CHEMISTRY LETTERS, pp. 595-598, 1985.

PHOTOCHEMICAL REACTION OF 2-ALKENOYL-1,4-QUINONES. FORMATION OF CHROMONE DERIVATIVES

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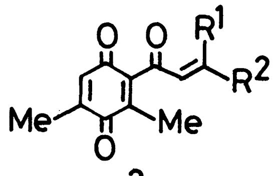
Irradiation of 5-methyl-2-(α-methylalkenoyl)-1,4-benzoquinones in alcohol under anaerobic conditions gave the two isomers of chromone derivatives being isomerization products of the quinones. Besides them other two adducts were produced. The mechanism of formation of these products is discussed.

The photochemical reaction of the quinones having olefinic double bond in the side chain such as plastoquinones has been intensively investigated[1)] and that of acyl quinones has been also reported.[2)] However, the photochemical behavior of alkenoyl-1,4-quinones having both olefinic double bond and carbonyl group in the side chain is scarcely known.[3,4)] In previous paper,[4)] we reported that irradiation of 2-alkenoyl-3,5-dimethyl-1,4-benzoquinones (2) in alcohol under nitrogen atmosphere afforded the two isomeric adducts; benzofuranone derivatives (type 3) and novel alkenyl ether derivatives (type 4). We wish to report herewith the photochemical reaction of 5-methyl-2-(α-methylalkenoyl)-1,4-benzoquinones (1) which have a methyl group at the α-position in the alkenoyl side chain. The photochemical reaction of 1 was noticeably different from that of 2 in the aspect to give 5 and 6 as given below.



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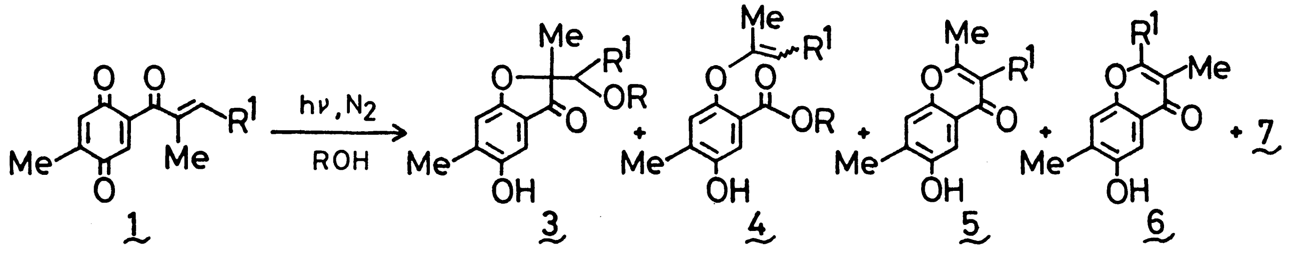
a R^1=H, R^2=C_6H_5

Typically, irradiation of an ethanol solution of 5-methyl-



a R^1=p-ClC_6H_4, b R^1=C_6H_5, c R^1=p-MeC_6H_4, d R^1=p-$MeOC_6H_4$
ROH = MeOH, EtOH, i-PrOH, and t-BuOH

2-(α-methylcinnamoyl)-1,4-benzoquinone (1b, 0.01 mol dm^{-3}) with a 300 W halogen lamp under the same conditions as described in the previous paper[4] gave a mixture of 2-(α-ethoxybenzyl)-5-hydroxy-2,6-dimethylbenzofuran-3-one (3b, 45%),[5] ethyl 5-hydroxy-4-methyl-2-(1-methylstyryloxy)benzoate (4b, 14%),[6] 6-hydroxy-2,7-dimethyl-3-phenylchromone (5b, 14%), 6-hydroxy-3,7-dimethyl-2-phenylchromone (6b, 12%), and 5-methyl-2-(α-methylcinnamoyl)hydroquinone (7b, 15%).[7] After separation of these products by column and thin layer chromatography on silica gel, the structures of 3b and 4b were determined by their spectral data.[4,5,6]

Since a mixture of 5b and 6b were obtained as colorless solids,[8] the mixture was separated into 6-methoxy-2,7-dimethyl-3-phenylchromone (8)[9] and 6-methoxy-3,7-dimethyl-2-phenylchromone (9)[10] after methylation by using methyl iodide and potassium carbonate by thin layer chromatography on silica gel. The structures of 8 and 9 were elucidated by their spectral data[9,10] and were confirmed by direct comparison with the authentic samples.[11] The structures of 5b and 6b were determined from these results. Surprisingly, 5b was an isoflavon derivative formed via skeletal rearrangement, while 6b was a flavone derivative formed by nomal cyclization.

Other 5-methyl-2-(α-methylalkenoyl)-1,4-benzoquinones (1a-1d) similarly reacted in ethanol to give the two isomers of chromone and the other two adducts.

