1,2-di-*O*-methylmandelates:[17] **1a**, δ 5.22 (m, 1 H); **1b**, δ 5.31 (m, 1 H).

Reaction of (*R*)-4-(Phenylmethoxy)butane-1,2-diol (1a) with CCl_4/Ph_3P. To a well-stirred solution of triphenylphosphine (421 mg, 1.61 mmol) in 10 mL of dry CCl_4 was added **1a** (300 mg, 1.53 mmol) in one portion at room temperature. The reaction mixture was allowed to stir at reflux temperature for 16 h and then cooled to room temperature. *n*-Pentane (5 mL) was added, and the resultant precipitate of triphenylphosphine oxide was separated by filtration. After evaporation of the filtrate under reduced pressure, the residual liquid was plug filtered (10% EtOAc in hexane) through a short silica gel column to give 62 mg (17% yield) of **4a** (R_f = 0.63, hexane:EtOAc = 5:3) and 205 mg (63% yield) mixture of **2a** and **3a** (2:1) as a colorless liquid (R_f = 0.40 (**2a**) and 0.32 (**3a**), hexane:EtOAc = 5:3). **4a**: IR (neat) 1255, 1020, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.24 (m, 5 H), 4.52 (s, 2 H), 4.32 (m, 1 H), 3.81–3.71 (dd, *J* = 8.4, 5.9 Hz, 2 H), 3.70–3.64 (m, 2 H), 2.36–2.27 (ddt, *J* = 3.7, 14.6, 7.1 Hz, 1 H), 1.98–1.89 (ddt, *J* = 4.7, 14.0, 4.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 138.25, 128.42, 127.63, 73.22, 66.41, 58.28, 48.70, 35.61; MS, *m/e* 232 (M^+), 125, 107, 91 (100), 79, 65, 51, 39. Anal. Calcd for $C_{11}H_{14}Cl_2O$: C, 56.67; H, 6.05. Found: C, 56.93; H, 6.17. Small portions of **2a** and **3a** were separated in order to obtain the spectral data as follows. **2a**: IR (neat) 3420 (OH), 1080, 742, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.25 (m, 5 H), 4.52 (s, 2 H), 4.02 (m, 1 H), 3.75–3.61 (m, 2 H), 3.57 (dd, *J* = 5.0, 11.2 Hz, 1 H), 3.51 (dd, *J* = 6.1, 11.1 Hz, 1 H), 3.15 (d, *J* = 3.9 Hz, 1 H, OH exchangeable), 1.87 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 137.79, 128.42, 127.74, 127.62, 73.24, 70.38, 67.66, 49.32, 33.72; MS, *m/e* 214, 107, 91 (100), 79, 65, 51, 39; HRMS for $C_{11}H_{15}O_2Cl$, calcd *m/e* 214.0760, obsd 214.0751. **3a**: IR (neat) 3400 (OH), 1080, 735, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.27 (m, 5 H), 4.52 (s, 2 H), 3.81–3.6 (m, 4 H), 2.70 (t, *J* = 6.7 Hz, 1 H, OH exchangeable), 2.15–2.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 137.79, 128.42, 127.74, 73.24, 66.67, 66.47, 61.35, 34.68; MS, m/e 214, 107, 91 (100), 79, 65, 51, 41; HRMS for $C_{11}H_{15}O_2Cl$, calcd *m/e* 214.0760, obsd 214.0757. Anal. Calcd for $C_{11}H_{15}ClO_2 \cdot 0.15H_2O$ (mixture of **2a** and **3a**): C, 60.78; H, 7.09. Found: C, 60.50; H, 6.98.

Reaction of (*S*)-4-(Phenylmethoxy)butane-1,2-diol (1b) with CCl_4/Ph_3P. The reaction was carried out with 1.0 g (5.1 mmol) of **1b** exactly as described above for the *R* enantiomer, **1a**, to give 159 mg (13%) of the corresponding dichloro derivative, **4b**, and 711 mg (65%) of a mixture of the monochloro alcohols, **2b** and **3b**. All spectral data (IR, ^1H NMR, ^{13}C NMR) for **2b–4b** were as reported above for **2a–4a**.

