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Metal-catalyzed Organic Photoreactions. Photoreaction of 2-Chloroacetophenone Derivatives with Olefins in the Presence of Silver Trifluoromethanesulfonate

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Key Words: Photoreaction; 2-chloroacetophenone; silver triflate; naphthalenone; oxetane

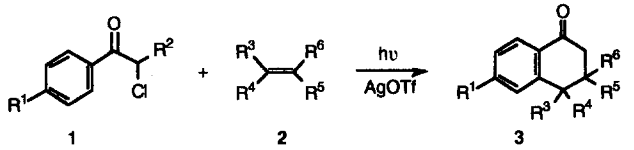
Abstract: UV-irradiation of 2-chloroacetophenones and olefins in the presence of silver triflate affords naphthalenone derivatives with high regio and stereoselectivity and chemical yields. A possible mechanism is proposed.

In the course of our investigations on the metal-catalyzed photoreactions, we have observed several systems where the presence of metal compounds exerts remarkable effects upon the photoreaction pattern of organic molecules.[1] Some of the reactions are characteristic in that cross coupling between two substrates proceeds quite efficiently, to which we proposed a reaction mechanism involving a metal-assisted interligand electron transfer upon photoexcitation. In our preliminary paper[2], we reported a novel coupling reaction between olefin and 2-chloroacetophenone upon UV irradiation in the presence of silver trifluoromethanesulfonate (triflate), and we schemed the reaction as involving the electron transfer mechanism. We will now describe the reaction in detail with new findings and propose a reaction scheme.

RESULTS

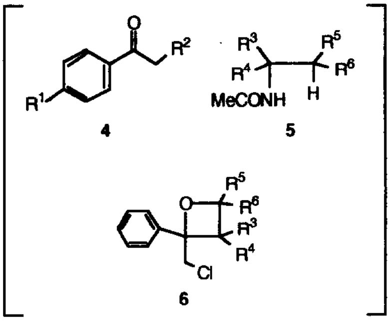
In our preliminary paper,[2] we described that the irradiation of an acetonitrile solution of 2-chloroacetophenone **1** (1 eq), olefins **2** (1.5 eq), and silver triflate (1 eq) with Pyrex-filtered light afforded naphthalenone derivatives **3** as major products. The reaction was generally clean, and the major byproducts were acetophenone **4**, amides **5**, and polymers of olefins which were removed easily by column chromatography. We have so far carried out the photoreaction by irradiating the reactant solutions in Pyrex tubes externally from the side while cooling the tubes by running water. Acetonitrile was the most convenient solvent in these experiments, because the precipitates of silver chloride which separated during the irradiation coagulated mostly at the bottom of the reaction tubes, and did not cause any appreciable disturbance for the light absorption by the reactants. With other solvents, however, black solid materials (silver chloride, silver metal, and in some cases, silver mirror) adhered on the glass surface where the incident light was passing, and the reaction terminated quite easily in most cases. Therefore we needed an apparatus in which the photoreaction could be performed without being disturbed even when solid material separated out during the irradiation. In the present study, we devised a rectanglar reaction vessel covered with a Pyrex glass lid having two holes serving as gas-inlet and outlet to fill the vessel with nitrogen. The whole vessel was cooled by externally circulating water, and the irradiation was carried out by a lamp located over the vessel, so that the light could reach the solution through the Pyrex lid which was kept from contacting with the solution. In this way we could carry out the photoreaction satisfactorily in any solvents. The results under various conditions are shown in Table 1. We designate **3ag**, as an instance, for the product obtained from **1a** and **2g**.

