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Reactions of methylenecyclobutanes with silver acetate and iodine

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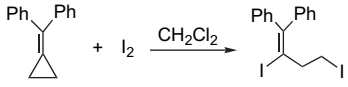
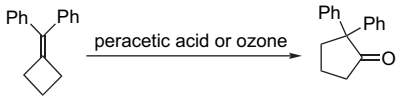
Abstract—Methylenecyclobutanes undergo an interesting rearrangement reaction in the presence of silver acetate and iodine at room temperature (20 °C) in dichloromethane to give the corresponding aryl-(1-arylcyclobutyl)methanones in good to high yields within short reaction time. A plausible reaction mechanism has been discussed on the basis of control and O^{18}-labeling experiments.

1. Introduction

Oxidation of alkenes using iodine and silver acetate has long been known to give the corresponding dihydroxy products.[1,2] Previously, we reported that using methylenecyclopropanes (MCPs), a kind of highly strained but readily accessible alkenes, as substrates, the ring-opening reaction takes place to produce the corresponding 2,4-diiodo-buta-1-enes in good yields in the presence of iodine or in the coexistence of silver acetate under mild conditions (Scheme 1).[3,4] On the other hand, it has been well known that methylenecyclobutanes (MCBs),[5] a class of moderately strained alkenes, could be oxidized by peracetic acid or ozone as well as thallium(III) oxide to give the corresponding cyclopentanone derivatives in good yields through a rearrangement (Scheme 2).[6] On the basis of the above results, we attempted to examine the reaction of MCBs in the presence of iodine (I_2) and silver acetate to understand their reaction pathway. In this paper, we wish to report that methylenecyclobutanes (MCBs) can undergo an interesting rearrangement reaction in the presence of iodine and silver acetate at room temperature (20 °C) in dichloromethane to give the corresponding cyclobutylmethanone derivatives in good to high yields within short reaction time rather than cyclopentanone derivatives.



Scheme 1. Ring-opening reaction of methylenecyclopropanes.



Scheme 2. Oxidation of methylenecyclobutanes to form cyclopentanone.

2. Results and discussion

At first, we investigated the rearrangement reaction of diphenylmethylenecyclobutane **1a** in the presence of silver acetate and iodine to develop the optimal conditions. The results are summarized in Table 1. Using **1a** (1.0 equiv) with I_2 (1.2 equiv) and AgOAc (2.4 equiv) in dichloromethane at room temperature (20 °C), **2a** was produced in 61% yield along with trace of cyclopentanone after 2 h under ambient atmosphere (Table 1, entry 1). When the ratio of **1a**/I_2/AgOAc increased to 1/1.5/3, the color of iodine immediately disappeared within 10 min and the yield of **2a** could be achieved in 87% (Table 1, entry 2). When $AgCO_3$ or $AgNO_3$ was used to replace AgOAc, the yield of **2a** decreased to 41% and 68%, respectively, under the similar conditions (Table 1, entries 3 and 4). In the presence of I_2 and Ag_2O, no reaction occurred (Table 1, entry 5). Using bromine to replace iodine, only 22% of **2a** was produced under identical conditions (Table 1, entry 6). When the reaction was carried out at 0 °C, **2a** was obtained in 75% yield under the standard conditions (Table 1, entry 7). Further examination of the solvent effects revealed that dichloromethane is the best one for this transformation (Table 1, entries 8–12).

