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

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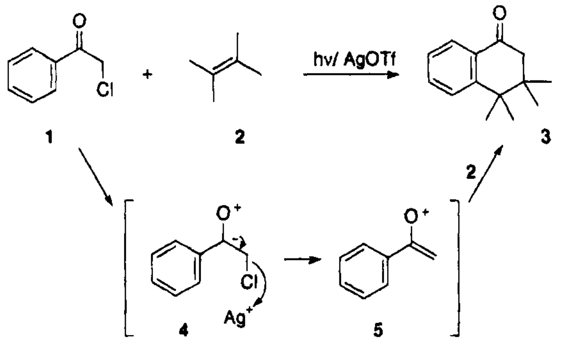
In our investigations of metal-catalyzed photoreactions, we have developed novel reactions induced by titanium(IV) chloride[1] and iron(III) chloride[2] for synthetic applications. In the continuation of that study, we discovered a novel coupling reaction between 2-chloroacetophenone (**1**) and simple olefins **2** that gives naphthalenone derivatives **3** upon UV irradiation in the presence of silver trifluoromethanesulfonate (triflate).[3,4]

The reaction is unique in that naphthalenone derivatives can be prepared as single isomers by a one-step photoreaction, where the more-substituted carbon of the olefin attaches to the benzene ring and the stereochemistry of the newly-created stereogenic centers reflects the *E*/*Z* geometry of the olefins. This reaction proceeds only under irradiation. A quantitative amount of **1** is recovered when an acetonitrile solution of **1** and cyclohexene is refluxed in the presence of silver triflate. The role of the silver triflate is critical. Although the cyclization proceeds in the absence of the metal compound with electron-rich olefins, such as 2,3-dimethyl-2-butene, the presence of silver triflate is required with less-substituted olefins. In the metal-free photoreaction, the reductive chlorine elimination and oxetane formation constitute the major reaction path. The oxetane formation is completely quenched by the presence of silver triflate.

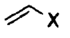
In our previous paper,[3b] we tentatively formulated the reaction as shown in Scheme 1, to involve a Diels−Alder type cycloaddition of olefins to a formal 1,3-diene **5**, formed by the ejection of chloride anion from the excited α-chloro carbonyl group in **4** with the assistance of silver ion. The justification for this scheme is the high stereospecificity observed in the reactions of cyclohexene derivatives, which afford only *cis*-fused products. Further support for a concerted process lies in the recent finding[5] that a stepwise annulation of benzoylmethyl radical and cyclohexene gave a naphthalenone derivative as a mixture of stereoisomers with a *cis*/*trans* ratio of 17/83. It seems that the cyclization step assists the ejection of the chloride ion, since the formation of silver chloride was very slow in the olefin-free photoreactions under the otherwise identical conditions. To investigate the potential of the reaction as a stereoselective one-step naphthalenone synthesis, we now investigated the reactions of olefins having several functional groups.

Scheme 1



As discussed in our previous papers,[3] the present photoreaction proceeds both in acetonitrile and in benzene. Acetonitrile is a convenient solvent for this reaction because silver chloride that separates during the reaction coagulates at the bottom of the reaction vessel, thus keeping the solution clean. When benzene is used as a solvent, silver chloride, and sometimes silver mirror, adheres to the wall of the reaction vessel, preventing the passage of incident light. Despite this drawback, the reactions in benzene exhibit more selectivity than those in acetonitrile and give lesser amounts of byproducts such as acetophenone, oxetanes, or acetonitrile adducts. The interference of silver chloride precipitate can be overcome by irradiating the sample with a lamp set above a Pyrex or quartz reaction vessel. By this technique, the photoreaction was conducted with several solvents, without the problem of precipitation on the surface of the incident light source. The reaction is normally carried out by irradiating benzene solutions of **1** (1 equiv) and **2** (1.5 equiv) in the presence of silver triflate (1 equiv) with a 450-W mercury lamp while cooling the solutions with running water (see Experimental Section).

Given the proposed reaction scheme, we expected that the present reaction would proceed better with electron-rich olefins. However, **6a−i** did not give any annulation products. Most of these reactants gave complex mixtures of products, and the only product identified in every case was acetophenone. With the stannyl compounds, interactions with silver triflate occurred immediately after mixing to afford black precipitates, and a small amount of a radical coupling product, 1-phenyl-4-penten-1-one, resulted from the reaction with **6f**.[6] Electron-deficient olefins **6j−k** and **7** also failed to undergo the photoreaction.



