The Photochemical Reaction of 1,2-Naphthoquinones with Aldehydes. III.[1] The Reactions with Aromatic Aldehydes and α,β-Unsaturated Aliphatic Aldehydes

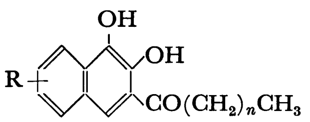
Akio TAKUWA

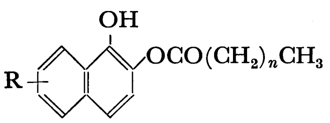
Department of Chemistry, Faculty of Literature and Science, Shimane University, Nishikawatsu-cho, Matsue 690

(Received December 24, 1976)

Photochemical reactions of 1,2-naphthoquinone and the substituted derivatives with a variety of aldehydes in the liquid phase have been investigated. The reaction with saturated aliphatic aldehydes gives a mixture of 3-acyl-1,2-naphthalenediol and 1,2-naphthalenediol monoacyl esters. On the other hand, the irradiation of the benzene solution of a 1,2-naphthoquinone derivative and an aromatic aldehyde gives, in general, 1,2-naphthalenediol monoaroyl esters, together with small amounts of other products. Unlike saturated aliphatic aldehydes, α,β-unsaturated aldehydes; *i.e.*, propenal, 2-butenal, *trans*-2-hexenal, 1-cyclopentenecarbaldehyde, and 1-cyclohexenecarbaldehyde, behave similary to the aromatic aldehydes in the photochemical reaction, giving only 1,2-naphthalenediol monoesters. However, 10-undecenal, 3-phenylpropanal, cyclopentanecarbaldehyde, cyclohexanecarbaldehyde, and 3-cyclohexenecarbaldehyde give mixtures of 3-acyl-1,2-naphthalenediols and 1,2-naphthalenediol monoacyl esters similar to those from saturated aliphatic aldehydes. The origin of these significant differences is discussed.

Light-induced reactions between quinone and aldehyde have been extensively studied by several workers,[2] but there have been few studies of those of 1,2-naphthoquinone derivatives, probably because of their instability.[3] Awad and Hafez, for example, failed to isolate photo-adducts by the photolysis of 1,2-naphthoquinone in the presence of acetaldehyde.[4] The successful isolation of photo-adducts in the photochemical reactions of 1,2-naphthoquinone with saturated aliphatic aldehydes was first reported by the present author.[1] Thus, 3-acyl-1,2-naphthalenediols, **1**, (C-attacking product) and 1,2-naphthalenediol monoacyl esters, **2**, (O-attacking product) were isolated as the reaction products.





and/or isomer

1 (C-attacking product) **2** (O-attacking product)

R=H, 4-CN, 6-Br, 6-CH_3; n=0—8

On the contrary, a preliminary investigation of the photochemical reactions of aromatic or α,β-unsaturated aliphatic aldehydes with 1,2-naphthoquinones revealed that the reaction products consisted exclusively of 1,2-naphthalenediol monoesters. On the other hand, *p*-quinones, in general, give C-attacking products as their major products in photochemical reactions with aliphatic or aromatic aldehydes.[2] In this paper, a detailed investigation of the reaction products, as well as of the effect of the structure of aldehydes and the substituent effect of 1,2-naphthoquinones on the product distributions, will be described.

Results and Discussion

The quinones examined in this work are 1,2-naphthoquinone and its 3-chloro-, 3-bromo-, 4-cyano-, 4-methyl-, 4-methoxy-, 6-bromo-, 6-chloro-, and 6-methyl derivatives. Benzaldehyde, and its *p*-nitro-, *m*-nitro-, *p*-methyl-, *p*-methoxy-, 2,4-dimethoxy-, 3,4,5-trimethoxy-, 2,4,6-trimethyl-, and 2,4,6-triisopropyl derivatives are examined as typical aromatic aldehydes. As representative α,β-unsaturated aliphatic aldehydes, propenal, 2-butenal, *trans*-2-hexenal, 1-cyclopentenecarbaldehyde, 1-cyclohexenecarbaldehyde, and cinnamaldehyde are used in this work. In addition, 10-undecenal, 3-phenylpropanal, cyclopentanecarbaldehyde, cyclohexanecarbaldehyde, 3-cyclohexenecarbaldehyde, and 3-chlorobutanal are also examined.

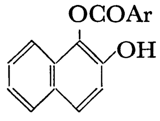
A benzene solution of a 1,2-naphthoquinone derivative and an aldehyde was irradiated by means of a 300-W high-pressure Hg arc lamp for a suitable time. The reaction mixture was then concentrated and chromatographed on silica gel. The products are summarized in Tables 1, 2, and 3.

In the reaction of 1,2-naphthoquinone with benzaldehyde, only 1,2-naphthalenediol monobenzoate, **3a**, is obtained. The other aromatic aldehydes used here behave much like benzaldehyde, giving the corresponding 1,2-naphthalenediol monoaroyl esters (O-attacking products), together with no ring-substituted derivatives (C-attacking products). Other substituted 1,2-naphthoquinone derivatives give O-attacking products exclusively in photochemical reactions with aromatic aldehydes (see Table 1).

These results are surprising because, in the photochemical reactions of 1,2-naphthoquinones with saturated aliphatic aldehydes, acetaldehyde, for example, gives 3-acetyl-1,2-naphthalenediols in a yield comparable to that of 1,2-naphthalenediol monoacetates. In addition, it is well known that *p*-benzoquinones and 1,4-naphthoquinones, in general, give C-attacking products predominantly, along with minor O-attacking products, in photochemical reactions with both aliphatic and aromatic aldehydes.[2]

In the photochemical reactions of 1,2-naphthoquinones with aromatic aldehydes, the larger steric requirement of the phenyl than of the alkyl group might be the cause of the absence of the C-attacking product. Cyclopentanecarbaldehyde and cyclohexanecarbaldehyde, however, give both C-attacking products and O-

Table 1. The photo-addition compounds from the photochemical reaction of 1,2-naphthoquinone derivatives with aromatic aldehydes



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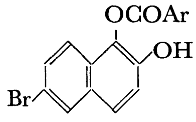

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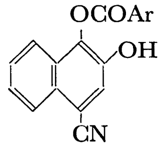

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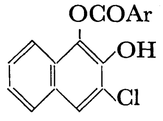

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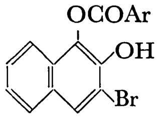

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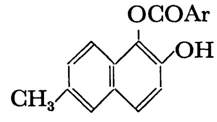

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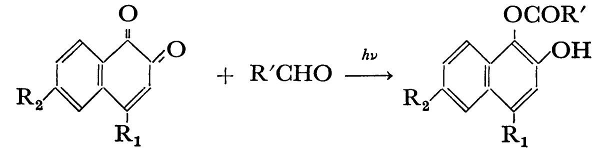
and/or isomer

