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PHOTOCHEMICAL ADDITION OF PROTIC SOLVENTS TO 1-PHENYLCYCLOALKENES

S. FUJITA, Y. HAYASHI, T. NÔMI and H. NOZAKI
Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

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Abstract—Direct photolysis of 6-8-membered 1-phenylcycloalkenes (**1a**–**1c**) dissolved in acetic or propionic acid gives mainly the corresponding esters (**2**), which are also obtained in the acetophenone-sensitized reactions. Minor products in the direct photolysis of **1a** and **1b** are hydrogenation (**3**) and alkylation products (**4**), while 8-membered **1c** yields 1-phenylbicyclo[5.1.0]octane (**5**) on UV irradiation. Compounds **3** and **4** are explained as the secondary photoproducts from **2**. Possible species affording **2** are discussed.

BTX-SENSITIZED reaction of 1-alkylcycloalkenes in protic solvents results in protonation of the double bonds followed by isomerization and/or the formation of ionic adducts.[1] The present paper deals with photochemical behaviour of cycloalkenes having a conjugated benzene chromophore.* †

In Table 1 and Scheme I are summarized the results of the irradiation of 1-phenylcycloalkenes (**1**) dissolved in carboxylic acids. 1-Phenylcyclohexene (**1a**) in acetic acid gave an acetate (**2a**), phenylcyclohexane (**3a**) and 1-methyl-1-phenylcyclohexane (**4a**).[4] The hydrocarbons **3a** and **4a** were identical with the authentic samples described in the literature. The ester **2a** exhibited IR bands at 1735 and 1250 cm^{-1} and an NMR signal at δ 1·93. Since the NMR spectrum shows no signal of a methine proton substituted by acetoxyl group, **2a** should be 1-acetoxy-1-phenylcyclohexane. The acetate (**2a**) easily decomposed to **1a** on GC and column chromatography. Direct irradiation of **1a** in propionic acid gave 1-propionyloxy-1-phenylcyclohexane (**2A**), **3a** and 1-ethyl-1-phenylcyclohexane (**4A**). Similarly, the main products of the photoreaction of 1-phenylcycloheptene (**1b**) in acetic and propionic acid were 1-acetoxy- (**2b**) and 1-propionyloxy-1-phenylcycloheptane (**2B**), respectively. Phenylcycloheptane (**3b**) and alkylation products (**4b**[5] and **4B**) were also detected. 1-Phenylcyclooctene‡ (**1c**) gave a slightly different pattern of product composition. Although the main product was again the corresponding acetate (**2c**, 34%), the conversion was less efficient and the hydrogeneration (**3c**) and alkylation products (**4c**) were absent. The hydrocarbon fraction was composed of 1-phenylbicyclo [5.1.0] octane (**5**, 5%) and two unidentified isomers of **1c** in minor amounts. Photoirradiation of 1-phenylcyclopentene in acetic acid did not give the corresponding acetate.

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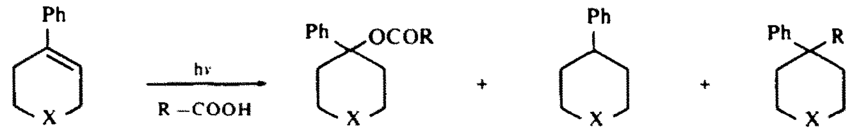
* The preliminary account of the present report has been described in Ref. 2.

† While the present paper was in preparation, Kropp reported similar photoaddition of methanol to the title olefins in the presence of sulphuric acid. See Ref. 3.

‡ For photochemical polar addition of cyclooctene, see Ref. 6.

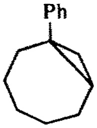
SCHEME I



1 **2** **3** **4**

a: X = $-CH_2-$
b: X = $-(CH_2)_2-$
c: X = $-(CH_2)_3-$

a: X = $-CH_2-$, R = Me
A: X = $-CH_2-$, R = Et
b: X = $-(CH_2)_2-$, R = Me
B: X = $-(CH_2)_2-$, R = Et
c: X = $-(CH_2)_3-$, R = Me .



