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Photo-Cleavage of Carbon–Carbon Bond of α-Iodocycloalkanones Giving ω,ω-Dialkoxyalkanoic Ester in Alcohol

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The irradiation at $\lambda > 300$ nm of α-iodocycloalkanones with a high-pressure mercury lamp in alcohols containing a small amount of water afforded the corresponding ω,ω-dialkoxyalkanoic ester (65—88%) by photochemical cleavage of the C(I)–C=O bond at room temperature. In the case of a commercial fluorescent lamp as the irradiating light source, photochemical ring-opening products were also obtained. The irradiation of 2α-iodo-5α- and 4β-iodo-5β-cholestan-3-ones in methanol gave methyl 2,2-dimethoxy-2,3-seco-5α-cholestan-3-oate and methyl 4,4-dimethoxy-3,4-seco-5β-cholestan-3-oate in 78 and 62% yields, respectively. The photochemical behavior of the cleavage reaction of α-iodocycloalkanones is also discussed on the basis of 2-hydroxycycloalkanone as an intermediate.

ω,ω-Dialkoxyalkanoic ester derivatives are important as intermediates in organic synthesis.[1] There are some syntheses of ω,ω-dialkoxyalkanoic ester involving a regiospecific oxidative ring cleavage of cycloalkenes with ozone in various alcohols;[2] ring-opening oxygenation on treatment with lead(IV) acetate,[3] sodium periodate,[4] perbenzoic acid,[5] iron(III) salt,[6] and oxovanadium(V)[7] in alcohol under oxygen; and electrochemical oxidation cleavage of α-substituted cycloalkanones and cycloalkanone enol acetates.[8] Recently, we have reported that the reaction of α-alkylcycloalkanones with iodine-cerium(IV) salts[9] and cerium(IV) salts[10] in alcohol yields the corresponding oxoalkanoic ester and ω,ω-dialkoxyalkanoic ester. Most of these processes suffer from disadvantages of using toxic reagents and heavy metals. Consequently, there is a need to develop the viewpoint of "green chemistry".

The photochemistry of organic halides RX (X = Cl, Br, I) has been intensively investigated for many years,[11] since it has become clear that cationic, as well as free-radical, intermediates play an important role in the solution phase photochemistry of these halides. Competing ionic and radical photobehaviors have been observed for haloalkenes, and cycloalkyl halides.[12,13] Recently, photoinduced alcoholysis and photodehalogenation[14] of α-halo ketones (Cl, Br) in alcohols have been intensively investigated by Tomioka et al.[15] In their interesting studies on the photosolvolysis of α-halo ketones, they have proposed that the homolysis of C–X bonds produces a radical pair, which may undergo a radical reaction or electron transfer to afford an ion pair, which would then cause a carbocation reaction. However, there are only a few reports on the study of the photochemistry of α-halo cyclic ketones. Recently, Orito et al. have reported that the photolysis of α-bromocamphor in methanol provide dimerized α-camphorylcamphors derivatives.[16] However, a photochemical reaction of α-iodocycloalkanones has been not reported until now. During the course of our studies, we investigated a novel self-coupling reaction of cyclic ketones with a high-pressure mercury lamp to give the corresponding pinacol-type compound in good yields.[17] Since α-iodocycloalkanones are important as intermediates in organic synthesis, which were synthesized by our laboratory by a new method.[18] These iodo ketones are unstable and are sensitive to light. We thus tried to afford useful products from these iodo compounds. In our previous paper in this series, we have already shown that the photo-dehydroiodination from α-iodocycloalkanones in hexane affords α,β-unsaturated ketones as major products, accompanied by photoreduced products as by-products. In the case of hexane containing a small amount of water, the substituted product 2-hydroxycycloalkanone was also obtained.[19] Herein, we report that the irradiation of α-iodocycloalkanones **1**—**7** in alcohols containing a small amount of water gave the corresponding ω,ω-dialkoxyalkanoic ester **1c**—**10c** by cleavage of the C–C bond under a high-pressure mercury lamp (Scheme 1 and Table 1). Moreover, probably photochemical behavior of ring-opening has been shown for α-iodocycloalkanones **1**—**7** in terms of 2-hydroxycycloalkanones and ω-formylalkanoic ester as intermediates.

Results and Discussion

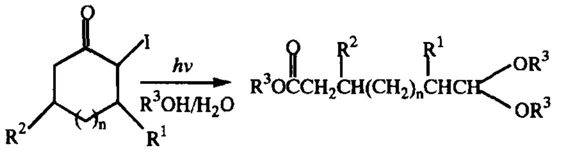
The photochemical reaction of α-iodocycloalkanones **1**—**7** in methanol afforded predominantly photocleavage products, methyl ω,ω-dimethoxyalkanoates **1c**—**10c**, in good yields with a high-pressure mercury lamp at room temperature. These reactions did not occur in the absence of light. Similarly, the reaction of α-iodocyclododecanone (**6**) in ethanol, 1-propanol, and 2-propanol yielded the corresponding ω,ω-dialkoxyalkanoates. These results are summarized in Scheme 1 and Table 1.