It was revealed that the reaction with unsymmetrical olefins **2h**, **2i**, and **2k** proceeded to give compounds having more substituents at the 4-position of the naphthalenone nucleus, and that the reaction with cyclohexenes **2j** and **2k** proceeded to give products exclusively having *cis* ring junction. The structure assignment will be discussed below.



a: R^1 = H; R^2 = H
b: R^1 = Me; R^2 = H
c: R^1 = OMe; R^2 = H
d: R^1 = OH; R^2 = H
e: R^1 = NO_2; R^2 = H
f: R^1 = H; R^2 = Me

g: R^3 = Me; R^4 = Me; R^5 = Me; R^6 = Me
h: R^3 = Me; R^4 = Me; R^5 = Me; R^6 = H
i: R^3 = n-Hex; R^4 = H; R^5 = H; R^6 = H
j: R^3 = H; R^4, R^5 = -$(CH_2)_4$-; R^6 = H
k: R^3 = Me; R^4, R^5 = -$(CH_2)_4$-; R^6 = H
l: R^3 = H; R^4, R^5 = -$(CH_2)_6$-; R^6 = H



The present reaction proceeded only under the irradiation. A quantitative amount of **1a** was recovered when a mixture of **1a** and **2j** was refluxed in the presence of silver triflate in acetonitrile for 10 h. The role of the silver triflate was characteristic. Although the cyclization proceeded even in the absence of the metal compound in some cases (runs 2, 4, 7, and 18), the presence of silver triflate was either requisite or preferable to attain a clean and selective reaction. In the metal-free photoreaction, the reductive chlorine elimination and oxetane formation became the major reaction path. Characteristically the oxetane formation was completely quenched by the presence of silver triflate.

It was found that the reaction proceeded more rapidly and selectively in benzene than in acetonitrile, affording **3** in higher yields with only trace amount of acetophenone (runs 1 *vs*. 3; 5 *vs*. 6; 9 *vs* 10; 15 *vs* 17). The photocyclization did not proceed at all in methanol or ether, producing only small amounts of **4** (runs 13 and 14). Hexane was not suitable because silver triflate was not soluble. The cyclization also proceeded satisfactorily with 2-chloroacetophenone derivatives having *p*-methyl (**1b**) or *p*-methoxyl group (**1c**) (runs 20 ~ 23), but not with *p*-hydroxy (**1d**) or *p*-nitro compound (**1e**) (runs 24 and 25). In contrast with the efficient cyclization with chloroacetophenone derivatives, 2-chloropropiophenone **1f** afforded only reduction product in benzene or acetonitrile (run 26).

It was evident that the olefin molecule is involved in the activation of **1a** because the formation of silver chloride was very slow in the olefin-free photoreactions under the otherwise same conditions. Under these conditions, the solution became brown, from which 72% of **1a** was recovered accompanied by a small amount of acetophenone. Although silver triflate was hardly soluble in benzene at room temperature, it dissolved easily upon addition of the olefins, suggesting a formation of olefin-silver ion complex. When silver nitrate was used in place of the triflate, the photoreaction also afforded **3**, but the reaction was slower accompanied by the formation of several byproducts.

The structures of the products were assigned by spectroscopic data. The NMR spectrum of **3ah** coincided with the reported datum, which differed definitely from that of the alternative regioisomer of 3,3,4-trimethyl-3,4-dihydro-1(2H)-naphthalenone.[3] The stereochemistry of **3aj** was assigned as *cis*, because the IR spectrum coincided with that of the *cis* isomer, which was clearly distinguishable from that of the *trans* isomer.[4] Both *cis* and *trans*-**3ak** are known compounds,[5] although no spectroscopic data have been reported.

Table 1. Photoreaction of 2-Chloroacetophenones with Olefins.

