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Highly Regio- and Stereoselective 1,4-Addition Reaction of β-Cyclopropyl-α,β-enones with Organocopper(I)–Aluminum Trichloride

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A highly regio- and stereoselective 1,4-addition reaction of β-cyclopropyl-α,β-enones with an equimolar mixture of organocopper(I) and aluminum trichloride ($RCu-AlCl_3$) is described.

Keywords——cyclopropylenone; conjugate addition; organometallic; stereoselectivity; regioselectivity; organocopper(I)-aluminum trichloride complex

The explosive growth of the literature on 1,4- or 1,6-addition reactions to carbon–carbon multiple bonds of unsaturated carbonyl compounds by organometallics over the past fifteen years has created a growing awareness of their utility to many organic chemists. Although many organometallics involving lithium,[1] boron,[2] aluminum,[3] aluminum–nickel,[4] silicon–titanium,[5] zirconium–nickel,[6] zinc,[7] and gallium[8] undergo the conjugate addition reaction to unsaturated carbonyl compounds, organocopper(I) reagents have received widespread acceptance due to their ease of preparation and their ability to effect the conjugate addition efficiently under mild reaction conditions.[9] Unfortunately, ordinary organocopper(I) reagents such as the Gilman reagent (R_2CuLi) have not been successfully applied for conjugate addition reactions to several types of substrates such as α,β-enoic acids[10] and γ-oxygenated-α,β-unsaturated carbonyl compounds.[11] Furthermore, although β-cyclopropyl-α,β-enones are useful compounds for the study of reaction mechanisms with organocopper(I) reagents,[12c-g] on successful regio- and stereoselective 1,4-addition with organometallics has been reported. Since the possibilities for mechanistically and synthetically useful organocopper(I) reagents have not yet been fully explored,[9] the solution of these problems would be a valuable addition to the arsenal of synthetic methodology. Recently, it has been reported that $RCu-BF_3$,[10] $Me_2CuLi-BF_3$,[13] and $RCu-AlCl_3$[11a] were very useful for conjugate addition reactions, and these reagents were successfully used for the synthesis of natural products.[13-15] In this paper, we present a highly regio- and stereoselective 1,4-addition reaction of β-cyclopropyl-α,β-enones with an equimolar mixture of organocopper(I) and aluminum trichloride ($RCu-AlCl_3$).[11a,16]

Synthesis of β-Cyclopropyl-α,β-enones

Substrates for the present investigation on the conjugate addition reaction were prepared by means of the following procedure.

Reaction of cyclopropyl methyl ketone (**1**) with the sodium salt of triethyl phosphonoacetate gave a 4:1 mixture of the esters (**2**) and (**3**) in 71% yield. Although the two isomers (**2** and **3**) were inseparable by silica gel column chromatography or by spinning band distillation, preparative gas chromatography of the mixture resulted in the separation of the pure enoates (**2**) and (**3**). The stereochemistries of the major product (**2**) and the minor product (**3**) were inferred from the results of a proton nuclear magnetic resonance (^{1}H-NMR) spectral investigation. It is well established that a methyl group attached to the double bond *cis* to the carbonyl function resonates downfield from its *trans* counterpart.[17]

The ^{1}H-NMR pectrum of the major product (**2**) showed the methyl group attached to the double bond at δ 1.98 as a doublet (J=1.5 Hz), whereas the spectrum of the minor compound

