of the 400-MHz NMR spectrometer. Special acknowledgement is drawn to Dr. Alan Tracey of Simon Fraser University for design execution and interpretation of the decoupling experiment.

Registry No. **9**, 14309-15-0; **10**, 108711-49-5; **11**, 108711-50-8; **12**, 22093-99-8; **13**, 69690-89-7; **14**, 108711-51-9; **15**, 10276-04-7; **16**, 69862-37-9; **17**, 108711-52-0; **18**, 1746-13-0; **19**, 84473-44-9; **20**, 5296-64-0; **21**, 108711-53-1; **22**, 108711-54-2; **23**, 10152-76-8; **24**, 22418-49-1; **25**, 84473-43-8; **26**, 108711-55-3; **27**, 16277-67-1; **28**, 76793-94-7; **29**, 76793-95-8; **30**, 108711-56-4; **32**, 65447-92-9; **33**, 108711-57-5; dichloroketene, 4591-28-0; phenol, 108-95-2; 1-bromo-3-methylbutene, 870-63-3; 2-methyl-3-butene-2-ol, 115-18-4; thiophenol, 108-98-5; trichloroacetyl chloride, 76-02-8.

α-Phenylation of Ketones. Reaction of Bromo Enamines with Phenylcopper Reagents

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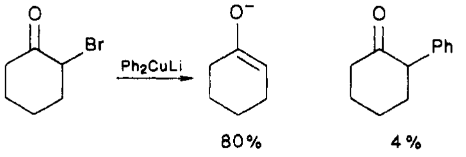
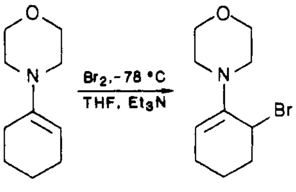
The introduction of a phenyl group α to a carbonyl is a useful step in the synthesis of a variety of biologically interesting compounds. Among the most successful phenylation procedures are the S_RN_1 reaction,[1] the reaction of arylboranes with α-bromo ketones[2] and the reaction of (*p*-tolylsulfonyl)azo olefins[3] or α,β-epoxy ketones[4] with lithium diphenylcuprate. The conceptually simple phenylation procedure based on reaction of α-halo ketones with phenylcopper reagents fails to give good yields because of a competing reduction (eq 1).[3] Our approach to this problem is based on the observation that enamines are readily brominated at low temperature in the presence of triethylamine.[5] Although we find that solutions of the brominated products are stable for at least several hours at room temperature, concentration of the solutions results in decomposition. However, ^{1}H NMR analysis of the reaction mixture obtained from the morpholine enamine of cyclohexanone revealed a quantitative yield of the allylic bromide **1** (eq 2). We examined the reaction of a freshly prepared THF solution of **1** with a variety of organometallics (PhM) with the results shown in eq 3. Results obtained with a variety of enamines by using Ph_2CuLi are shown in Table I. The sequence appears to provide a simple method for the phenylation of symmetrical ketones in good yield. The enamine of acetophenone, which can form only a vinylic bromide, is phenylated in relatively poor yield (19%, Table I).

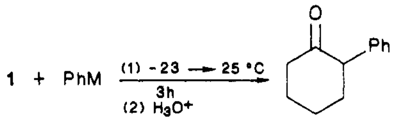


(1)



(2)

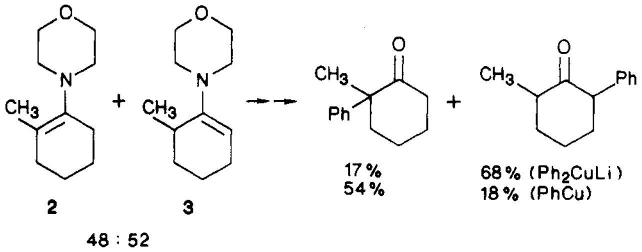
1



(3)

19%* (PhLi)
68% [$PhCuS(CH_3)_2$]
78% (PhCu)
94% (Ph_2CuLi)
*VPC yields

The regiochemistry of the phenylation reaction was briefly examined by using the equilibrium mixture of morpholine enamines of 2-methylcyclohexanone (**2** and **3**, eq 4). Interestingly, Ph_2CuLi and PhCu give a different regioisomer major product. In neither case, however, is the ratio of products related simply to the ratio of starting enamines. Presumably this is a result of the known ability of organocuprates to react with allylic substrates both with and without allylic rearrangement.[6]



(4)

Experimental Section

All the enamines except that of acetophenone were prepared by the azeotropic method.[7] The enamine of acetophenone was prepared by using $TiCl_4$ as a water scavenger.[8] Phenyllithium and copper(I) iodide were purchased from Aldrich and were used without any purification. A typical reaction sequence is described for the preparation of 2-phenylcyclohexanone.

