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Articles

Direct and Regiocontrolled Synthesis of α-Phenyl Ketones from Silyl Enol Ethers and Diphenyliodonium Fluoride

Kuanchiang Chen and Gerald F. Koser*

Department of Chemistry, The University of Akron, Akron, Ohio 44325

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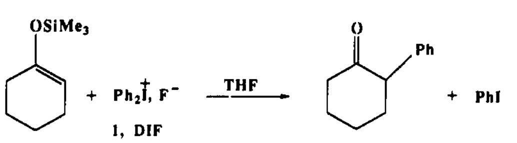
The efficacy of diphenyliodonium fluoride (1, DIF) for the phenylation of silyl enol ethers was investigated. When the silyl enol ethers of cyclopentanone, 2-methylcyclopentanone, cyclohexanone, 2-methylcyclohexanone, acetophenone, 2-pentanone, diisopropyl ketone, and pinacolone were mixed with DIF in tetrahydrofuran, either α-phenyl or α,α-diphenyl ketones were produced and isolated in yields ranging from 20 to 88%. That the regiochemistry of α-phenylation can be controlled by an appropriate choice of silyl enol ether was demonstrated with the kinetic and thermodynamic silyl enol ethers of 2-methylcyclohexanone, the thermodynamic silyl enol ether of 2-methylcyclopentanone, and the kinetic silyl enol ether of 2-pentanone. 3,3-Dimethyl-2-(silyloxy)-1-butene gave a dehydro dimer of pinacolone with DIF in addition to α-phenylpinacolone, thus suggesting that phenylations of silyl enol ethers with DIF may proceed via radical intermediates.

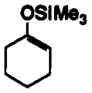
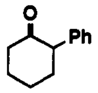
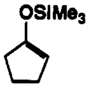
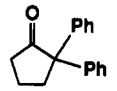
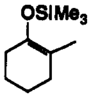
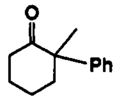
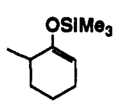
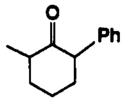
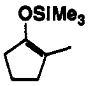
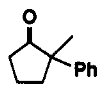
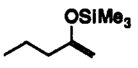
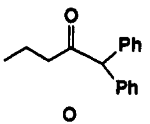
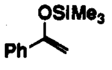
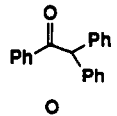
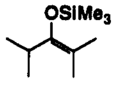
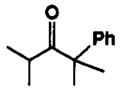
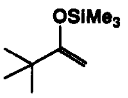
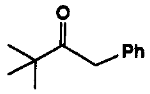
Mono- and/or diarylations of β-dicarbonyl compounds (via their enolates) with diaryliodonium salts (Ar_2I^+, X^-; $X^- = Cl^-, Br^-, I^-$) have been amply demonstrated.[1,2] However, similar arylations of unactivated ketones are restricted to the phenylation of several aryl alkyl ketones with diphenyliodonium chloride in the presence of tertiary alkoxides.[3] In an effort to generalize the iodonium salt method for the α-phenylation of ketones and to achieve regiochemical control under mild conditions, we investigated the treatment of silyl enol ethers with diphenyliodonium fluoride (1, DIF). Although DIF has been known since 1946 and can be obtained as the *anhydrous* salt,[4] it has apparently not yet been employed as a synthetic reagent. We now report that cyclic and acyclic silyl enol ethers react with DIF to give ether α-phenyl or α,α-diphenyl ketones, depending on the structure of the substrate.

