Selective, One-Pot Synthesis of 2,3,6-Trisubstituted Pyridine and 2-Cyclohexen-1-one Derivatives from Bicyclic Ketals

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Boron difluoromethanesulfonate, prepared from 5 equivalents of trimethylsilyl methanesulfonate and 1 equivalent of boron trifluoride etherate, has proved to be an active Lewis acid catalyst for the one-pot transformation reaction of bicyclic ketals in the 6,8-dioxabicyclo[3.2.1]octane series to 2,3,6-trisubstituted pyridine or 2-cyclohexen-1-one selectively, depending on conditions. A 1,5-diketone was the reaction intermediate for both products. Pyridine was formed selectively by using a nitrile as a solvent or a reagent, but cyclohexenone was prepared in methylene chloride instead of a nitrile.

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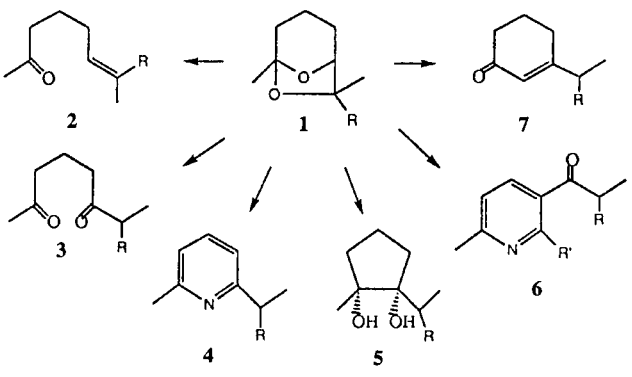
Bicyclic ketals in the 6,8-dioxabicyclo[3.2.1]octane series are very useful intermediates for the synthesis of other important structures. For example, a component of the glandular secretion of the Asian civet cat [1], a sex pheromone of the douglas fir tussock moth [2], a constituent of the venom of the fire ant [2], and a key intermediate for sirenin [3] were synthesized from this bicyclic ketal structure.

In the course of our continuing study into the bicyclic ketal **1**, we have carried out an investigation of reagents or reactions that would provide new chemistry. Fragmentation of **1** with acetyl iodide directly provided δ,ε-unsaturated ketone **2** stereoselectively that endo-ketals gave *cis*-alkenes and exo-ketals gave *trans*-alkenes [4] (Scheme 1). Lewis acid induced rearrangement of **1** with aluminum trichloride-sodium iodide at ambient temperature provided 1,5-diketone **3** [5]. Direct transformation of **1** with aluminum trichloride, acetic acid and hydroxylamine provided 2,6-disubstituted pyridine **4** [6]. A similar transformation of **1** with aluminum trichloride, acetic acid and zinc, however, provided *cis*-cyclopentane-1,2-diol **5** [7]. We also reported that the novel ketal fragmentation of **1** with aluminum iodide in acetonitrile provided the mixture of 2,3,6-trisubstituted pyridine **6** and 2-cyclohexen-1-one **7** in a ratio of about 5:1 in low yield [8].

Scheme 1



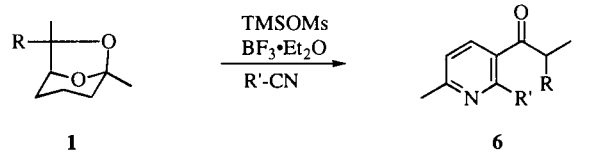
Results and Discussion.

In the continuous research to improve the selectivity and yield of this novel one-pot transformation of ketal **1** to pyridine **6**, we found a mild Lewis acid system, the combination of 5 equivalents of trimethylsilyl methanesulfonate and 1 equivalent of boron trifluoride etherate, provided the best results [9]. The use of this mild Lewis acid system was not well investigated since the first discovery for the reductive cleavage of methylated glycans in 1987 [10]. In recent years, only the nature of the trimethylsilyl methanesulfonate (5 equivalents)-boron trifluoride etherate (1 equivalent) complex was studied by proton and boron nmr in our group [9].