On the basis of these results, it was found that the pho-

Table 1. Irradiaton of α-Iodocycloalkanone in Alochols at Room Temperature

Entry	Substrates[a]	Solvents	Methods[b]	Time/h	Product/%[c]
1	**1**	MeOH	400 W	18	**1c** (65)
2	**2**	MeOH	400 W	14	**2c** (72)
3	**3**	MeOH	400 W	14	**3c** (70)
4	**4**	MeOH	400 W	15	**4c** (80)[d]
5	**5**	MeOH	400 W	18	**5c** (75)[d]
6	**6**	MeOH	100 W	12	**6c** (87)[d]
7	**6**	MeOH	400 W	10	**6c** (88)
8	**6**	EtOH	100 W	16	**7c** (77)[d]
9	**6**	EtOH	400 W	16	**7c** (80)
10	**6**	Pr^{n}OH	100 W	18	**8c** (69)
11	**6**	Pr^{n}OH	400 W	16	**8c** (70)
12	**6**	Pr^{i}OH	100 W	20	**9c** (n) **6a** (18) **9b** (64)
13	**6**	Pr^{i}OH	400 W	20	**9c** (n) **6a** (15) **9b** (65)
14	**7**	MeOH	100 W	20	**10c** (73)
15	**7**	MeOH	400 W	20	**10c** (75)

a) Substrate (15.7 mmol dm^{-3}) in hydrous alcohol (0.02%) was employed. b) Reactions were carried out with high-pressure mercury lamp as irradiation source under a nitrogen atmosphere. c) Isolated yields. n = no obtained. d) A trace of methyl 6-formylhexanoate (**4b**), methyl 7-formyl heptanoate (**5b**),[25a] methyl 11-formylundecanoate (**6b**), and ethyl 11-formylundecanoate (**7b**) were obtained, respectively.



1-7 **1c-10c**

		n	R^1	R^2	R^3
1	**1c**	1	H	H	Me
2	**2c**	1	H	Me	Me
3	**3c**	1	Me	H	Me
4	**4c**	2	H	H	Me
5	**5c**	3	H	H	Me
6	**6c**	7	H	H	Me
6	**7c**	7	H	H	Et
6	**8c**	7	H	H	Pr^n
6	**9c**	7	H	H	Pr^i
7	**10c**	10	H	H	Me

Scheme 1.

tochemical cleavage of the carbon–carbon bond occurred at the C^1 and C^2 positions of α-iodocycloalkanones finally to give ω,ω-dialkoxyalkanoic ester **1c**—**10c** in 65—88% yields. Also, it was found that in the case of methanol, the yield of the ring-opening product, methyl 12,12-dimethoxydodecanoate (**6c**),[2,8a] was higher and the reaction proceeded faster than in other alcohols (Entries 6—11). However, isopropyl 12,12-diisopropoxydodecanoate (**9c**) was not obtained in 2-propanol, and isopropyl 11-formylundecanoate (**9b**) and 2-hydroxycyclododecanone (**6a**)[8] were formed in 65 and 15% yields (Entries 12, 13), respectively. It seems that the acetalization of **9b** with 2-propanol is difficult due to the bulkier alkoxy group. The IR spectrum of this compound **9b** showed the characteristic absorption of formyl (2716 cm^{-1}, CHO) and ester carbonyl groups (1734 cm^{-1}). The ^{1}H NMR spectra exhibited the presence of a formyl group δ = 9.76 (1H, t, CHO) and the ^{13}C NMR spectrum exhibited signals at δ = 202.70 and 173.30, which were assigned to the formyl carbonyl carbon and ester carbonyl carbon, respectively. It is particular noteworthy that this photoreaction may provide a new synthetic method for the ω,ω-dialkoxyalkanoic ester, which is more convenient and cleaner than many methods reported heretofore.[2—10] Therefore, the new photocleavage products (**7c**, **8c**, and **9b**) were obtained in ethanol, 1-propanol, and 2-propanol containing a small amount of water for the α-iodocyclododecanone.

In order to investigate the reaction pathway of photocleavage for α-iodocycloalkanones in alcohol, irradiation of **6** was carried out. The results are summarized in Tables 2 and 3. From these results, it was found that in the cases of a high-pressure mercury lamp and a commercial fluorescent lamp

Table 2. Distribution of Photochemical Products of α-Iodocyclododecanone (**6**) at Room Temperature[a]

Entry	Methods[b]	Time/h	Products/%[c]		
			6a	**6b**	**6c**
1	100 W	3	33	38	7
2	100 W	6	25	28	36
3	100 W	9	8	15	60
4	100 W	12	t	5	87
5	400 W	3	23	27	40
6	400 W	6	10	16	60
7	400 W	10	t	3	88
8	F.L[d]	480	23	34	25
9	F.L[d]	960	5	3	78

a) A deoxygenated solution (15.7 mmol dm^{-3}) of α-iodocyclododecanone (**6**) in methanol (H_2O, 0.02%) was irradiated until complete consumption of substrate **6** which was apparent by TLC. b) The high-pressure mercury lamp in a water-cooled quartz immersion well as irradiation source. c) Isolated yields after purification by column chromatography on silica gel. A trace of **6e** and **6f** were also obtained. d) Reactions were carried out with a commercial fluorescent lamp. t = trace

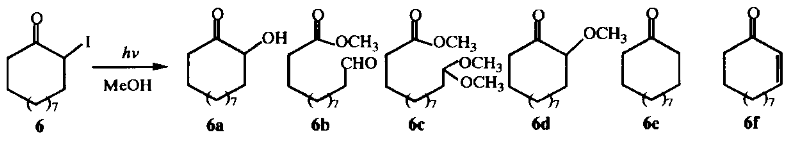


Table 3. Irradiation of α-Iodocyclododecanone (**6**) in Methanol at Room Temperature[a]

