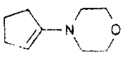
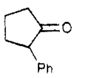
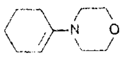
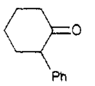
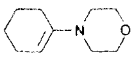
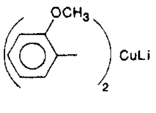
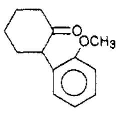
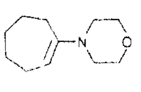
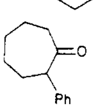
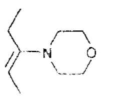
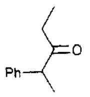
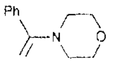
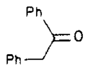
Table I. Bromination-Phenylation of Enamines with Ph_2CuLi

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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Received December 11, 1986

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.

(2) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 257-291.

(3) Viski, P.; Szeveremyi, Z.; Simandi, L. I. *J. Org. Chem.* **1986**, *51*, 3213.

(4) (a) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195. (b) Menger, F. M.; Rhee, J. U.; Rhee, H. K. *J. Org. Chem.* **1975**, *40*, 3803.

(5) (a) Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250. (b) Sam, D. J.; Simons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 4024. (c) Gokel, G. W.; Durst, H. D. *Aldrichimica Acta* **1976**, *9*, 3 and references cited therein.

(6) (a) McKillop, A.; Young, D. W. *Synthesis* **1979**, 401, 481 and references cited therein.

(7) Regen, S. L.; Koteel, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3837.

(8) Clark, H. J.; Cork, D. G. *J. Chem. Soc., Chem. Commun.* **1982**, 635.

(9) Wolf, S.; Ingold, C. F. *J. Am. Chem. Soc.* **1983**, *105*, 7755.

(10) Menger, F. M.; Lee, C. *J. Org. Chem.* **1979**, *44*, 3446.

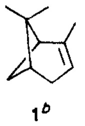
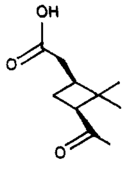
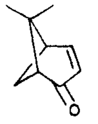
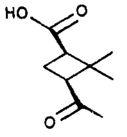
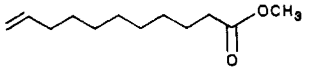
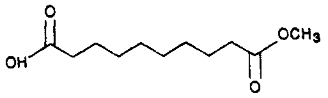
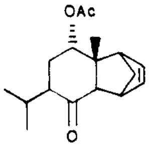
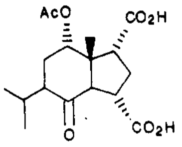
(11) Lee, D. G.; Noureldin, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 3188.

(12) Jazzaa, A. A.; Clark, J. H.; Robertson, M. *Chem. Lett.* **1982**, 405.

(13) Corrêa, A. G.; Brocksom, T. J.; Brocksom, U., personal comunication.

0022-3263/87/1952-3698$01.50/0

Table I. Carbon-Carbon Double Bond Cleavage by Silica Gel/$KMnO_4$

entry	compound	product	yield, %[a]
1	 **1**[b]	 **2**	84 (63)[c]
2	 **3**	 **4**	79
3	cyclohexene (**5**)	adipic acid (**6**)	74
4	cinnamyc acid (**7**)	benzoic acid (**8**)	73
5	cinnamyl acetate (**9**)	benzoic acid (**8**)	87
6	 **10**	 **11**	85
7	methyl oleate (**12**)	azelaic monomethyl acid (**13**) + nonanoic acid[d] (**14**)	79
8	 **15**	 **16**	62

[a] Yields refers to isolated product. [b] When optically active (+)-α-pinene was used the (+)-pinonic was obtained. [c] After column chromatography. [d] The two products were not separated; after extensive methylation with diazomethane, the mixture was analyzed by GC.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian FT-80A or Perkin-Elmer Hitachi R-24A spectrometer. Mass spectra were obtained on a Hewlett-Packard 5995 GC-MS with a ionizing voltage of 70 eV. Optical rotations were obtained on a Bellinghan + Stanley polarimeter. Gas chomatographic analyses were performed on a CG-2527 or Varian-3700 instrument. Melting points were determined on a Kofler apparatus and are uncorrected.