In a typical experiment, a solution of 1-[(trimethylsilyl)oxy]cyclohexene (10.1 mmol) in THF was added to a mixture of DIF (5.0 mmol) in THF at ca. −40 °C. The reaction mixture was stirred under nitrogen and allowed to warm gradually to room temperature. During that time, the *insoluble* DIF was consumed, and a clear solution resulted. After preliminary workup, an oil was obtained from which 2-phenylcyclohexanone was separated (column chromatography, silica gel) in 88% yield (eq 1). Little or no 2,2-diphenylcyclohexanone was produced.[5]



(1)

Table I. Major Products of Phenylation from Reactions of Silyl Enol Ethers with Diphenyliodonium Fluoride

silyl enol ether	product	% yield[a]
		88
		51[b]
		77
		78
		45
		24[b]
		47[b]
		20
		37

[a] Yields of isolated products. [b] Based on the assumption that 2 mol of DIF are required to give 1 mol of product.

Similar reactions of a variety of silyl enol ethers with DIF were conducted, the results of which are summarized

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[1] (a) Beringer, F. M.; Forgione, P. S.; Yudis, M. D. *Tetrahedron* **1960**, *8*, 49. (b) Beringer, F. M.; Galton, S. A.; Huang, S. J. *J. Am. Chem. Soc.* **1962**, *84*, 2819. (c) Beringer, F. M.; Forgione, P. S. *Tetrahedron* **1963**, *19*, 739. (d) Beringer, F. M.; Forgione, P. S. *J. Org. Chem.* **1963**, *28*, 714. (e) Chen, Z.-C.; Jin, Y.-Y.; Stang, P. J. *J. Org. Chem.* **1987**, *52*, 4115.

[2] For the phenylation of β-diketones (via their dianions) at γ-carbon with diphenyliodonium chloride in liquid ammonia, see: Hampton, K. G.; Harris, T. M.; Hauser, C. R. *J. Org. Chem.* **1964**, *29*, 3511.

[3] Beringer, F. M.; Daniel, W. J.; Galton, S. A.; Rubin, G. *J. Org. Chem.* **1966**, *31*, 4315.

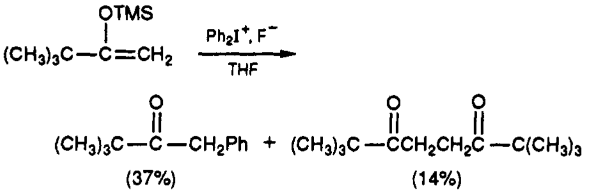
[4] Emeléus, H. J.; Heal, H. G. *J. Chem. Soc.* **1946**, 1126.

0022-3263/91/1956-5764$02.50/0

in Table I.

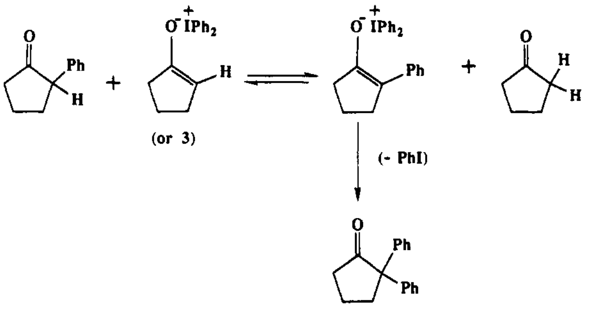
The reaction of 1-[(trimethylsilyl)oxy]cyclopentene with DIF provides an interesting contrast to that of the cyclohexene homologue. In this case, 2,2-diphenylcyclopentanone was isolated in 51% yield and only a trace of the monophenyl ketone was produced. Diphenylation was also dominant in the reactions of the silyl enol ethers of acetophenone and 2-pentanone with DIF. However, when DIF was added to 1-[(trimethylsilyl)oxy]-1-phenylethene (reverse mode of addition) under *homogeneous* conditions in CH_2Cl_2, monophenylation was competitive, and a 1.7/1.0 molar mixture of α,α-diphenylacetophenone and deoxybenzoin was obtained. The regiochemistry of phenylation at α-carbon can be controlled by an appropriate choice of silyl enol ether. This was demonstrated by the treatment of 2-methyl- and 6-methyl-1-[(trimethylsilyl)oxy]cyclohexenes, the kinetic silyl enol ether of 2-pentanone, and the thermodynamic silyl enol ether of 2-methylcyclopentanone with DIF.