Run	Substrate		Cond[a]	Add[b]	Solv[c]	Time (h)	Recvy[d]	Product and yield (%)				
	1	2					1	3	4	5	6	
1	1a	2g	B^2	Ag	BN	1.5	29	69	0			g)
2	1a	2g	A	None	BN	1.5	20	5	15		20	h)
3	1a	2g	A	Ag	AN	1.3	22	61	0	17		i)
4	1a	2g	A	None	AN	1.5	tr	20	10		6	h)
5	1a	2h	B^2	Ag	BN	1.5	tr	95	0			g)
6	1a	2h	A	Ag	AN	1.7	24	46	4	14		i)
7	1a	2h	A	None	AN	1.7	0	15	tr		50	i)
8	1a	2i	A	Ag	AN	1.7	24	36	8			i)
9	1a	2j	B^2	Ag	BN	1.5	6	83	0			g)
10	1a	2j	A	Ag	AN	5.6	0	39	7			i)
11	1a	2j	A	None	e), f)	2.0	0	0	0		~50	i)
12	1a	2j	A	None	DMSO[f]	2.0	0	0	~70			i)
13	1a	2j	B^1	Ag	MN	2.8	60	0	16			i)
14	1a	2j	B^1	Ag	EE	2.8	76	0	15			i)
15	1a	2k	B^2	Ag	BN	1.5	31	69	0			g)
16	1a	2k	B^2	None	BN	0.5	0	0	20		31	h)
17	1a	2k	A	Ag	AN	1.0	28	45	17	18		i)
18	1a	2k	A	None	AN	1.5	54	9	8		23	j)
19	1a	2l	A	Ag	AN	3.0	30	30	0			i)
20	1b	2j	B^2	Ag	BN	1.0	0	95	0			g)
21	1b	2k	B^2	Ag	BN	1.0	0	95	0			g)
22	1c	2j	B^2	Ag	BN	4.0	0	92	tr			g)
23	1c	2k	B^2	Ag	BN	0.5	15	84	tr			j)
24	1d	2j	B^2	Ag	BN	4.0	66	tr	0		tr	i)
25	1e	2j	B^2	Ag	BN	1.0	100	0	0			j)
26	1f	2j	B^2	Ag	BN	0.5	40	0	60			j)

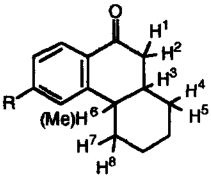
a) Conditions, molar ratio: 1/2/AgOTf = 1/1.5/1; the concentration refers to that of 1; A: apparatus A (see Experimental), 0.1 M; B: apparatus B, B^1: 0.025 M; B^2: 0.01 M. b) Additive, Ag: AgOTf. c) Solvent, AN: acetonitrile; MN: methanol; EE: diethyl ether; BN: benzene. d) Recovery. e) AN, BN, and CCl_4. f) The reactions in these solvents were not clean and yields were evaluated roughly from the NMR spectra of the crude products. g) Isolated yields. h) Determined by GC analysis using diethyl adipate as an internal reference. i) Determined by NMR and GC analyses of isolated mixture. j) Determined by NMR analysis using 1,1,2,2-tetrachloroethane as an internal reference.

An unambiguous proof for the regio and stereochemistry of **3ak** and **3ck** was obtained from 400 MHz ^{1}H NMR analysis. The chemical shifts and coupling constants of protons in δ 1.2 ~ 3.0 region of **3ak**, **3cj**, and **3ck** are shown in Table 2. The products **3ak** and **3ck** showed similar spectroscopic pattern with each other, in which a characteristic feature was a small coupling constants of $J_{\mathrm{H^1\text{-}H^3}}$ and $J_{\mathrm{H^2\text{-}H^3}}$ (2.7 ~ 5.5 Hz) for both compounds, suggestive of the conformer **7**. Although **3cj** showed larger $J_{\mathrm{H^2\text{-}H^3}}$ value (10.2 Hz), the possibility of *trans* structure **9** was definitely excluded by the smaller coupling constants for $J_{\mathrm{H^3\text{-}H^4}}$, $J_{\mathrm{H^3\text{-}H^5}}$, and $J_{\mathrm{H^3\text{-}H^6}}$ (4.5 Hz, each). In view of these NMR data, it is concluded that **3cj** adopts a conformer **8**, while **3ak** and **3ck** adopt a conformer **7**. Probably angular methyls in **3ak** and **3ck** are apt to occupy the equatorial position of the cyclohexane ring, forcing the conformation in favor of **7**. The splitting of H^1 and H^2 signals by

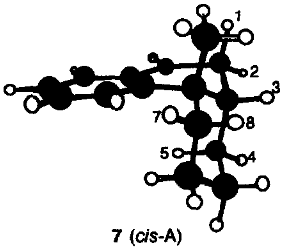
Table 2 Chemical Shifts and Coupling Constants of Phenanthrenones.