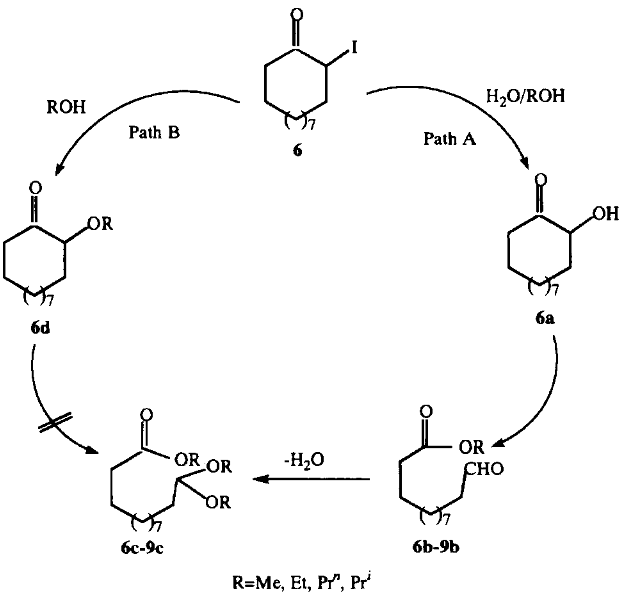
Entry	MeOH (H_2O%)	Method	Time / h	Products/%[c]					
				6a	**6b**	**6c**	**6d**	**6e**	**6f**
1	MeOH (0)	100 W[b,e]	12	t	t	t	65	17	8
2	MeOH (0)	F.L[d,e]	480	t	t	t	78	6	3
3	MeOH (0.01)	100 W	18	17	9	41	—	13	3
4	MeOH (0.02)	100 W	12	5	3	84	—	t	t
5	MeOH (0.04)	100 W	12	t	3	85	—	t	t
6	MeOH (1.68)	100 W[f]	10	t	t	86	—	t	t
7	MeOH (1.68)	F.L[f,d]	480	3	3	84	—	t	t

a) A deoxygenated solution (15.7 mmol dm^{-3}) of α-iodocyclododecanone (**6**) in solvents were irradiated until complete consumption of substrate **6** which was apparent by TLC. b) The high-pressure mercury lamp in a water-cooled quartz immersion well as irradiation source. c) Isolated yields after purification by column chromatography on silica gel. d) Reactions were carried out with a commercial fluorescent lamp. e) Methanol was dried completely by stored over 4A molecular sieves. f) The 2 ml water was added in methanol (150 ml). t = trace.

as the irradiation source, the photocleavage product, methyl 12,12-dimethoxydodecanoate (**6c**), was obtained preferentially. Also, it was found that the relative ratios of the photochemical products depend on the irradiated time and media. The irradiation of **6** for 3 h in MeOH–H_2O (0.02%) with a 100 W high-pressure mercury lamp gave **6a**, methyl 11-formylundecanoate (**6b**),[2,25a] and **6c** in 33, 38, and 7% yields, respectively (Table 2, Entry 1). In the irradiation of **6** for 12 h, **6a** and **6b** were nearly consumed; the major photoproduct **6c** was obtained in 87% yield (Table 2, Entry 4). In the cases of a 400 W high-pressure mercury lamp and a commercial fluorescent lamp, the same behavior was also observed for **6** (Table 2, Entries 5—9).

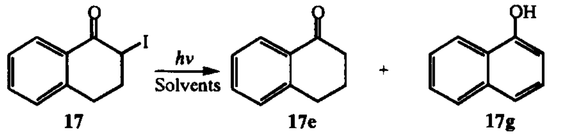
From the above results, it seems that **6a** and **6b** are intermediates of **6c**. The formation of **6a** may be due to the presence of a small amount of water in methanol. In order to clarify this hypothesis, the irradiation of **6** was carried out in absolute methanol and methanol containing a small amount of water. As can be seen from Table 3, the irradiation of **6** in absolute methanol gave a major photoalcoholysis product, 2-methoxycyclododecanone (**6d**) (65%), accompanied by a reduction product, cyclododecanone (**6e**) (17%), and an elimination product, cyclododecenone (**6f**)[26] (8%) (Table 3, Entry 1). In the case of methanol containing water (0.02 and 0.04%), ring-opening product **6c** was obtained in 84 and 85% yields, respectively (Table 3, Entries 4, 5). In the case of methanol containing water (0.01%), the ring-opening reaction was slower, accompanied by some reduction product **6e** and elimination product **6f** by a comparison with water (0.02 and 0.04%) (Table 3, Entry 3). It seems that the effects of the water content for the photochemical reaction of α-iodocycloalkanones are evident. From these results it was assumed that α-iodoketone **6** undergoes a displacement by an attack of the methoxy ion, and then α-hydroxyketone **6a** is formed by a small amount of water in methanol. This assumption was, however, denied by the facts that the transformation of α-methoxyketone **6d** into **6a** under photoirradiation conditions containing a small amount of water in methanol described above resulted in the recovery of **6d**.

Suginome et al. have recently reported that the irradiation of α-hydroxy cyclic ketones with mercury(II) oxide and iodine in benzene gives carbon–carbon bond-cleavage products.[20] On the basis of these results, it is considered that this reaction proceeds through photocleavage of the C(OH)–C=O bond of **6a** after a displacement by the hydroxide ion, followed by acetalization (Scheme 2).[21] Although the reason has not yet been clarified, it seems that α-substituted effects[22] of cycloalkanones for the present cleavage reaction of the C–C bond are apparent (Tables 3 and 5). Thus, in the case of **6a** in methanol containing iodine and HI, via an alkoxy radical as intermediates methyl ω,ω-dimethoxyalkanoate was obtained. This fact is apparently supported by the validity of **6a** as an intermediate (Fig. 1).