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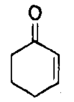
X: a: OMe b: $SiMe_3$ c: $SnMe_3$
d: CH_2Br e: CH_2SiMe_3 f: CH_2SnMe_3
g: $-(CH_2)_2SnMe_3$ h: $-(CH_2)_3SnMe_3$ i: $-(CH_2)_2COMe$
j: CN k: COMe



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In contrast, olefins such as **2a−j**, which have functional groups at remote positions, underwent the present reaction satisfactorily, as shown in Table 1. The cyclization products **3a−j** were obtained as single isomers, as revealed by ^{13}C and ^{1}H NMR and GC analyses. The only byproduct of these reactions was acetophenone. Designating protons

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[1] Ichikawa, S.; Takahashi, K.; Tanaka, M.; Sato, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 505−512.

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[4] Recently the effects of metal(II) salts on the photochemical cleavage of carbon−halogen bonds in 2-halonaphthalenones were reported: Zupancic, N.; Sket, B. *J. Photochem. Photobiol. A.* **1992**, *63*, 303−310.

[5] Russell, G. A.; Kulkarni, S. V. *J. Org. Chem.* **1993**, *58*, 2678−2685.

[6] Kosugi, M.; Arai, H.; Yoshino, A.; Migita, T. *Chem. Lett.* **1978**, 795−796.

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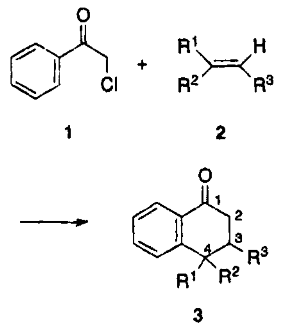


1 + **2** → **3**

	R^1	R^2	R^3
a	$-CH_2CN$	H	H
b	$-CH_2OMe$	H	H
c	$-(CH_2)_3COMe$	H	H
d	Me	Me	$-CH_2OMe$
e	H	$-CH_2-O-CH_2-$	
f	$-(CH_2)_2Br$	H	H
g	$-(CH_2)_3Br$	H	H
h	$-(CH_2)_2SiMe_3$	H	H
i	$-CH_2Ph$	H	H
j	$-(CH_2)_2Ph$	H	H
k	$-COOMe$	H	H

on the ring as H_2, $H_{2'}$, etc., all of the key protons for the structure determinations of **3a–e** and **3h,i** were assignable from 400-MHz and 270-MHz ^1H NMR as detailed in the Experimental Section. The regiochemistry of the monosubstituted naphthalenones was deduced from the presence of only one proton at the C4 position. The structure of the adduct from olefin **2d** was assigned as **3d** because each signal of the AB quartet of two protons (H_2 and $H_{2'}$) was further split into doublets, indicating that there is one proton at the neighboring position (C3). The *cis* ring junction of **3e** was assigned in view of the coupling constants of 8.80 Hz and 7.32 Hz for $J_{H_2-H_3}$ and $J_{H_{2'}-H_3}$, which are too small for an axial–axial coupling constant, as required for the *trans* junction. The regiochemistries of other products were assigned as shown, based on the results above.

Of all the olefins possessing conjugating groups that were used in the reactions, only methyl acrylate (**2k**) underwent the cyclization. Although the major product was assigned as **3k** from the 400-MHz ^1H NMR spectrum, the product material was impure. Since there was an extra methoxy signal in the ^1H NMR spectrum, there remains a possibility that the other regioisomer was formed, but no further evidence was obtained.

Our observations can be summarized as follows:

1. The positions of the functional groups are critical for the present reaction. The dependence of the yields of **3** upon the number of carbon atoms that separate the olefinic and respective functional groups of **8** is shown in Table 2. Apparently all of the functional groups tend to inhibit the cyclization as they are positioned closer to the olefinic group. The effect is the largest with an acetyl group: the cyclization proceeds only when it is separated from the double bond by three methylene groups. On the other hand, a methoxycarbonyl group showed the least effect on the reactivity: the reaction proceeds when it is attached directly to the double bond. A stannyl group completely prevents the cyclization, irrespective of its position, probably owing to the deactivation of the silver catalyst by tin.

2. The regiochemistry is controlled simply by the number of substituents, not by the nature of the functional group, as revealed by the comparison of the reactions of **2b** and **2d**.