Under these optimal reaction conditions, we next carried out this interesting rearrangement reaction of a variety of methylenecyclobutanes **1** with silver acetate and iodine. The results are summarized in Table 2. We found that the corresponding aryl-(1-arylcyclobutyl)methanone products **2** were

Keywords: Methylenecyclobutanes; Rearrangement; Iodine; Silver acetate.
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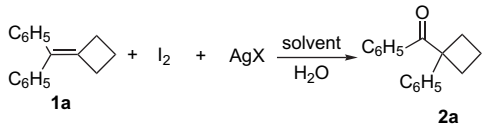
Table 1. Optimized reaction conditions of **1a** with X in the presence of I_2

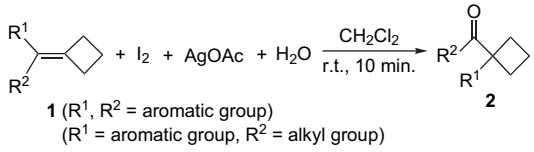


Entry[a]	Solvent	AgX	**1a**/I_2/AgX	Temp (°C)	Time	Yield[b] (%)
						2a
1	CH_2Cl_2	AgOAc	1/1.2/2.4	rt	2 h	61
2	CH_2Cl_2	AgOAc	1/1.5/3	rt	10 min	87
3	CH_2Cl_2	Ag_2CO_3	1/1.5/1.5	rt	1 h	41
4	CH_2Cl_2	$AgNO_3$	1/1.5/3	rt	2 h	68
5	CH_2Cl_2	Ag_2O	1/1.5/3	rt	2 h	N.R.
6	CH_2Cl_2	AgOAc	1/1.5/3	rt	40 min	22[c]
7	CH_2Cl_2	AgOAc	1/1.5/3	0	10 min	75
8	THF	AgOAc	1/1.5/3	rt	5 h	57
9	Et_2O	AgOAc	1/1.5/3	rt	5 h	49
10	CH_3CN	AgOAc	1/1.5/3	rt	5 h	23
11	DCE	AgOAc	1/1.5/3	rt	5 h	77
12	Toluene	AgOAc	1/1.5/3	rt	5 h	68

N.R. = no reaction.
[a] Reaction conditions: **1a** (0.3 mmol), I_2 (0.45 or 0.36 mmol), AgX (0.9 mmol), solvent (2.0 mL), and the reactions were carried out at room temperature or 0 °C.
[b] Isolated yields.
[c] Br_2 was used instead of I_2.

obtained in moderate to good yields within 10 min for a variety of MCBs **1** with electron-rich, electron-neutral, and electron-poor substituents on the benzene ring under ambient atmosphere. The effect of the nature of the substituents is not very significant. However, as can be seen from Table 2, in the presence of an electron-donating substituent at the *para*-position of benzene ring leads to a higher yield. For unsymmetrical MCBs **1f** and **1g**, the corresponding products **2f** and **2g** were obtained as isomeric mixtures in which the ratios were determined by GLC analysis (Table 2, entries 5 and 6) (Supplementary data). But for unsymmetrical MCBs **1i**, **1j**, **1k**, and **1l**, the corresponding products **2i**, **2j**, **2k**, and **2l** were obtained as single products through the phenyl migration (Table 2, entries 8–11). The possible reason is that the aromatic group can much more easily migrate than alkyl group, which exclusively results in the formation of alkyl ketone. For MCB **1h** (R^1=H, R^2=*p*-MeC_6H_4), complicated reaction products were formed without the formation of the expected product **2h** (Table 2, entry 7).

Table 2. Reaction of **1** with I_2 and AgOAc under the optimal conditions



Entry[a]	**1** (R^1/R^2)	Yield[b] (%)
		2
1	**1b** (*p*-ClC_6H_4/*p*-ClC_6H_4)	**2b**, 60
2	**1c** (*p*-MeC_6H_4/*p*-MeC_6H_4)	**2c**, 73
3	**1d** (*p*-FC_6H_4/*p*-FC_6H_4)	**2d**, 63
4	**1e** (*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$)	**2e**, 77
5	**1f** (*p*-ClC_6H_4/C_6H_5)	**2f**, 72 (2:1)[c]
6	**1g** (*m*,*p*-$Me_2C_6H_3$/C_6H_5)	**2g**, 81 (3.2:1)[c]
7	**1h** (*p*-MeC_6H_4/H)	**2h**, —[d]
8	**1i** (*p*-MeC_6H_4/Me)	**2i**, 43
9	**1j** (*p*-BrC_6H_4/Me)	**2j**, 73
10	**1k** (*p*-$CF_3C_6H_4$/Me)	**2k**, 36
11	**1l** (*p*-MeC_6H_4/$(CH_2)_4CH_3$)	**2l**, 41

[a] Reactions were carried out at room temperature. Reaction conditions: **1** (0.4 mmol), I_2 (0.6 mmol), AgOAc (1.2 mmol), and CH_2Cl_2 (3.0 mL).
[b] Isolated yields.
[c] Isomeric mixtures.
[d] No expected product.

