mmol) was added. The mixture was refluxed for 3.5 h and then filtered and concentrated. From the resulting residue crystalline **3** was obtained with EtOAc/pentane. Yield: 2.51 g (66%). Mp: 118–119 °C. $[\alpha]_D^{20}$: 10.5° (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{18}H_{26}O_{11}$: C, 51.67; H, 6.26. Found: C, 51.75; H, 6.26. Concentration of the mother liquor gave a syrup containing a mixture of **3** and methyl 2,3,4-tri-*O*-acetyl-1-*O*-*pivaloyl*-α-D-glucopyranuronate (0.57 g, ratio 2:1) as seen by NMR. ^{1}H NMR ($CDCl_3$): δ 5.72 (d, J_{12} = 8 Hz, H-1), 5.32, 5.25, 5.20 (3 t, H-2, H-3, H-4), 4.18 (d, J_{45} = 9 Hz, H-5), 3.74 (s, OMe), 2.02–2.06 (3 s, OAc's), and 1.20 (s, CCH_3's). ^{13}C NMR ($CDCl_3$): δ 176.9 (C=O), 169.6, 169.0, 168.6 (OAc's), 166.4 (C-6), 91.1 (C-1), 72.7, 71.5, 69.6, 68.8 (C-2, C-3, C-4, C-5), 52.6 (OMe), 38.4 (CMe_3), 26.4 (3 C, Me's), 20.2, 20.1, and 20.1 (OAc's).

2,3,4,6-Tetra-*O*-benzyl-1-*O*-pivaloyl-β-D-glucopyranose (5). 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (**4**) (10.0 g, 18.5 mmol) was dissolved in CH_2Cl_2 (100 mL), and (dimethylamino)pyridine (100 mg), pyridine (10 mL, 124 mmol), and pivaloyl chloride (9.0 g, 74 mmol) were added. The resulting solution was kept at 25 °C for 24 h. More CH_2Cl_2 (200 mL) was added, and the solution was washed with 1 N HCl (200 mL), saturated $NaHCO_3$ solution (200 mL), and H_2O (200 mL). Drying ($MgSO_4$) and concentrating the solution left an oily liquid (15 g). Crystallization from ether/pentane gave **5**. Yield: 9.91 g (86%). Mp: 89–90 °C (lit.[11] mp 87.9–88.5 °C). $[\alpha]_D^{20}$: 20.1° (*c* 1.0, $CHCl_3$) [lit.[11] $[\alpha]_D^{20}$ −14° (*c* 1.0, $CHCl_3$)]. ^{1}H NMR ($CDCl_3$): δ 7.14–7.35 (m, Phs), 5.62 (d, J_{12} = 8 Hz, H-1), 4.72–4.90 (m, 5 H), 4.48–4.64 (m, 3 H), 3.55–3.81 (m, 6 H), and 1.24 (s, Me's). ^{13}C NMR ($CDCl_3$): δ 176.9 (C=O), 138.0–138.4 (4 C, ipso Ph), 127.6–128.4 (20 C, Ph), 94.3 (C-1), 84.8, 81.0, 77.3 and 75.6 (C-2, C-3, C-4 and C-5), 75.6, 74.9 (2 C) and 73.4 (CH_2Ph's), 66.1 (C-6), 38.7 (CMe_3), and 27.0 (3 C, Me's). Anal. Calcd for $C_{39}H_{44}O_7$: C, 74.98; H, 7.10. Found: C, 75.11; H, 7.20.

1-*O*-Pivaloyl-β-D-glucopyranose (6). **5** (5.0 g, 8 mmol) was dissolved in EtOAc (100 mL) and EtOH (50 mL), and palladium on carbon (10%, 1.0 g) was added. The mixture was hydrogenolyzed (101 kPa) until the expected amount of H_2 had been consumed (5 h). Fitration and concentration left clear syrupy **6** (2.19 g). On addition of ether a white solid was obtained (1.77 g, 84%). Mp: 123–135 °C (lit.[13] syrup). $[\alpha]_D^{20}$: −7.7° (*c* 1.0, dioxane) (lit.[20] $[\alpha]_D^{20}$ 12° (dioxane)]. Anal. Cacd for $C_{11}H_{20}O_7$: C, 49.99; H, 7.63. Found: C, 49.61; H, 7.77. The mother liquor contained 0.27 g (13%) of **6** as syrup; pure as seen from NMR. ^{1}H NMR (CD_3OD): δ 5.44 (d, J_{12} = 8 Hz, H-1), 3.83 (br d, J_{6a6b} = 12 Hz, H-6a), 3.68 (dd, J_{56b} = 3 Hz, H-6b), 3.33–3.42 (m, H-2, H-3, H-4 and H-5), and 1.23 (s, Me's). ^{13}C NMR (CD_3OD): δ 178.8 (C=O), 95.8 (C-1), 78.8, 78.2, 74.0 and 71.0 (C-2, C-3, C-4 and C-5), 62.3 (C-6), 39.8 (CMe_3), and 27.4 (3 C, Me's).