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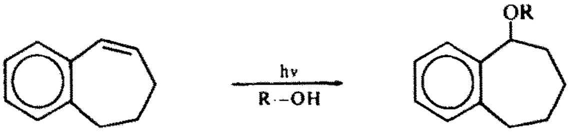
SCHEME II



6 **7**

a: R = Ac 22% (32%)*
b: R = Me 8% (14%)*

TABLE 1. UNSENSITIZED AND ACETOPHENONE-SENSITIZED REACTION OF **1a** AND **1b** IN CARBOXYLIC ACIDS (RCOOH)

Olefin	Time min	Conv. %	Product[a]				
			X	R	**2**, %	**3**, %	**4**, %
1a	30[b]	72	$-CH_2-$	Me	31	2	3
	30[c]	68	$-CH_2-$	Me	(42)	(d)	(d)
	45[b]	92	$-CH_2-$	Et	44	4	7
	30[c]	68	$-CH_2-$	Et	(44)	(d)	(d)
1b	30[b]	93	$-(CH_2)_2-$	Me	41	5	4
	30[c]	70	$-(CH_2)_2-$	Me	(56)	(d)	(d)
	45[b]	84	$-(CH_2)_2-$	Et	40	3	5
	30[c]	66	$-(CH_2)_2-$	Et	(42)	(d)	(d)

[a] Values in parentheses refer to the yields in the acetophenone-sensitized irradiation.

[b] Direct irradiation was effected on 0·04–0·05 M solutions placed in quartz tubes (1·5* × 18 cm) with an external 200 W high pressure Hg arc under N_2 atmosphere at room temp.

[c] Irradiation was effected by means of an external 200 W high pressure Hg arc and a 1·5 cm thick 9% $CuSO_4$ solution as a filter on 0·05 M solutions in Pyrex tubes containing *ca* equimolar amount of acetophenone. Acetophenone was recovered from the reaction mixture in more than 78%.

[d] Not detected.

Direct irradiation of 1,2-benzo-1,3-cycloheptadiene (**6**) in acetic acid gave the corresponding acetate (**7a**). Methanol addition to **6** proceeded in the presence of 0·5% sulphuric acid under unsensitized condition to produce **7b** (Scheme II). All the new compounds gave correct analyses and their spectral data reported in the experimental section and in Table 2 were consistent with the structure assigned. The esters (**2**) are not accessible by acylation of the corresponding tertiary alcohols because of the facile dehydration.

Acetophenone-sensitized reactions of **1a** and **1b** in carboxylic acids afforded the corresponding esters (**2**) (Table 2). Unexpectedly, the photoinduced addition of acetic acid to 8-membered **1c** was not photosensitized by acetophenone. Since **1c** must be very little different from 6- and 7-membered olefins with respect to the triplet energy, the energy accepted may be consumed by nonradiative or emission processes. These results of the sensitized reactions indicate the fact that the formation of ester (**2**) can be effected *via* π,π^* triplet states of **1a** and **1b**.* Since the photochemical behaviours of 6- and 7-membered olefins (**1a** and **1b**) are different from those of 5- and 8-membered ones, highly strained *trans* cycloalkenes would be the most plausible intermediates of the ionic addition reactions.† However, our data are insufficient to ascertain the possibility.‡ It should be added that the protonation of the ground state of **1a** gave 3-acetoxy-2-phenylcyclohexene.§

Whether the reactive intermediate is the π,π^* triplet state of an olefin or a *trans*-cycloalkene, three limiting cases may be considered: (1) a concerted four-centre addition to the excited triplet or *trans* cycloalkene, (2) a *trans* addition *via* a protonated olefin and (3) a stepwise addition proceeding through a cationic species (Scheme IV).[1c] Direct and acetophenone-sensitized irradiation of **1a** in a mixture of acetic acid and methanol (1 :3700) gave 1-methoxy-1-phenylcyclohexane (**8a**) as well as **2a**, whereas no ether (**8a**) was obtained in the absence of acetic acid (Scheme III). Similarly, the ether (**8b**) was obtained in the photoreaction of **1b**. If path 1 was the main course of the photoaddition, no ether (**8**) would be obtained. These competitive reactions suggest, therefore, that cationic intermediates are involved in the ionic addition reactions of polar solvents and that a concerted four-centre mechanism (path 1) is excluded. Moreover, the yields of **2a** and **2b** were more than two-third those of **8a** and **8b**, respectively, in spite of the small ratios of acetic acid to methanol (1 :3700). This means that the intermediate is sufficiently long-lived to attract the more favourable partner or carboxylic acid and form a benzyl cation and carboxylate anion pair, which recombine to give the ester **2** (path 3).