2-Phenylcyclohexanone. Bromine (5 mmol, 0.8 g) was added dropwise to a solution of the morpholine enamine of cyclohexanone (5 mmol, 0.84 mL) and triethylamine (5.5 mmol, 0.77 mL) in THF (5 mL) at -78 °C. After 10 min, the cold bath was removed, and the reaction mixture was stirred for 10 additional minutes. Ether (10 mL) was added to the flask, and the ammonium salt was filtered. The bromo enamine solution was injected to a flask containing 5 mmol of Ph_2CuLi in 5 mL of THF. [The organocopper reagent was prepared 5 min earlier by the addition of 5 mL of PhLi (10 mmol) to a suspension of CuI (5 mmol, 0.95 g) in THF (5 mL) at -23 °C.] The reaction mixture was stirred for 2 h at -23 °C and for 1 h at room temperature. Cold hydrochloric acid was added (10 mmol, 5 mL), and after 6 h, the organic layer was separated, the water layer was extracted twice with 10 mL of ether, the combined organic layers were dried with K_2CO_3, and the ether was evaporated. Silica gel chromatography [hexane-ether (60:40)] gave 2-phenylcyclohexanone as a white solid, mp 55-56 °C (0.76 g, 87% yield): ^{1}H NMR ($CDCl_3$) δ 1.5-2.6 (m, 8 H), 3.4-3.8 (m, 1 H), 7.2-7.4 (m, 5 H); MS, *m/e* (relative intensity) 174 (M^+, 3), 120 (25), 105 (100), 91 (8), 77 (64). In a separate experiment, solvent was removed from the bromo enamine solution and the residue (**1**) was examined: ^{1}H NMR (CD_3CN) δ 1.6-3.1 (m, 10 H), 3.7 (t, 4 H), 4.9 (m, 2 H).

With a similar procedure, the following compounds were prepared.

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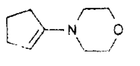
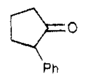
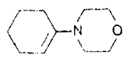
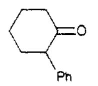
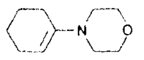
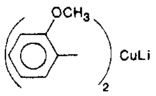
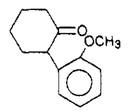
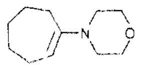
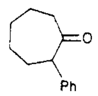
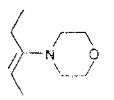
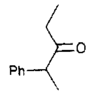
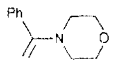
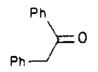
0022-3263/87/1952-3697$01.50/0

Table I. Bromination-Phenylation of Enamines with Ph_2CuLi

enamine	organocuprate	product (isolated yield, %)
	Ph_2CuLi	 (65)
	Ph_2CuLi	 (87)
		 (69)
	Ph_2CuLi	 (81)
	Ph_2CuLi	 (72)
	Ph_2CuLi	 (19)

2-Phenylcyclopentanone: ^1H NMR ($CDCl_3$) δ 1.76–2.6 (m, 6 H), 3.1–3.5 (m, 1 H), 7.2–7.4 (m, 5 H); MS, m/e (relative intensity) 161 (M^+ + 1, 12), 160 (27), 104 (100), 91 (17), 78 (19), 77 (15).

2-Phenylcycloheptanone: ^1H NMR ($CDCl_3$) δ 1.2–2.8 (m, 10 H), 3.5–3.8 (m, 1 H), 7.2–7.4 (m, 5 H); MS, m/e (relative intensity) 188 (M^+, 25), 117 (78), 104 (90), 91 (100), 84 (47), 78 (33), 77 (32), 51 (37).

2-Phenyl-3-pentanone: ^1H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.3 (d, 3 H), 2.2 (q, 2 H), 3.6 (q, 1 H), 7.2 (s, 5 H); MS, m/e (relative intensity) 163 (M^+ + 1), 70), 154 (25), 105 (89), 104 (50), 91 (18), 77 (39), 57 (100).