(*R*)-[2-(Phenylmethoxy)ethyl]oxirane (5a). The mixture (181 mg, 0.84 mmol) of monochloro alcohols **2a** and **3a** was dissolved in 4 mL of mixed solvent (H_2O:DMSO = 3:1), and 71 mg (1.27 mmol) of KOH was added into the reaction mixture. The reaction mixture was stirred at 60 °C and monitored by TLC until all the starting material was consumed (about 45 min). The reaction mixture was then poured into ice water (10 mL) and extracted with ether. The combined ether phase was washed with brine, dried (Na_2SO_4), and evaporated. The residue was applied to a silica gel column, and the desired oxirane was obtained by elution with 3% EtOAc in hexane to give 127 mg (85% yield) of **5a** as a colorless liquid: IR (neat) 1258, 1026, 738, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.25 (m, 5 H), 4.53 (s, 2 H), 3.64 (t, 2 H), 3.07 (m, 1 H), 2.79 (dd, *J* = 4.3, 4.9 Hz, 1 H), 2.52 (dd, *J* = 5.0, 2.7 Hz, 1 H), 1.98–1.76 (ddt, *J* = 4.7, 14.1, 6.5 Hz), 1.75–1.65 (ddt, *J* = 6.4, 14.1, 5.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 138.31, 128.36, 127.57, 73.1, 67.06, 50.04, 47.05, 33.0; $[\alpha]_D$ = +16.9 (*c* 2.51, $CHCl_3$); HRMS for $C_{11}H_{14}O_2$ ($M - H^+$), calcd *m/e* 177.0915, obsd 177.0915. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.12; H, 7.91. Found: C, 73.95; H, 7.90.

(*S*)-[2-(Phenylmethoxy)ethyl]oxirane (5b). The reaction was carried out with 636 mg (2.96 mmol) of the (*S*)-monochloro alcohols, **2b** and **3b**, exactly as described above for the *R* enantiomer to give 423 mg (80%) of **5b** as a colorless liquid: $[\alpha]_D$ = −14.5 (*c* 2.51, $CHCl_3$); HRMS for $C_{11}H_{14}O_2$ ($M - H^+$), calcd *m/e* 177.0915, obsd 177.0916. All spectral data (IR, ^1H NMR, ^{13}C NMR) for **5b** were as reported for **5a**.

(17) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370.

Determination of Percent Enantiomeric Excess of (*R*)- and (*S*)-Oxiranes by Shift Reagent ($Eu(hfc)_3$). A measured amount of the epoxide to be analyzed (2–4 mg) was transferred to a high-quality 5-mm NMR tube. One drop of deuteriochloroform containing 1% TMS was then added, followed by sufficient $CDCl_3$ (dried over 4A molecular sieves) to bring the total volume in the tube to 0.5 mL. A fresh solution of $Eu(hfc)_3$ was made up by transferring the sublimed $Eu(hfc)_3$ (65 mg) to a 1.0-mL volumetric flask. The material was then dissolved in sufficient CCl_4 to bring the solvent level to the mark. Shift reagent titration was carried out by transfer of the $Eu(hfc)_3$ solution (via a 25-μL syringe) to the oxirane sample solution in the NMR tube. Addition of the shift reagent was repeated until the desired separation of the signals due to the benzylic protons (Figure 1) was optimal.

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Supplementary Material Available: Figure 1, a portion of each of the ^1H NMR spectra obtained for the racemic (*R,S*)-oxirane, the *R* isomer (**5a**), and the *S* isomer (**5b**) (1 page). Ordering information is given on any current masthead page.

Oxovanadium(V)-Induced Oxidative Transformations of Cyclobutanones

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Transition-metal compounds can often act as catalysts or even reagents in organic reactions that involve electron transfer.[1] Some versatile synthetic methods based on one-electron transfer have been recently developed.[2] Vanadium(V) compounds, in which vanadium is in a high oxidation state, are known to promote one-electron oxidation reactions.[3] The utilization of such compounds is, however, limited because the reactions are usually performed in acidic aqueous media.[3b] In previous papers, we reported that $VO(OR)Cl_2$ works well as a Lewis acid with oxidative capability in organic solvents.[4]

Cyclobutanones are regarded as important sources of four-carbon synthetic building blocks via ring opening.[5]

(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

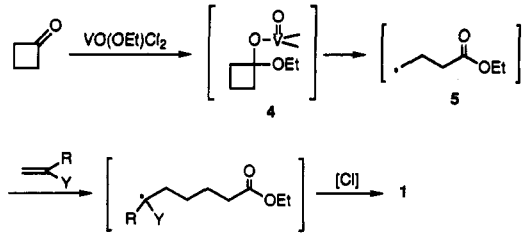
(2) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Curran, D. P. *Synthesis* **1989**, 417, 489. (c) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1974**, *39*, 3456. (d) Corey, E. J.; Kang, M.-C. *J. Am. Chem. Soc.* **1984**, *106*, 5384. (e) Yang, F. Z.; Trost, M. K.; Fristad, W. E. *Tetrahedron Lett.* **1987**, *28*, 1493. (f) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152, 6551. (g) RajanBabu, T. V.; Nugent, W. A. *Ibid.* **1989**, *111*, 4525. (h) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *Ibid.* **1989**, *111*, 8014.