On the basis of computational calculation on ^{13}C chemical shifts by gauge including atomic orbital (GIAO) method at B3LYP/6-31G* level using Gaussian03 program, we confirmed that electron-rich aromatic group migrates more preferentially than electron-poor ones for unsymmetrical MCBs **1f** and **1g** (Supplementary data).

The structures of all these products reported in this paper were determined by ^1H and ^{13}C NMR spectroscopic data, and HRMS or microanalysis. The structure of **2b** was unambiguously determined by X-ray diffraction (Fig. 1).[7]

Because these reactions were carried out under ambient atmosphere and all of the solvents and reagents were used without further drying, the ambient water may play a key role in this rearrangement reaction and the oxygen atom might be derived from the ambient water. Therefore, we carefully studied the water effect on the reaction in anhydrous dichloromethane under argon atmosphere. The results are summarized in Table 3. As can be seen from Table 3, with the addition of water from 0.5 equiv to 1.0 equiv, the yield of **2a** was indeed improved from 62% to 87%, although 2.0 equiv, 4.0 equiv or 5.0 equiv of water did not make any significant difference (Table 3, entries 2–5). In the absence of water, **2a** was obtained in 36% yield, suggesting that trace of water is still involved in this reaction even using anhydrous reagents and solvent under argon atmosphere (Table 1, entry 1). The best result was obtained with the addition of 1.0 equiv of water.

In order to clarify the reaction mechanism, $H_2{}^{18}O$ (^{18}O content 97.7%) was used in the reaction of **1a** with iodine and silver acetate under the standard conditions. It was found that the corresponding product **2a**-^{18}O was obtained in 82% yield along with 61% of ^{18}O content, indicating that

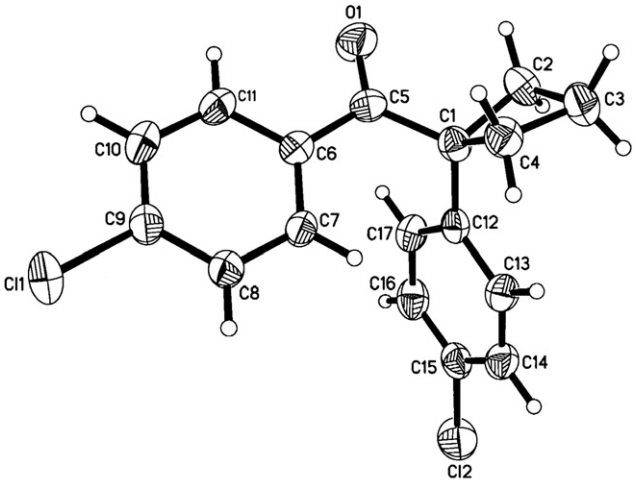
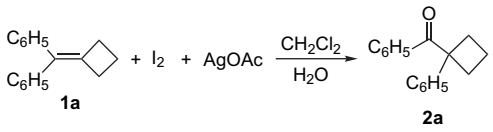


Figure 1. X-ray crystal structure of compound **2b**.