Although a polar mechanism for these reactions involving the initial production of diphenyliodonium enolates **2** followed by S_NAr phenylation of the enolate ions by the iodonium ion can be envisioned, the diphenyliodonium ion does not bear substituents (e.g., $-NO_2$ etc.) typically associated with the stabilization of Meisenheimer intermediates. An alternative mechanism involving the intermediate formation of tricovalent iodine adducts **4** and/or **5** is suggested (Scheme I). Homolytic decomposition of **4** and/or **5** to give an enol radical and the diphenyliodine radical, presumably in a solvent cage, and subsequent formal transfer of the phenyl radical from the latter to the former (at carbon) would give iodobenzene and the α-phenyl ketone. Analogy for this mechanism is provided by the known synthesis of triphenyliodine (Ph_3I) from diphenyliodonium chloride and phenyllithium at −80 °C and its decomposition at −10 °C to iodobenzene and biphenyl.[6] That enolic radicals can be produced and escape the solvent cage, at least with bulky substrates, is indicated by the iolation of 2,2,4,4-tetramethyl-3,6-octanedione in 14% yield along with the expected α-phenyl ketone when 3,3-dimethyl-2-[(trimethylsilyl)oxy]-1-butene was allowed to react with DIF (eq 2). It is recognized, of course, that the production of free radicals can also be accounted for by single electron-transfer from enolate ions to iodonium ions within ion pairs such as **2**.[7]



$$(CH_3)_3C-\overset{\overset{OTMS}{|}}{C}=CH_2 \xrightarrow[THF]{Ph_2I^+,\,F^-} \underset{(37\%)}{(CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_2Ph} + \underset{(14\%)}{(CH_3)_3C-\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}-C(CH_3)_3} \quad (2)$$

Whether onium enolates versus onium fluorosiliconates are generated in reactions of onium fluorides with silyl enol ethers has been a matter of some debate.[8] Thus, it is not clear if tricovalent iodine(III) intermediates such as **4** and **5** would originate from iodonium enolates **2** or iodonium enolfluorosiliconates **3**. In any event, it seems likely that the production of 2,2-diphenylcyclopentanone from 1-[(trimethylsilyl)oxy]cyclopentene and DIF proceeds in stepwise fashion via 2-phenylcyclopentanone and that the second phenylation would require the presence of 2-phenylcyclopentanone enolate. Either the enolate ion in **2** or the enolfluorosiliconate ion in **3**, present simultaneously with 2-phenylcyclopentanone, might function as the base for the deprotonation step (eq 3).



(3)

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Elemental analyses were performed by Midwest Microlab, LTD (Indianapolis, IN). Melting points are uncorrected.

The times given for reactions of silyl enol ethers with diphenyliodonium fluoride are estimated from the *beginning* of dropwise additions. Such reactions proceeded with the initial development of yellow color. Reaction temperatures refer to bath temperatures (e.g., dry ice/MeCN, surrounding air) and not to direct measurements on reaction mixtures. Those products isolated by column chromatography generally appeared by ^1H NMR analysis to be of reasonably high purity (probably ≥95% by weight in most cases).

Starting Materials. Except for 1-phenyl-1-[(trimethylsilyl)oxy]ethylene (purchased), the silyl enol ethers were prepared by literature methods. The silyl enol ethers of cyclopentanone, cyclohexanone, diisopropyl ketone, and *tert*-butyl methyl ketone and the kinetic silyl enol ethers of 2-pentanone, 2-methylcyclopentanone, and 2-methylcyclohexanone were made by the sequential treatment of the ketones with LDA and trimethylsilyl chloride in THF.[9a] The thermodynamic silyl enol ethers of 2-methylcyclopentanone and 2-methylcyclohexanone were prepared from the ketones with triethylamine and trimethylsilyl chloride in DMF under reflux.[9a,b] Molar ratios of silyl enol ether regioisomers were estimated from relative line intensities of their $-SiMe_3$ resonances in ^1H NMR spectra.