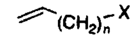
3. The reaction is accompanied by some polymerization of the olefins. In the cases of olefins with less tendency to polymerize, longer irradiation gave better yields of **3**, as observed in runs 9 and 10. In runs 2 and 5, however, the reactions stopped after 0.5 h, probably due to olefin polymerization. As evidenced by the results of runs 3 and 6, the addition of up to 3 equiv of the olefins, in portions during the irradiation, improved the yields.

Table 1. Silver Triflate-Catalyzed Cyclization of 2-Chloroacetophenone with Olefins

			yield (%)		
run	olefin **2**	time (h)	product **3**	recovered **1**	acetophenone
1	a	0.5	69	8	12
2	b	0.5	45	35	0
3[a]	b	1	65	25	0
4	c	2	65	25	0
5	d	0.5	50	50	0
6[a]	d	0.5	71	9	0
7	e	0.5	31	27	15
8	f	2	50	4	10
9	g	3	67	0	0
10	h	3	66	0	6
11	i	2	64	0	0
12	j	2	63	0	tr
13	k	1	53[b]	19	0

[a] The olefin was added during the irradiation in portions up to total of 3 equiv. [b] Contains some impurities.

Table 2. Yields (%) of Cyclization Products 3 Depending upon the Number of Carbons Separating the Respective Functional Groups and Olefinic Group of 8



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	X							
n	COOMe	OMe	CN	Ph	Br	COMe	$SiMe_3$	$SnMe_3$
0	53	0	0	0		0	0	0
1		71	69	64	0		0	0
2				63	50	0	66	0
3					67	65		0

Experimental Section

General Procedure and Instrumentation: GC experiments were carried out on a 2.5 m × 3 mm stainless steel column packed with Silicone SE 30 and PEG 20 M on silanized Chromosorb W, and 25 m × 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. Excluding **3k**, the spectroscopic data were determined on pure samples obtained by column chromatography, checking the purity by TLC and GC analyses. The mass spectra (low and high resolution) were obtained by EI method at 70 eV, the ^1H NMR data (400 MHz and 90 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: The irradiation was carried out in a rectangular vessel (6 cm (*l*) × 3.5 cm (*w*) × 4 cm (*h*)), which was cooled by circulating water around the vessel and covered with a Pyrex lid. After being flushed with nitrogen gas through two holes on the lid, the solution was irradiated by a lamp (medium-pressure mercury lamp, Ushio UM 452, 450 W), placed horizontally 5 cm above the vessel. The photoreaction was carried out in a benzene solution (20 mL) of 2-chloroacetophenone (30.9 mg, 0.2 mmol), olefins (0.3 mmol), and silver triflate (51.4 mg, 0.2 mmol). 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 products were extracted with ether. After being dried over Na_2SO_4 and concentrated *in vacuo*, the residue was purified by column chromatography to give pure materials.

4-(Cyanomethyl)-3,4-dihydro-1(2*H*)-naphthalenone (3a): MS *m/z* (rel intensity) 185 (M^+, 97), 146 (28), 145 (100), 130 (38), 117 (83), 115 (73), 77 (23); IR *ν* 2954, 1677, 1595, 1292, 959, 764 cm^{-1}; ^1H NMR (400 MHz) δ 2.16–2.26 (m, 1H), 2.37–2.47 (m, 1H), 2.67 (dd of ABq, $J = 17.6, 7.06, 5.04$ Hz, 1H), 2.77 (dd of ABq, $J = 17.6, 9.90, 4.76$ Hz, 1H), 2.80 (d, $J = 8.10$ Hz, 1H), 2.82 (d, $J = 6.60$ Hz, 1H), 3.35–3.43 (m, 1H), 7.34–7.43 (m, 2H), 7.57 (dt, $J = 7.50, 1.52$ Hz, 1H), 8.04 (dd, $J = 7.73, 1.11$ Hz, 1H); mp 76°–77.5 °C. Anal. Calcd for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.71; H, 5.95; N, 7.48.

4-(Methoxymethyl)-3,4-dihydro-1(2*H*)-naphthalenone (3b): MS *m/z* (rel intensity) 190 (M^+, 38), 145 (68) 144 (48) 117

(60), 115 (60), 91 (30), 77 (21), 45 (100); IR ν 2925, 1682, 1453, 1112, 768 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.21−2.27 (m, 2H), 2.61 (t of ABq, *J* = 17.9, 5.49 Hz, 1H), 2.80 (dd of ABq, *J* = 17.9, 9.26, 7.24 Hz, 1H), 3.19−3.27 (m, 1H), 3.40 (s, 3H), 3.63 (d, *J* = 6.96 Hz, 1H), 3.63 (d, *J* = 6.23 Hz, 1H), 7.32−7.39 (m, 2H), 7.51(d of t, *J* = 6.23, 1,46 Hz, 1H), 8.04 (dd, *J* = 6.60, 1.47 Hz, 1H); HRMS calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.1010.