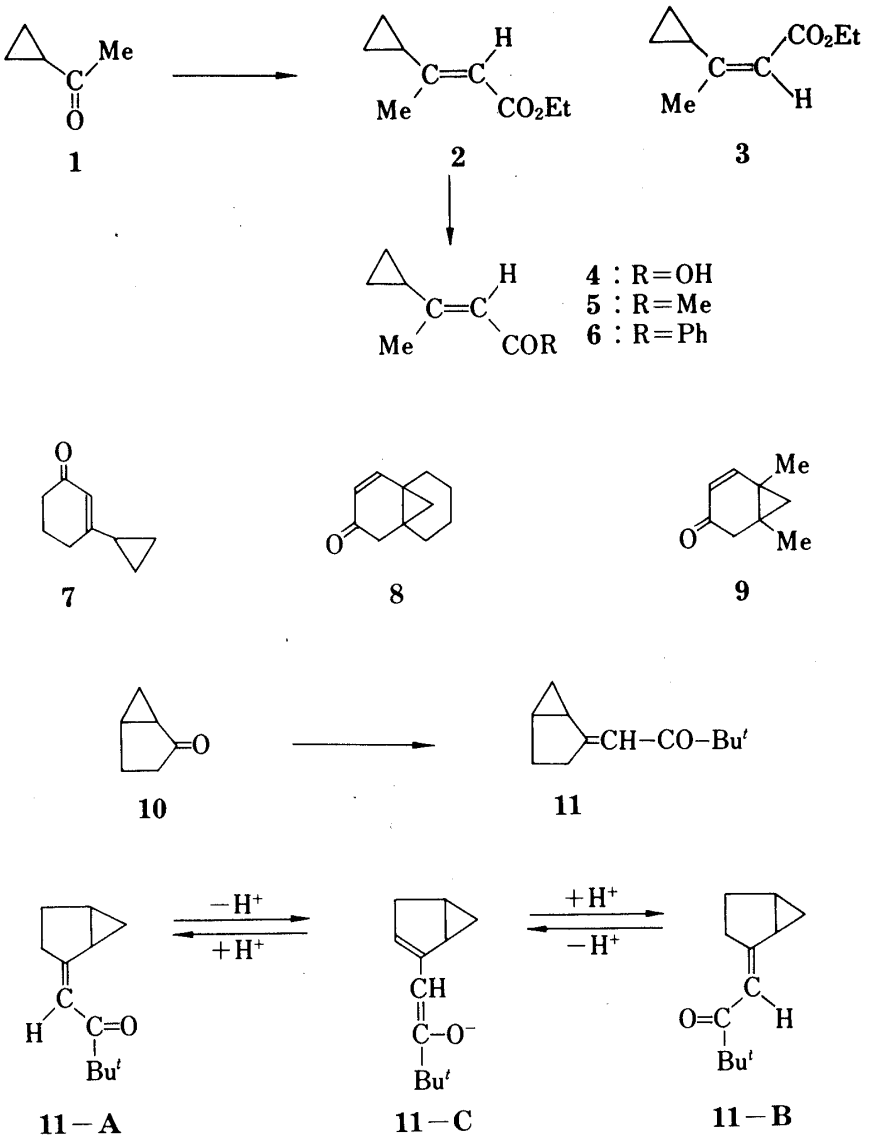


Chart 1

(**3**) revealed the methyl signal at δ 1.50 as a doublet (J=1.5 Hz). From these spectral data, (*E*)- and (*Z*)-configurations were assigned to the major product (**2**) and the minor product (**3**), respectively. Furthermore, the stereochemistry of **3** was ascertained by observation of the nuclear Overhauser effect (*ca.* 9% enhancement of the signal due to the olefinic proton) between the olefinic hydrogen and the methyl group.

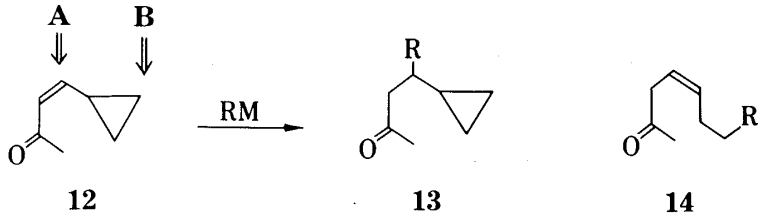
Hydrolysis of **2** gave the acid (**4**), which on treatment with methyllithium and phenyllithium gave the β-cyclopropyl-α,β-enones (**5**) and (**6**), respectively.

