Photocycloaddition of Chloromethyl Alkenyl Ketones with Olefins in the Presence of Silver Trifluoromethanesulfonate

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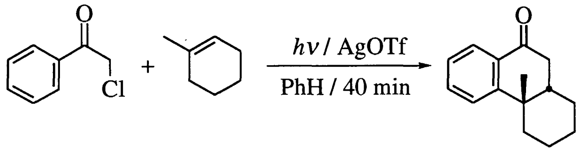
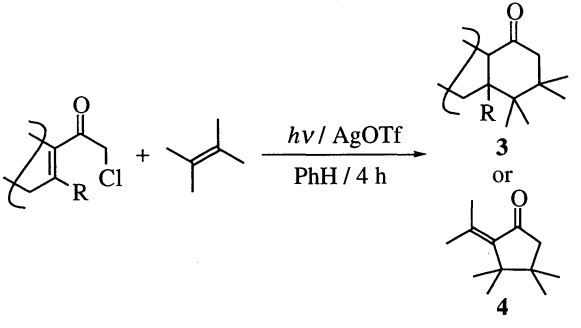
The photoreaction of chloromethyl alkenyl ketones with olefins in the presence of AgOTf proceeded to give five or six membered cyclic compounds.

Cycloaddition reactions to make five or six membered rings are useful synthetic methods.[1] In previous papers,[2-4] we reported that the reaction of α-chloroacetophenone with olefins upon UV irradiation in the presence of silver trifluoromethanesulfonate (AgOTf) gave 1-tetralones in good yields (eq. 1). The reaction was explained by a radical mechanism initiated by photo- and metal- promoted electron transfer. In the course of our studes, we have found that the photoreaction of chloromethyl alkenyl ketones with olefins under similar conditions proceeded to give five or six membered cyclic compounds (**3** or **4**, eq. 2).



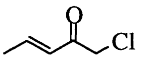
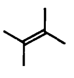
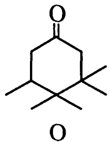
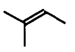
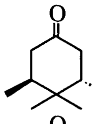
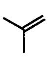
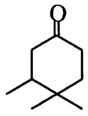
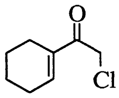
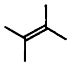
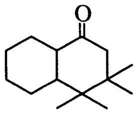
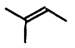
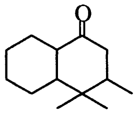
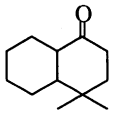
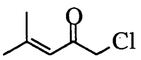
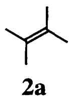
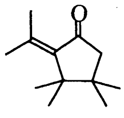
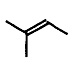
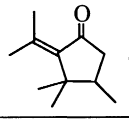


Irradiation of 1-chloro-3-penten-2-one (**1a**) and 2-methyl-2-butene in benzene in the presence of AgOTf with Pyrex filtered light for 4 h gave *trans*-3,4,4,5-tetramethylcyclohexanone (**3ab**) in 56% yield after purification by column chlomatography on SiO_2 (Method A, Run 3 in Table 1). The *trans* stereochemistry of the product **3ab** was confirmed by NMR analysis comparing with those reported.[5] No formation of the *cis* isomer was observed. Similarly, reaction of **1a** with 2,3-dimethyl-2-butene and 2-methylpropene gave 3,3,4,4,5-pentamethylcyclohexanone (**3aa**) and 3,4,4-trimethylcyclohexanone (**3ac**) in 19% and 21% yields, respectively. Bicyclic compounds, 1-decalones **3ba**-**3bc**, were obtained by the reaction of chloromethyl 1-cyclohexenyl ketone (**1b**) with olefins. Thus, the reaction of **1b** with 2-methylpropene gave *trans* -4,4-dimethyl-1-decalone (**3bc**) in 30% yield. Similarly, 3,3,4,4-tetramethyldecalone (**3ba**) and 3,4,4-trimethyl-1-decalone (**3bb**) were obtained in 33% and 25% yields in the reaction with 2,3-dimethyl-2-butene and 2-methyl-2-butene, respectively.

Although the six-membered ketones **3** were obtained from the α-chloro ketones **1a** and **1b**, only five membered enones **4** were obtained as the major cyclization product in the reaction of **1c**. Thus, the reaction of 1-chloro-4-methyl-3-penten-2-one (**1c**) with olefins **2a** and **2b** proceeded to give the isopropylidene cyclopentanones **4ca** and **4ab** in 77% and 52%, respectively.