Diphenyliodonium Fluoride (DIF). Ag_2O (24.6 g, 0.106 mol) was added portionwise to a heterogeneous mixture of diphenyliodonium iodide (50 g, 0.124 mol)[10] in H_2O (200 mL) at 0 °C. The reaction mixture was allowed to stir for 4 h at 0 °C and for 9 h at room temperature. The insoluble material (AgI, excess Ag_2O) was then removed by filtration and washed with H_2O. The filtrate and washings were combined, cooled below 5 °C, spiked with phenolphthalein (5 drops, 0.05%), and acidified with 10% aqueous HF. Concentration of the acidified solution on a rotary evaporator at 50 °C gave crude diphenyliodonium fluoride as a pale yellow solid. The crude iodonium salt was initially recrystallized from 200 mL of hot acetone. The large crystals and mother liquor together were concentrated to ca. half-volume on a rotary evaporator, the mechanical action converting the crystalline phase to a powder. Refrigeration and vacuum filtration gave diphenyliodonium fluoride as a white solid: yield, 23.53 g (63%); mp 79–102 °C (lit.[4] mp 85 °C dec and 110 °C dec).

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(5) In one experiment in which the molar ratio of silyl enol ether to DIF was about 1:1, 2,2-diphenylcyclohexanone was isolated in 4–5% yield (see the Experimental Section).

(6) Wittig, G.; Rieber, M. *Ann. Chem.* **1949**, *562*, 187.

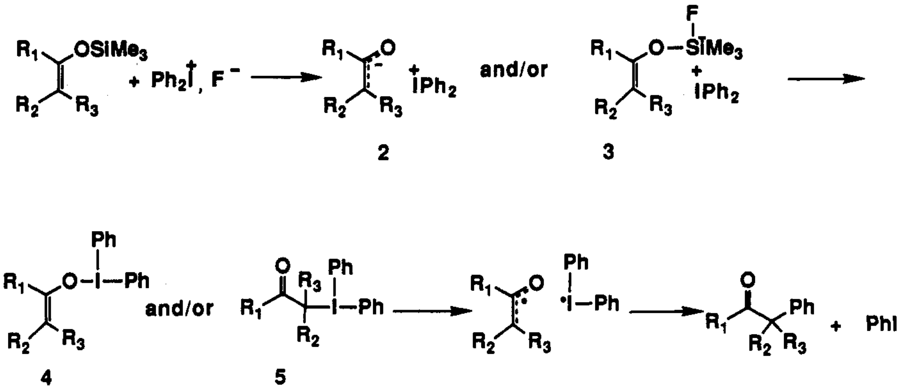
(7) Beringer, F. M.; Galton, S. A. *J. Org. Chem.* **1963**, *28*, 3417 and ref 1b.

(8) For example, see: (a) Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265. (b) Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 1223.

(9) (a) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736. (b) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(10) (a) Lucas, H. J.; Kennedy, E. R. *Organic Syntheses*; Wiley: New York, 1955, Collect. Vol. III, p 355. (b) Beringer, F. M.; Drexler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* **1953**, *75*, 2705. (c) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, *81*, 342.

Scheme I



Reactions of Silyl Enol Ethers with DIF. A detailed procedure for the phenylation of 1-[(trimethylsilyl)oxy]cyclohexene with DIF and the isolation of 2-phenylcyclohexanone is given below and serves as an example. The reactions of the remaining silyl enol ethers in Table I with DIF were conducted in similar fashion and abbreviated procedures are given; unless otherwise specified, the quantities of silyl enol ether and DIF, the total volumes of THF, reaction times and temperatures, chromatography solvents, and characterization data are presented *in that order*. In most cases, high boiling volatiles (e.g., PhI) were removed from the crude product mixtures by vacuum distillation prior to column chromatography.