1-*O*-Pivaloyl-β-D-glucopyranuronic Acid (1). **6** (0.50 g) in H_2O (50 mL) was stirred with platinum black (0.25 g) at 87–88 °C. A stream of O_2 was bubbled through the solution. When necessary, pH was adjusted to 7–8 by addition of 0.5 M $NaHCO_3$ solution (4.5 mL). After 3.5 h, TLC (EtOAc–MeOH (5:1)) showed the absence of starting material. The solution was filtered and treated with 5 mL of ion-exchange resin (Dowex 50W×8, H^+). The resin was filtered off after 15 min, and the filtrate was concentrated to a clear syrup of **1** that crystallized spontaneously (0.32 g, 60%, mp 164–6 °C). $[\alpha]_D^{20}$: −26.7° (*c* 1.0, H_2O). ^{1}H NMR (D_2O): δ 5.43 (d, J_{12} = 7.6 Hz, H-1), 3.97 (d, J_{45} = 9.6 Hz, H-5), 3.38–3.49 (m, H-2, H-3, H-4), and 1.08 (s, Me's). ^{13}C NMR (D_2O): δ 182.6 (COOH), 174.7 (C=O), 96.4 (C-1), 77.8 (2 C), 74.2, 73.7 (C-2, C-3, C-4 and C-5), 41.3 (CMe_3), and 28.7 (3 C, Me's). Anal. Calcd for $C_{11}H_{18}O_8 \cdot 0.5H_2O$: C, 45.99; H, 6.67. Found: C, 46.06; H, 6.73.

Acknowledgment. I thank Niels Rastrup Andersen and his staff for running the NMR spectra and Martin T. Sørensen for experimental assistance.

Registry No. **1**, 98299-37-7; **2**, 21085-72-3; **3**, 135505-23-6; **4**, 38768-81-9; **5**, 82561-63-5; **6**, 80928-26-3; Me_3CCOCl, 3282-30-2; $Me_3CCOOAg$, 7324-58-5.

(14) Silver pivalate was prepared as follows: 0.5 M $AgNO_3$ (100 mL) was slowly added to 1.67 M $Me_3CCOO^-Na^+$ (30 mL). After thorough stirring the precipitate was filtered off and washed with H_2O (4 × 25 mL) and acetone (4 × 25 mL). Overnight drying in a desiccator afforded 6.7 g of $Me_3CCOO^-Ag^+$.

Indirect Electroreduction of 2-Alkyl-2-(bromomethyl)cycloalkanones with Cobaloxime To Form 3-Alkyl-2-alkenones via 1,2-Acyl Migration

Tsutomu Inokuchi,† Michihiro Tsuji,† Hiroyuki Kawafuchi,‡ and Sigeru Torii*,†

Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama, Japan 700, and Toyama National College of Technology, Hongo 13, Toyama, Japan 939

Received March 18, 1991

Radical reactions mediated by organocobalt complexes[1,2] have proven to be useful for the construction of carbon[3] and hetero ring systems[4] directed toward the synthesis of bioactive compounds. In particular, carbon radicals, generated by a homolytic carbon–Co bond cleavage of alkylcobalt complexes, are likely to recombine reversibly in a matrix with the released cobalt complex.[5] These aspects are of benefit to the concomitant rearrangement of the carbon skeleton of the radical intermediates and the formation of olefins thereafter via β-elimination of the Co–H moiety.[6] However, few synthetic transformations have been achieved by recyclable cobalt complexes.[4d,7] We report here that 1,2-acyl migration[8–11] of alicyclic 2-alkyl-2-(bromomethyl)alkanones **1** is operative by an indirect electroreduction with (chloropyridine)cobaloxime(III) as a mediator.[12] This method can provide a facile access to α,β-unsaturated ketones[13] by a one-step operation.

External irradiation with a tungsten sunlump and heating at 55–60 °C were applied during the electroreduction in a divided cell in order to facilitate the ensuing carbon–Co bond cleavage of the alkylcobaloxime complexes.[4d] Thus, the electrolysis of 2-hexyl-2-(bromomethyl)cyclopentanone (**1a**) in the presence of cobaloxime (50 mol %) and a small amount of aqueous 50% potassium hydroxide in an MeOH–Et_4NOTs–(Pt) system under a constant applied voltage of 9–15 V (current density: 30 mA/cm^2), 5 F/mol of electricity being charged, gave the desired 3-hexyl-2-cyclohexenone (**2a**) in 74% yield together with minor products such as **3a** (4%), a saturated isomer of **1a**, and 2-hexyl-2-methylcyclopentanone (**4a**, 17%).[14] Similar electrolysis of **1a** in an undivided cell afforded the enone **2a** in 32–34% yield, and the run without use of the cobaloxime resulted in recovery of the starting material (Scheme I).

Authentic samples of **3a** and **4a** were prepared as follows. The compound **3a** was obtained by hydrogenation of the enone **2a** over palladium on carbon and the 2-methylcyclopentanone **4a** was derived from **1a** by exhaustive reduction with lithium aluminum hydride ($LiAlH_4$) followed by oxidation of the resulting cyclopentanol with pyridinium chlorochromate (PCC).[14]

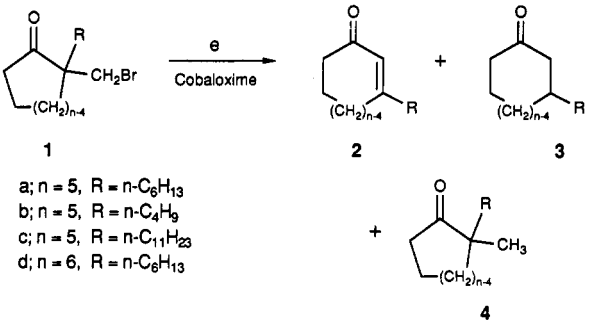
The correlation between yields of **2a**, **3a**, and **4a** under varying the amount of cobaloxime was explored as illustrated in Figure 1 in order to clarify the role of the cobaloxime in this electroreduction. Formation of the enone **2a** is favored in the presence of more than 20 mol % of the cobaloxime. The saturated **3a** yield increases to 14–28% at the expense of **2a** in the range of 5–10 mol % of cobaloxime. The unrearranged product **4a** is produced in about 5–17% yields regardless of the catalyst amount.

