(d, 1 H, J = 10.5 Hz), 3.59 (s, 3 H), 7.28 (s, 5 H).

13: IR (neat) 2950, 1740, 1240 cm^{-1}; NMR (CCl_4) δ 1.42 (d, 3 H, J = 7.0 Hz), 3.54 (q, 2 H, J = 7.0 Hz), 3.60 (s, 3 H), 3.74 (s, 3 H), 6.76 (d, 2 H, J = 7.0 Hz), 7.14 (d, 2 H, J = 7.0 Hz).

14: IR (neat) 1735, 1240, 790 cm^{-1}; NMR (CCl_4) δ 1.42 (d, 3 H, J = 7.0 Hz), 3.57 (s, 3 H), 3.57 (q, 1 H, J = 7.0 Hz), 5.00 (s, 2 H), 6.73–7.50 (m, 9 H). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.66; H, 6.67.

15: IR (neat) 2990, 1740 cm^{-1}; NMR (CCl_4) δ 1.43 (d, 3 H, J = 8.0 Hz), 3.60 (s, 3 H), 3.61 (q, 1 H, J = 8.0 Hz), 7.23 (s, 4 H).

16: IR (neat) 1950, 1740 cm^{-1}; NMR (CCl_4) δ 0.70 (d, 3 H, J = 6.0 Hz), 1.00 (d, 3 H, J = 6.0 Hz), 2.05–2.65 (m, 1 H), 3.04 (d, 1 H, J = 10.5 Hz), 3.45 (s, 3 H), 7.26 (s, 4 H). Anal. Calcd for $C_{12}H_{15}ClO_2$: C, 63.58; H, 6.69. Found: C, 63.34; H, 6.63.

17: IR (neat) 3050, 3000, 1740 cm^{-1}; NMR (CCl_4) δ 1.60 (d, 3 H, J = 7.0 Hz), 3.60 (s, 3 H), 4.41 (q, 1 H, J = 7.0 Hz), 7.30–8.10 (m, 1 H). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.40; H, 6.68.

Synthesis of 20. Synthesis of **19** was carried out according to the known method.[27] Into a solution of **2** (10 mmol) in 10 mL of DMF was added 2.5 mmol of **19** in 5 mL of DMF at −78 °C. After the reaction mixture was stirred for 15 min at the same temperature, the solution was added dropwise to a solution of methyl iodide (10 mmol) in 10 mL of DMF at −78 °C. The product **20** was isolated by using a silica gel column (CH_2Cl_2).

20: IR (KBr) 1730, 1670, 1610, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.51 (d, 3 H, J = 7.5 Hz), 3.65 (s, 3 H), 3.37 (q, 1 H, J = 7.5 Hz), 4.74 (s, 2 H), 7.30–8.00 (m, 8 H). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80. Found: C, 73.15; H, 5.73.

Registry No. **1**, 616-45-5; **2**, 45373-29-3; **4**, 101-41-7; **6**, 31508-44-8; **7**, 2294-71-5; **8**, 72615-27-1; **9**, 23786-14-3; **10**, 68641-16-7; **11**, 52449-43-1; **12**, 2876-78-0; **13**, 50415-73-1; **14**, 89618-33-7; **15**, 50415-70-8; **16**, 86618-06-6; **17**, 72221-62-6; MeI, 74-88-4; *i*-PrI, 75-30-9; EtI, 75-03-6.

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New Preparations of Lanthanide Alkoxides and Their Catalytical Activity in Meerwein–Ponndorf–Verley–Oppenauer Reactions