Scheme 2. Photochemical process of α-iodocycloalkanones.

Table 4. Irradiation of 3,4-Dihydro-2-iodo-1(2*H*)-naphthalenone (**17**) in Solvents at Room Temperature



Entry	Solvents[a)]	Time	Product/%[b)]	
		h	17e	17g
1	Hexane[c)]	1.0	46	53
2	Hexane[d)]	1.2	45	52
3	Hexane[e)]	10.0	25	71
4	Cyclohexane[c)]	1.0	52	47
5	Acetonitrile[c)]	3.5	51	47
6	Ethyl ether[c)]	2.0	57	42
7	Methanol[c)]	5.0	43	56
8	Methanol[f)]	5.0	46	53

a) Substrate (2.355 mmol) in solvents (150 ml) under nitrogen atmosphere with 100 W high-pressure mercury lamp was irradiated. b) Determined by GC. Isolated product **17g** had the same NMR spectra as authentic sample and was determined by HRMS. c) By dried. d) Hexane : H_2O = 10 : 1 (v/v). e) 1 molar amount of triethylamine was employed. f) Methanol containing a small amount of water (0.02%).

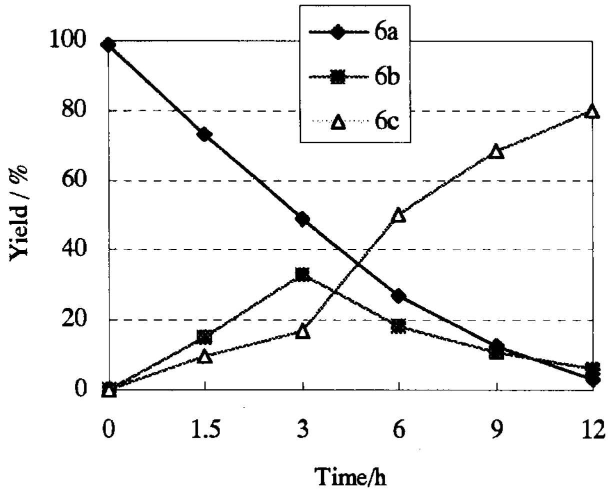
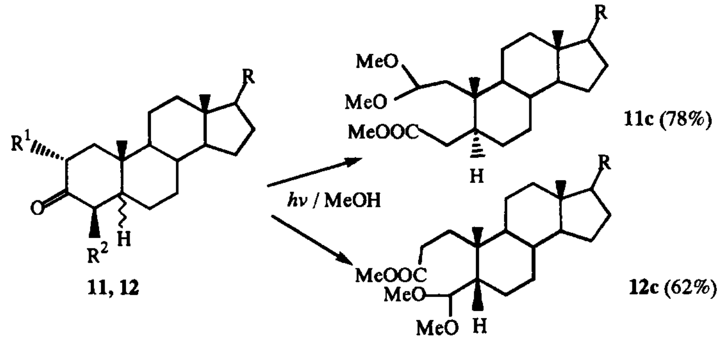


Fig. 1. Yields of **6b** and **6c** during irradiation of **6a** in degassed methanol.

2α-Iodo-5α-cholestan-3-one (**11**) and 4β-iodo-5β-isomer (**12**) were also treated with a high-pressure mercury lamp under the same conditions; the results are shown in Scheme 3. From these results, it was found that the reaction of **11** and **12** gave methyl 2,2-dimethoxy-2,3-seco-5α-cholestan-3-oate (**11c**, 78%) and methyl 4,4-dimethoxy-3,4-seco-5β-cholestan-3-oate (**12c**, 62%),[23] respectively. These results show that this photocleavage reaction is applicable to steroidal α-iodo ketones.

It is known that competing ionic and radical photobehaviors have been observed for a number of alkyl halides by Kropp and his co-workers.[12] The photolysis of α-halo ketones (RCO–C–X) is understood to proceed via competing homolysis of C–C and C–X bonds as primary processes.[11] Recently, Tomioka et al. have also proposed that the photochemical behavior of α-halo ketones in alcohols undergoes competition of the ionic and radical photobehaviors, resulting in the formation of photoalcoholysis products and photoreduction products.[15] During the course of our studies, it was found that the irradiation of α-iodocycloalkanones in nonpolar solvents (e.g., hexane) mainly afforded the elimination product, α,β-unsaturated cyclic ketone, accompanied by small photoreduction-product parent ketones.[19] It seems that the irradiation of α-iodocycloalkanones gave major novel photochemical cleavage products, ω,ω-dialkoxyalkanoic esters. Therefore, it is considered that this photochemical behavior can be explained, as shown in Fig. 2, on the basis of the results mentioned above.

As can be seen from Fig. 2, the irradiation of α-iodocycloalkanones via a process involving a light-induced homolytic cleavage of the C–I bond generates radical pair (**I**).[12,13] In the polar solvents, electron transfer competes efficiently with the escape from the solvent cage to produce an ion pair (**II**); then, photosubstituted product **6a** was formed preferentially, which clearly occurs from nucleophilic trapping of the ion pair (**II**). Under the present irradiated conditions, the ring opening of **6a** at the C^1 and C^2 position gave secondary photoproducts ω-formylalkanoic ester immediately, which probably arises from the cleavage of alkoxyl radical (**III**), to form radical (**IV**)[20] by the intermolecular addition of alcohols. It seems that acetalization occurs readily in these



11, 11c, R^1=I R^2=H R=C_8H_{17}

12, 12c, R^1=H R^2=I R=C_8H_{17}

Scheme 3.