Quinone[a]	Aldehyde	Ar	Compound No	Yield[b,c] (%)	Mp (°C)
1,2-NQ	Benzaldehyde	C_6H_5	**3a**	29	162—166
1,2-NQ	*p*-Nitrobenzaldehyde	*p*-$NO_2C_6H_4$	**3b**	39	182—183
1,2-NQ	*m*-Nitrobenzaldehyde	*m*-$NO_2C_6H_4$	**3c**	31	159—161
1,2-NQ	*p*-Methylbenzaldehyde	*p*-$CH_3C_6H_4$	**3d**	23	158—160
1,2-NQ	*p*-Methoxybenzaldehyde	*p*-$CH_3OC_6H_4$	**3e**	26	184—185
1,2-NQ	3,4,5-Trimethoxybenzaldehyde	3,4,5-$(CH_3O)_3C_6H_2$	**3f**	14	195—198
6-Br-1,2-NQ	Benzaldehyde[d]	C_6H_5	**4a**	47	173—174
6-Br-1,2-NQ	*p*-Nitrobenzaldehyde	*p*-$NO_2C_6H_4$	**4b**	49	201—202
6-Br-1,2-NQ	*m*-Nitrobenzaldehyde	*m*-$NO_2C_6H_4$	**4c**	39	177—178
6-Br-1,2-NQ	*p*-Methylbenzaldehyde[d]	*p*-$CH_3C_6H_4$	**4d**	35	189—190
6-Br-1,2-NQ	*p*-Methoxybenzaldehyde[d]	*p*-$CH_3OC_6H_4$	**4e**	54	193—194
6-Br-1,2-NQ	2,5-Dimethoxybenzaldehyde	2,5-$(CH_3O)_2C_6H_3$	**4f**	65	145—149
6-Br-1,2-NQ	3,4,5-Trimethoxybenzaldehyde	3,4,5-$(CH_3O)_3C_6H_2$	**4g**	15	211—214
6-Br-1,2-NQ	2,4,6-Trimethylbenzaldehyde	2,4,6-$(CH_3)_3C_6H_2$	**4h**	41	292—293
6-Br-1,2-NQ	2,4,6-Triisopropylbenzaldehyde	2,4,6-$[(CH_3)_2CH]_3C_6H_2$	**4i**	19	190—192
4-CN-1,2-NQ	Benzaldehyde	C_6H_5	**5a**	21	177—178
4-CN-1,2-NQ	*p*-Nitrobenzaldehyde[e]	*p*-$NO_2C_6H_4$	**5b**	39	253—255
4-CN-1,2-NQ	*m*-Nitrobenzaldehyde	*m*-$NO_2C_6H_4$	**5c**	35	225—227
4-CN-1,2-NQ	*p*-Methylbenzaldehyde	*p*-$CH_3C_6H_4$	**5d**	16	186—188
4-CN-1,2-NQ	*p*-Methoxybenzaldehyde[e]	*p*-$CH_3OC_6H_4$	**5e**	26	215—217
4-CN-1,2-NQ	3,4,5-Trimethoxybenzaldehyde	3,4,5-$(CH_3O)_3C_6H_2$	**5f**	27	151—152
4-CN-1,2-NQ	2,4,6-Trimethylbenzaldehyde	2,4,6-$(CH_3)_3C_6H_2$	**5g**	55	217—219
3-Cl-1,2-NQ	Benzaldehyde	C_6H_5	**6a**	26	141—144
3-Cl-1,2-NQ	Cinnamaldehyde	$C_6H_5CH=CH$	**6b**	25	180—181
3-Cl-1,2-NQ	*p*-Nitrobenzaldehyde	*p*-$NO_2C_6H_4$	**6c**	44	203—205
3-Cl-1,2-NQ	*m*-Nitrobenzaldehyde	*m*-$NO_2C_6H_4$	**6d**	26	194—196
3-Cl-1,2-NQ	*p*-Methylbenzaldehyde	*p*-$CH_3C_6H_4$	**6e**	40	164—166
3-Cl-1,2-NQ	*p*-Methoxybenzaldehyde	*p*-$CH_3OC_6H_4$	**6f**	26	184—186
3-Br-1,2-NQ	Benzaldehyde	C_6H_5	**7a**	21	150—153
3-Br-1,2-NQ	Cinnamaldehyde	$C_6H_5CH=CH$	**7b**	20	189—190
3-Br-1,2-NQ	*p*-Nitrobenzaldehyde	*p*-$NO_2C_6H_4$	**7c**	17	202—205
3-Br-1,2-NQ	*m*-Nitrobenzaldehyde	*m*-$NO_2C_6H_4$	**7d**	15	188—190
3-Br-1,2-NQ	*p*-Methylbenzaldehyde	*p*-$CH_3C_6H_4$	**7e**	22	176—178
3-Br-1,2-NQ	*p*-Methoxybenzaldehyde	*p*-$CH_3OC_6H_4$	**7f**	20	196—198
6-Me-1,2-NQ	Benzaldehyde	C_6H_5	**8a**	38	172—174
6-Me-1,2-NQ	Cinnamaldehyde	$C_6H_5CH=CH$	**8b**	35	145—146
6-Me-1,2-NQ	*p*-Nitrobenzaldehyde	*p*-$NO_2C_6H_4$	**8c**	23	187—189
6-Me-1,2-NQ	*m*-Nitrobenzaldehyde	*m*-$NO_2C_6H_4$	**8d**	24	172—175
6-Me-1,2-NQ	*p*-Methylbenzaldehyde	*p*-$CH_3C_6H_4$	**8e**	41	185—186
6-Me-1,2-NQ	*p*-Methoxybenzaldehyde	*p*-$CH_3OC_6H_4$	**8f**	53	184—185

a) 1,2-NQ: 1,2-naphthoquinone, 6-Br-1,2-NQ: 6-bromo-1,2-naphthoquinone, 4-CN-1,2-NQ: 4-cyano-1,2-naphthoquinone, 3-Cl-1,2-NQ: 3-chloro-1,2-naphthoquinone, 3-Br-1,2-NQ: 3-bromo-1,2-naphthoquinone, 6-Me-1,2-NQ: 6-methyl-1,2-naphthoquinone. b) The yield was calculated on the basis of the amount of quinone used. c) The relatively low yields may be due to the instability of 1,2-naphthoquinone and its derivatives, because they were not recovered from the reaction mixture. d) *Cf.* A. Mustafa *et al.*, *J. Am. Chem. Soc.*, **78**, 4306 (1956). e) *Cf.* A. Schönberg *et al.*, *J. Am. Chem. Soc.*, **77**, 3850 (1955).