The hydrogenation (**3**) and the alkylation products (**4**) appear to be the secondary photoproducts arising from the esters (**2**), since photolysis of **2a** in acetic acid afforded a considerable amount of **1a**, **3a** and **4a**. Their formation may be explained on the basis

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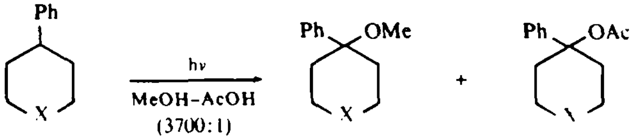
* Quenching studies with piperylene gave no reliable results. It is not clear, therefore, whether the formation of **2** *in direct irradiation* occurs through singlet or triplet excited states.

† Photoinduced additions of protic solvents to 6–8 membered cyclenones have been reported.[8] The highly strained *trans* isomers formed by photochemical *cis-trans* isomerization have been considered as the intermediates of the ionic addition reactions.[9]

‡ All attempts to detect highly strained ground state(s) by low temperature NMR proved futile.

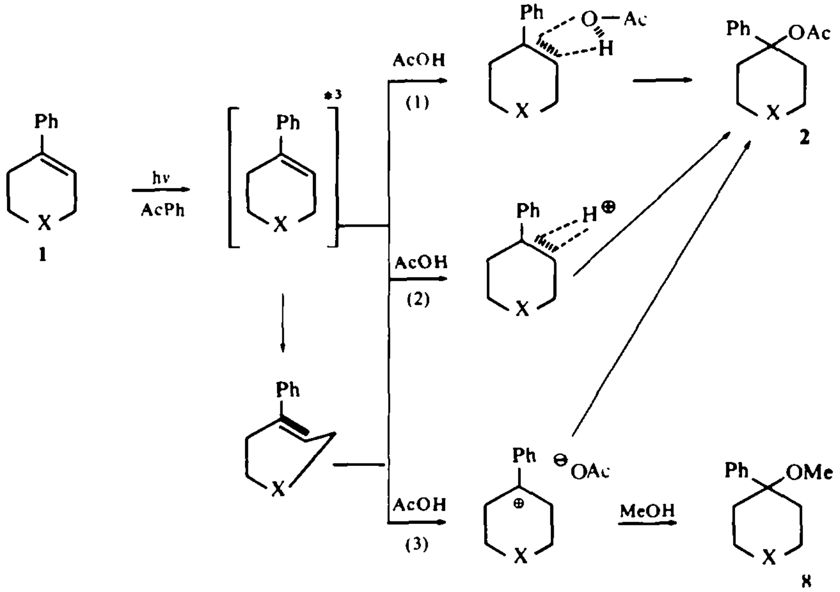
§ Similar reactions of carbonium ions have been reported. See Ref. 10.

Scheme III

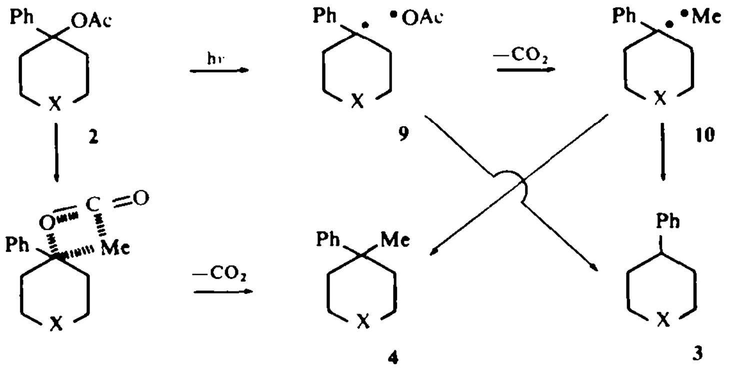


1	**8**	**2**
a: X = $-CH_2-$	26% (23%)*	19% (14%)*
b: X = $-(CH_2)_2-$	27% (25%)*	19% (18%)*

Scheme IV



Scheme V



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* Values in parentheses refer to the yields in the acetophenone-sensitized irradiations.

of a radical mechanism rather than ionic ones. The homolytic fission of C–O bond of **2** may give radical pairs (**9**). The following decarboxylation and recombination may afford the alkylation products (**4**).* Formation of **3** can be also explained in terms of the radical pairs **9** and/or **10**. However, the possibility of concerted decarboxylative alkylation is not excluded.

EXPERIMENTAL

NMR data were obtained on JEOL C-60-H spectrometer in CCl_4 at 60 MHz. Preparative TLC were performed on silica gel G (20 × 20 × 0·3 cm) using benzene as a solvent and the same solvent as an eluant. Preparative GC were performed on High Vacuum Silicone Grease 20% on Celite 545 (2 m, 160°, He as carrier gas). The contents of the hydrocarbons were determined by GC (Polyethylene glycol 30% on Celite 545 containing 3% $AgNO_3$, 2 m, 100°, H_2 as carrier gas).