The present reaction can be explained by assuming the path shown in Scheme II. The alkyl–Co(III)py complex

† Okayama University.
‡ Toyama National College of Technology.

0022-3263/91/1956-5945$02.50/0

Scheme I



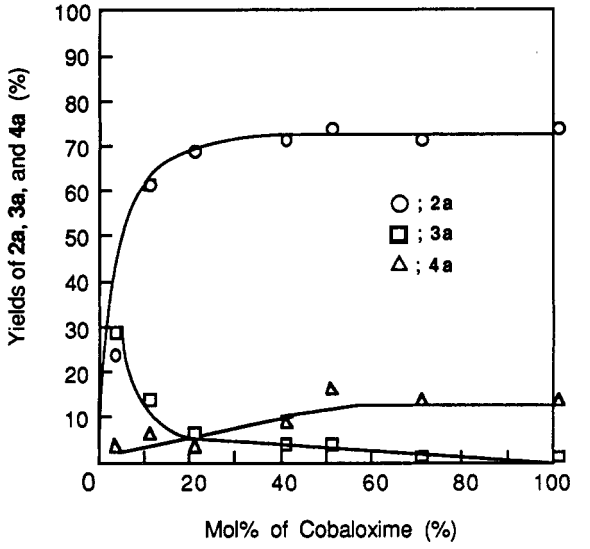


Figure 1. Profiles of the cobaloxime-mediated electroreduction of **1a** with varying amounts of the cobaloxime: **2a** (○); **3a** (□); **4a** (△).

A, formed by nucleophilic attack of the electrogenerated Co(I)py species to 1, would undergo a homolytic cleavage

Scheme II

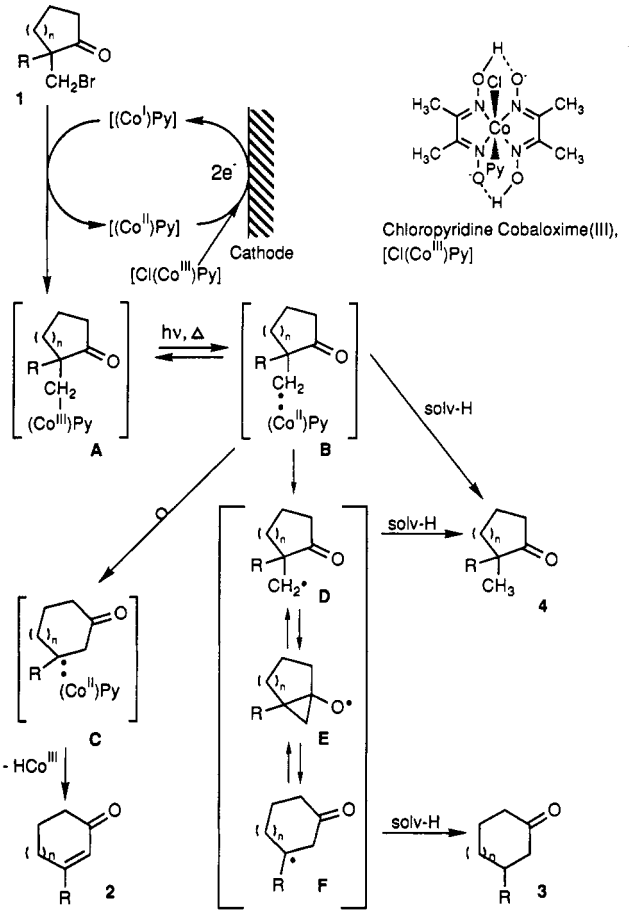


Table I. Cobaloxime-Mediated Indirect Electroreduction of Cycloalkanones 1[a]

entry	substr	products, yield, %[b] 2	3	4	rearrangmnt/ unrearrangmnt (2 + 3)/4
1	**1a**	74	4	17	4.6
2	**1b**	52	3	15	3.7
3	**1c**	69	2	18	3.6
4	**1d**	51	trace	23	2.2

[a] Carried out by using 1 (0.3–0.5 mmol) and cobaloxime (50 mol %) in an MeOH–Et_4NOTs–(Pt)–(Pt) system. A constant current of 20 mA/cm², 9–15 V (applied), was charged at 55–60 °C with irradiation. [b] Yields are based on isolated products.