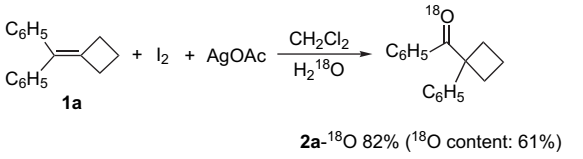
Table 3. Studies on the influence of the amount of water on the reaction using anhydrous reagents under argon atmosphere



Entry[a]	H_2O (equiv)	Time (min)	Yield[b] (%)
			2a
1	0	10	36
2	0.5	10	62
3	1.0	10	87
4	2.0	10	87
5	4.0	20	85
6	5.0	20	85

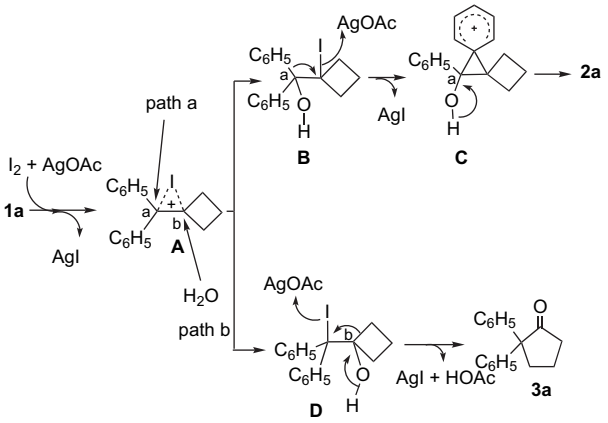
[a] Reaction conditions: **1a** (0.3 mmol), I_2 (0.45 mmol), AgOAc (0.9 mmol), CH_2Cl_2 (2.0 mL), H_2O (*x* equiv), and the reactions were carried out at room temperature.
[b] Isolated yields.

the oxygen atom is indeed derived from water (Scheme 3). The lower ^{18}O content of **2a** (61%) is due to that the ambient moisture (H_2O) takes part into the reaction as well.



Scheme 3. Isotopic labeling experiment using $H_2{}^{18}O$ under the reaction conditions.

A plausible reaction mechanism for this rearrangement reaction of methylenecyclobutanes is shown in Scheme 4. Initially, the reaction of **1a** with iodine and silver acetate generates iodonium intermediate **A**.[8,9] Then, cationic intermediate **B** is formed when water attacks the position a of intermediate **A**, which produces the corresponding rearranged product **2a** (path a) through the phenonium ion **C**.[10–12] As shown in Table 2, the relatively higher yields of **2** with an electron-donating substituent at the *para*-position of benzene ring can partially prove the existence of intermediate **C**, because it can be stabilized by an electron-donating



Scheme 4. Proposed mechanism for the reaction of **1a** with iodine and silver acetate.

substituent at the benzene ring more than an electron-withdrawing one.[12] However, when water attacks the position b of intermediate **A**, intermediate **D** can be formed, which produces the corresponding cyclopentanone **3a** as a by-product. In cationic intermediate **A**, the resonance-stabilized cationic intermediate **A-1** is more stable than the resonance-stabilized cationic intermediate **A-2** by two aromatic groups and a cyclobutane moiety (Fig. 2).[9a,13] Subsequently, phenonium ion intermediate **C** from intermediate **A-1** can be more easily formed, which has been disclosed by Kakis et al.[14] Therefore, the attack of water on the position a can exclusively take place to give the corresponding rearranged product **2a** as a major product.

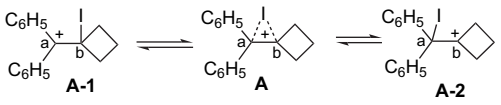
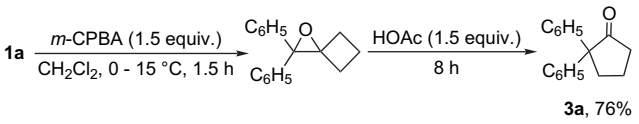


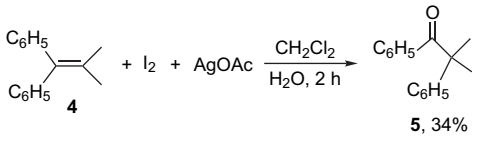
Figure 2. Cationic intermediates.