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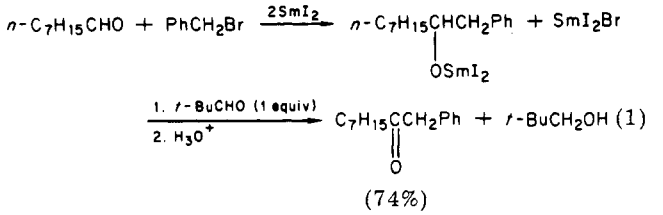
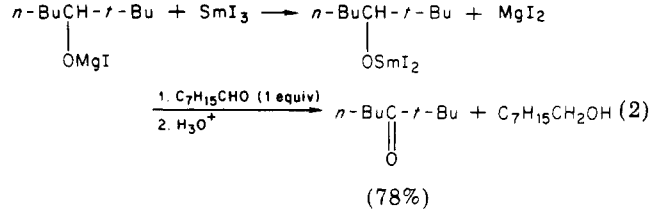
Meerwein–Ponndorf–Verley reductions of aldehydes and ketones[1] and Oppenauer oxidations of alcohols[2] have been known for a long time.[3] These reactions are useful tools for the synthesis of vitamins and steroids[4-6] but otherwise have restricted synthetic applications. Extensive studies of the experimental conditions of the reaction have been performed, dealing with the nature of oxidizing and reducing agents[1,2,7] or of catalysts. The most widely used catalysts are aluminum alkoxides,[3,8] but potassium,[9] sodium,[10] and zirconium[11] alkoxides, alumina,[12] and some transition-metal complexes have also been reported as catalysts.[13]

Oppenauer oxidations can be achieved under mild conditions as compared with many other oxidation methods. Moreover, oxidants (ketones or aldehydes) are cheap. However, a drastic limitation to its use for a wide range of organic substrates is the requirement of great amounts of metal alkoxides. Usually, stoichiometric quantities (or an excess) are used for these reactions. Recently, Seebach reported a system using a catalytic amount of zirconium *tert*-butoxide, but few examples using aluminum alkoxides in catalytic amounts have appeared in the literature.[7,14]

In 1977,[15] we mentioned the occurrence of a competitive Meerwein–Ponndorf reaction to explain the product distribution obtained in the "pseudo-Barbier" alkylation of aldehydes by organic halides using diiodosamarium. Recently, we prepared secondary samarium alkoxides in a similar way using a benzylic halide as the alkylating agent.[16] We directly verified their reducing activity in the Meerwein–Ponndorf reduction of pivalaldehyde. Reaction 1 has been performed in stoichiometric conditions, in THF, at room temperature.



When samarium triiodide is added to a magnesium alkoxide (reaction 2), the mixture reduces octanal, whereas no reaction occurs with the magnesium alkoxide alone. So



we assume an exchange reaction and formation of samarium alkoxide. Although this reaction needs a stoichiometric amount of samarium triiodide, it is interesting to point out that it can be considered as a quite general preparation of dissymmetrical ketones. Encouraged by these preliminary results, we explored the potential of samarium alkoxides in oxidoreduction reactions. We now report *new methods of synthesis* of samarium alkoxides and their *catalytic activity* in Meerwein–Ponndorf–Verley reductions and Oppenauer oxidations.

Catalysts

Several routes have been described for the synthesis of alkoxy lanthanide compounds:[8,17] (i) reaction of an alcohol

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Table I. Catalyzed Oppenauer Oxidations[a]

entry	alcohol	oxidant (equiv)	rctn time, h	oxidation product	% yield[b]
1	2-octanol	2-butanone (8)	24	2-octanone	90
2	2-octanol	propionaldehyde (4)	16		0[c]
3	α-methylbenzyl alcohol	2-butanone (8)	24	acetophenone	98
4	1-octanol	2-furaldehyde (8)	5	octanal	69
5	1-octanol	trichloroacetaldehyde (4)	24		0[d]
6	2,2-diphenylpropanol	2-furaldehyde (8)	5	2,2-diphenylpropionaldehyde	67
7	benzyl alcohol	trimethylacetaldehyde (4)	24	benzaldehyde	80[e]
8	4-*tert*-butylbenzyl alcohol	2-furaldehyde (1)	24	4-*tert*-butylbenzaldehyde	82
9	2-cyclohexen-1-ol	acetone (4)	24	2-cyclohexen-1-one	15[e,f]
10	2-cyclohexen-1-ol	acetone (4)	24	2-cyclohexen-1-one	85[e,g]
11	*cis*-carveol	acetone (4)	24	carvone	95[e]
12	geraniol	2-furaldehyde (3)	24	citral (*E* + *Z*)	62
13	geraniol	2-butanone (4)	24	citral (*E* + *Z*)	10[h]
14	cholesterol	cyclohexanone (4)	48	4-cholesten-3-one	78

[a] 65 °C, 0.1 equiv of *t*-BuOSmI$_2$. [b] Isolated yield. [c] Aldolization and crotonization products from propionaldehyde. [d] Product was $Cl_3CCH(OH)OCH_2C_7H_{15}$. [e] Yield determined by GLC and ^{1}H NMR. [f] Dicyclohexenyl ether (48%); cyclohexenyl isopropyl ether (4%). [g] Reaction with catalyst 1; no ether detected. [h] Myrcene (60%), limonene (18%), ocimene (8%).