Table II. Reduction of Cycloalkanones 1 with Tin Hydride

entry	substr	method[a]	products, yield, %[b] 3	4	rearrangmnt/ unrearrangmnt 3/4
1	**1a**	A	50	11	4.5
2	**1a**	B	70	4	71.5
3	**1b**	A	44	10	4.4
4	**1c**	A	56	5	11.2
5	**1d**	A	25	60	0.4
6	**1d**	B	65	18	3.6

[a] Method A: reduction with Ph_3SnH (1.5 equiv) in C_6H_6 (5 mL, 0.12 M solution) at 80 °C. Method B: reduction with Ph_3SnH (1.5 equiv) in C_6H_6 (100 mL, 0.006 M solution) at 80 °C. [b] Yields are based on isolated products.

of the Co–carbon bond, on heating or by exposure to sunlight, providing a β-keto alkyl radical **B**. This primary

(1) Scheffold, R.; Rytz, G.; Walder, L. *Modern Synthetic Methods*; Scheffold, R., Ed.; Otto Salle Verlag: Frankfurt, 1983; Vol. 3, pp 355–440.
(2) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986.
(3) Use of cobaloxime: (a) Giese, B.; Hartung, J.; He, J.; Hüter, O.; Koch, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 325. (b) Branchaud, B. P.; Meier, M. S.; Malekzadeh, M. N. *J. Org. Chem.* **1987**, *52*, 212. Use of Co(salophen): (c) Patel, V. F.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2703; *Tetrahedron Lett.* **1988**, *29*, 707.
(4) Use of cobaloxime: (a) Pattenden, G.; Reynolds, S. J. *Tetrahedron Lett.* **1991**, *32*, 259. (b) Baldwin, J. E.; Moloney, M. G.; Parsons, A. F. *Tetrahedron* **1991**, *47*, 155. (c) Baldwin, J. E.; Li, C.-S. *J. Chem. Soc., Chem. Commun.* **1987**, 166. (d) Torii, S.; Inokuchi, T.; Yukawa, T. *J. Org. Chem.* **1985**, *50*, 5875. Use of Co(salophen): (e) Gill, G. B.; Pattenden, G.; Reynolds, S. J. *Tetrahedron Lett.* **1989**, *30*, 3229. (f) Patel, V. F.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1987**, 871.
(5) (a) Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 423. (b) Maillard, P.; Giannotti, C. *Can. J. Chem.* **1982**, *60*, 1402.
(6) Other useful radical reactions by using cobaloxime: (a) Stang, P. J.; Datta, A. K. *J. Am. Chem. Soc.* **1989**, *111*, 1358. (b) Branchaud, B. P.; Meier, M. S. *J. Org. Chem.* **1989**, *54*, 1320. (c) Fukuzumi, S.; Kitano, T.; Ishikawa, K.; Tanaka, T. *Chem. Lett.* **1989**, 1599. (d) Ghosez, A.; Göbel, T.; Giese, B. *Chem. Ber.* **1988**, *121*, 1807. (e) Branchaud, B. P.; Choi, Y. L. *J. Org. Chem.* **1988**, *53*, 4638. (f) Kijima, M.; Miyamori, K.; Sato, T. *J. Org. Chem.* **1988**, *53*, 4147. (g) Kijima, M.; Miyamori, K.; Sato, T. *J. Org. Chem.* **1987**, *52*, 706. (h) Cabaret, D.; Maigrot, N.; Welvart, Z.; Duong, K. N. V.; Gaudemer, A. *J. Am. Chem. Soc.* **1984**, *106*, 2870.
(7) Recyclable use of cobalt reagents: (a) Orliński, R.; Stankiewicz, T. *Tetrahedron Lett.* **1988**, *29*, 1601. (b) Scheffold, R.; Dike, M.; Dike, S.; Herold, T.; Walder, L. *J. Am. Chem. Soc.* **1980**, *102*, 3642.
(8) (a) Tada, M.; Nakamura, T.; Matsumoto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4647. (b) Okabe, M.; Osawa, T.; Tada, T. *Tetrahedron Lett.* **1981**, *22*, 1899. (c) Tada, M.; Miura, K.; Okabe, M.; Seki, S.; Mizukami, H. *Chem. Lett.* **1981**, 33.
(9) (a) Murakami, Y.; Hisaeda, Y.; Song, X.-M.; Fan, S.-D. *Chem. Lett.* **1989**, 877. (b) Murakami, Y.; Hisaeda, Y.; Ozaki, T.; Tashiro, T.; Ohno, T.; Tani, Y.; Matsuda, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 311.
(10) (a) Best, W. M.; Widdowson, D. A. *Tetrahedron* **1989**, *45*, 5943. (b) Thoma, G.; Giese, B. *Tetrahedron Lett.* **1989**, *30*, 2907.

carbon radical, presumably existing in equilibrium with the alkyl–Co(III)py complex **A** in the matrix, can be converted to the thermodynamically more stable tertiary radical **C** via a 1,2-acyl migration. The enone **2** may be produced from **C** either by synchronous recombination with Co(II)py species in the matrix followed by β-elimination of Co(II)(py)H moiety or by direct abstraction of a hydrogen α to the carbonyl by Co(II)py species existing in the vicinity of the carbon radical **C**. On the other hand, the formation of the saturated compound **3** may be ascribed to H-abstraction of the tertiary radical **F** or its structural isomer **E**. The methylcyclopentanone **4** would be produced from **B** or **D** by a similar H-abstraction.

The Co(I)-mediated 1,2-acyl rearrangement can be extended to other 2-alkyl-2-(bromomethyl)cycloalkanones **1** and the results carried out by using 50 mol % of the cobaloxime are shown in Table I. Usually, the rearrangement is favored over a simple proton abstraction probably by the initially formed oxoalkyl radical, i.e., **B**, significantly in cyclopentanone series **1a–c** (Table I, entries 1–3).