Chemical shifts of H^n (δ)				Coupling constants of H^n–$H^{n'}$ (Hz)			
n	**3ak**	**3cj**	**3ck**	n–n'	**3ak**	**3cj**	**3ck**
1	3.06	2.42	3.00	1–2	17.4	17.1	17.3
2	2.45	2.83	2.38	1–3	5.1	4.5	5.5
3	2.39	2.50	2.31	2–3	3.8	10.2	2.7
4	b	a	b	3–4	~2	4.5	~2
5	b	a	b	3–5	12.3	4.5	13.8
6	–	2.89	–	3–6	–	4.5	–
7	2.10	a	1.97	6–7	c	13.0	c
8	b	a	b	6–8	c	4.5	c

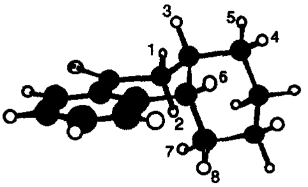
a) 1.4 ~ 1.8; b) 1.2 ~ 1.6; c) Not determined.



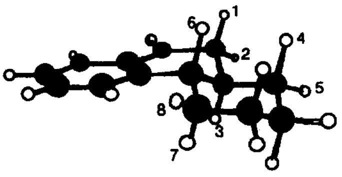
R = H or OMe



7 (*cis*-A)



8 (*cis*-B)



9 (*trans*)

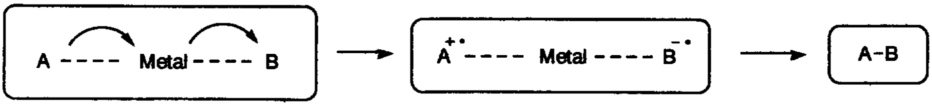
a neighboring proton in **3ak** and **3ck** confirms the regiochemistry assignment. The product **3al** showed two peaks (~1 : 1) on GC analysis. Since both fractions gave almost identical MS spectra, we concluded that the product was a mixture of *cis* and *trans* isomers.

Although the stereochemistry was not determined with oxetanes **6**, the isolated products were stereochemically single isomers. The regiochemical assignment of the oxetanes from unsymmetrical olefins were assigned as indicated, in view of the proton signals at δ 4.59 (q) for **6ah** and δ 4.82 (br) for **6ak**. The structures of the amides **5** were determined by comparing with the authentic samples prepared by the known methods.[6]

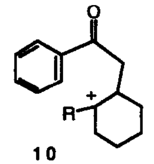
DISCUSSIONS

We have so far found several reactions in which the photochemical reactions are affected by the presence of metal compounds. For instance, titanium(IV) chloride induced a cross coupling between ketone and alcohol molecules,[1a] while iron(III) chloride or uranyl acetate induced a photooxidation of olefins to produce β-substituted hydroperoxides.[1b] These reactions are characteristic in that the cross coupling between the reactants proceeded favorably without producing any amounts of the geminal coupling products. We schemed the reaction as involving a metal-assisted interligand electron transfer, resulting in the formation of radical cation-radical anion pair, which couples with each other, as shown in Scheme 1. It was assumed that all the processes occur within the coordination sphere of the metal ion, thus favoring the cross coupling, and we proposed a term "long-range electron transfer" for this type of reaction.[1]

In our preliminary paper,[2] we proposed the long-range electron transfer for the present reaction in which the reaction was initiated by a silver ion-assisted photo-induced electron transfer from olefin to 2-chloroacetophenone. It was assumed that the electron transfer was followed by the coupling of the resulting radical cation-radical anion pair, and after the chloride ejection, by a Friedel-Crafts type cyclization of the cationic intermediate **10** to the final products. The mechanism seemed attractive to account for the regioselectivity, as well as the facts that the cyclization under silver-free irradiation proceeded only with electron-rich olefins, while the reaction with less-substituted olefins was realized only in the presence of silver ion. However, in view of the widely-known facts that the cyclization of the cationic species such as **10**, which has been extensively investigated in relation to the synthesis of naturally-occurring tricarbocyclic ring-C-aromatic diterpenoids,[7] usuallly affords *trans*-fused isomer exclusively or at least as a *cis, trans* mixture, the scheme presented earlier appeared questionable to account for the *cis*-selectivity now achieved in reactions in benzene.