4-(4-Oxopentyl)-3,4-dihydro-1(2*H*)-naphthalenone (3c): MS *m/z* (rel intensity) 230 (M^+, 15), 159 (29), 145 (35), 117 (32), 91 (25), 77 (10), 43 (100); IR ν 2940, 1714, 1683, 1600, 1284, 767 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.57−1.83 (m, 4H), 2.07 (q of ABq, *J* = 14.0, 4.95 Hz, 1H), 2.14 (s, 3H), 2.20−2.30 (m, 1H), 2.49 (t, *J* = 6.97 Hz), 2.58 (t of ABq, *J* = 17.9, 4.86 Hz, 1H), 2.76 (dd of ABq, *J* = 17.9, 11.7, 5.13 Hz, 1H), 2.90−2.97 (m, 1H), 7.27−7.33 (m, 2H), 7.48 (d of t, *J* = 7.33, 1.46 Hz, 1H), 8.03 (dd, *J* = 7.70, 1.46 Hz, 1H); HRMS calcd for $C_{15}H_{18}O_2$ 230.1307, found 230.1278.

3-(Methoxymethyl)-4,4-dimethyl-3,4-dihydro-1(2*H*)-naphthalenone (3d): MS *m/z* (rel intensity) 218 (M^+, 0.7), 174 (10), 173 (75), 145 (29), 131 (16), 117 (12), 115 (14), 77 (9), 45 (100); IR ν 2971, 1683, 1600, 1450, 1304, 1114, 767 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.35 (s, 3H), 1.46 (s, 3H), 2.25−2.32 (m, 1H), 2.81 (d of ABq, *J* = 17.6, 8.06 Hz, 1H), 2.93 (d of ABq, *J* = 17.6, 4.77 Hz, 1H), 3.25 (dd, *J* = 9.40, 8.20 Hz, 1H), 3.30 (s, 3H), 3.61 (dd, *J* = 9.35, 4.20 Hz, 1H), 7.25−7.33 (m, 1H), 7.42 (d, *J* = 8.07 Hz, 1H), 7.52−7.56 (m, 1H), 8.01 (dd, *J* = 7.71, 1.46 Hz, 1H); HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1277.

***cis*-1,3,3a,9b-Tetrahydronaphtho[1,2-*c*]furan-5(4*H*)-one (3e):** MS *m/z* (rel intensity) 188 (M^+, 32), 158 (100), 130 (63), 129 (98), 115 (84), 77 (30); IR ν 2933, 2867, 1683, 1599, 1454, 1290, 1062, 898, 770 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.76 (d, *J* = 8.80 Hz, 1H), 2.76 (d, *J* = 7.32 Hz, 1H), 3.01−3.11 (m, 1H, H_3), 3.63−3.69 (m, 1H), 3.74 (dd, *J* = 8.80, 3.30 Hz, 1H), 3.88 (t, *J* = 8.06 Hz, 1H), 4.10 (dd, *J* = 5.86, 2.93 Hz, 1H), 4.33 (t, *J* = 8.43 Hz, 1H), 7.25−7.28 (m, 1H), 7.33−7.40 (m, 1H), 7.51−7.56 (m, 1H), 8.00 (dd, *J* = 7.62, 0.74 Hz, 1H); HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0867.

4-(2-Bromoethyl)-3,4-dihydro-1(2*H*)-naphthalenone (3f): MS *m/z* (rel intensity) 254 ($M^+ + 2$, 11), 252 (M^+, 11), 145 (100), 131 (10), 117 (34), 115 (30); ^{1}H NMR (90 MHz) δ 1.6−2.4 (m, 4H), 2.4−2.8 (m, 2H), 3.0−3.3 (m, 1H), 3.49 (t, *J* = 6.6 Hz, 2H), 7.1−7.6 (m, 3H), 7.9−8.1 (m, 1H); ^{13}C NMR δ 26.47, 31.40, 34.59, 35.94, 37.16, 127.17, 127.64, 128.20, 131.94, 133.64, 146.41, 197.64; HRMS calcd for $C_{12}H_{13}OBr$ 252.0150, found 252.0168.