The enones (**7**), (**8**), and (**9**) were prepared according to the literature methods.[12b,c,18]

The enone (**11**) was prepared by reacting bicyclo[3.1.0]hexan-2-one (**10**)[19] with the sodium salt of diethyl 2-oxo-3,3-dimethylbutyl phosphonate.[20] The enone (**11**) was a mixture (*ca.* 1:1) of **11-A** and **11-B.** Separation of the mixture was effected by high pressure liquid chromatography (PORASIL column, hexane:ethyl acetate=99:1) to yield the enones (**11-A**) and (**11-B**). However, after removal of the solvent on a rotary evaporator at 18°C, the enones (**11-A**) and (**11-B**) attained equilibrium fairly rapidly presumably *via* an intermediate (**11-C**). Therefore, the enone (**11**) used for the present 1,4-addition reaction is a mixture of stereoisomers.

Reaction of β-Cyclopropyl-α,β-enones with Organocopper(I)–Aluminum Trichloride

The nucleophilic addition of an organometallic reagent (RM) to an enone (**12**) could be expected to form either a normal adduct (**13**) (attack **A**) or a ring-opened product (**14**) (attack **B**). However, it has been reported that β-cyclopropyl-α,β-enone, in which the plane of the cyclopropyl group is held approximately perpendicular to the plane of the enone system, undergoes competitive alkylating ring opening along with conjugate addition on reacting with an ordinary organocopper(I) reagent such as R_2CuLi.[12]



12 **13** **14**

Chart 2

On the other hand, treatment of $RCu–AlCl_3$ with the enones (**5**), (**6**), or (**7**) gave the corresponding 1,4-adduct in a high yield (see Chart 3). In these reactions, we did not detect any cyclopropane ring-opened by-product. Marshall and a collaborator have reported that the enone (**8**) gave a mixture of products involving the 1,4-adducts and the cyclopropane ring-opened products on reacting with Me_2CuLi.[12b] In contrast, reaction of the enone (**8**) with $MeCu–AlCl_3$ and $BuCu–AlCl_3$ gave the 1,4-adducts (**22**) and (**23**), respectively, in high yields. In a similar manner, the Casey system (**9**) gave the 1,4-adduct (**24**) as a sole product. The stereochemistries of **22** and **24** were ascertained by comparison of their infrared (IR) and ^{1}H-NMR spectra with the respective authentic spectra provided by Professors Marshall and Casey. The remarkable difference in reactivity between $MeCu–AlCl_3$ and Me_2CuLi is noteworthy. Thus, Me_2CuLi was rather unreactive to 1,4-addition with the enone (**11**) at −70 to −25°C, whereas $MeCu–AlCl_3$ readily underwent, 1,4-addition to yield the adduct (**25**) as a sole product in a high yield. The stereochemistry of the adduct (**25**) was inferred from the