In order to rule out the possibility of this rearrangement through an epoxide intermediate, we prepared the corresponding epoxide from **1a** using *m*-CPBA in dichloromethane, and found that the corresponding cyclopentanone **3a** was obtained in 76% yield in the presence of acetic acid, indicating that **2a** might be derived from the iodonium intermediate **A** (Scheme 5). In fact, Takada has already reported that cyclopentanone derivatives can be obtained via the ring enlargement of the corresponding epoxides derived from alkylidenecyclobutanes in the presence of Lewis acid such as $BF_3{\cdot}OEt_2$.[15]



Scheme 5. Rearrangement through the corresponding epoxide.

We also examined the reaction of alkene **4** with iodine and silver acetate in the presence of water under identical conditions. The corresponding product **5** was only isolated in 34% yield along with 51% of the starting material **4** was recovered after 2 h, suggesting that cyclobutane moiety is required in this interesting rearrangement reaction (Scheme 6).



Scheme 6. Reaction of alkene **4** with iodine and silver acetate.

3. Conclusion

In summary, we have disclosed an interesting rearrangement reaction of MCBs with silver acetate and iodine at room temperature in dichloromethane to give the corresponding rearranged products in moderate to good yields under mild

conditions.[14] The corresponding ketones **2** may be useful intermediates in organic synthesis. Efforts are in progress to elucidate the mechanistic details of this reaction and to determine its scope and limitations.

4. Experimental procedures

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values are given in Hertz. Mass spectra were recorded by EI methods and HRMS were measured on a Finnigan MA$^+$ mass spectrometer. CHN microanalyses were recorded on a Carlo-Erba 1106 analyzer. Solvents were used without further drying up. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

4.2. General procedure for rearrangement reaction of vinylidenecyclopropanes with silver acetate and iodine

Under ambient atmosphere, methylenecyclobutanes (MCBs) (0.4 mmol), AgOAc (1.2 mmol), and I_2 (0.6 mmol) were added into a Schlenk tube. The reaction mixture was stirred at room temperature until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **2** in moderate to good yields.

4.2.1. Phenyl(1-phenylcyclobutyl)methanone (2a). A colorless oil; IR (CH_2Cl_2): ν 3058, 3019, 2986, 2945, 2853, 1675, 1598, 1579, 1495, 1250, 1179, 957, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.80–1.97 (1H, m, CH_2), 1.99–2.18 (1H, m, CH_2), 2.16–2.62 (2H, m, CH_2), 2.85–3.03 (2H, m, CH_2), 7.20–7.44 (8H, m, ArH), 7.65–7.75 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.9, 32.2, 57.1, 125.6, 126.5, 128.1, 128.9, 129.7, 132.2, 134.1, 143.1, 201.0; MS (EI) *m*/*z* (%): 257 (1.39) [M$^+$], 131 (46.17), 105 (100.00), 91 (15.75), 77 (43.53), 51 (11.17), 41 (1.84); HRMS (EI) Calcd for $C_{17}H_{16}O$ (M$^+$) requires 236.1201, Found: 236.1208.

4.2.2. (4-Chlorophenyl)(1-(4-chlorophenyl)cyclobutyl)-methanone (2b). A white solid, mp 82–84 °C; IR (CH_2Cl_2): ν 3058, 2987, 2947, 2869, 1677, 1587, 1569, 1490, 1399, 1251, 1093, 967, 752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.85–2.03 (1H, m, CH_2), 2.05–2.14 (1H, m, CH_2), 2.44–2.57 (2H, m, CH_2), 2.62–3.02 (2H, m, CH_2), 7.22–7.33 (6H, m, ArH), 7.59–7.68 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.9, 32.1, 56.6, 127.0, 128.6, 129.2, 131.0, 132.2, 132.6, 138.8, 141.4, 199.3; MS (EI) *m*/*z* (%): 304 (2.27) [M$^+$], 241 (2.58), 165 (59.97), 139 (100.00), 111 (19.62), 102 (11.09), 75 (16.38), 51 (5.51), 41 (1.62); HRMS (EI) Calcd for $C_{17}H_{14}OCl_2$ (M$^+$) requires 304.0422, Found: 304.0410.