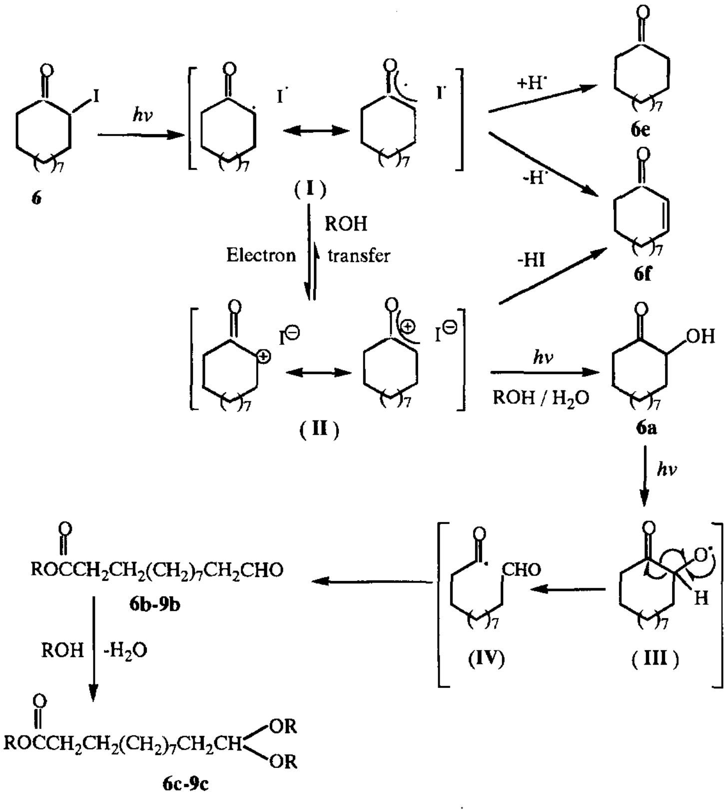


Fig. 2. Photchemical cleavage behavior of α-iodocyclododecanone.

formyl compounds, and that the formed acetals are stable.

In order to investigate the photochemical character from aliphatic to aromatic compounds, 3,4-dihydro-2-iodo-1(2*H*)-naphthalenone (**17**) was chosen as a model compound. The irradiation of **17** under same condition gave 1-naphthol (**17g**) and 3,4-dihydro-1(2*H*)-naphthalenone (**17e**). These results are summarized in Table 4. From these results, it was found that photochemical behavior is quite different compared with α-iodocycloalkanones. Moreover, the photochemical product has no relation to the polarity of solvents. It seems that the substrate **17** is easier to aromatize than cleaving the C–C bond. In the presence of 1 molar amount of triethylamine, aromatized product **17g** is evidently increased (Table 4, Entry 3).[11c,15f] This photochemical behavior is probably due to the fact that for the irradiation of 3,4-dihydro-2-iodo-1(2*H*)-naphthalenone, a photoinduced homolytic cleavage of the C–I bond generates a radical pair, (**A**) or (**B**), and an enol radical, (**C**) or (**D**), is formed via the migration of β-H or γ-H before an electron transfer occurs.[15d] Ultimately, aromatized product 1-naphthol (**17g**) was obtained by the elimination of β-H or γ-H, accompanied by the reduced product 3,4-dihydro-1(2*H*)-naphthalenone (**17**) by the abstraction of hydrogen (Fig. 3).

Thus, in order to discuss the reactivity of the α-iodo cyclic ketone, it was compared with that of the chloro or bromo derivative, as summarized in Table 5. On the basis of these results, it was found that the irradiation of 2-chloro- (**13**) or 2-bromocyclohexanone (**14**)[24] afforded mainly acetalization products 2-chloro- (**13d**) or 2-bromo-1,1-dimethoxycyclohexane (**14d**)[18d] in 90 and 85% yields, respectively. It is considered that the difference in the reactivity of the iodo compound is due to the unstable properties for lights compared with that of chloro or bromo ketone.

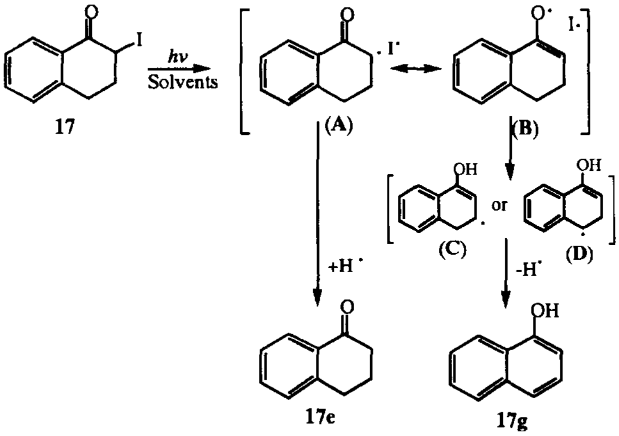
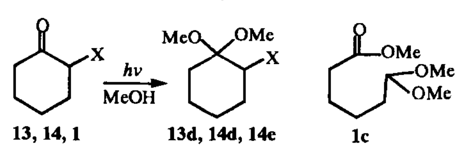


Fig. 3. Probable photchemical behavior of 3,4-dihydro-2-iodo-1(2*H*)-naphthalenone.

In conclusion, we have encountered a novel photochemical cleavage reaction of α-iodocycloalkanones in alcohols using a high-pressure mercury lamp and a commercial fluorescent lamp, resulting in an efficient and direct synthesis of ω,ω-dialkoxyalkanoic ester. It is noteworthy that the present photocleavage reaction affords a new synthetic method, more convenient and cleaner than the method used heretofore.