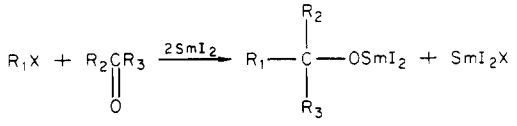
Table II. Catalyzed Meerwein–Ponndorf Reductions[a]

entry	ketone or aldehyde	redn product	% yield[b]	other product (%)
1	2-octanone	2-octanol	86	
2	octyl aldehyde	1-octanol	66[c]	octanoic acid (33)[c]
3	*p*-nitrobenzaldehyde	*p*-nitrobenzyl alcohol	94	
4	*p*-anisaldehyde	4-methoxybenzyl alcohol	58[c]	*p*-anisic acid (29)[c]
5	ethyl pyruvate	ethyl lactate	80[c]	
6	cinnamaldehyde	cinnamyl alcohol	58	cinnamyl isopropyl ether (3)[c]
7	cinnamaldehyde		0	cinnamyl isopropyl ether (85)[b]

[a] 65 °C; 0.1 equiv of *t*-BuOSmI$_2$; 4 equiv of 2-propanol; 24 h. [b] Isolated yield. [c] Yield determined by GLC and ^{1}H NMR. [d] Reaction time: 7 h.

with metal in the presence of a small amount of a mercuric salt, (ii) exchange reaction between an anhydrous lanthanide halide and an alkali or magnesium alkoxide, and (iii) reaction of an alcohol with an alkoxy lanthanide compound. These products are very moisture sensitive, and their preparation requires drastic anhydrous conditions.

Preparation of LnI_2 (Ln = Yb, Sm) and LnI_3 may be readily performed under anhydrous conditions in THF.[15] For this reason, we investigated some routes to alkoxy ytterbium and samarium compounds starting from their iodides. Coupling between an aldehyde or a ketone and an organic halide is mediated by SmI_2.[18] Various alkoxy samarium compounds are obtained in this way:



These products are efficient catalysts in Meerwein–Ponndorf reactions (see above). Catalyst 1 was prepared by reductive coupling between benzyl bromide and octanal:[16]

$$C_7H_{15}CHO + PhCH_2Br \xrightarrow{2SmI_2} C_7H_{15}CH(OSmI_2)CH_2Ph + SmI_2Br$$

We also prepared alkoxy samarium compounds by an exchange reaction between SmI_3 and sodium isopropoxide:

$$xi\text{-PrONa} + SmI_3 \rightarrow SmI_{(3-x)}(i\text{-PrO})_x + x\text{NaI}$$

$$x = 1\text{–}3$$

(Separation of the samarium compounds from NaI was not achieved.) These species are poor catalysts.

We investigated an original route to samarium and ytterbium alkoxide as follows: SmI_2 and YbI_2 smoothly react with di-*tert*-butyl peroxide to yield "*t*-BuOLnI$_2$":

$$t\text{-BuOO-}t\text{-Bu} + 2LnI_2 \xrightarrow[\text{room temp}]{\text{THF}} 2\text{"}t\text{-BuOLnI}_2\text{"}$$

catalyst 2: Ln = Sm; rctn time, 15 min; concn, 9×10^{-2} M

catalyst 3: Ln = Yb; rctn time, 2 h; concn, 4×10^{-2} M

We did not perform structural determinations and the formula "*t*-BuOLnI$_2$" only represents the stoichiometric composition of the products,[19] as indicated by titrations (see Experimental Section).

As cerium is the least expensive of the lanthanides we tried to prepare some alkoxides of this element. We succeeded in reacting cerium metal with iodine and 2-propanol in THF (catalyst 4):

$$Ce + I_2 + i\text{-PrOH} \xrightarrow[1\text{ h}]{\text{THF, room temp}} \text{"}i\text{-PrOCeI}_2\text{"} + {}^1/_2H_2$$

A yellow 0.08 M solution of the alkoxide is readily obtained as indicated by titrations. This method is probably quite general for *i*-PrOLnI$_2$ synthesis, except for Ln = Sm or Yb where, under these conditions, SmI_2 and YbI_2 are the end products.