This cobaloxime-mediated 1,2-acyl rearrangement of **1a** to the enone **2a** was operative by using sodium borohydride as reducing reagent to produce the cobaloxime(I) species. However, this chemical version requires an excess amount of pregenerated cobaloxime(I) in ethanol, giving the enone **2a** in lesser yield (27%) compared with that by the electrochemical method.

Alternatively, triphenyltin hydride (Ph_3SnH) was employed to induce rearrangement of **1** in a free-radical process.[2] Thus, the treatment of **1** with Ph_3SnH in refluxing benzene led either to **3** by a 1,2-acyl rearrangement or to **4** by a simple H-abstraction, respectively. In this case, the concentration of the reactants in benzene was found to be greatly influential. For instance, as shown in Table II, entries 1 and 2, the ratio of rearrangement/unrearrangement of **1a** increases to 17.5:1 from 4.5:1 when the substrate concentration is varied from 0.12 M to 0.006 M solution.[15] Similar improvement is also attained in the reduction of the six-membered **1d** (Table II, entries 5 and 6).

In conclusion, although the 1,2-acyl migrations thus far have mainly been attempted with 2-alkoxycarbonyl derivatives of **1**[11] or their diester analogues by the action of trialkyltin hydride or low-valent transition-metal reagents such as Co, Fe, Mn, etc.,[9] the similar 1,2-acyl migrations are shown, in this work, to be operative with 2-alkyl derivatives **1** by use of a low-valent cobalt complex and tin hydride reagent, giving one-carbon homologated 3-alkylalkenones or 3-alkylalkanones, respectively. Especially, the electrochemical cobaloxime-mediated 1,2-acyl migration method, catalytic with respect to the cobalt reagent, is useful as a means of obtaining alkenones by a simple operation.[13,16]

Experimental Section[17]

Electrolysis Apparatus. A modified H-type cell (40 mL volume) with a Nafion (No. 324) diaphragm was used. The cathodic compartment was fitted with a thermometer, a magnetic stirring bar, and an argon inlet glass tube. Two platinum foil electrodes (1.5 cm^2) immersed parallel to each other, 4 cm apart, were used and the vessel was warmed at 55–60 °C on an oil bath.

Indirect Electroreduction of 2-(Bromomethyl)-2-hexylcyclopentanone (1a): Typical Procedure. Into the cathodic compartment were placed **1a** (80 mg, 0.31 mmol) and (chloropyridine)cobaloxime(III) (66 mg, 0.16 mmol), and then into the both compartments were added two solutions of Et_4NOTs (0.08 M, 20 mL) in MeOH containing aqueous 50% KOH (0.1 mL), respectively. The entire mixture was electrolyzed under a constant current of 20 mA/cm^2 (applied voltage: 9–15 V) at 55–60 °C, during which an external irradiation by a tungsten lump (projector lamp, 750 W) from a distance of 15 cm was applied. In the course of the electrolysis, a stream of argon was passed through the cathodic chamber. After 5 F/mol of electricity has been charged, the mixture was partitioned with AcOEt and brine. The organic layers were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography (SiO_2, hexane–AcOEt = 30:1–3:1) to give 10 mg (17%) of **4a** (R_f 0.51 on Merck F-254 TLC, hexane–AcOEt = 5:1), 2 mg (4%) of **3a** (R_f 0.43), and 41 mg (74%) of **2a** (R_f 0.35) as oils. **2a**[18] (R = C_6H_{13}): bp 113–114 °C (9 Torr). **4a**[19] (R = C_6H_{13}): bp 80 °C (9 Torr). **3a**[20] (R = C_6H_{13}): bp 110 °C (19 Torr).

Preparation of 2-Hexyl-2-methylcyclopentanone (4a) from 1a. To a solution of **1a** (100 mg, 0.38 mmol) in THF (10 mL) was added $LiAlH_4$ (38 mg, 1.0 mmol) at 0 °C. After heating at reflux for 10 h, the reaction was quenched by consecutive addition of AcOEt, MeOH, and 5% $NaHCO_3$. Usual workup followed by purification by column chromatography (SiO_2, hexane–AcOEt = 5:1) gave 48 mg (68%) of 2-hexyl-2-methylcyclopentanol: IR (neat) 3370 (OH), 1673, 1466, 1377, 1296, 1149, 1122, 1081 cm^{-1}; ^1H NMR (500 MHz) δ 0.84 (s, 3, CH_3), 0.88 (t, J = 6.3 Hz, 3, CH_3), 1.29 (m, 14, CH_2), 1.53–1.65 (m, 2, CH_2), 1.95–2.05 (br, 1, OH), 3.72 (m, 1, CHOH); ^{13}C NMR (126 MHz) δ 14.10, 20.23, 22.68, 23.21, 24.89, 30.37, 31.91, 32.86, 35.14, 35.48, 45.92, 80.76. Without further purification, the carbinol (48 mg, 0.26 mmol) thus obtained was dissolved in CH_2Cl_2 (2 mL) and added to a suspension of PCC (233 mg, 1.1 mmol) and AcONa (107 mg, 1.3 mmol) in CH_2Cl_2 (10 mL). After being stirred at room temperature for 3 h, the mixture was diluted with ether and passed through a short silica gel pad. Concentration of eluents followed by column chromatography (SiO_2, hexane–AcOEt = 7:1) of the residue gave 20 mg (41%) of **4a**, bp 80 °C (9 Torr), whose IR and ^1H NMR spectra were identical with those of the same ketone **4a** obtained by the electroreduction of **1a**.