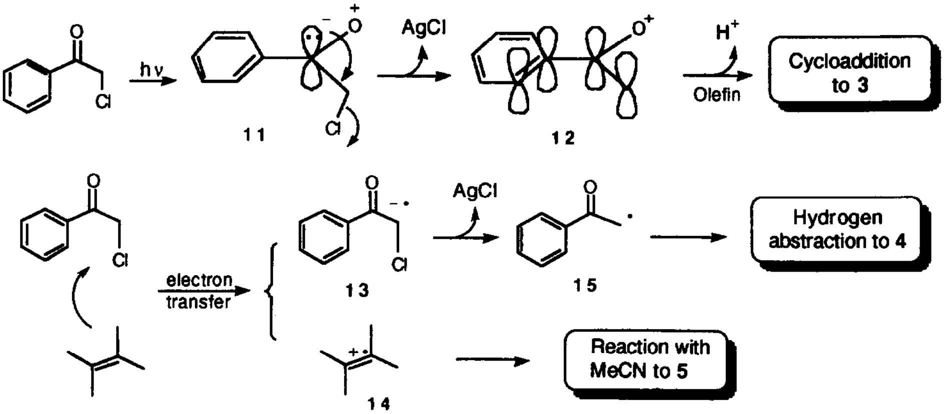
Scheme 1



10

The photoreaction of 2-chloroacetophenone derivatives in methanol has been reported to give acetophenone and phenylacetate ester through hydrogen abstraction and through rearrangement, respectively.[8] A radical species is believed to be responsible for the former type of reaction, while an ionic species for the latter. When the aromatic ring has *o*-methyl group, the initial photoenolization also competes.[9] The photoreaction of other cyclic 2-chloro ketones generally proceeds similarly to those of 2-chloroacetophenones.[10] It has been generally accepted that the nπ* excitation of α-chloro ketones provide the C-Cl bond with considerable antibonding character due to the mixing of antibonding orbitals of C=O and C-X bonds, and under ordinary conditions (without metal), the deactivation proceeds in dual way, resulting in homolytic or heterolytic fissions to afford α-keto radicals or α-keto carbonium ions, respectively.[11]

These considerations led us to propose a reaction scheme involving an excited state **11**, from which an intermediate qualitatively represented as **12** would be produced. Although the exact description of the photo processes, particularly in the presence of metal ion, is out of the scope of the present study,[12] **12** would serve as a potential diene system suitable for the concerted Diels-Alder type cycloaddition leading to the observed products. Presumably the presence of silver cation accelerates the ejection of chloride anion from **11**, which otherwise reacts with an olefin to form oxetane. In view of the fact that the formation of silver chloride was greatly accelerated by the presence of olefin, we speculate that the carbon-halogen heterolysis is assisted concertedly not only by pulling of the chloride by silver cation, but by pushing through electron donation from



olefin. In cases where the electron donation from the olefin is large enough to eject the chloride anion, the Diels-Alder type cyclization proceeds without the assistance of the silver cation.

As for the formation of **4**, it would be reasonable to assume a hydrogen abstraction by a radical species, as generally accepted. A plausible route would be an electron transfer from olefin to the chloro ketone to afford a chloro ketone radical anion **13**, from which chloride anion could be removed by silver cation to afford **15**. Since the electron transfer would be more facile in polar solvents, the formation of the reduction product would well compete with the cycloaddition in acetonitrile, as compared with the reaction in benzene. No methanol-incorporated products were identifed in run 13. It is known that the hydrogen abstraction is much faster with propiophenone derivatives than acetophenone derivatives.[9] The formation of the amide would be a good indication of intervention of olefin radical cation species **14** which would abstract hydrogen and react with acetonitrile through a Ritter type reaction to afford the amides **5**.

