were very hygroscopic. When Method A was apllied, a dirty colored syrup was left by the concentration of the filtered reaction solution. A method to avoid to contact with moisture was devised as follows. A solution of **1d** or **1e** (1 g) in acetonitrile (20 ml) was charged into a two-necked flask equipped with a rubber-serum cap. The flask was connected to a vacuum line, and the solution was then degassed by the thaw-freeze-pump method. Through the serum cap a solution of the calculated amount of DDQ in acetonitrile (10 ml) was syringed in. The change in the color of the reaction was the same as in method B. After *ca.* 15 min, the solvent was evaporated by bulb-to-bulb distillation through the vacuum line. The residual powder, composed of dichlorodicyanohydroquinone and **2**, was submitted to sublimation under a vacuum to isolate **2a**—**e**.

Preparation of the Dimers (3). Solutions of **2** were sealed in Pyrex glass tubes after having been degassed by the thaw-freeze-pump method and irradiated externally by means of a 300W high-pressure Hg-arc lamp for the appropriate times. The homogeneous reaction solutions, or the filtrates when solid products had been crystallized out, were concentrated to semi-solid residues, which were then submitted to sublimation under a vacuum to recover the **2**. The residues on sublimation were repeatedly rinsed with benzene to remove any tarry materials.[13] The remaining dirty yellow crystals, combined with the crystals which had been filtered off from the reaction solutions, were dissolved chloroform by slight warming. The solvent was evaporated in a desiccator by connecting it through a calcium chloride tube to a water pump. The solid residues were repeatedly rinsed with benzene. This process was repeated several times to give the pure dimers (**3**), *i. e.* **8**, which decomposed on silica-gel chromatography.

Table 4. Elemental analyses of the dimers **3**[a]

	Mp/°C[b]	Found (%) (Calcd (%)) C	H	X	Formula ($\mathrm{C}_l\mathrm{H}_m\mathrm{O}_n\mathrm{X}_x$): *l-m-n-x*
a	154—156	63.96 (64.00	4.25 4.03)	—	16-12-6
c	c	67.52 (67.40	5.61 5.66)	—	20-20-6
d	137—142	68.79 (68.73	6.41 6.29)	—	22-24-6
e	c	69.91 (69.88	6.99 6.84)	—	24-28-6
f	159—161	65.61 (65.85	4.80 4.91)	—	18-16-6
h	c	54.13 (54.41	3.46 3.53	18.09 17.88)	18-14-6-2
l	c	73.09 (72.89	4.40 4.71)	—	26-20-6
m	c	73.94 (73.67	5.44 5.30)	—	28-24-6

a) For **3b**,[c] **g**,[c] and **j**,[c] satisfactory results were not obtained because of the contamination by a trace amount of tarry materials, which could not be eliminated by repeated purification. b) Measured in a vacuum-sealed capillary. c) Melting gradually because of thermal decomposition.

The results of the elemental analyses are shown in Table 4. All the dimers gave the expected values of the molecular peaks in the mass spectrometry. Some of the dimers showed their melting points sharply in vacuum sealed capillaries, but the others melted gradually because of thermal decomposition. All the dimers showed similar IR and UV spectral data. Those of **3c** are representative; IR (KBr): ν 3500 (broad), 2980, 2950 (shoulder), 2880, 1720, 1695, 1680, 1645, 1610 (shoulder), 1595 cm^{-1}; UV (EtOH): $\lambda_{\max}$ (ε) 388 (5930), 300 (3650), 275 (3900), 222 (31200) nm.

The partially deuterated dimers (**6**) were similarly prepared from **5**. Elemental analyses were not performed for **6**, but satisfactory results were obtained in the mass spectrometry.

The Monoacetyl Derivative of 3h (7). A homogeneous solution obtained by the occasional swirling of a suspension of **3h** (0.5 g) in acetic anhydride (20 ml) containing one crop of *p*-toluenesulfonic acid was left standing at room temperature for 2 days. The solvent was then evaporated by bulb-to-bulb distillation through a vacuum line. Upon standing *in vacuo* overnight, the strupy residue became a semi-solid, which was subsequently dissolved in chloroform after rinsing with benzene.[14] The solution was concentrated to a solid, which was

