products observed in etherification of tertiary alkyl alcohols.

Experimental Section[12]

Typical Procedure for Preparation of Acyclic Ethers. To a stirred solution of α-methylbenzyl alcohol (245 mg, 2.0 mmol) in dichloroethane (10 mL) at room temperature was added anhydrous zinc chloride (270 mg, 2.0 mmol). The reaction mixture was stirred at room temperature for 4 h, diluted with dichloromethane (30 mL), and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was distilled with a Kugelrohr apparatus to afford bis(α-methylbenzyl) ether (206 mg, 91%) as a colorless oil. The spectral data and boiling point were identical with those of reported data.

Typical Procedure for Preparation of Cyclic Ethers. To a stirred solution of 1-phenyl-1,5-pentanediol (182 mg, 1.0 mmol) in dichloroethane (20 mL) at room temperature was added zinc chloride (135 mg, 1.0 mmol), and the reaction mixture was stirred at 80 °C for 2.5 h. The usual workup and distillation with a Kugelrohr apparatus gave 2-phenyltetrahydropyran (136 mg, 84%). The spectral data[13] and boiling point were in agreement with reported data.

Acknowledgment. This investigation was supported in part by a grant from the Korea Science and Engineering Foundation. We are grateful to Sung Soo Kim for the experimental assistance.

Registry No. $PhCH(Me)OH$, 98-85-1; Ph_2CHOH, 91-01-0; $PhCH_2OH$, 100-51-6; *p*-$MeOC_6H_4CH_2OH$, 105-13-5; EtOH, 64-17-5; $CH_2{=}CHCH_2OH$, 107-18-6; $PhCH(OH)(CH_2)_3OH$, 4850-50-4; $PhCH(OH)(CH_2)_4OH$, 1011-61-6; $PhCH(OH)(CH_2)_{10}OH$, 109217-58-5; $PhCH{=}CHCH(OH)(CH_2)_4OH$, 17303-68-3; *i*-$BuC(OH)(Me)(CH_2)_4OH$, 109217-59-6; $PhCH(Me)OCH(Me)Ph$, 93-96-9; $Ph_2CHOCHPh_2$, 574-42-5; $PhCH_2OCH_2Ph$, 103-50-4; *p*-$MeOC_6H_4CH_2OCH_2C_6H_4$-*p*-OMe, 5405-95-8; $PhCH(Me)OEt$, 3299-05-6; $PhCH(Me)OCh_2Ph$, 2040-37-1; $PhCH(Me)OCH_2CH{=}CH_2$, 27122-63-0; $\overline{\mathrm{CH(Ph)(CH_2)_3O}}$, 16133-83-8; $\overline{\mathrm{CH(Ph)(CH_2)_4O}}$, 4203-44-5; $\overline{\mathrm{CH(Ph)(CH_2)_{10}O}}$, 109217-60-9; $\mathrm{PhCH{=}CH}\overline{\mathrm{CH(CH_2)_4O}}$, 70028-17-0; *i*-$\mathrm{Bu}\overline{\mathrm{C(Me)(CH_2)_4O}}$, 109217-61-0; 2-cyclohexen-1-ol, 822-67-3; 1-hydroxy-1-cyclohexanepropanol, 6963-45-7; di(2-cyclohexenyl) ether, 15129-33-6; 1-oxaspiro[4.5]decane, 176-91-0.

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[12] ^1H NMR spectra were recorded in $CDCl_3$ with a Varian T-60A or FT-80A spectrometer, and chemical shifts are expressed as δ units relative to tetramethylsilane. Coupling constants are given in hertz. Infrared spectra were measured as a neat film or KBr pellets on a Perkim-Elmer 267 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5895A spectrometer. Melting points were taken on an Electrothermal apparatus, and reported boiling points are those observed during distillation with a Kugelrohr apparatus.

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Synthesis of α-Iodo Ketones

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A number of methods for the direct and indirect preparation of α-iodo ketone from the ketones, enol acetates, and enol silyl ethers have been reported.[1] Although methods such as lead tetraacetate/metal iodide,[2] pyridinium chlorochromate/iodine,[3] silver acetate/iodine,[4] thallium(I) acetate/iodine,[5] and electrolysis[6] represent significant advances, new and efficient methods for the preparation of α-iodo ketones are still desirable. Recently, during our study of natural products synthesis, we discovered a convenient new procedure for the preparation of α-iodo ketones from the ketones or enol silyl ethers under mild reaction conditions.