(3) (a) Schwartz, M. A.; Holton, R. A.; Scott, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 2800; **1970**, *92*, 1090. (b) Freeman, F. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Ed.; Plenum Press: New York, 1986; pp 1–39. (c) The imido derivative of $VOCl_3$ was reported to be useful for oxidative decarboxylations in organic solvents. See: Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 3069.

(4) Hirao, T.; Mori, M.; Ohshiro, Y. (a) *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399; (b) *J. Org. Chem.* **1990**, *55*, 358. (c) Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1990**, *31*, 3917. (d) Hirao, T.; Mikami, S.; Mori, M.; Ohshiro, Y. *Tetrahedron Lett.* In press.

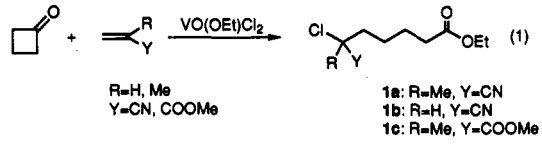
0022-3263/91/1956-2264$02.50/0

Scheme I



We now report a novel oxidative ring-opening reaction of cyclobutanones that is induced by $VO(OEt)Cl_2$.

Treatment of cyclobutanone with $VO(OEt)Cl_2$ in the presence of an olefin bearing an electron-withdrawing substituent gave the adduct **1** (eq 1). For example, the

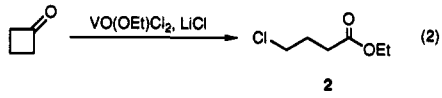


R=H, Me
Y=CN, COOMe

1a: R=Me, Y=CN
1b: R=H, Y=CN
1c: R=Me, Y=COOMe

$VO(OEt)Cl_2$-induced reaction of cyclobutanone with methacrylonitrile gave ethyl 6-chloro-6-cyanoheptanoate (**1a**). Ethyl 4-chlorobutyrate (**2**) was obtained as the other isolated product. Some other results are listed in Table I. Copper(II) chloride facilitated the oxidative addition reaction.[6] However, the use of lithium chloride instead of copper(II) chloride caused a decrease in the yield of **1a**.

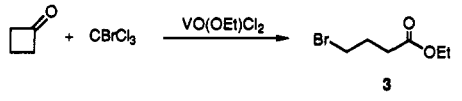
The reaction of cyclobutanone with $VO(OEt)Cl_2$ in the absence of an olefin gave **2** as the sole isolable product (eq 2). The chlorine atom was introduced regioselectively at



2

the γ-position of the product. The presence of lithium chloride (10 equiv) was required for a higher yield (43% instead of 28% in the absence of lithium chloride). A decrease to 2.0 equiv from 3.0 equiv in the amount of $VO(OEt)Cl_2$ led to a lower yield (29%) of **2**. $VO(OEt)_3$ did not induce oxidative ring opening under similar conditions, possibly due to the now lower acidity of the reaction medium.

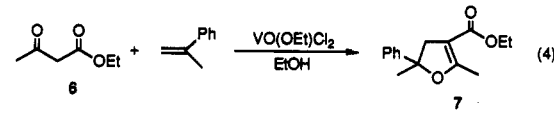
When cyclobutanone was treated with a combination of $VO(OEt)Cl_2$ and bromotrichloromethane, ethyl 4-bromobutyrate (**3**) was exclusively produced, in 60% yield (eq 3). The presence of **2** was not detected, indicating that bromotrichloromethane could also serve as a halogen source.



3

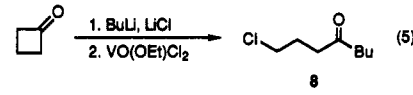
These findings suggested the intervention of a radical intermediate. A plausible reaction path is illustrated in Scheme I. Thus, a one-electron oxidation of the initial adduct **4**, which is obtained by attack of $VO(OEt)Cl_2$ on cyclobutanone, is followed by a ready ring opening, aided by relief of ring strain,[3b,7] to generate radical **5**.[8] This intermediate then adds the carbon–carbon double bond of the olefin. Reaction of the addition product with a chlorine source then gives **1**.