Direct irradiation of 1-*phenylcyclohexene* (**1a**) *and -cycloheptene* (**1b**) *in carboxylic acids*

General procedure. After 30–45 min irradiation of a 0·04–0·05 M soln (15 ml) of **1** in the respective carboxylic acid with a high pressure Hg arc under N_2, the photolysate was neutralized with $NaHCO_3$aq, extracted with ether and dried (Na_2SO_4). Concentration *in vacuo* and subsequent preparative TLC gave a mixture of hydrocarbons (**1**, **3** and **4**) and the corresponding ester (**2**). The two fractions separated were weighed and the hydrocarbon fraction was subjected directly to GC analysis. The results are summarized in Table 1. Preparative GC of the hydrocarbon fraction gave the starting olefin (**1**), **3** and **4**. The ester (**2**) was distilled and subjected to spectrometric analyses. The physical properties of **2** and **4** are given in Table 2. Preparative GC of **2** resulted in elimination of carboxylic acid to give the corresponding olefin (**1**).

Direct irradiation of 1-*phenylcyclooctene* (**1c**) *in acetic acid*

A 0·036 M soln (15 ml) of **1c** in AcOH was irradiated under N_2 for 30 min and worked up as described (conversion 51%). The hydrocarbon fraction consisted of **5**[7] and two unidentified isomers of **1c**. The acetate **2c** decomposed on distillation and gave no correct analysis. The compound (**2c**) was characterized by IR (1730, 1240 and 1120 cm^{-1}) and NMR spectra (δ 2·00, singlet).

The photolysis of 1-*acetoxy*-1-*phenylcyclohexane* (**2a**) *in acetic acid*

A 0·03 M soln (15 ml) of **2a** in AcOH was placed in a quartz tube and irradiated under N_2 with a 200 W high pressure Hg arc for 30 min. Work-up followed by GC indicated the presence of **3a** (rel retention time 0·43), **4a** (0·56) and **1a** (1·00).

Acetophenone-sensitized photoreaction of **1** *in carboxylic acids*

General procedure. A 0·05 M soln (15 ml) of **1** and equimolar amount of acetophenone in carboxylic acid was placed in a Pyrex tube and irradiated through a 9% $CuSO_4$aq (1·5 cm thick) under N_2 with a 200 W high pressure Hg arc for 30 min. Usual work-up afforded the corresponding esters (**2**). The hydrocarbons (**3** and **4**) were not detected by GC. The results are summarized in Table 1. Acetophenone-sensitized irradiation of **1c** resulted in the recovery of the starting olefin.

Direct irradiation of **1a** *and* **1b** *in* AcOH-MeOH

A 0·085 M soln (15 ml) of **1a** in MeOH containing 0·5 wt % of AcOH was placed in a quartz tube and irradiated for 60 min under N_2. Usual work-up afforded the corresponding acetate (**2a**) and **8a**, b.p. 70–72°/0·06 mm. NMR (CCl_4): δ 7·24 (5H, s), 2·90 (3H, s) and 2·2–1·3 (10H, m). IR (neat): 3040, 2925, 2850, 1600, 1490, 1450, 1340, 1265, 1245, 1200, 1135, 1065, 1010, 925, 910, 890, 835, 815, 750 and 695 cm^{-1}. (Found: C, 82·4; H, 9·6. $C_{13}H_{18}O$ requires: C, 82·1; H, 9·5%).

Similar irradiation of a 0·077 M soln (15 ml) of **1b** gave **2b** and **8b**, b.p. 82°/0·07 mm; NMR (CCl_4): δ 7·24 (5H, broad s), 2·92 (3H, s) and 2·1–1·4 (12H, m); IR (neat): 3060, 3030, 2925, 2850, 1600, 1490, 1445, 1180,

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* Similar decarboxylative alkylation was reported in the literature. See Ref. 11. The authors are grateful to Professor T. Mukai for valuable suggestions.