Under the same conditions, but in other alcohols, the quinone 1 gave fairly different results in the relative products ratio. For example, the experimental results of 1b in several alcohols were shown in Table 1. As given in Table 1, change of solvents from methanol to t-butyl alcohol induced remarkable variations of the amount of chromone derivatives (5b and 6b). They were produced as major products in t-butyl alcohol. In addition, other quinones, 1a and 1c, also gave the chromone derivatives as main products in t-butyl alcohol as given in Table 2. On the contrary, the quinone 2 which has no methyl group at the α-position in the alkenoyl side chain gave the isomeric adducts (type 3 and 4) as main products in any alcohols though the ratios 3/4 varied with the solvents. The experimental results of the photochemical reaction of 2-cinnamoyl-3,5-dimethyl-1,4-benzoquinone (2a) in several alcohols were shown together with that of 1b in Table 1.

A possible mechanism of the reaction is as follows. Initially the photoexcited species of 1 cyclizes intramolecularly to form a zwitterionic intermediate.[4] The intermediate will accept a proton from alcohols to form a cationic

Table 1. Photochemical Reaction of 2-Alkenoyl-1,4-benzoquinone (1b and 2a) in Alcohol

Alcohols	Reaction of 1b / Yield/%[a]					Reaction of 2a / Yield/%[a]	
	3b	4b	5b + 6b	(5b/6b)	7	type 3	type 4
MeOH	36	8	14	(46/54)	38	82	17
EtOH	45	14	26	(55/45)	14	75	23
i-PrOH	26	22	43	(64/36)	8	49	45
t-BuOH	4	22	72	(64/36)	1	13	70

[a] Isolated yields based on the quinone consumed.

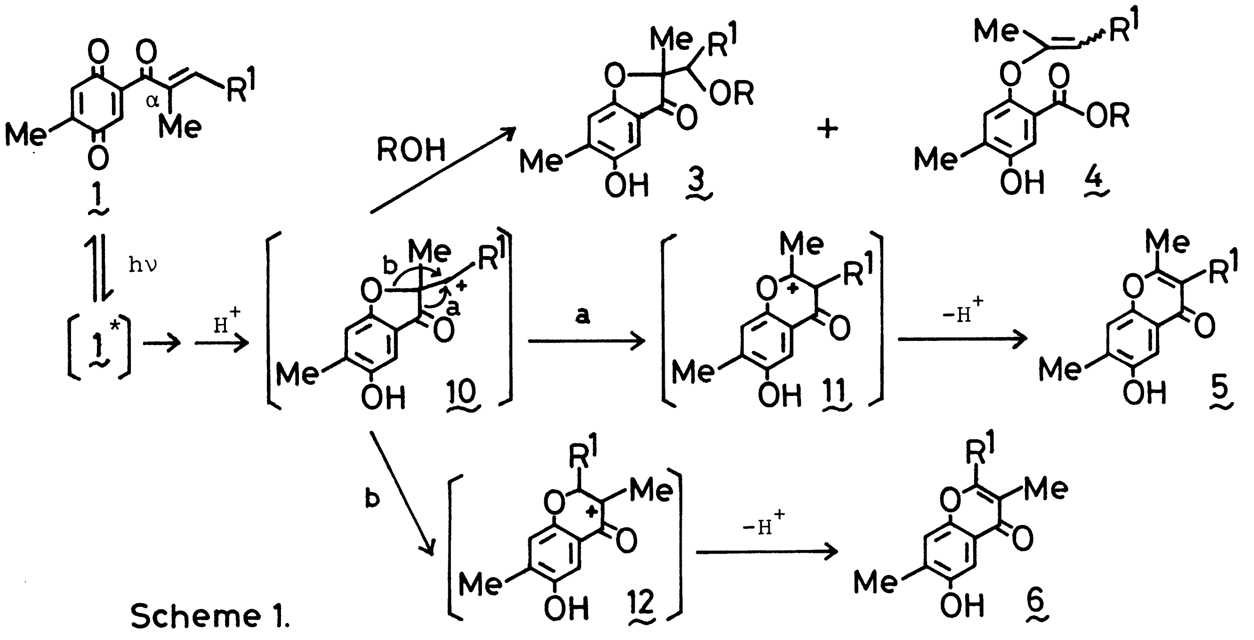
Table 2. Photochemical Reaction of 5-Methyl-2-(α-methylalkenoyl)-1,4-benzoquinones (1a-1d) in t-Butyl Alcohol

Quinone	R^1	Yield of products/%[a]				
		3	4	5 + 6	(5/6)	7
1a	p-ClC_6H_4	2	22	74	(73/27)	1
1b	C_6H_5	4	22	72	(64/36)	1
1c	p-MeC_6H_4	7	22	70	(63/37)	trace
1d	p-$MeOC_6H_4$	69	5	24	(60/40)	trace

a) Isolated yields based on the quinone consumed.

intermediate (10). When 10 is stable and/or solvents tend to add as in the reaction in methanol or ethanol, an alcohol adds to 10 to give the adduct 3. When 10 is unstable and/or solvents are hard to add as in the reaction in t-butyl alcohol, an alcohol adds to the carbonyl carbon of 10 to give the adduct 4 as described previously.4) At the same time, bond shift a of 10 results in the formation of 5, and bond shift b results in the formation of 6 as shown in Scheme 1.