The addition to the carbon–carbon double bond seems to involve the interaction of a half-filled orbital of the radical intermediate with the lowest unoccupied orbital of the olefin. On the other hand, an interaction with the highest occupied orbital apparently occurs in the $VO(OEt)Cl_2$-induced reaction of ethyl acetoacetate (**6**) with α-methylstyrene in ethanol to give 3-(ethoxycarbonyl)-2,5-dimethyl-5-phenyl-4,5-dihydrofuran (**7**) in 52% yield (eq 4).



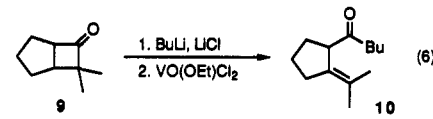
6 **7**

Oxovanadium cyclobutoxide intermediates, or their chemical equivalents, can be formed by transmetalation of the lithium cyclobutoxides prepared from cyclobutanones and alkyllithiums. This discovery expands the versatility of $VO(OEt)Cl_2$ in oxidative reactions. Thus, cyclobutanone was converted to 1-chloro-4-octanone (**8**, 70% yield) by treatment with butyllithium in the presence of lithium chloride, followed by treatment with $VO(OEt)Cl_2$ (eq 5). This reaction is also characteristic of $VO(OEt)Cl_2$; $VO(OEt)_3$ did not act as an oxidant in this system. The absence of lithium chloride resulted in a lower yield, as was the case in the reaction of $VO(OEt)Cl_2$ and cyclobutanone (eq 2).



8

Regioselective bond fission in the cyclobutoxide derived from the bicyclic cyclobutanone **9** gave the olefinic ketone **10** in 40% yield (eq 6).



9 **10**

The one-pot ring-cleavage reaction (eqs 5 and 6) may also be explained by a $VO(OEt)Cl_2$-induced one-electron oxidation of the oxovanadium cyclobutoxide adduct. The regioselectivity and lack of chlorination in the latter case can be assumed to be due to differences in the stability of the possible radical intermediates.

$VO(OEt)Cl_2$ is thus a useful one-electron oxidizing agent for oxidative ring-openings of cyclic carbonyl compounds.[4a]

Experimental Section

IR spectra were recorded with a Hitachi 270-30 spectrometer. ^1H NMR spectra were recorded with a JEOL JNM-FX90Q, a JEOL JNM-GSX270, or a JEOL JNM-GSX400 spectrometer. Chemical ionization and electron impact mass spectra were recorded with a JEOL JMS-DX303 instrument.

$VO(OEt)Cl_2$ was prepared by the drop-by-drop addition of ethanol to an equimolar amount of commercially available $VOCl_3$ in hexane, while nitrogen was bubbled through the reaction

(5) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1980**, 2639. Trost, B. M. *Top. Curr. Chem.* **1986**, *133*, 3. Wong, N.-C.; Lau, K.-L.; Tam, K.-F. *Ibid.* **1986**, *133*, 83. Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797.

(6) A similar rate acceleration was reported for Mn(III)-induced reactions. See: Nikishin, G. I.; Vinogradov, M. G.; Fedorova, T. M. *J. Chem. Soc., Chem. Commun.* **1973**, 693. Snider, B. B.; Mohan, R.; Kates, S. A. *J. Org. Chem.* **1985**, *50*, 3659. Oumar-Mahamat, H.; Moustrou, C.; Surzur, J.-M.; Bertrand, M. P. *Tetrahedron Lett.* **1989**, *30*, 331.

(7) Meyer, K.; Rocek, J. *J. Am. Chem. Soc.* **1972**, *94*, 1209. Rocek, J.; Aylward, D. E. *Ibid.* **1975**, *97*, 5452. Rocek, J.; Radkowsky, A. E. *J. Org. Chem.* **1973**, *38*, 89.

(8) Alternatively, the cyclobutoxide intermediate could undergo a one-electron oxidation by $VO(OEt)Cl_2$, followed by ring opening to **5**. Another species capable of reacting with an olefin may be a radical intermediate which displays some kind of interaction with the vanadium salt.