Table 2. The photo-addition compounds from the photochemical reaction of 1,2-naphthoquinone derivatives with α,β-unsaturated aliphatic aldehydes



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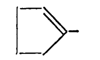
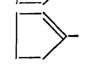
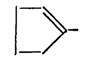
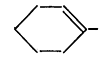
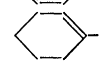
Quinone[a)]	Aldehyde	Product			Compound No	Yield[b,c)] (%)	Mp (°C)
		R_1	R_2	R′			
1,2-NQ	Propenal	H	H	CH_2=CH-	**9a**	47	111—113
6-Br-1,2-NQ	Propenal	H	Br	CH_2=CH-	**9b**	72	150—151
4-CN-1,2-NQ	Propenal	CN	H	CH_2=CH-	**9c**	51	165—166
1,2-NQ	2-Butenal	H	H	CH_3CH=CH-	**9d**	42	99—101
4-CN-1,2-NQ	2-Butenal	CN	H	CH_3CH=CH-	**9e**	28	153—154
1,2-NQ	*trans*-2-Hexenal	H	H	$CH_3(CH_2)_2$CH=CH-	**9f**	16	80— 81
6-Br-1,2-NQ	*trans*-2-Hexenal	H	Br	$CH_3(CH_2)_2$CH=CH-	**9g**	43	129—131
4-CN-1,2-NQ	*trans*-2-Hexenal	CN	H	$CH_3(CH_2)_2$CH=CH-	**9h**	20	135—137
1,2-NQ	1-Cyclopentenecarbaldehyde	H	H		**9i**	37	130—132
6-Br-1,2-NQ	1-Cyclopentenecarbaldehyde	H	Br		**9j**	30	176—177
4-CN-1,2-NQ	1-Cyclopentenecarbaldehyde	CN	H		**9k**	8	145—146
1,2-NQ	1-Cyclohexenecarbaldehyde	H	H		**9l**	28	140—142
6-Br-1,2-NQ	1-Cyclohexenecarbaldehyde	H	Br		**9m**	41	156—157
1,2-NQ	Cinnamaldehyde	H	H	C_6H_5CH=CH-	**9n**	57	179—180
6-Br-1,2-NQ	Cinnamaldehyde	H	Br	C_6H_5CH=CH-	**9o**	39	190—191
4-CN-1,2-NQ	Cinnamaldehyde[d)]	CN	H	C_6H_5CH=CH-	**9p**	58	178—180

a, b), c) See the footnotes in Table 1. d) *Cf.* A. Schönberg *et al.*, *J. Am. Chem. Soc.*, **77**, 3850 (1955).

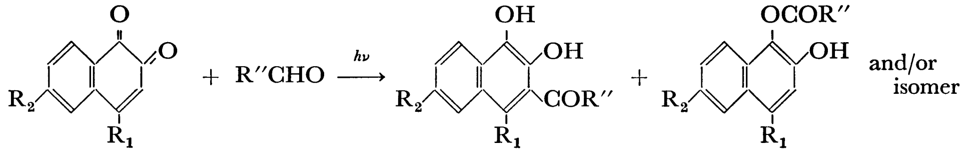
attacking products in reactions with 1,2-naphthoquinone. 4-Cyano-1,2-naphthoquinone behaves similarly to give both C-attacking and O-attacking products. In addition, α,β-unsaturated aliphatic aldehydes also give 1,2-naphthalenediol monoesters exclusively (see Table 2). Therefore, there is no reason to consider that the higher steric factor of the phenyl group could be the controlling factor of the product distribution.

What is, then, the controlling factor for the C-attacking or O-attacking products in these reactions? Since these photochemical reactions are undoubtedly initiated by hydrogen abstraction from aldehyde by the photoexcited 1,2-naphthoquinone molecule,[5)] giving an acyl radical and a 1,2-naphthosemiquinone radical,[6)] the structure of the combination product of the two resulting radicals must depend on the electronic character of the radical concerned. It has been reported that both the acetyl radical and the benzoyl radical have a nucleophilic character.[7)] However, considering the photochemical reactions of 1,2-naphthoqinone with acetaldehyde, propenal, and benzaldehyde, the present author could arrange the decreasing nucleophilic character of the acyl radicals concerned in the following order: $CH_3\dot{C}{=}O > CH_2{=}CH{-}\dot{C}{=}O > C_6H_5\dot{C}{=}O$, on the basis of the inductive effect of the methyl, vinyl, and phenyl groups. Acyl radicals are, in general, of a strong σ-radical character and most of the free spin localizes on the acyl carbon. This was confirmed by the ESR measurement of the benzoyl radical.[8)]

p-Methyl- and *p*-methoxybenzaldehyde, in reaction with *p*-benzoquinone, give 2-aroylhydroquinones as the predominant products.[9)] However, as is shown in Table 1, the introduction of three methyl or three methoxyl groups on the phenyl ring has no appreciable effects on the product distributions, giving 1,2-naphthalenediol monoesters exclusively. Thus, α,β-unsaturated aldehydes, including aromatic aldehydes, are characteristic in giving the O-attacking products selectively.

As for the reactions with 10-undecenal, 3-phenylpropanal, and 3-cyclohexenecarbaldehyde, which have no olefinic π-system conjugated to carbonyl, we obtained the C-attacking product together with the O-attacking product in the reaction with 1,2-naphthoquinone derivatives, as is shown in Table 3. Whereas the carbonyl carbon of the acyl radical derived from α,β-unsaturated aldehydes attaches to the sp^2 carbon, the carbonyl carbon derived from these three aldehydes attaches to the sp^3 carbon. Therefore, it is reasonable to consider that the former acyl radical is more electrophilic than the latter. Thus, the inherent polarity of an acyl radical could exert the controlling influence on determining the attacking position on the 1,2-naphthosemiquinone radical. To support the

TABLE 3. THE PHOTO-ADDITION COMPOUNDS FROM THE PHOTOCHEMICAL REACTION OF 1,2-NAPHTHOQUINONE DERIVATIVES WITH ALDEHYDES WHICH HAVE NO CONJUGATED OLEFINIC π-SYSTEM TO CARBONYL



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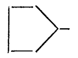
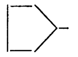
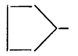
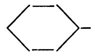
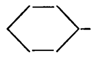
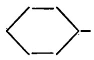
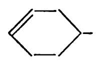
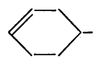
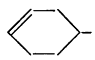
Quinone[a]	Aldehyde	Product R_1	Product R_2	Product R''	Compound No	Yield[b,c] (%)	Mp (°C)
1,2-NQ	Cyclopentanecarbaldehyde	H	H		10a 11a	8 25	148—149 107—109
6-Br-1,2-NQ	Cyclopentanecarbaldehyde	H	Br		10b 11b	14 37	133—134 156—158
4-CN-1,2-NQ	Cyclopentanecarbaldehyde	CN	H		10c 11c	21 6	181—182 130—131
1,2-NQ	Cyclohexanecarbaldehyde	H	H		10d 11d	9 34	186—187 104—105
6-Br-1,2-NQ	Cyclohexanecarbaldehyde	H	Br		10e 11e	20 36	138—139 180—181
4-CN-1,2-NQ	Cyclohexanecarbaldehyde	CN	H		10f 11f	17 8	149—150 165—167
1,2-NQ	10-Undecenal	H	H	$CH_2=CH(CH_2)_8-$	10g 11g	8 11	65— 67 68— 69
6-Br-1,2-NQ	10-Undecenal	H	Br	$CH_2=CH(CH_2)_8-$	10h 11h	12 32	65— 66 84— 87
4-CN-1,2-NQ	10-Undecenal	CN	H	$CH_2=CH(CH_2)_8-$	10i 11i	25 6	84— 85 82— 83
1,2-NQ	3-Phenylpropanal	H	H	$C_6H_5CH_2CH_2-$	10j 11j	5 33	128—129 103—104
6-Br-1,2-NQ	3-Phenylpropanal	H	Br	$C_6H_5CH_2CH_2-$	10k 11k	18 43	125—126 120—122
4-CN-1,2-NQ	3-Phenylpropanal	CN	H	$C_6H_5CH_2CH_2-$	10l 11l	32 8	165—166 149—150
1,2-NQ	3-Cyclohexenecarbaldehyde	H	H		10m 11m	5 34	109—110 139—140
6-Br-1,2-NQ	3-Cyclohexenecarbaldehyde	H	Br		10n 11n	12 42	143—144 163—165
4-CN-1,2-NQ	3-Cyclohexenecarbaldehyde	CN	H		10o 11o	10 17	157—158 147—148