Rearrangement by the Combined Use of Cobaloxime with $NaBH_4$. Sodium borohydride (16 mg, 0.42 mmol) was added to a solution of aqueous 10 N NaOH (0.1 mL) and pyridine (0.3 mL) in EtOH (3 mL). To this solution was added (chloropyridine)-cobaloxime(III) (194 mg, 0.46 mmol), and the resulting black solution of cobaloxime(I) was stirred for 1 min. A solution of **1a** (100 mg, 0.38 mmol) in ethyl ether (3 mL) was added to the above solution with cooling on an ice–water bath, and the reaction mixture was stirred for 30 min at the same temperature. After

(11) R_3SnH-induced 1,2-acyl rearrangements: (a) Dowd, P.; Choi, S.-C. *J. Am. Chem. Soc.* **1987**, *109*, 3493 and 6548. (b) Dowd, P.; Choi, S.-C. *Tetrahedron Lett.* **1989**, *30*, 6129.

(12) Electrochemistry of alkylcobaloximes: (a) Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558. (b) Reference 6d.

(13) Cycloalkenone syntheses by rearrangements: (a) Grieco, P. A.; Abood, N. *J. Org. Chem.* **1989**, *54*, 6008. (b) Greene, A. E.; Charbonnier, F. *Tetrahedron Lett.* **1985**, *26*, 5525. (c) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 534. (d) Sasaki, K.; Kushida, T.; Iyoda, M.; Oda, M. *Tetrahedron Lett.* **1982**, *23*, 2117.

(14) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(15) Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3112.

(16) Halpern, J. *Science* **1985**, *227*, 869.

(17) Melting points and boiling points indicated by air-bath temperature are uncorrected. IR spectra were recorded on a JASCO FT-5000 spectrometer. ^1H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ (Me_4Si as an internal standard). Column chromatography was carried out with Merck Kieselgel 60, Art. 7734 (silica gel), with hexane–AcOEt as eluent. The purity of all electrolyzed products, isolated, was judged to be >95% by ^1H NMR and ^{13}C NMR spectral determination. Elemental analyses were performed in our laboratory. Starting 2-(bromomethyl)-2-alkylcycloalkanones **1** were prepared from the corresponding 2-alkyl-2-(methoxycarbonyl)cycloalkanones in ca. 52–82% yields by the following sequence: (1) ethylenedioxy acetalization of the starting keto ester, (2) reduction of the resulting acetal ester with $LiAlH_4$, (3) methanesulfonylation of the primary hydroxyl group by the action of methanesulfonyl chloride and triethylamine, (4) hydrolysis of ethylenedioxy acetal group with perchloric acid, and (5) S_N2 replacement of the methanesulfonate to the bromide with lithium bromide.

(18) Boeckmann, R. K., Jr.; Bruza, K. J. *Tetrahedron Lett.* **1977**, 4187.

(19) Corey, E. J.; Beams, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210.

(20) Paterson, I.; Fleming, I. *Tetrahedron Lett.* **1979**, 2179.

removal of almost all of the ethanol under reduced pressure, the mixture was extracted with AcOEt (3 × 5 mL). The combined extracts were washed with brine and dried (Na_2SO_4). The residue was purified by column chromatography (SiO_2, hexane–AcOEt = 20:1) to give 18.3 mg (27%) of **2a** as an oil.

Rearrangement of 1 with Ph_3SnH in 0.12 M Solution; Typical Procedure. A mixture of **1a** (R = C_6H_{13}, 110 mg, 0.42 mmol), Ph_3SnH (250 mg, 0.71 mmol), and AIBN (7 mg) in benzene (10 mL) was heated at reflux for 20 h. The mixture was concentrated and the residue was flash-distilled at 130–140 °C (10–20 Torr) to exclude tin reagents. The distillate was purified by column chromatography (SiO_2, hexane–AcOEt = 10:1–7:1) to give **3a** (27 mg, 50%) and **4a** (8 mg, 11%).

Spectral data of the compounds listed in Tables I and II are as follows.

3-Butyl-2-cyclohexenone (2b): bp 92–95 °C (26 Torr); IR (neat) 1671 (C=O), 1626 (C=C), 1458, 1255, 1195, 967, 888, 758 cm^{-1}; ^1H NMR (200 MHz) δ 0.90 (t, J = 7.1 Hz, 3, CH_3), 1.21–1.55 (m, 4, CH_2), 1.90–2.00 (m, 2, CH_2), 2.16–2.37 (m, 6, CH_2), 5.86 (m, 1, HC=C); ^{13}C NMR (50 MHz) δ 13.80, 22.31, 22.69, 29.01, 29.63, 37.30, 37.74, 125.57, 166.81, 200.05.

3-Butylcyclohexanone (3b): bp 78–79 °C (14 Torr); IR (neat) 1715 (C=O), 1433, 1226, 731, 696 cm^{-1}; ^1H NMR (500 MHz) δ 0.88 (t, J = 6.5 Hz, 3, CH_3), 1.28 (m, 6, CH_2), 1.59–1.68 (m, 2, CH_2), 1.75 (m, 1, CH_2), 1.89 (d, J = 13.5 Hz, 1, CH_2), 1.97–2.02 (m, 1, CH_2), 2.00–2.06 (m, 1, CH_2CO), 2.22–2.28 (m, 1, CH_2CO), 2.34 (m, 1, CH_2CO), 2.42 (m, 1, CH_2CO); ^{13}C NMR (126 MHz) δ 14.02, 22.72, 25.32, 28.84, 31.32, 36.30, 39.07, 41.53, 48.26, 212.31.