Table I. $VO(OEt)Cl_2$-Induced Oxidative Addition Reaction of Cyclobutanone[a]

olefin[b] R	Y	additive, equiv	product yield, %[c] 1	2
Me	CN	$CuCl_2$ 3.0	1a 63 (55)	35 (25)
		LiCl 4.0	1a 23	35
			1b 38	16
H	CN	$CuCl_2$ 3.0	1b 55	13
Me	COOMe	$CuCl_2$ 3.0	1c 32	13

[a] Cyclobutanone (1.0 mmol), $VO(OEt)Cl_2$ (3.0 mmol, 3.0 equiv), CH_2Cl_2, -75 °C, 2 h; rt, 14–19 h; argon atmosphere. [b] 10–12 equiv. [c] Yields were determined by GLC. The numbers in parentheses represent the yields isolated from a fivefold scale-up of the reaction.

mixture at room temperature. The product was purified by distillation under reduced pressure [bp 52–54 °C (2 mmHg)].[9] $VO(OEt)_3$ was obtained from Shinko Chemical Co., Ltd.

Representative Procedure for the Oxidative Addition Reaction of Cyclobutanone with Olefins. To a suspension of dry $CuCl_2$ (15.0 mmol, 2.02 g) in dichloromethane (10 mL) was added $VO(OEt)Cl_2$ (15.0 mmol, 2.75 g) at room temperature under argon. The mixture was cooled to -75 °C, and methacrylonitrile (60 mmol, 4.03 g) was added drop-by-drop over 20 min. The resulting mixture was kept at -75 °C for 2 h. Cyclobutanone (5.0 mmol, 0.35 g) was then added drop-by-drop over 15 min at -75 °C. Stirring was continued at -75 °C for 2 h. The mixture was allowed to warm to room temperature and was stirred for 17 h. Ether (50 mL) and 5% aqueous $Na_2S_2O_3$ (5 mL) were then added, and the two liquid layers were separated. The aqueous layer was extracted with ether (3 × 100 mL). Concentrated aqueous HCl (2 mL) was added to the aqueous solution, which was again extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc, 10:1) to give **1a** (R_f = 0.17) and **2** in 55% and 25% yield, respectively.

The reaction of cyclobutanone (1.0 mmol) with other olefins was performed in a similar manner. The yield of **1** was determined by GLC (2.1 m 10% PEG 20M column, 200 °C) as shown in Table I.

Ethyl 6-chloro-6-cyanoheptanoate (1a): IR (neat) 2244, 1738 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.27 (t, 3 H, J = 7.1 Hz), 1.5–1.8 (m, 4 H), 1.92 (s, 3 H), 1.9–2.1 (m, 2 H), 2.36 (t, 2 H, J = 7.1 Hz), 4.15 (q, 2 H, J = 7.1 Hz); CIMS m/z 218 (M^+ + 1, 100), 172 (10).

Ethyl 6-chloro-6-cyanohexanoate (1b): IR (neat) 2248, 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.26 (t, 3 H, J = 7.2 Hz), 1.5–1.9 (m, 4 H), 1.9–2.2 (m, 2 H), 2.36 (t, 2 H, J = 6.7 Hz), 4.15 (q, 2 H, J = 7.2 Hz), 4.46 (t, 1 H, J = 6.6 Hz); CIMS m/z 204 (M^+ + 1, 100), 158 (25).

Ethyl 6-chloro-6-(methoxycarbonyl)heptanoate (1c): IR (neat) 1738 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.25 (t, 3 H, J = 7.1 Hz), 1.3–1.5 (m, 2 H), 1.6–1.7 (m, 2 H), 1.74 (s, 3 H), 1.9–2.1 (m, 2 H), 2.32 (t, 2 H, J = 7.3 Hz), 3.78 (s, 3 H), 4.13 (q, 2 H, J = 7.1 Hz); CIMS m/z 251 (M^+ + 1, 100), 205 (23).

Ring Opening of Cyclobutanone to Ethyl 4-Chlorobutyrate (2). To a suspension of dry LiCl (10 mmol, 0.424 g) in ether (2 mL) was added $VO(OEt)Cl_2$ (3.0 mmol, 0.549 g) at room temperature under nitrogen. Cyclobutanone (1.0 mmol, 70 mg) was then added drop-by-drop over 15 min at room temperature. Stirring was continued for 13 h. The mixture was then diluted with ether (10 mL) and was treated with 5% aqueous HCl (1 mL). The two liquid layers were separated. The aqueous layer was extracted with ether (5 × 20 mL). The combined organic layers were washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. GLC analysis (2.1 m 10% PEG 20M column, 160 °C) of the residue showed only the presence of **2** (43% yield). Ester **2** was identified by comparison of its spectra with those of a commercially available authentic sample.

The reaction with $VO(OEt)_3$ was carried out in a similar manner.