a), b), c) See the footnotes in Table 1.

above consideration it was confirmed that, in the reactions of 6-bromo-1,2-naphthoquinone with butyraldehyde[1] and with 3-chlorobutanal, the ratios of C-attacking to O-attacking products were 47 : 53 and 9 : 91 respectively.

On the other hand, the introduction of an electron-attracting group, such as halogen or cyano groups, into the quinone ring should facilitate the C-attacking on the basis of the same considerations. Since the electron densities on the C_3-carbon of the 1,2-naphthosemiquinone radical, of the 6-bromo-1,2-naphthosemiquinone radical, and of the 4-cyano-1,2-naphthosemiquinone radical may decrease in this order, the C-attacking product would increase in the same order. The results of the photochemical reactions of 1,2-naphthoquinone, 6-bromo-1,2-naphthoquinone, and 4-cyano-1,2-naphthoquinone with acetaldehyde, propanal and 3-phenylpropanal are compared in Table 4. In actual, the amounts of the C-attacking product relative to the amounts of the O-attacking product change regularly. That is, the relative yields of the C-attacking products are 13—27, 30—57, and 80—85 % respectively. In the cases of the reaction with other aliphatic aldehydes, as has been described in a previous paper[1] and as is shown in Table 3, these tendencies can also be recognized.

Contrary to the effect of introducing some electron-attracting groups into the quinone ring, the introduction of an electron-donating group, such as methyl or methoxyl group, should exert the opposite influences on the product distributions. Actually, 4-methyl- or 4-methoxy-1,2-naphthoquinone gives only O-attacking products, without any C-attacking product, as is shown in Table 4.

The 2-butenoyl radical is also of an O-attacking character for the 1,2-naphthosemiquinone radical, but it shows a somewhat C-attacking character for the 6-halo-1,2-naphthosemiquinone radical. This might be due to the fact that the introduction of the halogen atom at the 6-position of the 1,2-naphthosemiquinone

Table 4. The relative yields of the photo-addition compounds obtained in the reaction of 1,2-naphthoquinone derivatives with several aldehydes

Quinone[a)]	Aldehyde	Relative yields C-product (%)[e)]	Relative yields O-product (%)[f)]
1,2-NQ	CH_3CHO[b)]	24	76
6-Br-1,2-NQ	CH_3CHO[b)]	46	54
4-CN-1,2-NQ	CH_3CHO[b)]	82	18
4-Me-1,2-NQ	CH_3CHO[c)]	0	100
4-MeO-1,2-NQ	CH_3CHO[c)]	0	100
1,2-NQ	CH_3CH_2CHO[d)]	27	73
6-Br-1,2-NQ	CH_3CH_2CHO[d)]	57	43
4-CN-1,2-NQ	CH_3CH_2CHO[d)]	83	17
4-Me-1,2-NQ	CH_3CH_2CHO[c)]	0	100
4-MeO-1,2-NQ	CH_3CH_2CHO[c)]	0	100
1,2-NQ	$C_6H_5(CH_2)_2CHO$[c)]	12	88
6-Br-1,2-NQ	$C_6H_5(CH_2)_2CHO$[c)]	29	71
4-CN-1,2-NQ	$C_6H_5(CH_2)_2CHO$[c)]	80	20

a) 4-MeO-1,2-NQ: 4-Methoxy-1,2-naphthoquinone. The other quinones are shown in Table 1. The relative yields were determined by b) the integration of the ^{1}H-NMR signals of the concentrated reaction mixture, c) the weights of the isolated products, and d) the integration of the ^{1}H-NMR signals of the isolated products with TLC. e) 3-Acyl-1,2-naphthalenediol. f) 1,2-Napthalenediol monoacyl esters.

Table 5. The relative yields of the photo-addition compounds obtained in the reaction of 6-bromo- and 6-chloro-1,2-naphthoquinone with 2-butenal and 3-methyl-2-butenal

Quinone[a)]	Aldehyde	Relative yields (%)[b)] C-product[c)]	Relative yields (%)[b)] O-product[d)]
6-Br-1,2-NQ	$CH_3CH=CHCHO$	2.6	97.4
6-Cl-1,2-NQ	$CH_3CH=CHCHO$	4.9	95.1
6-Br-1,2-NQ	$(CH_3)_2C=CHCHO$	6.3	93.7

a) 6-Br-1,2-NQ: 6-bromo-1,2-naphthoquinone, 6-Cl-1,2-NQ: 6-chloro-1,2-naphthoqinone. b) Average of three experiments. c) C-attacking product. d) O-attacking product.

radical induces a change in the electron density of the radical. Thus, the relative ratio of the C-attacking product to the O-attakcing product in the photochemical reaction of 6-chloro-1,2-naphthoquinone with 2-butenal increases slightly compared with the case of 6-bromo-1,2-naphthoquinone(see Table 5).

The reaction of 6-bromo-1,2-naphthoquinone with propenal yields the O-attacking product exclusively, but with 2-butenal a minor C-attacking product arises along with the major O-attacking product, suggesting that the methyl group somewhat enhances the nucleophilic character of the derived acyl radical.[10)] However, as compared with 2-butenal, 3-methyl-2-butenal gives a slightly larger C-attacking product in the reaction with 6-bromo-1,2-naphthoquinone (Table 5).

Experimental

The melting points are uncorrected. The infrared spectra were obtained on a Hitachi 215 spectrometer, using a KBr disc. The ^{1}H-NMR spectra were taken with a JEOL MH-100 spectrometer, using TMS as the internal standard. Elemental analyses were carried out using a Yanaco MT-2 CHN corder.