2-Butyl-2-methylcyclopentanone (4b): bp 69–70 °C (14 Torr); IR (neat) 1740 (C=O), 1462, 1162, 1108, 1060, 808, 729, 665 cm^{-1}; ^1H NMR (500 MHz) δ 0.88 (t, J = 7.3 Hz, 3, CH_3), 0.99 (s, 3, CH_3), 1.08–1.16 (m, 1, CH_2), 1.24–1.31 (m, 3, CH_2), 1.33–1.42 (m, 2, CH_2), 1.67–1.73 (m, 1, CH_2), 1.82–1.94 (m, 3, CH_2), 2.16–2.32 (m, 2, CH_2CO); ^{13}C NMR (126 MHz) δ 13.99, 18.71, 21.84, 23.28, 26.48, 35.64, 36.40, 37.73, 48.31, 223.97.

3-Undecyl-2-cyclohexenone (2c): bp 159–161 °C (25 Torr); IR (neat) 1673 (C=O), 1628 (C=C), 1348, 1325, 1253, 1193, 967, 665 cm^{-1}; ^1H NMR (500 MHz) δ 0.88 (t, J = 7.0 Hz, 3, CH_3), 1.26 (m, 14, CH_2), 1.29 (m, 2, CH_2), 1.50 (m, 2, CH_2), 1.98 (m, 2, CH_2), 2.20 (t, J = 7.5 Hz, 2, CH_2), 2.28 (t, J = 6.1 Hz, 2, CH_2), 2.36 (m, 2, CH_2CO), 5.87 (s, 1, HC=C); ^{13}C NMR (126 MHz) δ 14.01, 22.67, 22.73, 26.92, 29.25, 29.31, 29.38, 29.49, 29.60, 29.66 (2 C), 31.89, 37.35, 38.08, 125.61, 166.81, 200.01. Anal. Calcd for $C_{17}H_{30}O$; C, 81.54; H, 12.07. Found: 81.56; H, 12.11.

3-Undecylcyclohexanone (3c): bp 150 °C (14 Torr); IR (neat) 1717 (C=O), 1466, 1226, 1058, 866, 729, 696 cm^{-1}; ^1H NMR (500 MHz) δ 0.88 (t, J = 7.0 Hz, 3, CH_3), 1.26 (m, 21, CH_2), 1.62–1.69 (m, 1, CH_2), 1.75 (m, 1, CH_2), 1.89 (m, 1, CH_2), 1.97–2.02 (m, 1, CH_2), 2.02–2.07 (m, 1, CH_2CO), 2.20–2.29 (m, 1, CH_2CO), 2.35 (m, 1, CH_2CO), 2.42 (m, 1, CH_2CO); ^{13}C NMR (126 MHz) δ 14.12, 22.68, 25.33, 26.65, 29.34, 29.58, 29.62 (2 C), 29.65 (2 C), 31.33, 31.90, 36.62, 39.09, 41.54, 48.25, 212.29. Anal. Calcd for $C_{17}H_{32}O$; C, 80.89; H, 12.78. Found: 81.15; H, 12.77.

2-Methyl-2-undecylcyclopentanone (4c): bp 131–133 °C (25 Torr); IR (neat) 1740 (C=O), 1464, 1162, 1064, 723 cm^{-1}; ^1H NMR (500 MHz) δ 0.87 (t, J = 7.0 Hz, 3, CH_3), 0.98 (s, 3, CH_3), 1.24 (m, 18, CH_2), 1.36 (m, 2, CH_2), 1.70 (m, 1, CH_2), 1.83–1.92 (m, 3, CH_2), 2.16–2.33 (m, 2, CH_2CO); ^{13}C NMR (126 MHz) δ 14.11, 18.72, 21.84, 22.68, 24.28, 29.34, 29.53, 29.60 (2 C), 29.64, 30.22, 31.90, 35.64, 36.68, 37.73, 48.35, 223.96.

3-Hexyl-2-cycloheptenone (2d): bp 120–123 °C (25 Torr); IR (neat) 1653 (C=O), 1456, 1346, 1201, 940, 884 cm^{-1}; ^1H NMR (500 MHz) δ 0.87 (t, J = 6.3 Hz, 3, CH_3), 1.28 (m, 6, CH_2), 1.46 (m, 4, CH_2), 1.77 (m, 2, CH_2), 2.17 (m, 2, CH_2), 2.40 (m, 2, CH_2), 2.56 (m, 2, CH_2CO), 5.90 (s, 1, HC=C); ^{13}C NMR (126 MHz) δ 14.02, 21.22, 22.51, 25.09, 27.51, 28.93, 31.60, 32.51, 41.09, 42.12, 129.13, 162.57, 204.27.