α-Phenylacetophenone: ^1H NMR ($CDCl_3$) δ 4.2 (s, 2 H), 7.2 (s, 5 H), 7.4–8.2 (m, 5 H); MS, m/e (relative intensity) 196 (M^+, 1), 105 (100), 91 (8), 77 (51), 65 (10).

2-Methyl-6-phenylcyclohexanone: ^1H NMR ($CDCl_3$) δ 0.9–2.8 (m, 10 H), 3.5–3.9 (m, 1 H), 7.1–7.5 (m, 5 H); MS, m/e (relative intensity) 188 (M^+, 53), 130 (78), 117 (81), 115 (33), 104 (74), 91 (100), 78 (23), 77 (27).

2-Methyl-2-phenylcyclohexanone: ^1H NMR ($CDCl_3$) δ 1.1–2.8 (m, 11 H), 7.2–7.4 (m, 5 H); MS, m/e (relative intensity) 188 (M^+, 63), 145 (80), 144 (97), 131 (97), 129 (48), 118 (80), 117 (71), 91 (100), 77 (40).

2-(2-Methoxyphenyl)cyclohexanone: ^1H NMR ($CDCl_3$) δ 1.6–2.8 (m, 8 H), 3.8 (s, 3 H), 3.7–4.1 (m, 1 H), 6.8–7.5 (m, 4 H); MS, m/e (relative intensity) 204 (M^+, 79), 160 (49), 147 (100), 121 (44), 119 (30), 91 (75), 77 (22), 65 (23).

Carbon-Carbon Double Bond Cleavage Using Solid-Supported Potassium Permanganate on Silica Gel[1]

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Potassium permanganate has been widely used as an oxidant in aqueous solutions, which frequently cause problems due to the low solubility of organic substrates.[2,3] To overcome this problem, phase-transfer catalysis[4] and cyclic polyethers[5] have been used to solubilize the oxidant into the organic phase. A great number of organic reactions using solid-supported reagents have been developed in the past,[6] where permanganate oxidations play a main role. Potassium permanganate supported on molecular sieves[7] or silica gel[8] have been used to oxidize alcohols to carbonyl compounds and to convert γ-nitro ketone into the corresponding 1,4-diketones with great advantage compared with the previous methods. Zinc permanganate supported on silica gel has been reported[9] to perform the following transformations: acetylene to α-diketone and cyclic olefin to ketol, among others.

Permanganate on solid supports such as copper sulfate[10,11] has been used in the oxidation of alcohols to the corresponding carbonyl compounds where the authors have come to the conclusion that this reagent does not react with carbon–carbon double bonds.

In this paper we would like to present our results on the use of potassium permanganate, supported on silica gel, to achieve carbon–carbon double bond cleavage under very mild conditions.

Clark and collaborators[12] have been studying the nature of the silica gel supported permanganate. However, at the present time we can not offer any explanation as to why silica gel changes the reaction course so dramatically.

Potential synthetic advantages of this silica gel/$KMnO_4$ reagent are as follows: (1) the reaction occurs at room temperature and within a very short reaction time (20–30 min); (2) the method is equally effective for cleaving terminal, secondary, tertiary, and electron-withdrawing substituted double bonds; (3) when optically active α-pinene ($[\alpha]_D^{25}$ +40.6° (c 1, neat)) was cleaved and we obtained (+)-pinonic acid ($[\alpha]_D^{25}$ +47.1° (c 1, $CHCl_3$)); (4) in the case of compound 15 (entry 8), where all the traditional methods such as aqueous potassium permanganate in neutral, acidic, or basic medium, $KMnO_4/MgSO_4$, or $KMnO_4/NaIO_4$ failed,[13] the reaction occurred in reasonable yield under our conditions.

Our results are summarized in Table I and show that despite no attempt having been made to maximize yields, good to excellent yields of cleavage products were obtained. Due to the high solubility of some products (entries 1–3), they need to be continuously extracted from the aqueous phase. When we used toluene as the solvent the cleavage product was contamined with benzoic acid, which was formed from the direct oxidation of toluene.

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[1] A preliminary account of this research was presented at the VI International Conference on Organic Synthesis, Moscow, August 1986.

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