Table 5. Photochemical Reaction of α-Halocycloalkanone in Methanol at Room Temperature



Entry	Substrates[a)]	Method	Time/h	Product/%[b)]
1	**13** (X = Cl)	100 W	20	**13d** (X = Cl) (90)
2	**13** (X = Cl)	400 W	18	**13d** (X = Cl) (86)
3	**14** (X = Br)	100 W	20	**14d** (X = Br) (85) **14e** (7)
4	**14** (X = Br)	400 W	18	**14d** (X = Br) (82) **14e** (8)
5	**1** (X = I)	100 W	20	**14e** (X = OMe) (13) **1c** (68)
6	**1** (X = I)	400 W	18	**14e** (X = OMe) (15) **1c** (65)

a) Substrate (2.355 mmol) in methanol (150 ml) under nitrogen atmosphere with 100 W high-pressure mercury lamp was irradiated. b) Isolated yields.

Experimental

The melting points are uncorrected and were measured by a Yanaco Mp-52777 (Yanaco Co., Ltd., Kyoto, Japan). IR spectra were recorded using a JASCO FT/IR-230 grating infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured using a JEOL GSX 400 Model spectrometer in deuteriochloroform solutions with tetramethylsilane used as an internal standard. The high-resolution mass spectra were performed at 75 eV on a JEOL JMS-01SG-2 instrument with a direct inlet. UVL-100P and UVL-400P high-pressure mercury lamps (Riko-Kagaku Sangyo Co.) and a commercial fluorescent lamp (FLR-40S.W-E/M) were used as the irradiation source. The starting material used in our experiments, α-iodocycloalkanones **1**—**7**, were prepared according to the literature.[18] All irradiations were carried out under a nitrogen atmosphere, that was achieved by bubbling nitrogen gas through the solvent for 20 min prior.

General Procedure for the Irradiation of α-Iodocycloalkanones (1—7) with a High-Pressure Mercury Lamp in Methanol: 2-Iodocycloheptanone (**4**) (0.747 g, 3.14 mmol) was added in methanol (200 ml) at room temperature under a nitrogen atmosphere. The stirred solution was irradiated with a 400 W high-pressure mercury lamp in a water-cooled quartz immersion well for 15 h. After the irradiation had been completed, the mixture was concentrated, poured into water, and extracted with Et_2O (3×40 ml). The ethereal solution was washed with a saturated solution of sodium thiosulfate and brine, dried over anhydrous sodium sulfate, and filtered. Subsequently, the solvent was removed. The resulting oil was purified by column chromatograph on silica gel using hexane–ethyl acetate (10 : 1) as an eluent to give product **4c** as colorless oil (0.512 g, 80.0%).

Methyl 7,7-Dimethoxyheptanoate (4c):[2a] (No spectral data): Colorless oil; IR (NaCl) 1738 and 1127 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.34—1.38 (m, 4H), 1.57—1.67 (m, 4H), 2.31 (t, J = 7.51 Hz, 2H, C2), 3.31 (s, 6H, C7–OCH_3), 3.66 (s, 3H, C1–OCH_3), and 4.35 (t, J = 5.86 Hz, 1H, C7); ^{13}C NMR ($CDCl_3$) δ = 24.26, 24.86, 28.97, 32.32, 33.82, 33.95, 51.43, 52.65, 104.45, and 174.11. HRMS Found: m/z 204.1381 (M$^+$). Calcd for $C_{10}H_{20}O_4$: M, 204.1352.

Methyl 6,6-Dimethoxyhexanoate (1c):[2a] (No spectral data): Colorless oil; IR (NaCl) 1739 and 1076 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.38—1.40 (m, 2H), 1.59—1.67 (m, 4H), 2.32 (t, J = 7.51 Hz, 2H, C2), 3.31 (s, 6H C6–OCH_3), 3.67 (s, 3H, C1–OCH_3), and 4.36 (t, J = 5.68 Hz, 1H, C6); ^{13}C NMR ($CDCl_3$) δ = 24.19, 24.79, 32.20, 33.67, 33.99, 51.49, 52.71, 104.34, and 174.04. HRMS Found: m/z 190.1227 (M$^+$). Calcd for $C_9H_{18}O_4$: M, 190.1205.

Methyl 6,6-Dimethoxy-3-methylhexanoate (2c): Colorless oil; IR (NaCl) 1740 and 1126 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.95 (d, J = 6.48 Hz, 3H, C3–CH_3), 2.29 (d, J = 5.87 Hz, 2H, C2), 3.30 (s, 6H, C6–OCH_3), 3.66 (s, 3H, C1–OCH_3), and 4.34 (t, J = 5.68 Hz, 1H, C6); ^{13}C NMR ($CDCl_3$) δ = 14.33, 22.51, 30.24, 31.43, 35.59, 51.33, 51.59, 53.89, 104.60, and 173.39. HRMS Found: m/z 204.1409 (M$^+$). Calcd for $C_{10}H_{20}O_4$: M, 204.1352.

Methyl 6,6-Dimethoxy-5-methylhexanoate (3c): Colorless oil; IR (NaCl) 1740 and 1057 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.90 (d, J = 6.59 Hz, 3H, C5–CH_3), 2.15 (t, J = 7.51 Hz, 2H, C2), 3.33 (s, 6H, C6–OCH_3), 3.66 (s, 3H, C1–OCH_3), and 4.03 (d, J = 6.23 Hz, 1H, C6); ^{13}C NMR ($CDCl_3$) δ = 19.69, 30.00, 31.26, 34.31, 41.47, 51.39, 52.61, 54.14, 108.74, and 173.99. HRMS Found: m/z 204.1400 (M$^+$). Calcd for $C_{10}H_{20}O_4$: M, 204.1352.