Results and Discussion

We found experimental conditions under which truly catalytic Oppenauer oxidations of any type of alcohols

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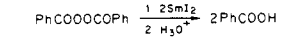
(18) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

(19) Reductive cleavage of the O–O bond by LnI_2 seems to be a general reaction: SmI_2 was found to react instantaneously in THF with benzoyl peroxide:



(primary, secondary, allylic, aliphatic, aromatic) and Meerwein–Ponndorf reductions of various aldehydes and ketones can be performed. Results are listed in Tables I and II. Our reactions involve 0.1 mol of catalyst 2 (in the general case) per mole of substrate.

In the Meerwein–Ponndorf reductions, 2-propanol (4 equiv) was an excellent hydride donor. As for Oppenauer oxidations, the choice of the hydride acceptor depends on several parameters.

(1) Thermodynamic considerations were clearly established by Adkins and Cox.[20] Aldehydes are more efficient oxidants than ketones and conjugated systems should be preferred to saturated ones. These conclusions apply well in our case. Thus, use of 2-furaldehyde in order to oxidize primary alcohols succeeds (entries 4 and 6, Table I), but attempts with 2-butanone failed. Moreover, oxidation of geraniol with 2-butanone leads mainly to intramolecular dehydration products, whereas 2-furaldehyde[7] leads to citral formation (entries 12 and 13, Table I). Lastly, oxidations of cinnamyl alcohol and ethyl lactate failed, while consequently, and conversely, reduction of cinnamaldehyde and ethyl pyruvate with 2-propanol were successful (entries 6 and 5, Table II).

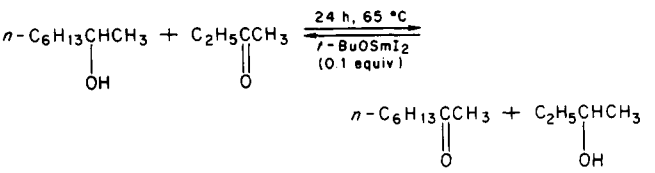
(2) Secondary reactions occurred with some aldehydes used as oxidant. Chloral leads to hemiacetal formation from the starting alcohol (entry 5, Table I); such reactions are known to be catalyzed by trivalent lanthanides.[21] Enolizable aldehydes such as propionaldehyde or isobutyraldehyde give products arising from aldolization and crotonization (entry 2, Table I). Of course this is not the case with 2-furaldehyde or trimethylacetaldehyde, which are not enolizable (entries 4, 6–8, and 12, Table I).

Secondary reactions may also involve the substrates and/or the products. In several experiments involving allylic alcohols, symmetrical and unsymmetrical ethers or polyenes are obtained as major products from intra- or intermolecular dehydration reactions (entries 9 and 138 Table I; entry 7, Table II). These reactions, catalyzed by a trivalent samarium salt, have been previously observed.[22] Oxidations of primary alcohols lead to aldehydes, but the reaction must be stopped in the case of enolizable aldehydes after a 5-h reaction time because of secondary processes; indeed, after 24 h, no more aldehyde can be recovered (entry 4, Table I).

We must point out that appreciable amounts of water have to be avoided in the reaction media. Substrates and reagents must be anhydrous. For example, oxidation of 2-octanol with 2-butanone leads to 2-octanone in 90% yield (entry 1, Table I) when the ketone (commercial sample, 0.20% water) has been dried on molecular sieves for 24 h; but the yield drops to 27% when such a precaution has not been taken.

Besides catalyst 2, we also tried to perform catalytic Oppenauer oxidations with other lanthanide alkoxides. Catalyst 1 is as efficient as Catalyst 2 (for oxidation of 2-cyclohexen-1-ol, it is even better (entry 10, Table I)); nevertheless, we did not use it because we cannot easily remove the corresponding alcohol or ketone after reaction. Catalyst 3 catalyzes oxidations of aliphatic alcohols in good yields, but allylic alcohols follow a dehydration pathway (more important with Yb^{3+} than Sm^{3+}). Since Yb is much more expensive than Sm, we selected t-$BuOSmI_2$ as catalyst. Catalyst 4 is efficient in the oxidation of 2-octanol and methylphenyl carbinol by 2-butanone (90% yield in both cases). Nevertheless, only 50% yield was obtained in the oxidation of carveol to carvone (using acetone) and no benzaldehyde could be observed after attempted oxidation of benzyl alcohol by trimethyl acetaldehyde. Consequently, we must consider catalyst 2 as the best among the catalysts we prepared.