In the reaction of **1a** or **1b**, the cyclized products **3** were

Table 1. Reaction of chloromethyl alkenyl ketones with olefins

Run	Ketone	Olefin	Method[a]	Product	Yield/%[b]
1	 **1a**	 **2a**	A	 **3aa**	19
2			B		45
3	**1a**	 **2b**	A	 **3ab**	56
4			B		77
5	**1a**	 **2c**	A	 **3ac**	21
6	 **1b**	 **2a**	A	 **3ba**	33
7			B		79
8	**1b**	 **2b**	A	 **3bb**	25
9			B		22
10	**1b**	 **2c**	A	 **3bc**	30
11			B		60
12	 **1c**	 **2a**	A	 **4ca**	77
13	**1c**	 **2b**	A	 **4cb**	52

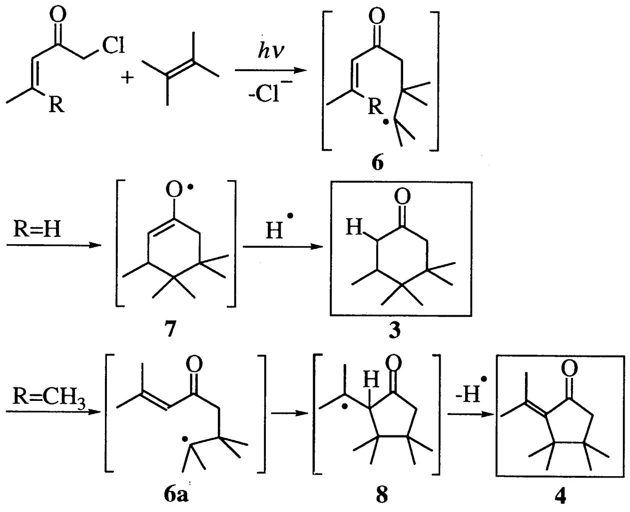
[a] Method A: Reaction was carried out with the α-chloroketone (0.2 mmol), AgOTf (0.2 mmol), and the olefin (0.3 mmol) in benzene (20 ml) in a Pyrex tube under irradiation.

Method B: Reaction was carried out in the presence of thiophenol (0.2 mmol) in Method A.

[b] Products were isolated by column chromatography.

obtained reductively. The reaction is considered to involve hydrogen radical transfer or electron transfer. Accordingly hydrogen radical donors are necessary for formation of the cyclized products **3**. The ketones **1a** and **1b** themselves may play as the source of hydrogen donors, which causes the low yields of the cyclized products **3**. Indeed, when the reaction of **1b** was carried out with thiophenol as the added hydrogen radical donor, the yield of the cyclized product **3ba** was raised dramatically (79% yield, Run 7).[6] On the contrary, when triethylamine was used as an electron donor,[7] no organic product was obtained, instead silver metal was deposited. Thus only the electron transfer from triethylamine to the silver cation proceeded.

Although the precise mechanism for the cycloaddition is uncertain, the reaction is considered to involve a radical mechanism. Electron transfer from the olefin to a photo excited state of chloromethyl alkenyl ketone, then abstraction of chloride anion from the chloro enone by the silver cation gives a radical species, which reacts with the olefin at the less substituted site giving the radical intermediate **6**. When R in the enone is a hydrogen, the radical species adds at the ß-position to give **7** followed by hydrogen abstraction provides the saturated ketones **3**. On the contrary, when the R is a methyl group, the intramolecular C-C bond formation of **6a** at the less hindered α-position gives **8**, followed by release of an active α-hydrogen of the ketone gives the five membered enone **4**. (Scheme 1)



Scheme 1.

The present reaction provides a useful method for the preparation of cyclic compounds. Further mechanistic investigations and synthetic applications are in due course.