Experimental Section

General Procedure and Instrumentation. GC experiments were carried out on a 2.5 m x 3 mm stainless steel column packed with Silicone SE 30 and PEG 20 M on silanized Chromosorb W and 25 m x 0.25 mm capillary column (SE 30 and PEG 20 M). Column chromatography was carried out on Kieselgel 60, Art. 7734 (70 ~ 230 mesh ASTM) using CH_2Cl_2. Unless otherwise stated, the spectroscopic data were determined on pure samples obtained by column chromatography, checking the purity by TLC or GC analyses; the mass spectra were obtained by EI method at 70 eV, the ^{1}H-NMR data on the 60 MHz machines with CCl_4 solutions, the ^{1}H-NMR data (400 MHz) and ^{13}C-NMR data (22.5 MHz) with $CDCl_3$ solutions, and IR spectra with CCl_4 solutions.

General Procedure for the Photoreaction. Apparatus A: The irradiation was carried out with a solution (20 ml) in a Pyrex test tube (17ϕ mm x 40 cm), flushed with nitrogen gas, and placed vertically at 3 cm from a mercury lamp (Ushio UM 452 (450 W)) in running water. **Apparatus B:** The irradiation was carried out in a rectangular vessel (6 cm (*l*) x 3.5 cm (*w*) x 4 cm (*h*)), which was cooled by circulating water around the vessel, and covered with a Pyrex lid. After flushed with nitrogen gas through two holes on the lid, the solution (20 ml) was irradiated by the lamp placed horizontally 5 cm above the vessel. After the irradiation, the solution was added to an aqueous solution containing NaCl and $NaHCO_3$, and stirred for a while. The silver chloride was filtered off, and the organic phase was extracted with ether, dried over $CaCl_2$, and concentrated *in vacuo*. The residue was purified on a column chromatography to give pure materials.

3,3,4,4-Tetramethyl-3,4-dihydro-1(2H)-naphthalenone (3ag). MS, m/z (rel int) 202 (M^+, 24), 187 (12), 146 (100), 131 (90), 117 (31). IR, 2960, 1688, 1594, 1298, 766 cm^{-1}. ^{1}H NMR, δ 1.00 (s, 6H), 1.33 (s, 6H), 2.49 (s, 2H), 7.1 ~ 7.5 (m, 3H), 7.8 ~ 8.0 (m, 1H). Exact mass: calcd for $C_{14}H_{18}O$ (M) 202.1358, obsd 202.1380.

3ah. MS, m/z 188 (M^+, 44), 173 (100), 145 (44), 131 (40), 117 (21), 115 (15), 91 (14). IR, 1685, 1302, 767 cm^{-1} ^{1}H NMR, δ 1.00 (d, J = 7 Hz, 3H), 1.22 (s, 3H), 1.37 (s, 3H), 1.7 ~ 2.9 (m, 3H), 7.0 ~ 7.5 (m, 3H), 7.8 ~ 8.0 (m, 1H). Exact mass: calcd for $C_{13}H_{16}O$ (M) 188.1202, obsd 188.1181.

3ai. MS, m/z 230 (M^+), 145 (100), 117 (30). IR, 1686, 1286, 764 cm^{-1}. ^{1}H NMR, δ 0.89 (t, J = 6 Hz, 3H), 1.1 ~ 1.8 (br.s, 10H), 1.9 ~ 3.0 (m, 5H), 7.0 ~ 7.5 (m, 3H), 7.8 ~ 8.0 (m, 1H).

***cis*-2,3,4,4a,10,10a-Hexahydro-9(1H)-phenanthrenone (3aj).** MS, m/z 200 (M^+, 92), 158 (100), 131 (34), 118 (35), 115 (35). IR, 1684, 1295, 763 cm^{-1}. ^{1}H NMR, δ 1.2 ~ 2.1 (br.s, 8H), 2.2 ~ 3.0 (m, 4H), 7.1 ~ 7.5 (m, 3H), 7.8 ~ 8.0 (m, 1H). Exact mass: calcd for $C_{14}H_{16}O$ (M) 200.1201, obsd 200.1176.