Ring Opening of Cyclobutanone to Ethyl 4-Bromobutyrate (3). To a solution of $VO(OEt)Cl_2$ (3.0 mmol, 0.549 g) in ether (2 mL) was added bromotrichloromethane (5.0 mmol, 0.992 g) over 10 min at room temperature under nitrogen. Cyclobutanone (1.0 mmol, 70 mg) was then added drop-by-drop over 20 min. Stirring was continued for 13 h. The reaction mixture was then diluted with ether (10 mL) and was treated with saturated aqueous $NaHCO_3$ (1 mL). The two liquid layers were separated. The aqueous layer was extracted with ether (4 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. GLC analysis (2.1 m 10% PEG 20M column, 160 °C) of the residue showed only the presence of **3** (60% yield). Ester **3** was identified by comparison of its spectra with those of a commercially available authentic sample.

$VO(OEt)Cl_2$-Induced Reaction of Ethyl Acetoacetate (6) with α-Methylstyrene. To a solution of $VO(OEt)Cl_2$ (3.0 mmol, 0.549 g) in ethanol (2 mL) was added drop-by-drop α-methylstyrene (2.0 mmol, 0.236 g) over 15 min at -75 °C under argon. Stirring was continued at -75 °C for 2 h. Ethyl acetoacetate (**6**, 1.0 mmol, 0.130 g) was then added drop-by-drop over 15 min. Stirring was continued for 2 h. The mixture was then warmed to room temperature and was stirred for 20 h. Ether (10 mL) and 5% aqueous $Na_2S_2O_3$ (1 mL) were added, and the two liquid layers were separated. The aqueous layer was extracted with ether (3 × 20 mL), then was treated with concentrated aqueous HCl (0.5 mL), and was again extracted with ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried ($MgSO_4$), and concentrated. GLC analysis (2.1 m 10% PEG 20M column, 200 °C) of the residue showed the presence of 3-(ethoxycarbonyl)-2,5-dimethyl-5-phenyl-4,5-dihydrofuran (**7**) in 52% yield. It was identified by comparison of its spectra with those of an authentic sample.[2c]

Representative Procedure for the Oxidative Transformation of Cyclobutanones to Ketones 8 and 10. To a mixture of butyllithium (1.0 mmol, 1.6 M in hexane) and lithium chloride (3–10 mmol) in dichloromethane (2 mL) was added cyclobutanone (1.0 mmol, 70 mg) drop-by-drop over 20 min under nitrogen at -75 °C. The mixture was kept at -75 °C for 2–3 h. $VO(OEt)Cl_2$ (3.0 mmol, 0.549 g) was then added and stirring was continued at -75 °C for 2 h. The mixture was warmed to room temperature and was stirred for 2 h. Workup with 5% aqueous HCl, as described above, gave **8**. GLC analysis (2.1 m 10% PEG 20M column, 160 °C) showed the presence of **8** (70% yield).[10] Ketone **10** was obtained in 40% yield in a similar manner.

8: IR (neat) 1718 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.87 (t, 3 H, J = 6.8 Hz), 1.0–2.1 (m, 6 H), 2.37 (t, 2 H, J = 7.2 Hz), 2.53 (t, 2 H, J = 6.9 Hz), 3.50 (t, 2 H, J = 6.4 Hz); EIMS m/z 162 (M^+, 6), 120 (21), 105 (50), 85 (95), 77 (24), 58 (100).

10: IR (neat) 1708 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, 3 H, J = 7.3 Hz), 1.29 (tq, 2 H, J = 7.3, 7.0 Hz), 1.5–1.6 (m, 2 H), 1.56 (s, 3 H), 1.69 (s, 3 H), 1.7–2.0 (m, 4 H), 2.2–2.4 (m, 2 H), 2.41 (dt, 2 H, J = 7.3, 1.8 Hz), 3.4–3.6 (m, 1 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 13.8, 21.5, 21.6, 22.5, 25.3, 26.0, 31.2, 31.3, 39.7, 55.6, 125.4, 134.1, 212.7; EIMS m/z 194 (M^+).

Elemental analyses of **1a–c** and **10** gave satisfactory results.

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(9) Funk, von H.; Weiss, W.; Zeising, M. *Z. Anorg. Allg. Chem.* **1958**, *296*, 36.

(10) Uchida, M.; Komatsu, M.; Morita, S.; Kanbe, T.; Yamasaki, K.; Nakagawa, K. *Chem. Pharm. Bull.* **1989**, *37*, 958.