The active reagent in this complex turned out to be the boron difluoromethanesulfonate which was formed instantly *via* ligand exchange. The 5:1 ratio of the combi-

Table 1

Synthesis of 2,3,6-Trisubstituted Pyridines **6**

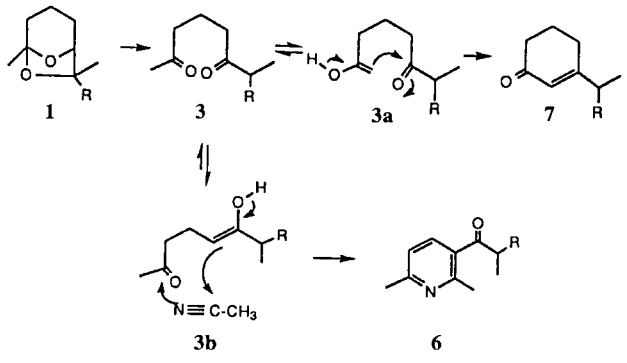


1 **6**

Entry	R	R'	Reaction hours	Yield (%)
a	Me	Me	30	73
b	Pr^i	Me	30	83
c	Bu	Me	30	88
d	Bu^t	Me	30	85
e	Ph	Me	48	52
f	Me	Pr	30	66
g	Me	Ph	30	58

nation of trimethylsilyl methanesulfonate-boron trifluoride etherate was required for the best formation of boron difluoromethanesulfonate yielding only the 2,3,6-trisubstituted pyridine **6** from the bicyclic ketal **1** without forming cyclohexenone **7**. The bicyclic ketal **1** was refluxed with the trimethylsilyl methanesulfonate (5 equivalents)-boron trifluoride etherate (1 equivalent) complex in acetonitrile solvent affording pyridine **6** directly in good yield as a single product (**6a-6e** in Table 1). In mechanism of this transformation reaction, the 1,5-diketone intermediate **3** was enolized to **3b**, and the following reaction with nitrile and aromatization yielded pyridine **6** as shown in

Scheme 2

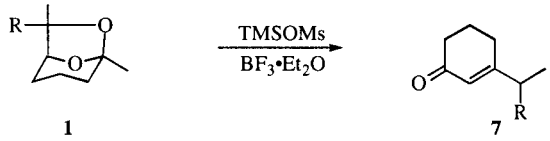


Scheme 2. In order to prove this approach as a general method to make **6** by using diverse nitriles, we used butyronitrile and benzonitrile instead of acetonitrile to give the expected results, (**6f** and **6g**).

Cyclohexenone **7** *via* intramolecular aldol condensation of **3a** was not formed and this indicated that the enol **3b** was more preferred than **3a** in this reaction. If there is no electrophile such as a nitrile in this reaction, the cyclohexenone **7** is the only product from the direct aldol condensation through the enol **3a** *via* equilibrium because of the destability for the intramolecular aldol condensation of **3b**. The ketal **1** was heated to reflux with the trimethylsilyl methanesulfonate (5 equivalents)-boron trifluoride etherate (1 equivalent) mixture in methylene chloride for 15 hours to give the cyclohexenone **7** in good yield as a single product shown in Table 2. The bicyclic ketals [11] having a substituent could be utilized for the synthesis of substituted cyclohexenone, especially at the α'-position [12-18].

Table 2

Synthesis of Cyclohexenones **7**



Entry	R	Reaction hours	Yield (%)
a	Me	15	80
b	Et	15	90
c	Pr	15	88
d	Pr^i	15	83
e	Ph	15	72

In conclusion, boron difluoromethanesulfonate is a very useful catalyst for the selective synthesis of 2,3,6-trisubstituted pyridine of the 2-cyclohexen-1-one from the bicyclic ketal in one step. Both products were formed through the 1,5-diketone as an intermediate [8]. Intermolecular reaction of 1,5-diketone with nitrile provided the pyridine, which intramolecular aldol condensation of 1,5-diketone provided the cyclohexenone.

EXPERIMENTAL

The proton and carbon nuclear magnetic resonance (nmr) spectra were recorded on a Varian Gemini-200 spectrometer at 200 and 50 MHz respectively, with the chemical shifts (δ) reported in parts per million (ppm) relative to tetramethylsilane. Deuteriochloroform was used as a solvent and an internal standard. Infrared (ir) spectra were recorded on a Shimadzu IR-435 spectrometer. Mass spectra (ms) were obtained using a VG MM16 mass spectrometer. Gas chromatography (gc) was performed using a Varian Aerograph series 2700 equipped with a 11 ft x 1/4 in, 10% OV-17 column.