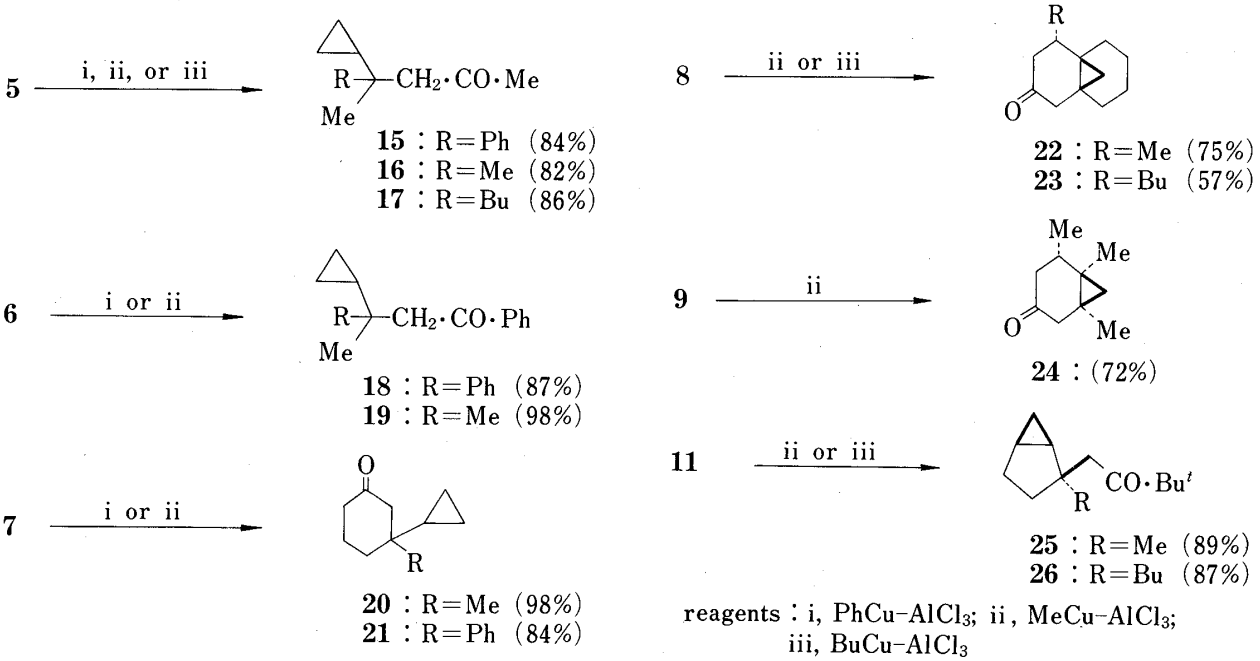


Chart 3

nuclear Overhauser effect between one of the hydrogens of the methylene group of the cyclopropane ring and the methylene hydrogens adjacent to the carbonyl group.

Although the exact reason for the high regioselectivity in the present conjugate addition reactions remains uncertain, the high stereoselectivity of the addition reaction with $RCu-AlCl_3$ is probably a result of 1,4-addition in which $RCu-AlCl_3$ approaches the face of the enone molecule opposite to the cyclopropyl group.

The present methodology for 1,4-addition of β-cyclopropyl-α,β-enones with $RCu-AlCl_3$ has several advantages over the use of the Gilman reagent in terms of the stereo- and regioselectivity, and efficiency.[21]

Experimental

General Methods———All reactions were performed under an argon atmosphere. Melting point was determined on a Yanagimoto melting point apparatus and is uncorrected. The evaporative bulb-to-bulb distillations were done by using a Büchi Kgelrohrofen apparatus at the pressure and the temperature indicated. All IR spectra were recorded on a Shimadzu IR 400 spectrometer. Nominal and accurate mass spectra were recorded on a JEOL JMS-01SG-2 mass spectrometer. All proton magnetic resonance spectra (^{1}H-NMR) were recorded on one of the following spectrometers: JEOL PMX-60, Varian A-60, Varian HA-100 D, and JEOL FX-200. Chemical shifts are quoted in parts per million downfield from internal tetramethylsilane (s=singlet, d=doublet, dd=double doublet, t=triplet, q=quartet, m=multiplet). Elemental analyses were carried out by the Microanalytical Center of Kyoto University. For column chromatographies, silica gel (Mallinckrodt, 100 mesh) was employed. For preparative thin-layer chromatographies, Silica gel GF_{254} (Merck) was used.

Ethyl β-Cyclopropylenoates (2) and (3)———Triethyl phosphonoacetate (107 g, 0.476 mol) was added dropwise to a stirred suspension of sodium hydride (11.5 g, 0.476 mol) in dry ether (200 ml) at 0°C and the mixture was stirred for 1 h. Cyclopropyl methyl ketone (**1**) (40.58 g, 0.476 mol) was added dropwise to the above mixture with stirring at 0°C. Ice-water (200 ml) was added with stirring at 0°C after the mixture had been allowed to stand for 24 h at ambient temperature. The usual work-up led to a yellow oil which was distilled at 80°C (9 mmHg) to give a mixture of **2** and **3** (**2**:**3**=4:1) as a colorless oil (52 g, 71% yield). Separation of the mixture was effected by preparative gas chromatography (Varian aerograph; column, 15% FFAP on Chromosorb W; column temperature, 110°C) to yield the enoates (**2**) and (**3**). **2**, Kugelrohr distillation, 110°C (45 mm Hg). IR ($CHCl_3$): 1701, 1630 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.60—0.85 (4H, m, cyclopropyl methylene protons), 1.25 (3H, t, J=7 Hz, $CO_2CH_2C\underline{H}_3$), 1.98 (3H, d, J=1.5 Hz, CH_3 attached to the double bond), 5.70 (1H, m, olefinic proton). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.83; H, 9.38. **3**, Kugelrohr distillation, 110°C (45 mmHg). IR ($CHCl_3$): 1700, 1625 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.65—0.95 (4H, m, cyclopropyl methylene protons), 1.50 (3H, d, J=1.5 Hz, CH_3 attached to the double bond), 3.24 (1H, m, ), 5.73 (1H, m, olefinic proton). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.38; H, 9.11.