4.2.3. *p*-Tolyl(1-*p*-tolylcyclobutyl)methanone (2c). A colorless oil; IR (CH_2Cl_2): ν 3024, 2986, 2945, 2867, 1672, 1607, 1572, 1512, 1444, 1267, 1180, 966, 737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.80–1.95 (1H, m, CH_2), 1.98–2.14 (1H, m, CH_2), 2.27 (6H, s, CH_3), 2.45–2.59 (2H, m, CH_2), 2.82–3.01 (2H, m, CH_2), 7.06 (2H, d, *J*=8.1 Hz, ArH), 7.12 (2H, d, *J*=8.1 Hz, ArH), 7.29 (2H, d, *J*=8.4 Hz, ArH), 7.64 (2H, d, *J*=8.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.9, 20.9, 21.4, 32.3, 56.7, 125.4, 128.7, 129.6, 139.8, 131.5, 135.9, 140.3, 142.8, 200.8; MS (EI) *m*/*z* (%): 264 (8.11) [M$^+$], 236 (3.53), 145 (83.75), 119 (100.00), 105 (10.19), 91 (48.04), 77 (2.87), 65 (19.59), 51 (4.53); HRMS (EI) Calcd for $C_{19}H_{20}O$ (M$^+$) requires 264.1514, Found: 264.1513.

4.2.4. (4-Fluorophenyl)(1-(4-fluorophenyl)cyclobutyl)-methanone (2d). A colorless oil; IR (CH_2Cl_2): ν 3072, 2988, 2948, 2870, 1888, 1675, 1598, 1508, 1410, 1268, 1156, 967, 833, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.84–2.03 (1H, m, CH_2), 2.06–2.16 (1H, m, CH_2), 2.43–2.57 (2H, m, CH_2), 2.85–2.99 (2H, m, CH_2), 6.92–7.09 (4H, m, ArH), 7.30–7.39 (2H, m, ArH), 7.69–7.78 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.8, 32.3, 56.4, 115.3 (d, J_{C-F}=21.2 Hz), 115.9 (d, J_{C-F}=21.2 Hz), 127.2 (d, J_{C-F}=8.0 Hz), 130.2 (d, J_{C-F}=2.8 Hz), 132.3 (d, J_{C-F}=9.2 Hz), 138.7 (d, J_{C-F}=3.5 Hz), 161.6 (d, J_{C-F}=258.2 Hz), 164.9 (d, J_{C-F}=267.9 Hz), 199.3; MS (EI) *m*/*z* (%): 272 (3.18) [M$^+$], 244 (3.24), 149 (89.13), 123 (100.00), 101 (30.52), 95 (68.88), 75 (38.32), 69 (6.17), 51 (10.49); HRMS (EI) Calcd for $C_{17}H_{14}OF_2$ (M$^+$) requires 272.1013, Found: 272.1000.

4.2.5. (4-Methoxyphenyl)(1-(4-methoxyphenyl)cyclobutyl)methanone (2e). A colorless oil; IR (CH_2Cl_2): ν 3056, 2948, 2867, 2837, 1875, 1672, 1610, 1505, 1512, 1441, 1245, 1170, 1031, 968, 736 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.80–1.95 (1H, m, CH_2), 1.98–2.14 (1H, m, CH_2), 2.43–2.55 (2H, m, CH_2), 2.83–2.97 (2H, m, CH_2), 3.74 (3H, s, CH_3), 3.75 (3H, s, CH_3), 6.76 (2H, d, *J*=8.4 Hz, ArH), 6.86 (2H, d, *J*=8.4 Hz, ArH), 7.32 (2H, d, *J*=9.0 Hz, ArH), 7.73 (2H, d, *J*=9.0 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.9, 32.4, 55.1, 55.2, 56.2, 113.3, 114.2, 126.7, 126.9, 132.0, 135.6, 158.0, 162.6, 200.8; MS (EI) *m*/*z* (%): 296 (9.72) [M$^+$], 268 (4.35), 161 (100.00), 135 (69.25), 107 (7.29), 92 (8.43), 64 (5.92), 55 (3.12), 43 (4.51); HRMS (EI) Calcd for $C_{19}H_{20}O_3$ (M$^+$) requires 296.1412, Found: 296.1403.