Materials.

Most of the chemicals used were purchased from Aldrich and were used without further purification unless noted otherwise. Bicyclic ketals **1** were prepared from methyl vinyl ketone [19]. Flash chromatography was carried out using silica gel Merck 60 (230-400 mesh). Thin-layer chromatography (tlc) was performed on DC-Plastikfolien 60, F_{254} (Merck, layer thickness 0.2 mm) plastic-backed silica gel plates with visualization by uv light (254 nm) or by treatment with *p*-anisaldehyde.

Typical Procedure for the Preparation of Pyridines **6** from Bicyclic Ketal **1**.

To a stirred solution of bicyclic ketal **1a** (0.1 g, 0.64 mmole) in dry acetonitrile (4 ml) at room temperature was added 5 equivalents of trimethylsilyl methanesulfonate (0.48 ml) and 1 equivalent of boron trifluoride etherate (0.073 ml) sequentially by syringe. Alternatively, the pre-made mixture of 5 equivalents of trimethylsilyl methanesulfonate and 1 equivalent of boron trifluoride etherate, which is quite stable in the refrigerator for a long time (~one month), can be used. The mixture was refluxed for 30 hours. After cooling to room temperature, 10% aqueous sodium hydroxide solution (10 ml) was added. The organic product was extracted with diethyl ether (3 x 20 ml). The ether layer was washed with saturated sodium bicarbonate (30 ml) and saturated brine (30 ml), dried over magnesium sulfate, and the solvent was evaporated. Flash chromatography (diethyl ether-hexane 3:7) gave the pyridine **6a** (83 mg, 73%, R_f 0.4).

1-(2,6-Dimethyl-3-pyridyl)-2-methyl-1-propanone (**6a**).

This compound was obtained as a pale yellow oil; ^{1}H nmr, ^{13}C nmr, ir and ms data were reported [9].

Anal. Calcd. for $C_{11},H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.48; H, 8.60; N, 7.76.

1-(2,6-Dimethyl-3-pyridyl)-2,3-dimethyl-1-butanone (**6b**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): 7.71 (1H, d, J = 8 Hz, pyridyl C4-H), 7.04 (1H, d, J = 8 Hz, pyridyl C5-H), 3.04 (1H, m, COCH), 2.63 (3H, s, pyridyl CH_3), 2.54 (3H, s, pyridyl CH_3), 2.01 (1H, m, isopropyl CH), 1.09 (3H, d, J = 7 Hz, $CHCH_3$), 0.92 (3H, d, J = 7 Hz, isopropyl methyl), 0.85 (3H, d, J = 7 Hz, isopropyl methyl); ^{13}C nmr (deuteriochloroform): 207.3 (s, CO), 159.9 (s, pyridyl C), 157.2 (s, pyridyl C), 135.7 (d, pyridyl C4), 121.2 (s, pyridyl C), 119.9 (d, pyridyl C5), 50.0 (d, COCH), 30.2 (d, isopropyl CH), 24.4 (q, pyridyl CH_3), 23.9 (q, pyridyl CH_3), 21.4 (q, $CHCH_3$), 18.4 (q, isopropyl methyl) and 12.5 (q, isopropyl methyl); ir (neat): 1681 (C=0), 1587 (C=C), 1447, 1370, 919, 732 cm^{-1}; uv (ethanol): λ_{max} (ε) 274 nm (4140), 239 (6640); ms: m/z 205 (M^+), 190 (M^+-CH_3), 163 (M^+-CMe_2), 134 (base, M^+-CHMeCHMe$_2$), 106 (M^+-COCHMeCHMe$_2$), 79, 63, 53, 41.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.21; H, 9.09; N, 6.60.