(*E*)-3-Cyclopropyl-2-butenoic Acid (4)———A mixture of **2** (15.4 mg, 0.1 mmol), potassium hydroxide (30 mg), MeOH (5 ml), and water (1 ml) was heated at 60°C for 2 h. The residual semisolid obtained from the solution by evaporation of the solvent was made acidic with 5% HCl at 0°C, and the solution was extracted with $CHCl_3$. Removal of the solvent gave the acid (**4**) (6.4 mg, 51% yield) as a crystalline mass. Recrystallization from hexane-CH_2Cl_2 (9:1) gave colorless crystals. mp 102—104°C. IR ($CHCl_3$): 2200—3500, 1683, 1625 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.67—0.93 (4H, m, cyclopropyl methylene protons), 1.56 (1H, m, ), 1.99 (3H, d, J=1.2 Hz, CH_3 attached to the double bond), 5.70 (1H, m, olefinic proton), 8.77 (1H, broad s, OH). *Anal.* Calcd for $C_7H_{10}O_2$: C, 66.64: H, 7.99. Found: C, 66.88; H, 8.11.

The Enone (5)———Ethereal methyllithium (22 ml, 15 mmol) was added dropwise to a stirred solution of **4** (473 mg, 3.75 mmol) in 35 ml of a mixture of hexane-ether (2:5) with stirring at 0°C, and the whole was stirred for 3 h. The reaction mixture was poured into a mixture of NH_4Cl (3 g), water (30 ml), and ice (10 g) under stirring. The mixture was extracted with ether, and the ethereal layer was successively washed with 5% sodium thiosulfate, 5% sodium bicarbonate, and water. The organic layer was dried and concentrated to leave an oily residue. Kugelrohr distillation at 110°C (25 mmHg) gave the enone (**5**) (252 mg, 54% yield) as a colorless oil. IR ($CHCl_3$): 1673, 1597 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.63—0.93 (4H, m, cyclopropyl methylene protons), 1.50 (1H, m, ), 1.93 (3H, d, J=1.2 Hz, CH_3 attached to the double bond), 2.13 (3H, s, $COCH_3$), 6.12 (1H, m, olefinic proton). *Anal.* Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 76.59; H, 9.95. MS m/z Calcd for $C_8H_{12}O$: 124.0880. Found: 124.0891.

The Enone (6)———The enone (**6**) was prepared from **4** in 15% yield by a procedure similar to the preparation of **5** but using ethereal phenyllithium instead of methyllithium. IR ($CHCl_3$): 1653, 1593 cm^{-1}

^{1}H-NMR ($CDCl_3$) δ: 0.86—1.05 (4H, m, cyclopropyl methylene protons), 1.66 (1H, m, ), 2.02 (3H, d, J=1.2 Hz, CH_3 attached to the double bond), 6.8 (1H, m, olefinic proton), 7.33—8.10 (5H, m, phenyl group). *Anal.* Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.83; H, 7.61.

The Enone (11)———Diethyl 2-oxo-3,3-dimethylbutyl phosphonate[20] (5.17 g, 21.9 mmol) was added dropwise to a stirred suspension of sodium hydride (490 mg, 20.4 mmol) in dimethoxyethane (15 ml) at 0°C with stirring, and the mixture was stirred for 45 min. Then, bicyclo[3.2.1]hexan-2-one (**10**) (700 mg, 7.3 mmol) was added to the above mixture, and the whole was refluxed for 8 h. The usual work-up of the reaction mixture led to a yellow oil which was purified by silica gel column chromatography with hexane–$CHCl_3$ (1:1) to give the enone (**11**). Kugelrohr distillation at 90—95°C (2 mmHg) gave the enone (**11**) as a colorless oil (733 mg, 55% yield). Gas chromatographic analysis (1.5% FFAP on chromosorb W, glass column (2 m), 120°C) revealed that the enone (**11**) was a mixture (*ca.* 1:1) of stereoisomers. IR ($CHCl_3$): 1672, 1605 cm^{-1}. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.61; H, 10.47.