Table 5A. Final atomic coordinates ($\times 10^4$) and thermal parameters* ($\times 10^4$), with their estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	7568(2)	−2130(1)	3896(1)	275(3)	56(1)	68(1)	36(2)	−67(2)	−3(1)
Cl(2)	2906(2)	344(1)	619(1)	329(3)	93(1)	33(1)	27(3)	−33(2)	−20(1)
O(1)	9036(4)	−230(3)	3835(3)	198(6)	78(3)	116(3)	52(6)	102(7)	54(4)
O(2)	3465(3)	226(3)	4148(2)	179(5)	98(3)	45(1)	−34(6)	66(4)	20(3)
O(3)	3032(3)	411(2)	2372(2)	159(4)	53(2)	38(1)	11(4)	12(3)	−18(2)
O(4)	8164(5)	1621(3)	1293(2)	316(8)	112(3)	68(2)	−19(8)	−184(7)	38(4)
O(5)	9365(4)	1897(3)	2737(2)	176(5)	88(3)	84(2)	−15(6)	94(5)	36(4)
O(6)	5151(4)	2221(3)	4559(2)	257(6)	92(3)	36(1)	31(7)	8(4)	−39(3)
O(7)	3332(3)	−1209(2)	2153(2)	183(5)	58(2)	67(2)	17(5)	29(5)	−20(3)
C(1)	7756(5)	−126(3)	3926(2)	147(6)	71(3)	41(2)	23(7)	16(5)	35(4)
C(2)	6729(5)	−987(3)	3895(2)	206(7)	54(2)	28(1)	−2(7)	−11(5)	15(3)
C(3)	5282(5)	−894(3)	3877(2)	193(7)	61(3)	32(2)	−26(7)	1(5)	14(3)
C(4)	4616(5)	106(3)	3883(2)	153(6)	76(3)	24(1)	−37(7)	21(4)	13(3)
C(4a)	5498(4)	972(3)	3601(2)	135(5)	50(2)	26(1)	−5(6)	20(4)	7(3)
C(4b)	5588(4)	958(3)	2696(2)	157(6)	39(2)	26(1)	26(5)	30(4)	10(3)
C(5)	4388(4)	651(3)	2132(2)	162(6)	46(2)	31(1)	31(6)	35(5)	0(3)
C(6)	4456(5)	694(3)	1306(2)	246(8)	49(2)	29(1)	51(7)	10(6)	−9(3)
C(7)	5712(6)	1026(4)	1027(3)	294(10)	69(3)	34(2)	33(9)	74(7)	4(4)
C(8)	6940(6)	1304(3)	1581(3)	260(9)	56(3)	46(2)	38(8)	120(7)	26(4)
C(8a)	6907(5)	1287(3)	2421(2)	157(6)	49(2)	41(2)	15(6)	61(5)	21(3)
C(9)	8218(5)	1648(3)	2986(3)	148(6)	52(3)	60(2)	12(7)	60(6)	38(4)
C(10)	8071(5)	1744(3)	3865(3)	143(6)	66(3)	46(2)	−46(7)	13(5)	18(4)
C(10a)	7107(4)	879(3)	4086(2)	149(6)	53(2)	34(1)	−17(6)	2(5)	15(3)
C(11)	4769(5)	1943(3)	3874(2)	158(6)	57(2)	31(1)	−24(6)	32(5)	−15(3)
C(12)	3615(5)	2451(3)	3280(3)	162(7)	63(3)	42(2)	46(7)	2(6)	−18(4)
C(13)	3034(5)	3403(4)	3599(3)	192(8)	67(3)	71(3)	29(8)	39(8)	−46(5)
C(14)	9569(6)	1875(4)	4441(4)	184(8)	106(5)	79(3)	−101(10)	−45(8)	32(6)
C(15)	2539(5)	−553(3)	2304(3)	178(7)	63(3)	44(2)	6(7)	1(6)	−23(4)
C(16)	952(6)	−609(5)	2452(4)	153(8)	106(5)	121(5)	−50(10)	83(10)	−72(8)

*The anisotropic thermal factors are of the form: exp $\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$.

Table 5B. Final atomic coordinates ($\times 10^3$), with their estimated standard deviations in parentheses

	x	y	z
H(1)	458(5)	−146(4)	386(3)
H(2)	563(6)	109(4)	43(3)
H(3)	747(5)	241(4)	390(3)
H(4)	706(5)	90(4)	467(3)
H(5)	284(6)	199(4)	308(3)
H(6)	410(6)	271(4)	278(3)

again rinsed with benzene. By repeating this process, faint yellow crystals of **7** were obtained; 150 mg. These crystals gradually melted at 180—190 °C. Found: C, 54.30; H, 3.48; Cl, 16.01%. Calcd for $C_{20}H_{16}O_7Cl_2$: C, 54.66; H, 3.64; Cl, 16.17%. ^1H NMR ($CDCl_3$): δ 1.06 (3H, t, J=7 Hz, Me_A), 1.49 (3H, d, J=7 Hz, Me_B), 2.23 (3H, s, OAc), 2.68 (1H, dq, J=7 and 3.5 Hz, H_B), 4.21 (1H, d, J=3.5 Hz, H_A), 7.16 (1H, s, H_C), 7.32 (1H, s, H_D), 12.88 (1H, s, chelated OH) ($COC\mathbf{H_2}$–Me_A: unclear). MS: m/e 440 and 438 (M^+).

X-Ray Structure Analysis. The molecular structure of **7** was determined by X-ray structure analysis. The crystal data were: monoclinic, $P2_1/c$, a=9.052 (2), b=13.512 (2), c=16.750 (3) Å, β=99.39 (2)°, V=2021.1 (7) Å^3. Z=4, D_m=1.449, D_c=1.445 g·cm^{-3}. A single crystal of approximately 0.26×0.25×0.18 mm was used for the intensity measurement. The cell constants were determined by the least-squares treatment of the angular settings of 20 reflections measured on a Rigaku computer-controlled four-circle diffractometer with Ni-filtered Mo $K\alpha$ radiation. The intensities were measured by the θ-2θ scan technique, with a scan speed of 2° min^{-1} in θ. The intensities of 3248 independent reflections were collected within $\sin\theta/\lambda \leqq 0.65$. The structure of **7** was solved by the heavy-atom method and refined by the blok-diagonal least-squares method. The difference Fourier synthesis computed after the anisotropic refinement of the non-hydrogen atoms revealed the positions of all the hydrogen atoms except the methyl and hydroxyl hydrogen atoms. The final refinement, including the contribution of these hydrogen atoms with isotropic temperature factors, reduced the R-value to 0.074 without F_{obsd}=0. The final atomic coordinates are given in Table 5, while the bond lengths and angles are shown in Figs. 4 and 5 respectively.

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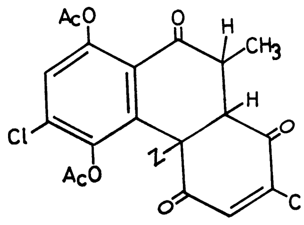
13) The dimers were hardly soluble in benzene after having been purified once but they did not crystallize out from the reaction solutions in benzene.

14) The washings contained **7** and the diacetyl derivative, **14**.



($Z=COC_2H_5$)

14