1-(2,6-Dimethyl-3-pyridyl)-2-methyl-1-hexanone (**6c**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 7.87 (1H, d, J = 8 Hz, pyridyl C4-H), 7.03 (1H, d, J = 8 Hz, pyridyl C5-H), 2.88 (1H, m, COCH), 2.72 (3H, s, pyridyl CH_3), 2.57 (3H, s, pyridyl CH_3), 1.70 (2H, m), 1.25 (3H, d, J = 7 Hz, $CHCH_3$), 1.23 (4H, m), 0.84 (3H, t, J = 7 Hz, CH_2CH_3); ^{13}C nmr (deuteriochloroform): δ 208.1 (s, CO), 159.0 (s), 156.1 (s), 139.5 (d, pyridyl C4), 134.8 (s), 122.9 (d, pyridyl C5), 53.0 (d, COCH), 34.5 (t), 28.0 (q, $CHCH_3$), 24.5 (q, pyridyl CH_3), 23.5 (q, pyridyl CH_3), 22.5 (t), 15.5 (t) and 13.0 (q, CH_2CH_3); ir (neat): 1681 (C=O), 1579 (C=C), 1363, 1252, 955, 829 cm^{-1}; ms: m/z 219 (M^+), 134 (base, M^+-CHMeCH$_2$-CH$_2$CH$_2$CH$_3$), 106 (M^+-COCHMeCH$_2$CH$_2$CH$_2$CH$_3$), 85, 57, 43.

Anal. Calcd. for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.51; H, 9.89; N, 6.11.

1-(2,6-Dimethyl-3-pyridyl)-2,3,3-trimethyl-1-butanone (**6d**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 7.88 (1H, d, J = 8 Hz, pyridyl C4-H), 7.15 (1H, d, J = 8 Hz, pyridyl C5-H), 3.18 (1H, q, J = 7 Hz, COCH), 2.76 (3H, s, pyridyl CH_3), 2.68 (3H, s, pyridyl CH_3), 1.21 (3H, d, J = 7 Hz, $CHCH_3$), 0.98 (9H, s, *t*-butyl); ^{13}C nmr (deuteriochloroform): δ 208.0 (s, CO), 159.5 (s), 157.1 (s), 138.9 (d, pyridyl C4), 130.0 (s), 120.1 (d, pyridyl C5), 52.2 (d, COCH), 34.2 (s), 31.2 (q, pyridyl CH_3), 29.7 (q, pyridyl CH_3), 27.9 (q x 3, *t*-butyl methyls) and 13.1 (q, $CHCH_3$); ir (neat): 1678 (C=O), 1654, 1586 (C=C), 1491, 1384, 907, 729 cm^{-1}; ms: m/z 219 (M^+), 164, 135 (base, M^+-CMeCMe$_3$), 106 (M^+-COCHMeCMe$_3$), 85, 58, 43.

Anal. Calcd. for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.47; H, 9.49; N, 6.18.

1-(2,6-Dimethyl-3-pyridyl)-2-phenyl-1-propanone (**6e**).

This compound was obtained as a pale yellow oil; ^{1}H nmr (deuteriochloroform): δ 7.60 (1H, d, J = 8 Hz, pyridyl C4-H), 7.16 (5H, m, phenyl protons), 6.88 (1H, d, J = 8 Hz, pyridyl C5-H), 4.37 (1H, q, J = 7 Hz, COCH), 2.49 (3H, s, pyridyl CH_3), 2.41 (3H, s, pyridyl CH_3),1.20 (3H, d, J = 7 Hz, $CHCH_3$); ^{13}C nmr (deuteriochloroform): δ 212.6 (s, CO), 159.3 (s), 157.6 (s), 151.3 (s), 139.2 (d), 132.4 (s), 129.3 (d x 2), 128.4 (d x 2), 121.5 (d), 121.3 (d), 56.3 (d, COCH), 30.4 (q), 29.3 (q) and 24.3 (q); ir (neat): 1681 (C=O), 1582 (C=C), 1401, 1369, 716 cm^{-1}; ms: m/z 239 (M^+), 223, 208, 160, 145, 134 (base, M^+-CH-MePh).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.13; H, 6.94; N, 5.51.