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References and Notes

1 "Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford (1991) vol 5.
2 T. Sato and K. Tamura, *Tetrahedron Lett.*, **50**, 1646 (1985).
3 S.-H. Oh, K. Tamura and T. Sato, *Tetrahedron*, **48**, 9687 (1992).
4 S.-H. Oh and T. Sato, *J. Org. Chem.*, **59**, 3744 (1994).
5 F. Fringuelli, *J. Org. Chem.*, **47**, 5056 (1982).
6 In the reaction of 1**a** by the method B (run 2, in Table 1) 1-chloro-4-phenylthio-2-pentanone (**5**) was obtained as a by-product by 1,4-addition reaction with PhSH.
7 R. S. Givens and B. W. Atwater, *J. Am. Chem. Soc.*, **108**, 5028 (1986).
8 **3aa**: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.90 (s, 3H, Me), 0.92 (s, 3H, Me), 0.93 (d, *J* = 5.61Hz, 3H, 5Me), 0.981 (s, 3H, Me), 0.986 (s, 3H, Me), 1.92 (d, *J* = 14.2Hz, 1H), 1.99-2.20 (m, 3H), 2.51 (d, *J* = 14.2Hz, 1H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 15.55, 16.61, 21.94, 25.52, 37.83, 37.88, 41.31, 46.92, 52.88, 211.52.

3ab: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.88 (d, *J* = 6.13Hz, 6H), 1.01 (s, 6H, 4Me), 1.82-1.97 (m, 2H, 3,5-H), 2.05-2.13 (ddd, *J* = 14.51, 7.76, 1.65Hz, 1H), 2.38-2.46 (ddd, *J* = 9.60, 5.12, 1.65Hz, 1H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 15.92, 23.72, 34.95, 39.41, 46.08, 212.25.

3ac: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.89 (d, *J* = 6.60Hz, 3H, 3Me), 0.97 (s,3H, 4Me), 1.01 (s, 3H, 4Me), 1.50-1.78 (m, 3H, 3,5-H), 2.03-2.45 (m, 4H, 2,5-H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 16.46, 19.07, 32.62, 38.42, 40.02, 46.04, 212.11.

3ba: ^{1}H-NMR (270 MHz, CDCl$_3$,) δ 0.86 (s, 3H, Me), 0.90 (s, 3H, Me), 0.96 (s, 3H, Me), 1.06 (s, 3H, Me), 1.10-1.30 (m, 4H), 1.45-1.57 (m, 1H), 1.70-1.85 (m, 3H), 1.89 (d, *J* = 13.2 Hz, 1H), 1.95-2.10 (m, 2H), 2.56 (d, *J* = 13.5 Hz, 1H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 17.16, 23.34, 25.28, 25.55, 25.82, 26.56, 27.73, 38.20, 41.80, 50.26, 52.56, 212.31.

3bb: ^{1}H-NMR (400 MHz, CDCl$_3$) δ 0.86-0.88 (d, *J* = 6.97Hz, 3H, Me), 0.93 (s, 3H, Me), 1.10-1.20 (s and m, 7H), 1.39-1.47 (ddd, *J* = 11.36, 11.36, 2.93, 1H), 1.67-1.81 (m, 3H), 1.83-1.93 (n, 1H), 1.94-2.10 (m, 3H), 2.74-2.82 (dd, *J* = 13.56, 5.64, 1H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 15.58 22.93, 25.42, 25.60, 26.31, 26.37, 27.48, 35.23, 44.03, 45.71, 46.88, 49.96, 213.13.

3bc: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.96 (s, 3H, Me), 1.07 (s, 3H,Me), 1.11-1.26 (m, 4H), 1.55-1.62 (m, 1H), 1.65-1.82 (m, 3H), 1.98-2.15 (m, 2H), 2.21-2.29 (ddd, *J* = 14.10, 4.37, 2.64 Hz, 1H), 2.40-2.54 (ddd, *J* = 14.20, 14.20, 6.26 Hz, 1H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 19.46 (α-Me), 25.38, 25.81, 27.79, 28.88 (ß-Me), 32.92, 38.40, 41.99, 49.54, 52.42, 212.92.

4ca: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.93 (s, 6H), 1.16 (s, 6H), 1.95 (s, 3H), 2.81 (s, 2H), 2.23 (s, 3H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 23.24, 23.33, 23.45, 38.82, 46.08, 52.71, 139.75, 148.80, 207.29.

4cb: ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.95 (d, *J* = 6.60Hz, 3H, 4Me), 1.03 (s, 3H), 1.24 (s, 3H), 1.72-1.90 (m, 1H), 1.94 (s, 3H), 2.00-2.05, (d, *J* = 11.6Hz, 1H), 2.20 (s, 3H), 2.29-2.40 (dd, *J* = 16.8 7.26Hz, 1H). ^{13}C-NMR (67.9 MHz, CDCl$_3$) δ 13.71, 20.81, 23.24, 23.43, 26.99, 39.39, 43.07, 45.61, 140.34, 149.02, 207.37.