2-Phenylcyclohexanone. A solution of 1-[(trimethylsilyl)oxy]cyclohexene (1.714 g, 10.06 mmol) in THF (5 mL) was added dropwise (2.5 min) under N_2 to a stirred mixture of diphenyliodonium fluoride (1.51 g, 5.03 mmol) in THF (15 mL) at ca. -40 °C (dry ice/MeCN). The reaction mixture was kept below -38 °C for 2 h and 50 min, allowed to warm slowly (2 h) to 10 °C, and kept at room temperature for 30 min. The resulting solution was treated with H_2O (ca. 3 mL) and concentrated on a rotary evaporator. The residual material was taken up in CH_2Cl_2 (100 mL), and the solution was washed with H_2O (2 × 20 mL) and saturated aqueous NaCl (15 mL), dried ($MgSO_4$), and concentrated to a light yellow oil (2.24 g). Flash column chromatography on silica gel (66.5 g, 22 cm × 28 mm) with hexanes (250 mL) and hexanes/CH_2Cl_2 (10:1 (110 mL), 5:1 (120 mL), 2:1 (75 mL), 1:1 (100 mL), 1:2 (150 mL), 1:3 (300 mL)) gave 2-phenylcyclohexanone as a white solid: yield, 0.775 g (88%); mp 54-57 °C, 55-57.5 °C (two crops) (lit.[11] fp 53-55 °C; lit.[12] mp 58-59 °C); IR (film) 1701 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ ~1.7-2.56 (five closely spaced m, 8 H), 3.59 (dd, J = 11.9, 5.5 Hz, 1 H), ~7.10-7.4 (arom m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.9, 27.5, 34.8, 41.9, 57.1, 126.9, 128.4, 128.6, 138.9, 210.5.

In another run (-70 °C to room temperature), 2,2-diphenylcyclohexanone, contaminated with about 7 mol % of 2-phenylcyclohexanone, was isolated by column chromatography (40 mg (4.7% crude yield)), mp 81-85 °C (lit.[13] mp (pure compound) 98.5-99.5 °C) and purified further by preparative TLC; ^1H NMR ($CDCl_3$) δ 1.77-1.88 and 1.88-2.0 (m's, 4 H), 2.45-2.54 (m, 2 H), 2.54-2.65 (m, 2 H), 7.0-7.08 (arom m, 4 H), 7.2-7.36 (arom, m, 6 H). The yield of 2-phenylcyclohexanone (mp 52-56 °C) was 0.51 g (43%).

2,2-Diphenylcyclopentanone: 1.563 g (10.0 mmol), 1.50 g (5.00 mmol); 21 mL; 1.8 h (ca. -40 °C), 1 h (rt); hexanes, hexanes/benzene (1:1-1:4); white solid; yield 0.30 g (51%); mp 85-87 °C (lit.[14] mp 87-88 °C; lit.[15] mp 88-90 °C, IR, ^1H NMR); IR (film) 1736, 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.93 (quintet, 2 H), 2.45 (t, J = 7.5 Hz, 2 H), 2.72 (t, J = 6.7 Hz, 2 H), ~7.15-7.38 (arom m, 10 H); ^{13}C NMR ($CDCl_3$) δ 18.6, 38.0, 38.1, 62.4, 126.9, 128.2, 128.5, 142.4, 218.2. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.89; H, 7.04. The analytical sample was purified by preparative TLC.