TABLE 2. PHYSICAL PROPERTIES OF **2** AND **4**

Compound	b.p. (m.p.) °/mm	IR[a] cm^{-1}	NMR[b] δ ppm
2a[c]	(58–59°)	1735, 1250, 1210, 1125	7·20 (5H, s), 2·7–1·0 (13H, m + s (δ 1·93))
2A[d]	100–102°/0·06	1735, 1260, 1175, 1130	7·23 (5H, s), 2·7–0·9 (15H, m)[e]
2b[f]	100–102°/0·06	1735, 1235, 1186, 1135	7·25 (5H, s), 2·4–0·9 (15H, m + s (δ 1·97))
2B[g]	112–115°/0·09	1735, 1260, 1200, 1175	7·20 (5H, s), 2·5–0·9 (17H, m)[h]
4A[i]	105–108°/5	1600, 1498, 1375	7·20 (5H, s), 2·5–1·2 (12H, m), 0·58 (3H, t)
4B[j]	85°/0·2	1600, 1495, 1370	7·03 (5H, s), 2·0–1·0 (14H, m), 0·53 (3H, t)

[a] Taken with neat liquid.

[b] Measured in CCl_4, at 60 MHz and 24°.

[c] Found: C, 77·3; H, 8·4. $C_{14}H_{18}O_2$ requires: C, 77·0; H, 8·3.

[d] Found: C, 77·6; H, 8·6. $C_{15}H_{20}O_2$ requires: C, 77·6; H, 8·7.

[e] The signals of the ethyl group appeared at δ 1·10 (t) and at δ 2·27 (q).

[f] Found: C, 77·8; H, 8·7. $C_{15}H_{20}O_2$ requires: C, 77·6; H, 8·7.

[g] Found: C, 78·2; H, 9·2. $C_{16}H_{22}O_2$ requires: C, 78·1; H, 9·0.

[h] The signals of the ethyl group appeared at δ 1·11 (t) and at δ 2·2 (m).

[i] Found: C, 89·4; H, 10·6. $C_{14}H_{20}$ requires: C, 89·3; H, 10·7.

[j] Found: C, 88·9; H, 10·9. $C_{15}H_{22}$ requires: C, 89·0; H, 11·0.

1130, 1075, 1060, 880, 745 and 690 cm^{-1}. (Found: C, 82·5; H, 9·8. $C_{14}H_{20}O$ requires: C, 82·3; H, 9·9%). The results are summarized in Scheme III.

Acetophenone-sensitized irradiation of **1a** *and* **1b** *in* AcOH-MeOH

A soln (15 ml) of **1a** (0·83 M) and equimolar amount of acetophenone in 0·5 wt % methanolic AcOH was irradiated for 30 min through Pyrex and aq $CuSO_4$ filters with a 200 W high pressure Hg arc. Usual work-up afforded **2a** and **8a**. Similarly, acetophenone-sensitized irradiation of **1b** yielded **2b** and **8b**. The results are collected in Scheme III.

Protonation of **1a** *in* AcOH-H_2SO_4 *in the dark*

A 0·05 M soln (20 ml) of **1a** in AcOH containing 0·5 wt % of H_2SO_4 was allowed to stand at room temp in dark under N_2 for 4 hr. Usual work-up gave 3-acetoxy-2-phenylcyclohexene which was identical with an authentic sample.[11]

Irradiation of **6** *in acetic acid*

A 0·05 M soln (15 ml) of **6** in AcOH was irradiated as described. Usual work-up gave **7a**, m.p. 36·6–37·3°. NMR (CCl_4): δ 7·04 (5H, s), 5·0–4·5 (1H, m) and 3·4–1·5 (11H, m + s (δ 1·94, 3H)). IR (Nujol): 1740, 1498, 1232, 1210, 1020, 980, 936, 908, 839, 750 and 725 cm^{-1}. (Found: C, 76·3; H, 7·9. $C_{13}H_{16}O_2$ requires: C, 76·4; H, 7·9%).

Acetophenone-sensitized reaction of **6** in AcOH was performed as described in the general procedure. The results are collected in Scheme II.

Irradiation of **6** *in methanol*

Direct irradiation of a 0·05 M soln (15 ml) of **6** in MeOH containing 0·5% H_2SO_4 gave **7b**, b.p. 80°/0·2 mm; NMR (CCl_4): δ 6·99 (4H, s), 3·27 (3H, s), 3·2–2·6 (5H, m) and 2·2–1·4 (4H, m); IR (neat): 3060, 3030, 2925, 2850, 2820, 1496, 1453, 1365, 1250, 1185, 1105, 1090, 1050, 975, 910, 860, 830, 745 and 720 cm^{-1}. (Found: C, 82·0; H, 9·1. $C_{12}H_{16}O$ requires: C, 81·8; H, 9·2%).

Acetophenone-sensitized reaction was conducted as described. The results are found in Scheme II.

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