4.2.6. (1-(4-Chlorophenyl)cyclobutyl)(phenyl)methanone and (4-chlorophenyl)(1-phenylcyclobutyl)methanone (2f). A colorless oil; IR (CH_2Cl_2): ν 3058, 2987, 2946, 2868, 1978, 1894, 1675, 1587, 1490, 1399, 1250, 1176, 966, 824, 780 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.83–1.99 (1H, m, CH_2), 2.01–2.17 (1H, m, CH_2), 2.45–2.58 (2H, m, CH_2), 2.83–2.97 (2H, m, CH_2), 7.15–7.44 (7H, m, ArH), 7.64–7.70 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.92, 15.96, 32.1, 32.3, 56.7, 57.0, 125.5, 126.7, 127.1, 128.1, 128.2, 128.5, 129.0, 129.1, 129.7, 131.1, 132.3, 132.41, 132.49, 133.7, 141.7, 142.8, 199.8, 200.7; MS (EI) *m*/*z* (%): 270 (2.10) [M$^+$], 242 (1.02), 139 (36.81), 131 (100.00), 111 (21.04), 103 (59.58), 91 (23.60), 77 (28.11), 51 (15.58); HRMS (EI) Calcd for $C_{17}H_{14}OCl$ (M$^+$) requires 270.0811, Found: 270.0816.

4.2.7. (1-(3,4-Dimethylphenyl)cyclobutyl)(phenyl)methanone and (3,4-dimethylphenyl)(1-phenylcyclobutyl)methanone (2g). A colorless oil; IR (CH_2Cl_2): ν 3058, 2943, 2864, 1675, 1598, 1504, 1447, 1250, 1180, 967, 818, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.82–2.02 (1H, m, CH_2), 2.04–2.12 (1H, m, CH_2), 2.20 (3H, s, CH_3), 2.22 (3H, s, CH_3), 2.47–2.59 (2H, m, CH_2), 2.82–2.96 (2H, m, CH_2), 6.99–7.43 (6H, m, ArH), 7.74 (2H, d, J=7.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 16.0, 18.8, 19.3, 19.7, 19.8, 19.9, 32.3, 38.2, 56.7, 57.1, 122.8, 125.5, 126.4, 127.0, 127.6, 128.1, 128.9, 129.2, 129.7, 130.1, 130.9, 131.9, 132.2, 134.2, 134.8, 136.5, 137.2, 140.5, 141.7, 143.5, 201.0, 201.3; MS (EI) *m/z* (%): 264 (8.04) [M^+], 236 (4.16), 159 (100.00), 131 (79.89), 105 (29.64), 77 (36.26), 51 (12.51), 41 (3.64); HRMS (EI) Calcd for $C_{19}H_{20}O$ (M^+) requires 264.1514, Found: 264.1525.

4.2.8. 1-(1-*p*-Tolylcyclobutyl)ethanone (2i). A colorless oil; IR (CH_2Cl_2): ν 2945, 2865, 1706, 1512, 1430, 1352, 1246, 1189, 1107, 827, 815 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.83–1.93 (2H, m, CH_2), 1.92 (3H, s, CH_3), 2.34 (3H, s, CH_3), 2.32–2.45 (2H, m, CH_2), 2.66–2.78 (2H, m, CH_2), 7.10–7.26 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.8, 21.0, 24.3, 30.4, 58.9, 126.1, 129.3, 136.3, 140.1, 209.0; MS (EI) *m/z* (%): 188 (4.87) [M^+], 160 (2.04), 145 (72.35), 117 (100.00), 105 (14.56), 91 (19.25), 77 (6.06), 63 (20.24), 43 (25.98); HRMS (EI) Calcd for $C_{13}H_{16}O$ (M^+) requires 188.1201, Found: 188.1194.