Results and Discussion

Treatment of cyclohexanone (**1**) with trimethylsilyl iodide/hexamethyldisilazane[7] followed by *m*–chloroperbenzoic acid (MCPBA) oxidation afforded 2-iodo-1-cyclohexanone (**5**) cleanly. Apparently, trimethylsilyl iodide/hexamethyldisilazane reacted with cyclohexanone to give the enol silyl ether (**2**) and hexamethyldisilazane hydroiodide salt (**3**). Treatment of the reaction mixture with MCPBA oxidized the iodide ion to an "I^+" species which reacted with the enol silyl ether to give the α-iodo ketone upon aqueous workup, presumably via intermediate **4** as shown in Scheme I. Addition of sodium iodide to the reaction mixture before the treatment with MCPBA increased the yield of α-iodo ketone by 10–20% (Table I).

Alternatively, performed enol silyl ethers could be treated sequentially with sodium iodide and then MCPBA to give α-iodo ketones in slightly lower yields (see Table II). In contrast, it has been reported that direct treatment of ketone enolate or enol silyl ether with molecular iodine does not give useful yield of iodo ketones.[4] Additionally, we also found that enamine **19** (Table II) could also be treated with NaI/MCPBA followed by hydrolysis to give α-iodo ketone **5**. With the enol silyl ethers of the aromatic ketones **17** and **18**, only the α-iodo ketones **21**[9] and **22** were obtained. Ring iodination reaction did not occur by this procedure.

In summary, we have discovered a convenient procedure for the preparation of α-iodo ketones. This method is complementary to the existing procedures and sometimes could be the method of choice because of its simplicity and high yield.

Experimental Section

General experimental conditions and instruments used in analyses were identical with those described in our earlier work.[8] *m*-Chloroperbenzoic acid and hexamethyldisilazane were purchased from Aldrich Co. All the known iodo ketones were identified by comparison of their IR, ^1H NMR, and MS spectra with the published data.

General Procedures for the Preparation of α-Iodo Ketones from Ketones. To a solution of ketone (1 mmol) in dry dichloromethane (5 mL) was added hexamethyldisilazane (1.2 mmol), and then trimethylsilyl iodide (1.1 mmol) was added dropwise at 0 °C. A solution of sodium iodide (1.0 mmol) in THF (3 mL) was then added. To this reaction mixture was added dropwise a solution of MCPBA (1.2 mmol) in dry CH_2Cl_2 (3 mL) at 0 °C, and the reaction was stirred for 10 min. The reaction solution was diluted with ether (50 mL), washed with 10% HCl (5 mL), saturated sodium thiosulfate solution (10 mL), and

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Scheme I

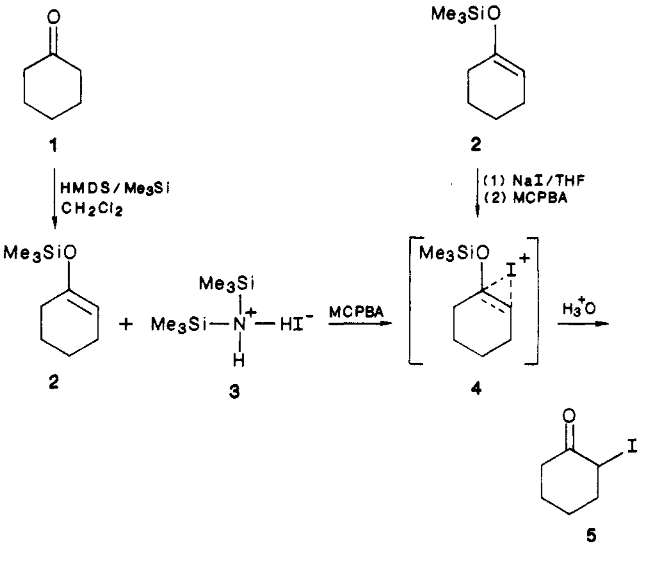
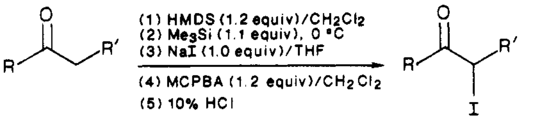


Table I



ketone	α-iodo ketone	isolated yield, %	ref
cyclohexanone (1)	2-iodo-1-cyclohexanone (5)	84	3
cyclopentanone (6)	2-iodo-1-cyclopentanone (10)	83	4b
4-methyl-2-pentanone (7)	1-iodo-4-methyl-2-pentanone (11) 3-iodo-4-methyl-2-pentanone (12)	11/12 = 1/4 84	
2-heptanone (8)	1-iodo-2-heptanone (13) 3-iodo-2-heptanone (14)	13/14 = 1/20 89	5
2,6-dimethyl-1-cyclohexanone (9)	2,6-dimethyl-2-iodo-1-cyclohexanone (15)	87	

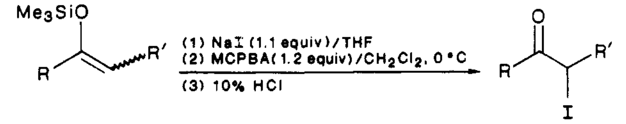
saturated sodium bicarbonate (10 mL), and then dried with anhydrous sodium sulfate. Concentrations and silica gel chromatography gave α-iodo ketones as the products. See Table I for yields.