Materials. *Quinones*: The 1,2-naphthoquinone (mp 121—122 °C),[11)] 3-chloro-(mp 171 °C),[12)] 3-bromo-(mp 164 °C),[13)] 4-cyano-(mp 175—176 °C),[14)] 4-methoxy-(mp 191—192 °C),[15)] 6-bromo-(mp 156 °C),[16)] and 6-chloro-1,2-naphthoquinone (mp 160—161 °C)[16)] were prepared according to the methods described in the literature. 6-Methyl-1,2-naphthoquinone(mp 126—127 °C)[17)] and 4-methyl-1,2-naphthoquinone(mp 77—80 °C)[18)] were prepared by the oxidation of 6-methyl-2-naphthol and 4-methyl-1-naphthol respectively with Fremy's salt.

Aldehydes: The *p*-nitro-, *m*-nitro-, *p*-methyl-, *p*-methoxy-, 2,4-dimethoxy-, and 3,4,5-trimethoxybenzaldehyde, and cinnamaldehyde were commercially available and were used without further purification. The acetaldehyde, propanal, propenal, 2-butenal, *trans*-2-hexenal, 10-undecenal, 3-phenylpropanal, and benzaldehyde were commercially available and were further purified by distillation before use. The 2,4,6-trimethylbenzaldehyde(bp 94—95 °C/5 mmHg),[19)] 2,4,6-triisopropylbenzaldehyde(bp 110—114 °C/3 mmHg),[19)] cyclohexanecarbaldehyde(bp 75—77 °C/21 mmHg),[20)] 1-cyclohexenecarbaldehyde(bp 82 °C/24 mmHg),[20)] 3-cyclohexenecarbaldehyde(bp 70—73 °C/20 mmHg),[21)] cyclopentenecarbaldehyde(bp 57—59 °C/28 mmHg),[22)] 1-cyclopentenecarbaldehyde(bp 49 °C/20 mmHg),[23)] 3-methyl-2-butenal(bp 67 °C/81 mmHg),[24)] and 3-chlorobutanal(bp 65 °C/64 mmHg),[25)] were prepared according to the methods given in the literature.

General Procedures. A 1,2-naphthoquinone derivative (1—2.5 mmol) and an aldehyde(1—10 mmol) were dissolved in benzene(25—80 ml), and the solution was irradiated for an appropriate time from outside in an ordinary glass tube by means of 300-W high-pressure mercury arc lamp through a 5-cm-thick layer of flowing water(15—20 °C) or of cold water (0—5 °C). After the removal of the solvent under reduced pressure, the residue was chromatographed on silica gel 60 (Merck, Art 7734, 0.063—0.200 mm), using benzene as the eluent. The photo-adducts thus obtained were further purified by recrystallization from benzene or benzene-light petroleum, or by TLC.

Structure Determination of Photo-adducts. 3-Acyl-1,2-naphthalenediols have characteristic IR bands at 3300—3500 (OH) and 1620—1650 (C=O) cm^{-1}. The 2-hydroxyl proton of them appeared at δ: 11—12 as a result of intramolecularly bonded hydrogen bonding with the carbonyl of the 3-acyl group. The 1,2-naphthalenediol monoesters show IR bands corresponding to carbonyl(1700—1740 cm^{-1}) and hydroxyl(3300—3400 cm^{-1}) groups. The existence of two isomers in these esters was confirmed by ^{1}H-NMR analyses. The yields and melting points of the adducts are listed in Tables 1, 2, and 3. Their physical properties and elemental analyses are shown in Table 6.

Detection of C-attacking Products. The presence of 3-acyl-1,2-naphthalenediol in a reacting system has been confirmed by inspecting the ^{1}H-NMR signal at δ: 11—12 in the concentrated reaction mixture. Thin-layer chromatography has been also used to detect the C-attacking products.

Irradiation of 6-Bromo-1,2-naphthoquinone with 2-Butenal: A benzene solution of the quinone (355.5 mg, 1.5 mmol) and

TABLE 6. SPECTRAL PROPERTIES AND ANALYTICAL DATA OF THE PHOTO-ADDITION COMPOUNDS OBTAINED IN THE REACTION OF 1,2-NAPHTHOQUINONE DERIVATIVES WITH ALDEHYDES