3ak. MS, m/z 214 (M^+, 28), 199 (100), 158 (30), 131 (48). IR, 1684, 765 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 ~ 1,68 (m, 7H), 1.35 (s, 3H), 1.97 ~ 2.05 (m, 1H), 2.39 (br.d, J = 12.3 Hz, 1H), 2.45 (dd, J = 17.4, 3.8 Hz, 1H), 3.06 (dd, J = 17.4, 5.1 Hz, 1H), 7.27 ~ 7.37 (m, 2H), 7.54 (br.t, J = 7.2 Hz, 1H), 8.05 (dd, J = 8.1, 1.6 Hz, 1H). Exact mass: calcd for $C_{15}H_{18}O$ (M) 214.1358, obsd 214.1364.

3,4-Hexamethylene-3,4-dihydro-1(2H)-naphthalenone (3al). For fraction 1: MS, m/z 228 (M^+, 24), 158 (100), 145 (37), 144 (64), 131(84), 129 (43), 118 (70), 115 (88), 77 (41). For fraction 2: MS, m/z 228 (M^+, 25), 158 (83), 145 (48), 144 (56), 131 (100), 129 (51), 118 (54), 115 (59). For mixture: IR, 1683, 1299, 759 cm^{-1}. ^{1}H NMR, δ 1.4 ~ 1.9 (br.s, 12H), 2.0 ~ 3.0 (m, 4H), 7.0 ~ 7.5 (m, 3H), 7.8 ~ 8.0 (m, 1H).

3bj: MS, m/z 214 (M^+, 100), 200 (13), 172 (92), 145 (32), 132 (23), 129 (18). IR, 2928, 1682, 1607, 1292 cm^{-1}. ^{1}H NMR, δ 1.4 ~ 1.9 (br.s, 8H), 2.2 ~ 3.0 (m, 4H), 2.3 (s, 3H), 6.7 ~ 7.0 (m, 2H), 7.6 ~ 7.9 (m, 1H). Exact mass: calcd for $C_{15}H_{18}O$ (M) 214.1358, obsd 214.1364.

3bk: MS, m/z 228 (M^+, 47), 213 (100), 172 (26), 145 (37). IR, 2926, 1682, 1606 cm^{-1}. ^{1}H NMR, δ 1.30 (s, 3H), 2.33 (s, 3H), 1.2 ~ 2.5 (m, 9H), 2.25 and 2.90 (ABq, J = 17 Hz, upper and lower halves split into doublets, J = 4 and 5 Hz, respectively), 6.8 ~ 7.0 (m, 2H), 7.55 ~ 7.7 (m, 1H). Exact mass: calcd for $C_{16}H_{20}O$ (M) 228.1514, obsd 228.1501.

3cj: MS, m/z 230 (M^+, 100), 188 (31), 161 (32), 148 (15). IR, 2926, 1674, 1600, 1270 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.40 ~ 1.79 (m, 8H), 2.42 (dd, J = 17.1, 4.5 Hz, 1H), 2.45 ~ 2.54 (m, 1H), 2.83 (dd, J = 17.1, 10.2 Hz, 1H), 2.86 ~ 2.93 (m, 1H), 3.86 (s, 3H), 6.73 (d, J = 1.5 Hz, 1H), 6.82 (dd, J = 7.2, 1.5 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H). Exact mass: calcd for $C_{15}H_{18}O_2$ (M) 230.1307, obsd 230.1271.