Methyl 6-Formylhexanoate (4b):[2a] (No spectral data): Colorless oil; IR (NaCl) 2724, 1736, and 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.32 (t, J = 4.40 Hz, 2H, C2), 2.46 (dt, J = 8.24, 1.83 Hz, 2H, C5), 3.67 (s, 3H, C1–OCH_3), and 9.76 (t, J = 1.83 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ = 21.69, 24.64, 28.59, 33.77, 43.63, 51.49, 173.97, and 202.47. HRMS Found: m/z 158.0971 (M$^+$). Calcd for $C_8H_{14}O_3$: M, 158.0963.

Methyl 8,8-Dimethoxyoctanoate (5c):[2b] Colorless oil; IR (NaCl) 1740 and 1127 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.33 (s, 6H), 1.57—1.66 (m, 4H), 2.29 (t, J = 8.06 Hz, 2H, C2), 3.30 (s, 6H, C8–OCH_3), 3.66 (s, 3H, C1–OCH_3), and 4.35 (t, J = 5.86 Hz, 1H, C8); ^{13}C NMR ($CDCl_3$) δ = 24.48, 24.77, 24.89, 28.80, 29.16, 32.47, 33.95, 51.38, 52.56, 104.51, and 174.10. HRMS Found: m/z 218.1533 (M$^+$). Calcd for $C_{11}H_{22}O_4$: M, 218.1508.

Irradiation of α-Iodocyclododecanone (6) with a 400 W High-Pressure Mercury Lamp in Alcohol at Room Temperature: α-Iodocyclododecanone (**6**) (0.967 g, 3.14 mmol) in methanol (200 ml) was irradiated for 3 h. After the usual work-up, the resulting oil was chromatographed on silica gel. Elution with hexane–ethyl acetate (8 : 1) (180 ml) gave 2-hydroxycyclododecanone (**6a**) (0.143 g, 23%), methyl 11-formylundecanoate (**6b**) (0.193 g, 27%), and methyl 12,12-dimethoxydodecanoate (**6c**) (0.344 g, 40%). When **6** was irradiated under a comparable condition as mentioned above for 10 h, it predominantly afforded **6c** (0.757 g, 88%).

Ethyl 12,12-Diethoxydodecanoate (7c): Colorless oil; IR (NaCl) 1738 and 1127 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.18—1.36 (m, 14H), 1.57—1.63 (m, 4H), 2.28 (t, J = 7.56 Hz, 2H, C2), 3.49 (q, J = 8.24, 3.66 Hz, 2H, $OC\underline{H}_2CH_3$), 3.63 (q, J = 8.25, 3.48 Hz, 2H, $OC\underline{H}_2CH_3$), 4.11 (q, J = 10.81, 3.66 Hz, 2H, $CH_3C\underline{H}_2OC(=O)$), and 4.47 (t, J = 5.87 Hz, 1H, C12); ^{13}C NMR ($CDCl_3$) δ = 14.29, 15.40, 24.80, 25.02, 29.19, 29.23, 29.25, 29.31, 29.42, 29.48, 29.54, 29.59, 33.63, 34.36, 60.08, 60.78, 103.00, and 173.70. HRMS Found: *m/z* 316.2569 (M^+). Calcd for $C_{18}H_{36}O_4$: M, 316.2600.

Propyl 12,12-Dipropoxydodecanoate (8c): Colorless oil; IR (NaCl) 1738 and 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.29 (t, J = 7.56 Hz, 2H, C2), 3.37 (t, J = 5.59 Hz, 2H, $OC\underline{H}_2CH_2CH_3$), 3.54 (t, J = 5.59 Hz, 2H, $OC\underline{H}_2CH_2CH_3$), 4.02 (t, J = 6.78 Hz, 2H, $CH_3CH_2C\underline{H}_2OC(=O)$), and 4.46 (t, J = 5.87 Hz, 1H, C12); ^{13}C NMR ($CDCl_3$) δ = 10.44, 10.75, 10.81, 22.08, 23.19, 24.83, 25.07, 29.20, 29.28, 29.31, 29.39, 29.41, 29.48, 29.53, 29.59, 33.55, 34.37, 65.77, 67.10, 103.16, and 173.84. HRMS Found: *m/z* 358.3062 (M^+). Calcd for $C_{21}H_{42}O_4$: M, 358.3068.

2-Hydroxycyclododecanone (6a): Colorless needles; mp 75.3—77.2 °C (from hexane : Et_2O = 10 : 1) (lit,[8] mp 75—76 °C or 78—79 °C).

Ethyl 11-Formylundecanoate (7b): Colorless oil; IR (NaCl) 2718, 1735, and 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.23—1.37 (m, 15H), 1.57—1.66 (m, 4H), 2.28 (t, J = 7.51 Hz, 2H, C2), 2.42 (dt, J = 8.24, 1.82 Hz, 2H, C11), 4.13 (q, J = 10.62, 3.48 Hz, 2H, $OC\underline{H}_2CH_3$), and 9.76 (t, J = 1.84 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ = 22.09, 24.97, 24.99, 29.12, 29.16, 29.23, 29.27, 29.33, 29.35, 34.36, 43.91, 60.12, 173.8, and 202.8. HRMS Found: *m/z* 242.1910 (M^+). Calcd for $C_{14}H_{26}O_3$: M, 242.1872

Isopropyl 11-Formylundecanoate (9b): Colorless oil; IR (NaCl) 2716, 1734, and 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.25 (t, J = 7.51 Hz, 2H, C2), 2.42 (dt, J = 8.06, 1.46 Hz, 2H, C11), 4.95—5.01 (m, 1H, $OC\underline{H}(CH_3)_2$), and 9.76 (t, J = 1.83 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ = 21.85, 22.06, 24.95, 25.01, 29.08, 29.14, 29.23, 29.33, 29.34, 29.36, 34.67, 43.89, 67.26, 173.3, and 202.70. HRMS Found: *m/z* 256.2015 (M^+). Calcd for $C_{15}H_{28}O_3$: M, 256.2028.