4-(3-Bromopropyl)-3,4-dihydro-1(2*H*)-naphthalenone (3g): MS *m/z* (rel intensity) 268 ($M^+ + 2$, 4), 266 (M^+, 4), 187 (5), 145 (100), 131 (17), 117 (35), 115 (29); ^{1}H NMR (90 MHz) δ 1.6−2.4 (m, 6H), 2.4−3.0 (m, 3H), 3.38 (t, *J* = 6.2 Hz, 2H), 7.1−7.5 (m, 3H), 7.9−8.1 (m, 1H); ^{13}C NMR δ 26.86, 30.68, 33.15, 33.35, 34.92, 37.43, 126.81, 127.44, 128.02, 131.94, 133.42, 147.36, 197.67; HRMS calcd for $C_{13}H_{15}OBr$ 266.0307, found 266.0347.

4-(2-Trimethylsilylethyl)-3,4-dihydro-1(2*H*)-naphthalenone (3h): MS *m/z* (rel intensity) 231 ($M^+ - 15$, 1.5), 218 (73), 203 (10), 190 (11), 157 (6), 73 (100); ^{1}H NMR (270 MHz) δ 0.36−0.62 (m, 2H), 1.54−1.63 (m, 2H), 2.00−2.19 (m, 2H), 2.47 (t of ABq, *J* = 17.8, 5.3, 1H), 2.64 (dd of ABq, *J* = 17.8, 11.1, 5.1 Hz, 1H), 7.2−7.4 (m, 3H), 7.91−7.94 (m, 1H); HRMS calcd for $C_{14}H_{19}OSi$ (M − Me) 231.1205, found 231.1253.

4-Benzyl-3,4-dihydro-1(2*H*)-naphthalenone (3i): MS *m/z* (rel intensity) 236 (M^+, 15), 144 (100), 143 (69), 116 (47), 114 (35), 90 (75); IR ν 3061, 3026, 2926, 2867, 1682, 1598, 1495, 1454, 1285, 1030, 766, 699 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.95 (q of ABq, *J* = 13.5, 4.9 Hz, 1H), 2.14 (dt of ABq, *J* = 13.5, 11.9, 4.9 Hz, 1H), 2.56 (t of ABq, *J* = 17.8, 4.9 Hz, 1H), 2.82 (dd of ABq, *J* = 17.8, 11.8, 4.9 Hz, 1H), 2.85 (d of ABq, *J* = 13.5, 9.5 Hz, 1H), 3.11 (d of ABq, *J* = 13.5, 5.9 Hz, 1H), 3.23 (m, 1H), 7.15−7.49 (m, 8H), 7.94−8.07 (m, 1H); HRMS calcd for $C_{17}H_{16}O$ 236.1201, found 236.1208.

4-(2-Phenylethyl)-3,4-dihydro-1(2*H*)-naphthalenone (3j): MS *m/z* (rel intensity) 250 (M^+, 3), 145 (100), 144 (18), 130 (19); IR ν 3060, 3025, 2933, 1683, 1600, 1496, 1453, 1284, 766, 700 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.78−2.35 (m, 4H), 2.50−3.10 (m, 5H), 7.03−7.65 (m, 8H), 7.95−8.17 (m, 1H); ^{13}C NMR δ 26.57, 33.70, 3480, 3625, 3747, 125.98, 126.69, 127.37, 128.19, 128.26, 128.45, 131,90 133.41, 141.63, 147.98, 198.17; HRMS calcd for $C_{18}H_{18}O$ 250.1358, found 250.1404.

4-(Methoxycarbonyl)-3,4-dihydro-1(2*H*)-naphthalenone (3k): MS *m/z* (rel intensity) 204 (M^+, 37), 176 (100), 148 (98), 145 (86), 133 (73), 115 (81), 77 (22); IR ν 2952, 1734, 1684, 1598, 1452, 1285, 1030, 759 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.25−2.55 (m, 2H), 2.64 (dd of ABq, *J* = 17.6, 5.86, 5.13 Hz, 1H), 2.92 (dd of ABq, *J* = 17.6, 11.36, 4.76 Hz, 1H), 3.74 (s, 3H), 4.00 (dd, *J* = 5.13, 4.76 Hz, 1H), 7.32−7.42 (m, 2H), 7.51−7.55 (m, 1H), 8.06 (dd, *J* = 7.33, 0.73 Hz, 1H); HRMS calcd for $C_{12}H_{12}O_3$ 204.0786, found 204.0805.

Supplementary Material Available: Copies of NMR spectra and NMR data complete with peak assignments, for **3a−k** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.