2-Methyl-2-phenylcyclohexanone: 1.93 g (10.5 mmol, 19 mol % 6-methyl regioisomer), 1.56 g (5.20 mmol); 20 mL; 1.4 h (-38 °C), 3.7 h (-38 to 10 °C), 1 h (rt); hexanes, hexanes/benzene (1:1-1:4); colorless oil;[11] yield, 0.752 g (77%); IR (neat) 1705, 1709 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3 H), ~1.56-1.82 (complex m, 4 H, ~1.85-1.99 (complex m, 1 H), ~2.22-2.42 (complex m, 2 H), ~2.59-2.74 (complex m, 1 H), ~7.12-7.36 (arom m, 5 H) (lit.[16] ^1H NMR); ^{13}C NMR ($CDCl_3$) δ 21.6, 28.2, 37.9, 39.7, 54.2, 126.2, 126.7, 129.1, 143.4, 214.4. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.85; H, 8.37. The analytical sample was purified by preparative TLC.

A small quantity (20 mg) of 6-phenyl- and 2-phenyl-2-methylcyclohexanones (1.34:1.00, NMR) was also obtained. Thus, the yield of the 6-phenyl regioisomer was about 1%.

6-Methyl-2-phenylcyclohexanone: 1.87 g (10.1 mmol, 11 mol % of 2-methyl regioisomer), 1.51 g (5.03 mmol); 20 mL; 1.6 h (below -38 °C), 1.7 h (-35 °C to -25 °C), 2.3 h (warmed to 15 °C) 1 h (rt); hexanes, hexanes/benzene (1:1-1:4). Two "fractions" of 6-methyl-2-phenylcyclohexanone were isolated, each consisting of major and minor geometric isomers: 0.230 g (colorless oil, ca. 10:1 molar mixture) and 0.533 g (colorless oil, ca. molar 22:1 mixture). The second fraction was contaminated with 6-8 mol % of the 2-methyl-2-phenyl regioisomer. Thus, the combined (and corrected) yield of 6-methyl-2-phenylcyclohexanone was 0.74 g (78%): IR (neat) 1705, 1709 cm^{-1} (C=O); ^1H NMR (CD_2Cl_2) δ 1.02 (d, J = 6.5 Hz, minor isomer) and 1.11 (d, J = 6.9 Hz, major isomer) (combined integration, 3 H), 1.57-1.7 (complex m, 1 H), 1.8-1.93 (complex m, 2 H), 1.95-2.17 (two complex m's, 2 H), 2.25-2.39 (complex m, 1 H), 2.48-2.62 (complex m, 1 H), 3.74 and 3.77 (overlapping d's, J = 7.3, 5.8 Hz, 1 H), 7.1-7.38 (arom m, 5 H) (lit.[16] ^1H NMR); ^{13}C NMR ($CDCl_3$, major isomer) δ 15.3, 20.8, 31.7, 35.1, 42.9, 53.8, 126.8, 127.7, 128.8, 138.6, 214.3. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.72; H, 8.51. The analytical sample (column fraction 1) was purified by preparative TLC.

2-Methyl-2-phenylcyclopentanone: 1.72 g (10.0 mmol, ca. 3 mol % of 5-methyl regioisomer), 1.40 g (4.67 mmol); 15 mL; 1.9 h (below -38 °C), ca. 1 day (rt); hexanes, hexanes/benzene (2:1-1:2), benzene, benzene/Et_2O (10:1, 4:1); oil;[17] yield, 0.370 g (45%); IR (neat) 1739 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.37 (s, 3 H), 1.74-2.06 (complex multiplets, 3 H), 2.33 (t, 2 H), 2.47-2.59 (complex m, 1 H), ~7.17-7.4 (arom m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.5, 24.8, 37.4, 37.9, 53.0, 126.4, 126.8, 128.7, 142.8, 221.1. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.41; H, 8.08. The above characterization data were collected on material from a similar run. The analytical sample was purified by preparative TLC.