Methyl 15,15-Dimethoxypentadecanoate (10c): Colorless oil; IR (NaCl) 1741 and 1126 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.30 (t, J = 7.51 Hz, 2H, C2), 3.31 (s, 6H, C14–OCH_3), 3.66 (s, 3H, C1–OCH_3), and 4.35 (t, J = 5.87 Hz, 1H, C14); ^{13}C NMR ($CDCl_3$) δ = 24.64, 24.98, 29.18, 29.23, 29.30, 29.36, 29.39, 29.49, 29.52, 29.59, 29.61, 29.65, 32.51, 34.11, 51.40, 52.36, 104.58, and 174.28. HRMS Found: *m/z* 316.2585 (M^+). Calcd for $C_{18}H_{36}O_4$: M, 316.2604.

Methyl 14-Formyltetradecanoate (10b): Colorless oil; IR (NaCl) 2715, 1740, and 1171 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.30 (t, J = 7.51 Hz, 2H, C2), 2.43 (dt, J = 8.25, 1.83 Hz, 2H, C14), 3.66 (s, 3H, C1–OCH_3), and 9.76 (t, J = 1.65 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ = 22.12, 24.99, 29.19, 29.21, 29.30, 29.41, 29.47, 29.61, 29.63, 32.52, 34.10, 43.94, 51.39, 52.53, 174.26, and 202.74. HRMS Found: *m/z* 270.2238 (M^+). Calcd for $C_{16}H_{30}O_3$: M, 270.2187.

Methyl 4,4-Dimethoxy-3,4-seco-5β-cholestan-3-oate (12c): Colorless oil; IR (NaCl) 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.33 (s, 3H, C4–OCH_3), 3.50 (s, 3H, C4–OCH_3), 3.67 (s, 3H, C3–OCH_3), and 4.50 (d, J = 3.30 Hz, 1H, C4); ^{13}C NMR ($CDCl_3$) δ = 11.96, 17.13, 18.66, 21.93, 22.56, 22.82, 23.81, 24.12, 27.28, 28.01, 28.30, 31.79, 35.56, 35.77, 35.81, 36.13, 37.05, 39.49, 39.53, 40.32, 41.00, 42.44, 47.18, 51.44, 52.56, 55.12, 56.30, 56.51, 105.36, and 175.49. MS (EI) 478 (M^+), 447 (M-31). HRMS Found: *m/z* 478.4053 (M^+). Calcd for $C_{30}H_{54}O_4$: M, 478.4008.

Irradiation of 2-Iodocyclododecanone (6) with a Commercial Fluorescent Lamp at Room Temperature: 2-Iodocyclododecanone (**6**) (0.967 g, 3.14 mmol) in methanol (200 ml) was irradiated with a fluorescent lamp at room temperature for 20 d. After the usual work-up, the residue was chromatographed on silica gel. The eluent with hexane–ethyl acetate (8 : 1) (180 ml) mainly gave the 2-methoxycyclododecanone (**6d**) (0.519 g, 78%), the reduction product **6e** (0.034 g, 6%) and the elimination product **6f** (0.017 g, 3%).

2-Methoxycyclododecanone (6d): Colorless needles; mp 65.8—67.0 °C (from hexane : EtOAc = 8 : 1) IR (KBr) 1741 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.30 (t, J = 7.51 Hz, 2H, C12), 3.66 (s, 3H, C2–OCH_3), and 4.83 (t, J = 5.32 Hz, 1H, C2); ^{13}C NMR ($CDCl_3$) δ = 23.57, 24.96, 29.15, 29.25, 29.37, 29.42, 29.46, 29.49, 34.11, 34.43, 51.45, 101.70, and 174.36. HRMS Found: *m/z* 212.1805 (M^+). Calcd for $C_{13}H_{24}O_2$: M, 212.1777.

Irradiation of 2-Chlorocyclohexanone (13): A solution of 2-chlorocyclohexanone (0.312 g, 2.355 mmol) in methanol (150 ml) was bubbled with nitrogen for 20 min prior. The mixture was then irradiated with a 100 W high-pressure mercury lamp inside a water-cooled quartz immersion well for 18 h. After the usual work-up, a crude product was obtained and chromatographed on silica gel. Elution with hexane–ether (5 : 1) gave pure 2-chloro-1, 1-dimethoxycyclohexane (**13d**) (0.378 g, 90%) as a colorless oil.

2-Chloro-1,1-dimethoxycyclohexane (13d): Colorless oil; IR (NaCl) 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.19 (s, 3H, OCH_3), 3.23 (s, 3H, OCH_3), and 4.20 (t, J = 2.39 Hz, 1H, C2); ^{13}C NMR ($CDCl_3$) δ = 19.40, 21.92, 26.78, 31.29, 47.04, 48.09, 59.20, and 100.30. HRMS Found: *m/z* 178.0725 (M^+). Calcd for $C_8H_{15}ClO_2$: M, 178.0762.

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