General Procedure for 1,4-Addition Reaction with Organocopper(I)–Aluminum Trichloride———The following procedure for the 1,4-addition is typical. A solution of $AlCl_3$ (2.8 mmol) in dry ether (2 ml) was added dropwise to a stirred suspension of MeCu (2.8 mmol) in dry ether (10 ml) under an argon atmosphere at −70°C, and the mixture was stirred for 1 h. The enone (**11**) (100 mg, 0.56 mmol) in dry ether (6 ml) was added dropwise to the above mixture with stirring at −70°C, and the temperature of the mixture was allowed to rise to −40°C. After the usual work-up, the product was purified by silica gel column chromatography or preparative silica gel TLC with $CHCl_3$ to give the adduct (**25**) (96 mg, 89% yield). All 1,4-addition reactions were carried out following the general procedure described above, and physical and spectral data of 1,4-adducts are presented below.

The Methyl Ketone (15)———Purification by preparative TLC with hexane–$CHCl_3$ (7:3), followed by Kugelrohr distillation of the product at 110°C (4 mmHg) gave the ketone (**15**) (84% yield) as a colorless oil. IR ($CHCl_3$): 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.20—0.65 (4H, m, cyclopropyl methylene protons), 1.20 (3H, s, CH_3), 1.87 (3H, s, $COCH_3$), 2.70 (1H, d, J=14 Hz, COC(H)H–), 2.96 (1H, d, J=14 Hz, COC(H)H–), 7.10—7.56 (5H, m, phenyl). *Anal.* Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.82; H, 9.03.

The Methyl Ketone (16)———Kugelrohr distillation of the product at 90°C (2 mmHg) gave the ketone (**16**) (82% yield) as a colorless oil. IR ($CHCl_3$): 1703 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.10—0.40 (4H, m, cyclopropyl methylene protons), 0.87 (6H, s, CH_3×2), 2.16 (3H, s, $COCH_3$), 2.37 (2H, s, $COCH_2$). MS m/z Calcd for $C_9H_{16}O$: 140.1201. Found: 140.1209.

The Methyl Ketone (17)———Purification by chromatography on a short silica gel column with hexane–$CHCl_3$ (1:1), followed by Kugelrohr distillation of the product at 90°C (10 mmHg) gave the ketone (**17**, 86% yield) as a colorless oil. IR ($CHCl_3$): 1705 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.13—0.43 (4H, m, cyclopropyl methylene protons), 0.65 (3H, s, CH_3), 0.88 (3H, tripletoid m, CH_3), 2.13 (3H, s, $COCH_3$), 2.33 (2H, s, $COCH_2$). *Anal.* Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.88; H, 12.39.

The Phenyl Ketone (18)———Purification by preparative TLC with hexane–$CHCl_3$ (2:1), followed by Kugelrohr distillation of the product at 145°C (2 mmHg) gave the ketone (**18**) (87% yield) as a colorless oil. IR ($CHCl_3$): 1680 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.16—0.50 (4H, m, cyclopropyl methylene protons), 1.22 (3H, s, CH_3), 3.42 (2H, s, $COCH_2$), 7.00—7.93 (10H, m, phenyl×2). *Anal.* Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.07; H, 7.73.

The Phenyl Ketone (19)———Purification by preparative TLC with $CHCl_3$, followed by Kugelrohr distillation of the product gave the ketone (**19**) (98% yield) as a colorless oil. IR ($CHCl_3$): 1675 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.16—0.36 (4H, m, cyclopropyl methylene protons), 0.90 (6H, s, CH_3×2), 2.92 (2H, s, $COCH_2$), 7.30—8.10 (5H, m, phenyl). *Anal.* Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.78; H, 9.11. MS m/z Calcd for $C_{14}H_{18}O$: 202.1355. Found: 202.1353.