α,α-Diphenylacetophenone: 2.04 g (10.6 mmol), 1.59 g (5.30 mmol); 20 mL; 3.7 h (below -38 °C, 1.1 mL more of silyl enol ether added), ca. 1 h (warmed to -15 °C to -10 °C). Initial workup (H_2O quenching, washing, removal of volatiles in vacuo) left 0.74 g of a light yellow solid containing little, if any, deoxybenzoin (mon-

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ophenylation). Recrystallization from CH_2Cl_2/hexanes (1:4) gave α,α-diphenylacetophenone as a crystalline solid: yield, 0.341 g (47%); mp 131–134 °C (lit.[18] mp 135–136 °C; lit.[19] 136–137 °C; lit.[20] 137 °C); IR (film) 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 6.03 (s, 1 H), ~7.2–7.55 (arom m, 13 H), ~7.95–8.03 (arom m, 2 H); ^{13}C NMR ($CDCl_3$) δ 59.4, 127.3, 128.8, 128.9, 129.1, 129.3, 133.2, 137.1, 139.3, 199.6.

1,1-Diphenyl-2-pentanone: reverse addition; DIF (1.61 g, 5.36 mmol) in CH_2Cl_2 (6 mL), precooled at 0 °C, added dropwise (5 min) under N_2 to 2-[(trimethylsilyl)oxy]-1-pentene (3.42 g, 21.6 mmol) in THF (20 mL) at -40 °C (dry ice/MeCN); 1.3 h (below −38 °C), warmed slowly to rt, ca. 0.5 day (rt); hexanes, benzene, benzene/Et_2O (10:1); 200 mg of a mixture of mono- and diphenyl-2-pentanones was obtained. Preparative thin-layer chromatography (silica gel GF, 20 cm × 20 cm, 1000 μm) with benzene/Et_2O (30:1) gave 1,1-diphenyl-2-pentanone as a light yellow oil: yield 0.154 g (24%); IR (neat) 1717, 1721 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.4 Hz, 3 H), 1.61 (sextet, J = 7.4 Hz, 2 H), 2.52 (t, J = 7.3 Hz, 2 H), 5.12 (s, 1 H), ~7.2–7.4 (arom m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.4, 17.2, 44.7, 64.1, 127.3, 128.8, 129.1, 138.7, 209.0. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.98; H, 7.64.

A second TLC fraction appeared (^1H NMR) to be a crude mixture of 1- and 3-phenyl-2-pentanones (30 mg, 3% yield).

2,4-Dimethyl-2-phenyl-3-pentanone: 2.92 g (15.7 mmol), 2.34 g (7.80 mmol); 20 mL; 80 min (below −38 °C), warmed to 0 °C, ca. 13 h (rt); hexanes, hexanes/CH_2Cl_2 (10:1–1:2); colorless oil; yield 0.30 g (20%); IR (neat) 1709 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.85 (d, J = 6.7 Hz, 6 H), 1.47 (s, 6 H), 2.65 (septet, J = 6.7 Hz, 1 H), ~7.19–7.35 (arom m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 24.6, 35.4, 52.7, 126.6, 127.0, 128.7, 143.5, 217.9 (lit.[21] IR; lit.[22] IR, ^1H NMR). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.81; H, 9.60. The analytical sample was purified by preparative TLC.

1-Phenyl-3,3-dimethyl-2-butanone: 3.81 g (22.1 mmol), 2.17 g (7.23 mmol); 35 mL; 37 min (−40 °C), 1.8 h (warmed to 6 °C), 5.5 h (rt); hexanes, hexanes/benzene (1:1, 1:2), benzene; colorless oil; yield, 0.480 g (38%); ^1H NMR (CD_2Cl_2) δ 1.19 (s, 8.6 H), 3.80 (s, 2 H), 7.11–7.35 (arom m, 5.4 H), very minor impurities (*tert*-butyl region); ^{13}C NMR ($CDCl_3$) δ 26.2, 43.1, 44.5, 126.8, 128.5, 129.7, 135.1, 213.3; IR (neat) 1713 cm^{-1} (C=O) (lit.[21,23] IR, NMR). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.08; H, 9.03.