Compound No	IR(KBr, cm^{-1}) OH	CN	C=O	PMR ($CDCl_3$, δ)[a,b]	Found (%) C	H	N	Calcd (%) C	H	N	Molecular formula
3a	3410	—	1720	—	77.35	4.61		77.26	4.58		$C_{17}H_{12}O_3$
3b	3400	—	1740 1720	—	65.88	3.40	4.61	66.02	3.58	4.53	$C_{17}H_{11}NO_5$
3c	3430	—	1740 1718	—	65.92	3.63	4.51	66.02	3.58	4.53	$C_{17}H_{11}NO_5$
3d	3380	—	1710	2.44(s), 2.47(s)	77.62	5.17		77.68	5.07		$C_{18}H_{14}O_3$
3e	3380	—	1728 1700	3.89(s), 3.91(s)[c]	73.60	4.71		73.46	4.79		$C_{18}H_{14}O_4$
3f	3425	—	1725	4.02(s), 4.05(s)	67.62	5.00		67.79	5.12		$C_{20}H_{18}O_6$
4a	3375	—	1720	—	59.21	3.28		59.50	3.23		$C_{17}H_{11}BrO_3$
4b	3380	—	1715	—	52.23	2.64	3.81	52.58	2.58	3.61	$C_{17}H_{10}NBrO_5$
4c	3330	—	1715	—[c]	52.67	2.52	3.69	52.58	2.58	3.61	$C_{17}H_{10}NBrO_5$
4d	3350	—	1705	2.43(s), 2.54(s)[c]	60.55	3.52		60.53	3.67		$C_{18}H_{13}BrO_3$
4e	3320	—	1700	3.89(s), 3.92(s)[c]	57.80	3.42		57.73	3.51		$C_{18}H_{13}BrO_4$
4f	3350	—	1710	3.75(s), 3.78(s), 3.90(s), 3.93(s)	56.79	3.77		56.60	3.75		$C_{19}H_{15}BrO_3$
4g	3420	—	1735	3.72(s), 8.81(s)[c]	55.27	3.77		55.45	3.96		$C_{20}H_{17}BrO_6$
4h	3320	—	1720	2.29(s), 2.42(s), 2.48(s)	62.30	4.53		62.35	4.45		$C_{20}H_{17}BrO_3$
4i	3380	—	1720	1.26(t), 1.29(t), 2.82—3.27(m)	66.30	6.48		66.53	6.23		$C_{26}H_{29}BrO_3$
5a	3325	2220	1735	—	74.71	3.88	4.69	74.73	3.83	4.84	$C_{18}H_{11}NO_3$
5b	3255	2240	1745	—[c]	64.77	2.95	8.46	64.67	3.02	8.38	$C_{18}H_{10}N_2O_5$
5c	3274	2237	1745	—[c]	64.51	3.14	8.45	64.67	3.02	8.38	$C_{18}H_{10}N_2O_5$
5d	3345	2238	1735	2.51(s)	75.34	4.33	4.58	75.24	4.32	4.62	$C_{19}H_{13}NO_3$
5e	3275	2250	1725	3.80(s), 3.83(s)	71.40	4.00	4.46	71.47	4.10	4.39	$C_{19}H_{13}NO_4$
5f	3420	2225	1683	3.66(s), 3.75(s)	66.53	4.50	3.52	66.49	4.52	3.69	$C_{21}H_{17}NO_6$
5g	3325	2230	1720	2.40(s), 2.53(s)	76.18	5.06	4.19	76.12	5.17	4.23	$C_{21}H_{17}NO_3$
6a	3330	—	1722	—	68.30	3.77		68.35	3.71		$C_{17}H_{11}ClO_3$
6b	3350	—	1715	6.81(d), 6.90(d), 7.89(d), 7.97(d)[c]	70.14	4.08		70.27	4.03		$C_{19}H_{13}ClO_3$
6c	3375	—	1720	—	59.40	2.85	4.11	59.39	2.91	4.08	$C_{17}H_{10}NClO_5$
6d	3345	—	1718	—[c]	59.27	2.88	3.93	59.39	2.91	4.08	$C_{17}H_{10}NClO_5$
6e	3360	—	1717	2.43(s)	69.22	4.15		69.13	4.19		$C_{18}H_{13}ClO_3$
6f	3310	—	1710	8.89(s), 3.91(s)[c]	65.67	4.01		65.76	3.99		$C_{18}H_{13}ClO_4$
7a	3340	—	1720	—[c]	59.47	3.23		59.50	3.23		$C_{17}H_{11}BrO_3$
7b	3300	—	1700	6.83(d), 6.89(d), 7.89(d), 7.92(d)[c]	61.78	3.61		61.81	3.55		$C_{19}H_{13}BrO_3$
7c	3375	—	1720	—	52.55	2.52	3.68	52.58	2.58	3.61	$C_{17}H_{10}NBrO_5$
7d	3370	—	1720	—	52.44	2.59	3.56	52.58	2.58	3.61	$C_{17}H_{10}NBrO_5$
7e	3325	—	1715	2.44(s)	60.50	3.69		60.53	3.67		$C_{18}H_{13}BrO_3$
7f	3320	—	1710	3.90(s), 3.91(s)[c]	57.77	3.44		57.73	3.51		$C_{18}H_{13}BrO_4$
8a	3380	—	1705	2.46(s)[d]	77.77	5.13		77.67	5.07		$C_{18}H_{14}O_3$
8b	3490	—	1705	2.53(s), 6.07(d)	78.85	5.21		78.93	5.30		$C_{20}H_{16}O_3$
8c	3420	—	1719	2.50(s), 2.54(s)	66.63	4.09	4.44	66.87	4.05	4.33	$C_{18}H_{13}NO_5$
8d	3360	—	1710	2.51(s)	66.85	3.96	4.41	66.87	4.05	4.33	$C_{18}H_{13}NO_5$
8e	3375	—	1710	2.44(s), 2.46(s), 2.50(s)	77.98	5.56		78.06	5.52		$C_{19}H_{16}O_3$
8f	3450	—	1739 1707	2.45(s), 2.50(s) 3.90(s), 3.91(s)	74.05	5.30		74.01	5.23		$C_{19}H_{16}O_4$
9a	3410	—	1725	—[d]	72.89	4.61		72.89	4.71		$C_{13}H_{10}O_3$
9b	3340	—	1710	—	53.24	3.12		53.27	3.09		$C_{13}H_9BrO_3$
9c	3250	2226	1738	—	70.14	3.73	5.80	70.29	3.79	5.85	$C_{14}H_9NO_3$
9d	3375	—	1910	1.90(dd), 1.95(dd)	73.57	5.31		73.67	5.30		$C_{14}H_{12}O_3$
9e	3300	2230	1740	2.04(dd), 6.25(m)	71.11	4.40	5.22	71.14	4.38	5.53	$C_{15}H_{11}NO_3$
9d	3390	—	1710	1.03(t), 1.50—1.75(m), 2.33(q), 6.15(d)	74.99	6.25		74.98	6.29		$C_{16}H_{16}O_3$
9g	3340	—	1700	0.97(t), 1.37—1.67(m), 2.24(q), 5.98(d)	57.42	4.56		57.33	4.51		$C_{16}H_{15}BrO_3$
9h	3330	2240	1745	1.03(t), 1.50—1.75(m), 2.37(q), 6.22(d)	72.56	5.32	4.89	72.58	5.37	4.89	$C_{17}H_{15}NO_3$

TABLE 6. (Continued)