The quinone 2 having no methyl group at the α-position in the alkenoyl side chain gave little chromone derivatives in every alcohol [with exception of 2-crotonoyl-3,5-dimethyl-1,4-benzoquinone (2b) in t-butyl alcohol],12) while the quinone 1 havihg α-methyl group gave the chromone derivatives (Tables 1 and 2). Possibly, the presence of a methyl group in the 2-position of benzofuranone skeleton of 10 enhances the process a and b and results in the formation of the greater amounts of 5 and 6 (Table 1).



Scheme 1.

References

1) J. M. Bruce, Quart. Rev., 21, 405 (1967); R. M. Wilson, T. F. Walsh, and S. K. Gee, Tetrahedron Lett., 21, 3459 (1980), and the literatures cited in it.

2) K. Maruyama and N. Narita, J. Org. Chem., 45, 1421 (1980).

3) K. Maruyama, M. Muraoka, and Y. Naruta, J. Chem. Soc., Chem. Commun., 1980, 1282.

4) K. Maruyama, H. Iwamoto, O. Soga, and A. Takuwa, Chem. Lett., 1984, 1343.

5) **3b** (mixture of diastereoisomers; ca. 2:1): IR (CHCl$_3$) 3330, 1680, 1620 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.86 and 0.93 (3H, each t, J=7 Hz), 1.10 and 1.31 (3H, each s), 2.23 (3H, s), 3.0-3.6 (2H, m), 3.67 and 4.50 (1H, each s), 6.66, 6.75, 6.81, and 6.99 (2H, each s), 7.1-7.5 (6H, m).

6) **4b** (mixture of cis-trans isomers; ca. 1:1): IR (CHCl$_3$) 3570, 3370, 1680, 1655, 1175 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.23 and 1.30 (3H, each t, J=7 Hz), 1.84, 2.13, 2.16, and 2.22 (6H, each s), 4.26 (2H, q, J=7 Hz), 5.36 and 5.60 (1H, each s), 5.90 (1H, brs), 6.69 and 6.81 (1H, each s), 6.95-7.60 (6H, m).

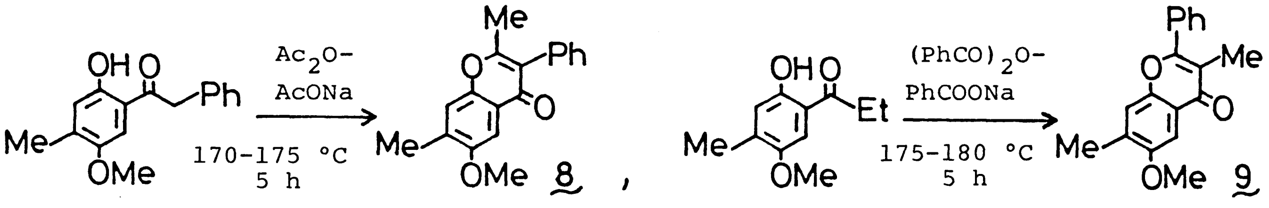
7) F. Farina and J. Valderrama, Synthesis, 1971, 315. When an ethanol solution of **1b** was allowed to stand for 3h in the dark at 35 °C, a mixture of hydroquinone (7b, 30%), 3-ethoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (30%), and **1b** (40%) was obtained. Therefore, **7** was thermochemical reaction product.

8) Mixture of **5b** and **6b**: IR (KBr) 3300, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.14, 2.24, and 2.30 (6H, each s), 7.10-7.65 (6H, m), 7.99 and 8.03 (1H, each s), 8.40 (1H, brs).

9) **8**: IR (CCl$_4$) 1645, 1630, 1470, 1425 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=2.20 (3H, s), 2.27 (3H, s), 3.88 (3H, s), 7.0-7.5 (7H, m). Found: C, 76.85; H, 5.71%; M$^+$, 280. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75%; M, 280.

10) **9**: IR (CCl$_4$) 1630, 1470, 1425 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=2.03 (3H, s), 2.26 (3H, s), 3.86 (3H, s), 7.14 (1H, s), 7.4-7.7 (6H, m). Found: C, 77.22; C, 5.75%; M$^+$, 280. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75%; M, 280.

11) Authentic samples, **8** and **9**, were synthesized according to Allan-Robinson methods[a] as follows.



a) J. Allan and R. Robinson, J. Chem. Soc., 125, 2192 (1924); T. C. Chadha, H. S. Mahal, and K. Venkataraman, ibid., 1933, 1459.

12) Irradiation of **2b** in t-butyl alcohol gave 6-hydroxy-3,5,7-trimethylchromone (type **5**) in 35% yield besides the other two adducts.

(Received February 18, 1985)