A second oil was isolated from the column and identified as 2,2,7,7-tetramethyl-3,6-octanedione: yield 0.202 g (14%); ^1H NMR ($CDCl_3$) δ 1.1 (s, 18 H), 2.72 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 26.4, 30.3, 43.8, 215.3.

Except for the ^{13}C spectrum of the phenyl ketone, the spectral and analytical data were obtained on products from another run first isolated by column chromatography and purified by preparative TLC.

Addition of Diphenyliodonium Fluoride to 1-Phenyl-1-[(trimethylsilyl)oxy]ethene in Dichloromethane. A solution of DIF (0.69 g, 2.3 mmol) in CH_2Cl_2 (3 mL) was added dropwise (2 min) under N_2 to a solution of 1-phenyl-1-[(trimethylsilyl)oxy]ethene (1.33 g, 6.91 mmol) in CH_2Cl_2 (5 mL) at -40 °C (dry ice/MeCN). The reaction mixture was kept at ca. -40 °C for 33 min, allowed to warm to −19 °C, kept at 0 °C (ice bath) for 1.7 h, and finally allowed to stand at room temperature for 2.6 h. After the reaction mixture was treated with H_2O (ca. 3 mL), CH_2Cl_2 (100 mL) was added, and the solution was washed with H_2O (2 × 20 mL) and saturated aqueous NaCl (15 mL), dried (M_9SO_4), and concentrated to a yellow oil (1.255 g). A portion of the oil (69.2 mg) was mixed with pinacolone (8.9 mg, 0.089 mmol) and subjected to ^1H NMR analysis. On the basis of the integration ratio (174:21:18) of the methyl singlet of pinacolone (δ 2.11), the methylene singlet of deoxybenzoin (δ 4.26) and the methine singlet of α,α-diphenylacetophenone (δ 6.03), the total yield of deoxybenzoin in the crude oil was estimated to be 0.28 mmol (12%) while that of α,α-diphenylacetophenone was estimated to be 0.48 mmol (42%, based on 2 equiv of DIF).

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Registry No. DIF, 322-23-6; diphenyliodonium iodide, 2217-79-0; 1-[(trimethylsilyl)oxy]cyclohexene, 6651-36-1; 2-phenylcyclohexanone, 1444-65-1; 2,2-diphenylcyclohexanone, 22612-62-0; 2,2-diphenylcyclopentanone, 15324-42-2; 2-methyl-2-phenylcyclohexanone, 17206-54-1; *trans*-6-methyl-2-phenylcyclohexanone, 77326-20-6; *cis*-6-methyl-2-phenylcyclohexanone, 50987-04-7; 2-methyl-2-phenylcyclopentanone, 50390-68-6; α,α-diphenylacetophenone, 1733-63-7; 1,1-diphenyl-2-pentanone, 41997-44-8; 2,4-dimethyl-2-phenyl-3-pentanone, 25097-60-3; 1-phenyl-3,3-dimethyl-2-butanone, 6721-67-1; 2,2,7,7-tetramethyl-3,6-octanedione, 27610-88-4; 1-phenyl-1-[(trimethylsilyl)oxy]ethene, 13735-81-4; pinacolone, 75-97-8; 1-[(trimethylsilyl)oxy]cyclopentene, 19980-43-9; 2-methyl-1-[(trimethylsilyl)oxy]cyclohexene, 19980-35-9; 6-methyl-1-[(trimethylsilyl)oxy]cyclohexene, 19980-33-7; 2-methyl-1-[(trimethylsilyl)oxy]cyclopentene, 19980-34-8; 2-[(trimethylsilyl)oxy]-1-pentene, 40911-68-0; 2,4-dimethyl-3-[(trimethylsilyl)oxy]-2-pentene, 55339-64-5; 3,3-dimethyl-2-[(trimethylsilyl)oxy]-1-butene, 17510-46-2.

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