Compound No	IR(KBr, cm^{-1})			PMR ($CDCl_3$, δ)[a,b]	Found (%)			Calcd (%)			Molecular formula
	OH	CN	C=O		C	H	N	C	H	N	
9i	3300	—	1700	1.91—2.28, 2.46—2.85(m)	75.33	5.58		75.58	5.55		$C_{16}H_{14}O_3$
9j	3360	—	1700	1.94—2.20, 2.49—2.84(m)	57.77	3.90		57.68	3.93		$C_{16}H_{13}BrO_3$
9k	3240	2220	1700	1.92—2.16, 2.49—2.84(m)	73.16	4.66	5.01	73.11	4.69	5.01	$C_{17}H_{13}NO_3$
9l	3350	—	1690	1.56—1.87, 2.15—2.56(m)	76.24	6.04		76.10	6.01		$C_{17}H_{16}O_3$
9m	3360	—	1700	1.48—1.82, 2.17—2.47(m)	58.75	4.31		58.81	4.35		$C_{17}H_{15}BrO_3$
9n	3330	—	1708	6.76(d), 6.88(d)[c]	78.39	4.95		78.61	4.86		$C_{19}H_{14}O_3$
9o	3380	—	1705	6.76(d), 6.88(d), 8.03(d), 8.13(d)[c]	62.00	3.62		61.81	3.55		$C_{19}H_{13}BrO_3$
9p	3275	2236	1740	6.75(d)[c]	76.01	4.32	4.47	76.18	4.16	4.44	$C_{20}H_{13}NO_3$
10a	3480	—	1650	1.48—2.14(m), 3.78—4.03(m), 11.78(s)[d]	74.90	6.31		74.98	6.29		$C_{16}H_{16}O_3$
11a	3320	—	1720	1.48—2.20(m), 2.89—3.24(m)	75.11	6.26		74.98	6.29		$C_{16}H_{16}O_3$
10b	3450	—	1640	1.63—2.16(m), 3.70—4.01(m), 11.69(s)[d]	57.33	4.44		57.33	4.51		$C_{16}H_{15}BrO_3$
11b	3420	—	1720	1.60—2.21(m), 2.90—3.33(m)	57.28	4.62		57.33	4.51		$C_{16}H_{15}BrO_3$
10c	3310	2220	1640	1.55—2.30(m), 4.40—4.62(m), 11.51(s)	72.47	5.35	4.79	72.58	5.37	4.98	$C_{17}H_{15}NO_3$
11c	3220	2235	1755	1.53—2.20(m), 2.90—3.29(m)	72.58	5.30	4.99	72.58	5.37	4.98	$C_{17}H_{15}NO_3$
10d	3460	—	1635	1.20—2.20(m), 3.28—3.68(m), 11.87(s)[d]	75·51	6.60		75.53	6.71		$C_{17}H_{18}O_3$
11d	3310	—	1710	1.20—2.20(m), 2.37—2.64(m)[d]	75.60	6.78		75.53	6.71		$C_{17}H_{18}O_3$
10e	3440	—	1645	1.20—2.07(m), 3.23—3.57(m), 11.87(s)[d]	58.28	4.96		58.47	4.91		$C_{17}H_{17}BrO_3$
11e	3400	—	1720	1.18—2.18(m), 2.58—2.82(m)	58.48	4.83		58.47	4.91		$C_{17}H_{17}BrO_3$
10f	3370	2210	1625	1.20—2.15(m), 3.95—4.22(m), 11.60(s)	73.28	5.86	4.65	73.20	5.80	4.74	$C_{18}H_{17}NO_3$
11f	3250	2220	1745	1.20—2.20(m), 2.54—2.80(m)	73.19	5.86	4.71	73.20	5.80	4.74	$C_{18}H_{17}NO_3$
10g	3470	—	1650	1.17—2.12(m), 3.06(t), 4.70—5.01(m), 11.55(s)[d]	77.07	8.03		77.27	8.03		$C_{21}H_{26}O_3$
11g	3430	—	1735	1.17—2.14(m), 2.48—2.80(m), 4.72—4.97(m)[d]	77.25	7.94		77.27	8.03		$C_{21}H_{26}O_3$
10h	3440	—	1650	1.16—2.13(m), 2.97(t), 4.73—4.98(m), 5.50—5.80(m), 11.84(s)[d]	62.02	6.27		62.23	6.22		$C_{21}H_{25}BrO_3$
11h	3400	—	1735	1.30—2.20(m), 2.70(t), 4.95—5.18(m), 5.76—6.25(m)	62.28	6.16		62.23	6.22		$C_{21}H_{25}BrO_3$
10i	3300	2220	1630	1.20—2.10(m), 3.42(t), 4.70—4.96(m), 5.44—5.84(m), 12.01(s)[d]	75.15	7.15	3.95	75.19	7.17	3.99	$C_{22}H_{25}NO_3$
11i	3370	2230	1745	1.10—2.20(m), 2.63(t), 4.80—4.98(m), 5.60—5.90(m)	75.23	7.01	4.04	75.19	7.17	3.99	$C_{22}H_{25}NO_3$
10j	3450	—	1660	3.02(t), 3.39(t), 11.36(s)	78.02	5.54		78.06	5.52		$C_{19}H_{16}O_3$
11j	3320	—	1725	2.92—3.10(m)	78.16	5.50		78.06	5.52		$C_{19}H_{16}O_3$
10k	3450	—	1660	2.96(t), 3.27(t), 11.31(s)[d]	61.47	4.13		61.47	4.07		$C_{19}H_{15}BrO_3$
11k	3320	—	1730	2.83—3.02(m)[d]	61.35	3.98		61.47	3.98		$C_{19}H_{15}BrO_3$
10l	3280	2225	1638	3.07(t), 3.76(t), 11.57(s)	75.61	4.80	4.44	75.70	4.76	4.41	$C_{20}H_{15}NO_3$
11l	3275	2230	1760	3.00(m)	75.72	4.70	4.33	75.70	4.76	4.41	$C_{20}H_{15}NO_3$
10m	3470	—	1630	1.78—2.43(m), 3.68(m), 5.68(m), 11.68(s)[d]	76.00	6.05		76.10	6.01		$C_{17}H_{16}O_3$
11m	3380	—	1720	1.77—2.67(m), 2.91(m), 5.67(m)[d]	75.99	5.87		76.10	6.01		$C_{17}H_{16}O_3$
10n	3450	—	1640	1.63—2.45(m), 3.65(m), 5.69(m), 11.66(s)[d]	58.84	4.30		58.81	4.35		$C_{17}H_{15}BrO_3$
11n	3400	—	1720	1.80—2.54(m), 1.96(m), 5.75(m)	58.88	4.26		58.81	4.35		$C_{17}H_{15}BrO_3$
10o	3450	2215	1630	1.95—2.52(m), 4.22(m), 5.68(m), 11.58(s)[d]	73.76	5.01	4.78	73.71	5.15	4.78	$C_{18}H_{15}NO_3$
11o	3250	2230	1750	1.97—2.53(m), 2.96(m), 5.77(m)	73.81	5.03	4.87	73.71	5.15	4.78	$C_{18}H_{15}NO_3$

a) The protons appeared in the aromatic region, and the hydroxyl protons, except for the 2-hydroxyl proton which shifted to the low field of 3-acyl-1,2-naphthalenediols, are not listed. b) s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, dd: double doublet. c) The solvent is acetone-d_6. d) The solvent is carbon tetrachloride.

the aldehyde (350 mg, 5 mmol) was irradiated for 2 days. The reaction mixture was then worked-up as usual. 3-(2-Butenoyl)-6-bromo-1,2-naphthalenediol: orange-red needles (7.5 mg, 1.6%), mp 185—186.5 °C. IR: 3450(OH), 1655 (C=O) cm^{-1}. PMR($CDCl_3$), δ: 2.02(dd, 3H, J=1.5, 7.0 Hz), 5.96(s, 1H, removed by D_2O), 7.05—7.97(m, 6H), 11.37 (s, 1H, removed by D_2O). 6-Bromo-1,2-naphthalenediol mono-2-butenoate: white crystals (283 mg, 61.6%), mp 173.5—175 °C. IR: 3340(OH), 1710(C=O) cm^{-1}. PMR ($CDCl_3$), δ: 1.94 (dd, 3H, J=1.5, 7.0 Hz), 1.99 (dd, 3H, J=1.5, 7.0 Hz), 5.82—6.10 (m, 4H), 7.04—8.06 (m, 14H).

Irradiation of 6-Chloro-1,2-naphthoquinone with 2-Butenal: A benzene solution of the quinone (192.5 mg, 1 mmol) and the aldehyde (350 mg, 5 mmol) was irradiated for 3 days. The reaction mixture was then worked-up as usual. 3-(2-Butenoyl)-6-chloro-1,2-naphthalenediol: red crystals (6.5 mg, 2.5 %), mp 151—154 °C. IR: 3460(OH), 1655 (C=O) cm^{-1}. PMR (CCl_4), δ: 2.08 (dd, 3H, J=1.5, 7.0 Hz), 6.13 (s, 1H, removed by D_2O), 7.07—8.13 (m, 6H), 11.93 (s, 1H, removed by D_2O). 6-Chloro-1,2-naphthalenediol mono-2-butenoate: white crystals (125 mg, 47.6%), mp 179—180 °C. IR: 3340 (OH), 1708 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 2.00 (dd, 3H, J=1.5, 7.0 Hz), 2.05 (dd, 3H, J=1.5, 7.0 Hz), 6.21 (s, 2H, removed by D_2O), 7.25—8.24 (m, 14H).