4.2.9. 1-(1-(4-Bromophenyl)cyclobutyl)ethanone (2j). A colorless oil; IR (CH_2Cl_2): ν 2986, 2944, 1894, 1705, 1487, 1427, 1394, 1352, 1189, 1074, 1009, 831, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.76–1.92 (2H, m, CH_2), 1.93 (3H, s, CH_3), 2.31–2.44 (2H, m, CH_2), 2.68–2.79 (2H, m, CH_2), 7.12 (2H, d, J=8.7 Hz, ArH), 7.48 (2H, d, J=8.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.8, 24.3, 30.4, 58.8, 120.7, 128.0, 131.7, 142.1, 207.9; MS (EI) *m/z* (%): 252 (5.81) [M^+], 209 (90.83), 183 (68.34), 173 (22.09), 130 (93.11), 102 (84.44), 75 (25.53), 63 (13.14), 43 (100); HRMS (EI) Calcd for $C_{12}H_{13}OBr$ (M^+) requires 252.0150, Found: 252.0157.

4.2.10. 1-(1-(4-(Trifluoromethyl)phenyl)cyclobutyl)ethanone (2k). A colorless oil; IR (CH_2Cl_2): ν 2947, 2856, 1709, 1593, 1489, 1354, 1332, 1225, 1125, 1075, 902, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.83–1.98 (2H, m, CH_2), 1.95 (3H, s, CH_3), 2.37–2.50 (2H, m, CH_2), 2.73–2.86 (2H, m, CH_2), 7.38–7.56 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.9, 24.4, 30.6, 59.1, 122.8 (q, J_{C-F}= 4.5 Hz), 123.6 (q, J_{C-F}=3.8 Hz), 124.0 (q, J_{C-F}=270.6 Hz), 129.2, 129.7 (q, J_{C-F}=1.2 Hz), 131.1 (q, J_{C-F}=32.0 Hz), 144.2, 207.6; MS (EI) *m/z* (%): 242 (3.63) [M^+], 199 (100.00), 171 (40.53), 159 (20.69), 145 (10.01), 130 (8.19), 117 (6.59), 91 (1.53), 43 (93.90); HRMS (EI) Calcd for $C_{13}H_{13}OF_3$ (M^+) requires 242.0918, Found: 242.0922.

4.2.11. 1-(1-(4-(Trifluoromethyl)phenyl)cyclobutyl)-hexan-1-one (2l). A colorless oil; IR (CH_2Cl_2): ν 3021, 2955, 2861, 1706, 1512, 1459, 1378, 1355, 1168, 1085, 1018, 814, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.80 (3H, t, J=7.2 Hz, CH_3), 1.01–1.35 (4H, m, CH_2), 1.38–1.46 (2H, m, CH_2), 1.77–1.92 (2H, m, CH_2), 2.20 (2H, t, J=7.2 Hz, CH_2), 2.33 (3H, s, CH_3), 2.30–2.45 (2H, m, CH_2), 2.66–2.78 (2H, m, CH_2), 7.10–7.16 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.8, 15.9, 20.9, 22.3, 23.8, 30.4, 31.2, 36.3, 58.6, 126.2, 129.2, 136.2, 140.1, 211.1; MS (EI) *m/z* (%): 244 (1.60) [M^+], 145 (100.00), 117 (78.57), 115 (16.76), 105 (11.17), 91 (12.06), 43 (18.68), 41 (10.48); HRMS (EI) Calcd for $C_{17}H_{24}O$ (M^+) requires 244.1827, Found: 244.1827.

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Supplementary data

It includes ^1H and ^{13}C NMR spectroscopic charts for compounds **2a–2l**. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.07.046.

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