The Ketone (20)———Purification by preparative TLC with $CHCl_3$, followed by Kugelrohr distillation of the product at 60°C (5 mmHg) gave the ketone (**20**) (98% yield) as a colorless oil. IR ($CHCl_3$): 1705 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.13—0.47 (4H, m, cyclopropyl methylene protons), 0.73 (1H, m, ), 0.77 (3H, s, CH_3). *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.03; H, 10.81.

The Phenyl Ketone (21)———Purification by chromatography on a short silica gel column with $CHCl_3$–hexane (7:3), followed by Kugelrohr distillation of the product at 140°C (1 mmHg) gave the ketone (**21**) (84% yield) as a colorless oil. IR ($CHCl_3$): 1704 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.17—0.57 (4H, m, cyclopropyl methylene protons), 1.00 (1H, m, ), 7.23 (5H, m, phenyl). *Anal.* Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.13; H, 8.57.

The Methyl Ketone (22)———Purification by chromatography on a silica gel column with $CHCl_3$–hexane (3:7), followed by Kugelrohr distillation of the product at 90°C (1 mmHg) gave the ketone (**22**) (75% yield) as a colorless oil. IR ($CHCl_3$): 1703 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.44 (1H, dd, J=6 and 1.2 Hz, one of the cyclopropyl methylene protons), 0.66 (1H, d, J=6 Hz, the other cyclopropyl methylene protons), 1.10 (3H, d, J=7 Hz, CH_3), 2.62 (1H, d, J=17.5 Hz, COC(H)H–), 2.42 (1H, dd, J=17.5 and 1.2 Hz, COC(H)H–). MS

m/z Calcd for $C_{12}H_{18}O$: 178.1357. Found: 178.1370.

The Butyl Ketone (23)———Purification by chromatography on a short silica gel column with hexane–$CHCl_3$ (7:3) gave the ketone (**23**) (57% yield) as a colorless oil. IR ($CHCl_3$): 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.46 (1H, d, J=5.5 Hz, one of the cyclopropyl methylene protons), 0.62 (1H, d, J=5.5 Hz, the other cyclopropyl methylene protons), 0.90 (3H, tripletoid m, CH_3). MS *m/z* Calcd for $C_{15}H_{24}O$: 220.1824. Found: 220.1821.

The Methyl Ketone (24)———Purification by silica gel column chromatography with $CHCl_3$–hexane (7:3) followed by Kugelrohr distillation of the product at 30—40°C (3 mmHg) gave the ketone (**24**) (72% yield) as a colorless oil. IR ($CHCl_3$): 1703 cm^{-1}. The ^{1}H-NMR spectrum (in $CDCl_3$ 200 MHz) of **24** was identical with that of an authentic spectrum provided by Professor Casey.[12c] MS *m/z* Calcd for $C_{10}H_{16}O$: 152.1202. Found: 152.1207.

The Methyl Ketone (25)———Purification by silica gel column chromatography with $CHCl_3$, followed by Kugelrohr distillation of the product at 105—110°C (4 mmHg) gave the ketone (**25**) (89% yield) as a colorless oil. IR ($CHCl_3$): 1703 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.06 (1H, m, one of the cyclopropyl methylene protons), 0.25 (1H, m, the other cyclopropyl methylene protons), 1.04 (3H, s, CH_3), 1.13 (9H, s, *tert*-Bu), 2.54 (2H, s, $COCH_2$). *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.62; H, 11.29.

The Butyl Ketone (26)———Purification by silica gel column chromatography with $CHCl_3$–hexane (1:4), followed by Kugelrohr distillation gave the ketone (**26**) (87% yield) as a colorless oil. IR ($CHCl_3$): 1704 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.04 (1H, m, one of the cyclopropyl methylene protons), 0.25 (1H, m, the other cyclopropyl methylene protons), 0.88 (3H, t, J=7 Hz, CH_3), 1.13 (9H, s, *tert*-Bu), 2.53 (2H, s, $COCH_2$). MS *m/z* Calcd for $C_{16}H_{28}O$: 236.2140. Found: 236.2140.

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