Preparation of the Silica Gel/$KMnO_4$ Reagent. Silica gel (15 g) was added to a 6 × 10^{-2} M of aqueous potassium permanganate (375 mL), and the resulting slurry was evaporated in a rotary evaporator (70–80 °C) to give a free flowing solid.

Cleavage of Carbon–Carbon Double Bond: a Typical Procedure. Sebacic Acid Monomethyl Ester (11). To 15.0 g of silica gel supported $KMnO_4$ in a chromatographic column (25 mm i.d.) was added methyl undecenoate (**10**) (269 mg, 1.36 mmol) dissolved in benzene (80 mL). After all the solution was percolated, more solvent (30 mL) was added, and pressure was applied on top of the column. After evaporation of the solvent, 16 mg of the starting material was recovered. Then, water was added (150 mL) and eluted under pressure. The aqueous phase was acidified (HCl), treated with solid ($NaHSO_3$), and extracted with ethyl ether (3 × 50 mL). After drying with anhydrous Na_2SO_4 the solvent was removed at reduced pressure, affording **11** (249 mg, 85% yield): ^{1}H NMR δ 1.31 (br s, 8 H), 1.5–1.8 (m, 4 H), 2.1–2.4 (m, 4 H), 3.66 (s, 3 H), 8.25 (br s, 1 OH); IR (film) 3600–2600 (OH), 1740 (COOMe), 1720 (COOH) cm^{-1}.

Adipic Acid (6). Cyclohexene (112 mg, 1.36 mmol) was cleaved by using the above procedure. When the aqueous phase was extracted with ether only a small quantity of adipic acid was recovered. Continuous extraction of the aqueous phase with the same solvent gave an additional amount of the desired product. Combination of both fractions afforded (147 mg, yield 74%) of adipic acid, mp 151–154 °C (acetone/petroleum ether), (lit.[14] mp 151–153 °C).

Acknowledgment. We thank Conselho de Desenvolvimento Cientifico e Tecnológico (CNPq) and Fundação de Amparo a Pesquisas do Estado de São Paulo (FAPESP) for financial support. One of us (W.O.C.) thankfully acknowledges FAPESP for an undergraduate fellowship.

Registry No. **1**, 80-56-8; **2**, 61826-55-9; **3**, 1123-46-2; **4**, 28587-41-9; **5**, 110-83-8; **6**, 124-04-9; **7**, 621-82-9; **8**, 65-85-0; **9**, 103-54-8; **10**, 111-81-9; **11**, 818-88-2; **12**, 112-62-9; **13**, 1732-10-1; **14**, 112-05-0; **15**, 108817-94-3; **16**, 108817-95-4.

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[14] Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1 p 15.

Sodium Metal Promoted Condensations of Carbamates

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Received August 11, 1986

The well-known acyloin condensation[1] of esters has been used widely for the synthesis of both carbocycles and heterocycles. It has been used with acid chlorides,[2] anhydrides,[3] half-ester amides,[4] and other nitrogen-containing

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[1] (a) Bloomfield, J. J.; Owsley, D. C.; Nelke, J. M. *Org. React. (N.Y.)* **1975**, *23*, 259. (b) Ruhlmann, K. *Synthesis* **1971**, 236. (c) Finley, K. T. *Chem. Rev.* **1964**, 573. (d) McElvain, S. M. *Org. React. (N.Y.)* **1948**, *4*, 256.

[2] (a) Ralston, A. W.; Selby, W. M. *J. Am. Chem. Soc.* **1939**, *61*, 1019. (b) Egorova, V. I. *Russ. Phys.-Chem. Soc.* **1928**, *60*, 1199; *Chem. Abstr.* **1929**, *23*, 2935. (c) Basse, A.; Klinger, H. *Chem. Ber.* **1898**, *31*, 1217. (d) Klinger, H.; Sandke, O. *Chem. Ber.* **1891**, *24*, 1217. (e) Klinger, H.; Schmitz, A. *Chem. Ber.* **1891**, *24*, 1217.