3ck. MS, m/z 244 (M^+, 100), 229 (90), 188 (40), 161 (51), 115 (15). IR, 2930, 1674, 1600, 1267 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.16 ~ 1.64 (m, 7H), 1.33 (s, 3H), 1.93 ~ 2.01 (m, 1H), 2.31 (br.d J = 13.8 Hz, 1H), 2.38 (dd, J = 17.3, 2.7 Hz, 1H), 3.00 (dd, J = 17.3, 5.5 Hz, 1H), 3.87 (s, 3H), 6.70 ~ 6.85 (m, 2H), 8.05 (d, J = 7.2 Hz, 1H). Exact mass: calcd for $C_{16}H_{20}O_2$ (M) 244.1463, obsd 244.1492.

2-Chloromethyl-2-phenyl-3,3,4,4-tetramethyloxetane (6ag). MS, m/z 180 (M^+ − 58, 2), 145 (15), 105 (32), 84 (100), 69 (69). IR (KBr), 2997, 1456, 1374, 1147, 1014, 771, 705 cm^{-1}. ^{1}H NMR, δ 1.00 (s, 3H), 1.43 (s, 3H), 1.55 (s, 3H), 1.65 (s, 3H), 4.06 (s, 2H), 7.34 (s, 5H). mp 98 ~ 98.5 °C. Anal, Found, C, 69.83; H, 7.99. Calcd for $C_{14}H_{19}ClO$, C, 70.43; H, 8.02%.[13]

6ah. MS, m/z 157 (M^+ + 2 − 69, 3), 155 (M^+ − 69, 9), 145 (6), 105 (14), 77 (12), 70 (100). IR, 2964, 1448, 1373, 1006, 706 cm^{-1}. ^{1}H NMR, δ 0.67 (s, 3H), 1.15 (d, J = 7 Hz, 3H), 1.23 (s, 3H), 3.79 and 4.06 (ABq, J = 11 Hz, 2H), 4.59 (q, J = 7 Hz, 1H), 7.16 (s, 5H). Exact mass (CI): calcd for $C_{13}H_{18}ClO$ (M + H) 225.1046, obsd 225.1071.

8-Chloromethyl-8-phenyl-7-oxabicyclo[4.2.0]octane (6aj). MS, m/z 187 (M^+ − CH_2Cl, 19), 157 (10), 155 (30), 105 (100). IR, 2940, 1447, 952, 703 cm^{-1}. ^{1}H NMR, δ 1.1 ~ 2.1 (m, 8H), 3.25 (q, J = 7 Hz, 1H), 3.92 (s, 2H), 5.10 (dt, J = 7 and 5 Hz, 1H), 7.30 (s, 5H). Exact mass (CI): calcd for $C_{14}H_{18}ClO$ (M + H) 237.1046, obsd 237.1009.

6ak. MS, m/z 201 (M^+ − CH_2Cl, 3), 157 (5), 155 (11), 105 (29), 96 (70), 81 (100). IR (KBr), 2926, 1446, 1010, 944, 710 cm^{-1}. ^{1}H NMR, δ 1.1 ~ 2.1 (m, 8H), 1.46 (s, 3H), 4.02 and 4.21 (ABq, J = 12 Hz, 2H), 4.82 (br, 1H), 7.29 (s, 5H). mp 100 ~ 101 °C. Anal, Found, C, 71.44; H, 7.61. Calcd for $C_{15}H_{19}ClO$, C, 71.85; H, 7.64%.

N-(1,1,2-Trimethylpropyl)acetamide (5g). Identical with the authentic sample prepared according to the reported method.[6] mp 65 ~ 66 °C (lit,[14] mp 62 ~ 64 °C). IR, 3300, 1675, 1545 cm^{-1}. ^{1}H NMR, δ 0.88 (d, J = 7 Hz, 6H), 1.22 (s, 6H), 1.85 (s, 3H), 2.41 (heptet, J = 7 Hz, 1H), 6.63 (br.s, 1H).

N-(1,1-Dimethylpropyl)acetamide (5h). Identical with the authentic sample prepared according to the reported method.[6] mp 77 ~ 78 °C (lit,[6] mp 78 ~ 79 °C). ^{1}H NMR, δ 0.80 (t, J = 8 Hz, 3H), 1.34 (s, 3H), 1.64 (q, J = 8 Hz, 2H), 1.82 (s, 3H).

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