3-Hexylcycloheptanone (3d): bp 111 °C (14 Torr); IR (neat) 1700 (C=O), 1456, 1350, 1251, 727 cm^{-1}; ^1H NMR (500 MHz) δ 0.87 (t, J = 6.5 Hz, 3, CH_3), 1.25, 1.27 (m, 9, CH_2), 1.36–1.43 (m, 1, CH_2), 1.50–1.70 (m, 4, CH_2), 1.83–1.93 (m, 3, CH_2), 2.37 (dd, J = 14.1, 10.6 Hz, 1, CH_2CO), 2.44–2.49 (m, 3, CH_2CO); ^{13}C NMR (126 MHz) δ 14.07, 22.60, 24.40, 26.87, 28.54, 29.36, 31.78, 36.04, 36.86, 37.28, 43.90, 49.99, 214.90.

2-Hexyl-2-methylcyclohexanone (4d): bp 99–102 °C (14 Torr); IR (neat) 1709 (C=O), 1456, 1431, 1125, 986, 727, 698 cm^{-1}; ^1H NMR (200 MHz) δ 0.87 (t, J = 6.5 Hz, 3, CH_3), 1.02 (s, 3, CH_3), 1.26 (m, 9, CH_2), 1.36 (td, J = 14.0, 4.0 Hz, 1, CH_2), 1.50–1.57 (m, 1, CH_2), 1.69 (m, 2, CH_2), 1.78 (m, 2, CH_2), 1.92 (m, 1, CH_2), 2.28–2.34 (m, 1, CH_2CO), 2.37–2.48 (m, 1, CH_2CO); ^{13}C NMR (126 MHz) δ 14.05, 21.03, 22.53, 22.60, 23.64, 27.54, 29.95, 31.67, 37.54, 38.80, 39.46, 48.65, 216.36.

Acknowledgment. We are thankful to the SC-NMR Laboratory of Okayama University for experiments with the Varian VXR-500 instrument. H.K. appreciates generous encouragement from Professor T. Sekiba of Toyama National College of Technology.

Registry No. **1a**, 135480-94-3; **1b**, 135454-90-9; **1c**, 135454-91-0; **1d**, 135454-92-1; **2a**, 66262-12-2; **2b**, 6301-49-1; **2c**, 135454-93-2; **2d**, 135454-94-3; **3a**, 69824-93-7; **3b**, 39178-69-3; **3c**, 103539-05-5; **3d**, 135454-94-3; **4a**, 135454-95-4; **4b**, 72653-69-1; **4c**, 135454-96-5; **4d**, 135454-97-6; cobaloxime, 3252-99-1.

Supplementary Material Available: Spectral data of **2a**, **3a**, and **4a** and ^1H NMR spectra of the compounds **2b,d**, **3b,d**, and **4b–d** (9 pages). Ordering information is given on any current masthead page.

Oxidation of Alcohols Using Bis(trichloromethyl) Carbonate as Activator of Dimethyl Sulfoxide

Claudio Palomo,* Fernando P. Cossio, Jesús M. Ontoria, and José M. Odriozola

Departamento de Química Orgánica, Facultad de Química, Universidad del País Vasco, Aptdo. 1072, 20080-San Sebastián, Spain

Received April 2, 1991

Mild oxidation of alcohols to carbonyl compounds is a very important synthetic operation in organic synthesis.[1] One useful method involves the combination of DMSO with a variety of electrophilic reagents.[2] DMSO–oxalyl chloride system,[3] DMSO–phosgene,[4] and DMSO–diphosgene dimer[5] have resulted in high yield conversions of alcohols to carbonyl compounds. However, the potential hazards associated with these reagents render them inappropriate for large-scale production of carbonyl compounds. In connection with studies directed toward the synthesis of (±)-PS-5 and (±)-PS-6 carbapenem antibiotics and their 6-epi analogues[6] we needed multigram quantities of aldehydes **8** and **9** (Scheme I). After examining some oxidizing reagents, we found that bis(trichloromethyl)carbonate (triphosgene), recently developed by Eckert and Forster,[7] is an excellent activator of DMSO to perform mild oxidations of alcohols to carbonyl compounds and this system is adaptable for a large-scale operations. Triphosgene, is a white crystalline solid, which has been successfully employed in a variety of synthetic transformations[7-10] as a safe alternative to phosgene and diphosgene dimer. Surprisingly, the oxidations of alcohols to carbonyl compounds promoted by triphosgene–DMSO has,

(1) For a recent review, see: Haines, A. H. In *Methods for the Oxidation of Organic Compounds*; Academic Press: New York, 1988.
(2) For reviews, see: Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165. Tidwell, T. T. *Org. React.* **1990**, *39*, 297; *Synthesis* **1990**, 857.
(3) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(4) Barton, D. H. R.; Garner, B. J.; Wightman, R. H. *J. Chem. Soc.* **1964**, 1855.
(5) Takano, S.; Inomata, K.; Tomita, S.; Yanase, M.; Samizu, K.; Ogasawara, K. *Tetrahedron Lett* **1988**, *29*, 6619.
(6) Palomo, C.; Ontoria, J. M.; Odriozola, J. M.; Aizpurua, J. M.; Ganboa, I. *J. Chem. Soc., Chem. Commun.* **1990**, 248.
(7) Eckert, H.; Forster, B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 894.
(8) Daly, W. H.; Pouché, D. *Tetrahedron Lett.* **1988**, *29*, 5859.
(9) Coghan, M. J.; Caley, B. A. *Tetrahedron Lett.* **1989**, *30*, 2033.
(10) Jochims, J. C.; Hehl, S.; Herzberger, S. *Synthesis* **1990**, 1128.

0022-3263/91/1956-5948$02.50/0