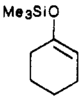
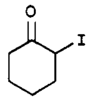
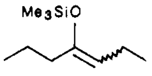
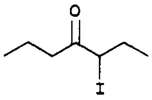
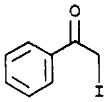
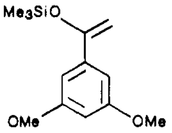
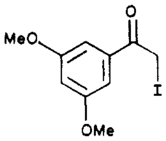
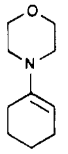
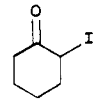
General Procedures for the Preparation of α-Iodo Ketones from Enol Silyl Ethers. To a solution of enol silyl ether (1 mmol) and sodium iodide (1.1 mmol) in THF (10 mL) was added dropwise a solution of MCPBA (1.2 mmol) in dry dichloromethane (3 mL) at 0 °C. The reaction mixture was stirred for 5 min, then diluted with ether (50 mL), and washed with 10% hydrochloric acid (10 mL), saturated sodium thiosulfate (10 mL), saturated sodium carbonate (2 × 10 mL), and then brine (10 mL). The organic layer was dried with anhydrous magnesium sulfate and concentrated. Silica gel chromatography gave α-iodo ketones as the products. See Table II for yields.

Data for the mixture of 1-iodo-4-methyl-2-pentanone (11) and 3-iodo-4-methyl-2-pentanone (12): IR (neat) 1715 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) [peaks for 11] δ 0.92 (d, J = 6.6 Hz, 6 H), 2.09–2.19 (m, 1 H), 2.58 (d, J = 7.1 Hz, 2 H), 3.76 (s, 2 H), [peaks for 12] δ 0.97 (d, J = 6.6 Hz, 3 H), 1.12 (d, J = 6.6 Hz, 3 H), 1.96–2.04 (m, 1 H), 2.39 (s, 3 H), 4.23 (d, J = 9.1 Hz, 1 H); ratio of 11/12 = 1/4; MS, m/e (relative intensity) 226 (M$^+$, 21), 167 (12), 156 (20), 99 (47), 85 (33), 43 (100); high-resolution mass spectrum, exact mass calcd for $C_6H_{11}IO$ (M$^+$) 225.9855, found 225.9892.

Data for 2-iodo-2,6-dimethylcyclohexanone (15): IR (CHCl$_3$) 1700 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.03 (d, J = 4.4 Hz, 3 H), 1.26–1.37 (m, 2 H), 1.80–1.85 (m, 1 H), 2.01–2.14 (m, 2 H), 2.06 (s, 3 H), 2.26–2.31 (m, 1 H), 3.63–3.72 (m, 1 H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 14.87 (q), 24.01 (t), 31.74 (q), 35.95 (t), 38.92 (d), 46.38 (t), 50.43 (s), 207.4 (s); MS, m/e (relative intensity) 252 (M$^+$, 13), 125 (100), 97 (51), 69 (10), 55 (73); high-resolution mass spectrum, exact mass calcd for $C_8H_{13}IO$ (M$^+$) 252.0012, found 252.0029.

Table II



enol ether	α-iodo ketone	isolated yield, %	ref
 2	 5	80	3
 16	 20	82	3
 17	 21	90	9
 18	 22	81	
 19	 5	69	3

Data for 2-iodo-1-(3,5-dimethoxyphenyl)ethanone (22): IR (CHCl$_3$) 1710 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.82 (s, 6 H), 4.31 (s, 2 H), 6.65 (t, J = 2.3 Hz, 1 H), 7.09 (d, J = 2.3 Hz, 2 H); MS, m/e (relative intensity) 306 (M$^+$, 90), 180 (25), 165 (100); high-resolution mass spectrum, exact mass calcd for $C_{10}H_{11}IO_3$ (M$^+$) 305.9753, found 305.9785.

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Registry No. 1, 108-94-1; 2, 6651-36-1; 5, 35365-19-6; 6, 120-92-3; 7, 108-10-1; 8, 110-43-0; 9, 2816-57-1; 10, 69381-32-4; 11, 109125-18-0; 12, 109125-19-1; 13, 66446-96-6; 14, 2033-49-0; 15, 109125-20-4; 16, 63547-54-6; 17, 13735-81-4; 18, 109125-22-6; 19, 670-80-4; 20, 85515-53-3; 21, 4636-16-2; 22, 109125-21-5.

A Convenient Method for the Stereoselective Synthesis of 3-Phenyl-1-alkynes

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In connection with our studies directed to the synthesis of optically active materials from chiral acetylenes,[1] we are