1-(6-Methyl-2-propyl-3-pyridyl)-2-methyl-1-propanone (**6f**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 7.79 (1H, d, J = 8 Hz, pyridyl C4-H), 7.13 (1H, d, J = 8 Hz, pyridyl C5-H), 3.29 (1H, m, isopropyl CH), 2.94 (2H, t, J = 7 Hz, pyridyl C2-CH_2), 2.67 (3H, s, pyridyl C6-CH_3), 1.76 (2H, m, CH_3CH_2), 1.18 (6H, d, J = 7 Hz, isopropyl methyls), 1.04 (3H, t, J = 7 Hz, CH_2CH_3); ^{13}C nmr (deuteriochloroform): δ 207.3 (s, CO), 159.1 (s), 156.6 (s), 142.5 (d, pyridyl C4), 134.0 (s), 124.7 (d, pyridyl C5), 39.2 (d, isopropyl CH), 33.2 (t, pyridyl C2-CH_2), 24.9 (q, pyridyl C6-CH_3), 19.9 (t, CH_3CH_2), 18.2 (q x 2, isopropyl methyls) and 14.1 (q, CH_2CH_3); ir (neat): 1682 (C=O), 1605 (C=C), 1370, 907, 730 cm^{-1}; ms: m/z 205 (M^+), 190 (M^+-CH_3), 177, 162 (M^+-isopropyl), 86, 84, 49 (base).

Anal. Calcd. for $C_{13}H_{19}NO$ C, 76.06; H, 9.33; N, 6.82. Found: C, 75.89; H, 9.08; N, 6.57.

1-(6-Methyl-2-phenyl-3-pyridyl)-2-methyl-1-propanone (**6g**).

This compound was obtained as a pale yellow oil; ^{1}H nmr (deuteriochloroform): δ 7.65 (1H, d, J = 8 Hz, pyridyl C4-H), 7.53 (2H, m, phenyl protons), 7.45 (3H, m, phenyl protons), 7.20 (1H, d, J = 8 Hz, pyridyl C5-H), 2.67 (3H, s, pyridyl C6-CH_3), 2.49 (1H, m, isopropyl CH), 0.89 (6H, d, J = 7 Hz, isopropyl methyls); ^{13}C nmr (deuteriochloroform): δ 204.7 (s, CO), 159.9 (s), 156.0 (s), 152.0 (s), 145.9 (s), 139.9 (d), 136.8 (d), 129.0 (d x 2), 128.7 (d x 2), 121.4 (d), 40.2 (d), 29.8 (q, pyridyl C6-CH_3) and 18.8 (q x 2, isopropyl methyls); ir (neat): 1682 (C=O), 1580 (C=C), 1428, 1374, 794, 696 cm^{-1}; ms: m/z 239 (M^+), 196 (M^+-isopropyl), 168 (M^+-$COCHMe_2$), 153, 84 (base), 47.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.08; H, 6.97; N, 5.61.

Typical Procedure for the Preparation of Cyclohexenone **7** from Bicyclic Ketal **1**.

After a mixture of 5 equivalents of trimethylsilyl methanesulfonate (0.48 ml) and 1 equivalent of boron trifluoride etherate (0.073 ml) was added to bicyclic ketal **1a** (0.1 g, 0.64 mmole) in methylene chloride (4 ml) while stirring at room temperature, the solution was refluxed for 15 hours. The reaction mixture was cooled to room temperature and mixed with an aqueous 10% sodium hydroxide solution (10 ml), and the organic product was extracted with diethyl ether (3 x 20 ml). The ether layer was washed with saturated sodium bicarbonate (30 ml) and saturated brine (30 ml), dried over magnesium sulfate, and the solvent was evaporated. Flash chromatography (diethyl ether-hexane 3:7) gave the cyclohexenone **7a** (78 mg, 80%, R_f 0.26).

3-Isopropyl-2-cyclohexen-1-one (**7a**).

This compound was obtained as a pale yellow oil; ^{1}H nmr

(deuteriochloroform): δ 5.83 (1H, br s, 2-H), 2.33 (5H, m), 1.97 (2H, m), 1.05 (6H, d, J = 7 Hz, isopropyl methyls); ^{13}C nmr (deuteriochloroform): δ 200.7 (s, CO), 172.4 (s, C3), 124.0 (d, C2), 38.1 (t), 36.2 (d, isopropyl CH), 28.2 (t), 23.5 (t) and 21.1 (q, 2 x Me); ir (neat): 1662 (C=O), 1619 (C=C), 1284, 906, 729 cm^{-1}; ms: m/z 138 (M^+), 123 (base, M^+-CH_3), 108, 95 (M^+-isopropyl), 80, 71, 41.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 10.05.