Irradiation of 6-Bromo-1,2-naphthoquinone with 3-Methyl-2-butenal: A benzene solution of the quinone (476 mg, 2 mmol) and the aldehyde (504 mg, 6 mmol) was irradiated for 3 days. The reaction mixture was then worked-up as usual. 3-(3-Methyl-2-butenoyl)-6-bromo-1,2-naphthalenediol: red crystals (22 mg, 3.4%), mp 148—150 °C. IR: 3400 (OH), 1635 (C=O) cm^{-1}. PMR (CCl_4), δ: 2.10 (s, 3H), 2.27 (s, 3H), 5.94 (s, 1H, removed by D_2O), 6.93—8.00 (m, 5H), 12.04 (s, 1H, removed by D_2O). 6-Bromo-1,2-naphthalenediol mono(3-methyl-2-butenoate): white crystals, mp 147—148 °C. IR: 3345 (OH), 1700 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 2.02 (s, 3H), 2.27 (s, 3H), 6.02 (br, 1H), 6.24 (s, 1H, removed by D_2O), 7.23—8.15 (m, 5H).

Irradiation of 4-Methyl-1,2-naphthoquinone with Acetaldehyde: A benzene solution (80 ml) of the quinone (258 mg, 1.5 mmol) and the aldehyde (660 mg, 15 mmol) was irradiated for 42 h. No C-attacking product was detected by ^{1}H-NMR or TLC in the concentrated reaction mixture. The reaction mixture was then worked-up as usual. 4-Methyl-1,2-naphthalenediol monoacetate: white needles (165 mg, 51%), mp 174 °C (dec). IR: 3410 (OH), 1740 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 2.40 (s, 3H), 2.52 (s, 3H), 5.45 (br, 1H), 7.14—7.74 (m, 4H). Found: C, 72.01; H, 6.04%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

Irradiation of 4-Methyl-1,2-naphthoquinone with Propanal: A benzene solution (25 ml) of the quinone (86 mg, 0.5 mmol) and the aldehyde (87 mg, 1.5 mmol) was irradiated for 24 h. The reaction mixture was then worked-up as usual. 4-Methyl-1,2-naphthalenediol monopropanoate: white needles (52 mg, 45%), mp 112 °C. IR: 3400 (OH), 1730 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 1.25 (t, 3H), 1.32 (t, 3H), 2.51 (s, 6H), 2.64 (q, 2H), 2.67 (q, 2H), 5.46 (bs, 1H), 5.63 (br, 1H), 6.85 (s, 2H), 7.16—7.75 (m, 8H). The ratio of the isomer contents was 1 : 1, as estimated on the basis of the integration of the ^{1}H-NMR signals of the mixture. Found: C, 73.12; H, 6.08%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%.

Irradiation of 4-Methoxy-1,2-naphthoquinone with Acetaldehyde: A benzene solution (25 ml) of the quinone (200 mg, 1.06 mmol) and the aldehyde (500 mg, 11.4 mmol) was irradiated for 2 days at 0—5 °C. The reaction mixture was then worked-up as usual. 4-Methoxy-1,2-naphthalenediol monoacetate: white needles (186 mg, 76%), mp 105—106 °C (dec). IR: 3360 (OH), 1728 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 2.30 (s, 18%), 2.38 (s, 82%), 3.66 (s, 82%), 3.81 (s, 18%), 5.81 (br, removed by D_2O), 6.32 (s, 82%), 6.35 (s, 18%), 7.09—7.96 (m). Found: C, 67.22; H, 5.10%. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21%.

Irradiation of 4-Methoxy-1,2-naphthoqinone with Propanal: A benzene solution of the quinone (188 mg, 1 mmol) and the aldehyde (87 mg, 1.5 mmol) was irradiated for 2 days. The reaction mixture was then chromatographed on silica gel, using benzene–ether (8 : 2) as the eluent. 4-Methoxy-1,2-naphthalenediol monopropanoate: white needles (200 mg, 81%), mp 90—91 °C (dec). IR: 3320 (OH), 1725 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 1.33 (t, 21%), 1.40 (t, 79%), 2.73 (q, 21%), 2.83 (q, 79%), 3.82 (s, 79%), 3.99 (s, 21%), 6.47 (s, 79%), 6.58 (s, 21%), 7.36—8.20 (m). Found: C, 68.09; H, 5.71%. Calcd for $C_{14}H_{14}O_4$: C, 68.23; H, 5.73%.

Irradiation of 6-Bromo-1,2-naphthoquinone with 3-Chlorobutanal: A benzene solution (25 ml) of the quinone (237 mg, 1 mmol) and the aldehyde (211 mg, 2 mmol) was irradiated for 2 days. The concentrated reaction mixture was then chromatographed on silica gel, using benzene as the eluent. 3-(3-Chlorobutanoyl)-6-bromo-1,2-naphthalenediol: orange yellow needles (22.3 mg), mp 138—141 °C. IR: 3420 (OH), 1642 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 1.70 (d, 3H), 3.58 (m, 2H), 4.72 (m, 1H), 6.11 (s, 1H), 7.55—8.03 (m, 4H), 11.40 (s, 1H). 6-Bromo-1,2-naphthalenediol mono (3-chlorobutanoate): white needles (203.3 mg), mp 135—137.5 °C. IR: 3410 (OH), 1725 (C=O) cm^{-1}. PMR ($CDCl_3$), δ: 1.66 (d, 3H), 1.69 (d, 3H), 3.03 (m, 4H), 4.75 (m, 2H), 5.62 (br. 1H), 5.92 (s, 1H), 7.20—7.93 (m, 10H).

The author wishes to express his deep gratitude to Professor Kazuhiro Maruyama, Kyoto University, and Professor Osamu Soga, Shimane University, for their fruitful suggestions and invaluable encouragement. He also wishes to thank the Ministry of Education for its financial support for this research.

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6) Bruce and Cutts reported on the mechanism of the formation of 2-acetylhydroquinone in the photochemical reaction of *p*-benzoquinone with acetaldehyde. In their paper they considered the attack of the acetyl radical on the quinone in its ground state, followed by the subsequent enolization of the primary adduct. However, the present author confirmed that 3-acetyl-1,2-naphthalenediols were not obtained in the reaction of the acetyl radical with 1,2-naphthoquinone

derivatives in their ground state. The experimental conditions were as follows: a mixture of a 1,2-naphthoquinone (200 mg) and di-*t*-butyl peroxyoxalate (200 mg) in acetaldehyde (20 ml) was kept in the dark at room temperature for 7 days. Furthermore, CIDNP signals were observed in the photochemical reaction of 1,2-naphthoquinone with acetaldehyde in hexadeuteriobenzene. In addition, the photoinduced Fries rearrangement of the O-attacking product to C-attacking product did not occur under the experimental conditions used in this work. *Cf.* a) J. M. Bruce and E. Cutts, *J. Chem. Soc., C*, **1966**, 449; b) K. Maruyama and Y. Miyagi, *Bull. Chem. Soc. Jpn.*, **47**, 1303 (1974).

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