3-(1-Methylpropyl)-2-cyclohexen-1-one (**7b**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 5.83 (1H, br s, 2-H), 2.34 (2H, t, J = 6.6 Hz), 2.26-2.08 (3H, m), 1.94 (2H, quintet, J = 6.2 Hz), 1.41 (2H, m), 1.05 (3H, d, J = 6.8 Hz, $CHCH_3$), 0.82 (3H, t, J = 7.4 Hz, CH_2CH_3); ^{13}C nmr (deuteriochloroform): δ 200.2 (s, CO), 170.8 (s, C3), 125.1 (d, C2), 43.2 (d, MeCH), 37.6 (t), 27.5 (t), 26.9 (t), 22.9 (t), 18.4 (q), 11.8 (q); ir (neat): 1671 (C=O), 1622 (C=C), 1277, 912, 728 cm^{-1}; ms: m/z 152 (M^+), 137 (M^+-CH_3), 96 (M^+-CMeEt), 84 (base), 55.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.69; H, 10.36.

3-(1-Methylbutyl)-2-cyclohexen-1-one (**7c**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 5.82 (1H, br s, 2-H), 2.32 (2H, t, J = 6.6 Hz), 2.27-2.19 (3H, m), 1.92 (2H, quintet, J = 6.2 Hz), 1.48-1.22 (4H, m), 1.03 (3H, d, J = 6.6 Hz, $CHCH_3$), 0.81 (3H, t, J = 6.8 Hz, CH_2CH_3); ^{13}C nmr (deuteriochloroform): δ 200.2 (s, CO),171.1 (s, C3), 125.0 (d, C2), 41.3 (d, MeCH), 37.6 (t), 36.9 (t), 26.9 (t), 22.9 (t), 20.5 (t), 18.8 (q), 14.0 (q); ir (neat): 1670 (C=O), 1621 (C=C), 1288, 800, 708 cm^{-1}; ms: m/z 166 (M^+), 137 (M^+-CH_2CH_3), 124, 96 (M^+-$CMeCH_2CH_2CH_3$), 84 (base), 49.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.23; H, 10.79.

3-(1,2-Dimethylpropyl)-2-cyclohexen-1-one (**7d**).

This compound was obtained as a colorless oil; ^{1}H nmr (deuteriochloroform): 5.84 (1H, br s, 2-H), 2.36 (1H, m, MeCH), 2.24 (2H, t, J = 6 Hz), 2.02-1.88 (4H, m), 1.65 (1H, m, isopropyl CH), 1.04 (3H, d, J = 7 Hz, $CHCH_3$), 0.88 (3H, d, J = 7 Hz, isopropyl CH_3), 0.83 (3H, d, J = 7 Hz, isopropyl CH_3); ^{13}C nmr (deuteriochloroform): δ 199.9 (s, CO), 170.7 (s, C3), 125.8 (d, C2), 48.8 (d, MeCH), 37.7 (t), 31.1 (d, isopropyl CH), 27.4 (t), 22.9 (t), 21.6 (q), 19.5 (q) and 15.8 (q); ir (neat): 1669 (C=O), 1620 (C=C), 1245, 890, 731 cm^{-1}; ms: m/z 166 (M^+), 151 (M^+-CH_3), 148, 124 (base, M^+-CMe_2), 109, 96 (M^+-$CMeCMe_2$), 81, 67, 55, 41.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.69; H, 11.14.

3-(1-Phenylethyl)-2-cyclohexen-1-one (**7e**).

This compound was obtained as a pale yellow oil; ^{1}H nmr (deuteriochloroform): δ 7.36-7.15 (5H, m, phenyl protons), 6.06 (1H, d, J = 2 Hz, 2-H), 3.56 (1H, q, J = 7 Hz, MeCH), 2.36 (2H, m), 2.16 (2H, m), 1.92 (2H, m), 1.44 (3H, d, J = 7 Hz, $CHCH_3$); ^{13}C nmr (deuteriochloroform): δ 220.8 (s, CO), 169.2 (s),143.3 (s), 129.2 (d x 2), 127.9 (d x 2), 127.4 (d), 125.4 (d), 47.4 (d, MeCH), 38.1 (t), 29.0 (t), 23.4 (t) and 19.6 (q, $CHCH_3$); ir (neat): 1669 (C=O), 1620 (C=C), 1581, 1492, 1113, 762, 699 cm^{-1}; ms: m/z 200 (M^+), 185 (M^+-CH_3), 123 (base, M^+-Ph), 108, 93, 78, 65, 41.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.88; H, 8.12.

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