Beyond the synthetic interest of the reactions we performed, we studied a particular case in order to evaluate the degree of reversibility of the reaction. We chose the "2-octanone/2-octanol" system opposed to the "2-butanone/2-butanol" one:



Starting from an equimolar mixture of 2-octanol and 2-butanone or of 2-octanone and 2-butanol, we obtained after 24 h at 65 °C, in the presence of 0.1 equiv of t-$BuOSmI_2$, the same composition: 2-octanone/2-octanol = 0.95.

Assuming that, after workup, 2-octanone and 2-octanol were the only products of the reaction,[23] we can conclude that, whatever the starting composition (2-octanol/2-butanone/2-octanone/2-butanol = 1:1:0:0 or 0:0:1:1) is, the system reaches finally the (0.51; 0.51; 0.49; 0.49) one. This latter can then be considered as the equilibrium composition. Consequently, the equilibrium constant at 65 °C is close to 0.90. Oxidation of 2-octanol with 8 equiv of 2-butanone (entry 1, Table I) starts from the (1; 8; 0; 0) composition and should lead to the $(1 - x; 8 - x; x; x)$ one. Using the previous value of the equilibrium constant, we find $x = 0.88$. The experimental value ($x = 0.90$) is in good agreement with the calculated one.

Conclusions

Various lanthanide iodo alkoxides, especially t-$BuOSmI_2$, showed promising activity in Meerwein–Ponndorf–Verley–Oppenauer reactions. An interesting feature of these compounds is their ability to react as catalysts and the need to use an amount of reagent (ketone or alcohol) only dictated by the thermodynamical considerations of the system under investigation. The major limitation is their deactivation by water; experimental conditions have been found where fairly good results were obtained with 0.1 mol equiv of catalyst with respect to substrate. Some side reactions (crotonization of enolizable aldehydes, dehydration reactions of allylic alcohols) have been controlled by adjusting the experimental conditions. Clearly the catalytic activity depends strongly on the nature of the lanthanide catalyst; it would be interesting to find structural modifications improving the activity and to make detailed comparisons with catalysts on the basis of other metals.[26]

Experimental Section

Apparatus. Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer. Proton magnetic resonance spectra (^1H NMR) were recorded with a Perkin-Elmer Model R 32 spec-

(20) Adkins, H.; Cox, F. W. *J. Am. Chem. Soc.* **1938**, *60*, 1151.
(21) Luche, J. L.; Gemal, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 976.
(22) Ouertani, M., Thèse de Doctorat 3ème cycle, Université Paris-Sud, 1982.
(23) No other products could be detected by either ^1H NMR or GLC (even after a long period with a hot oven).
(24) This should be used preferentially within 2 h.
(25) Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. *Nouv. J. Chim.* **1981**, *5*, 479.
(26) Under the experimental conditions as indicated in Table I (entry 1), the preliminary experiments showed that t-$BuOAlCl_2$ is completely inactive in Oppenauer oxidation of 2-octanol.

trometer at 90 MHz. Chemical shifts in $CDCl_3$ are reported in parts per million from Me_4Si as an internal standard. Mass spectra were obtained on a GC-MS Ribermag R 10-10 instrument. Gas chromatographic analyses were carried out on a Carlo Erba Fractovap 2101 chromatograph. Peak area integration was performed with a Delsi Icap 5 calculator. Flash chromatography was performed on silica gel (Merck, 230–240 mesh; 0.040–0.063 mm).

Reagents and Solvent. THF must be anhydrous and deoxygenated. It was carefully distilled under nitrogen from sodium benzophenone ketyl. Commercial cerium powder is kept in oil and must be cleaned with pentane in a drybox filled with N_2. Samarium diiodide was prepared according to the procedure formerly described.[18] All organic compounds were commercial samples purified by distillation and dried over molecular sieves (4-Å type).

Stoichiometric Meerwein–Ponndorf Reaction with a Samarium Homobenzylic Alkoxide. A 192-mg sample of octanal (1.5 mmol) and 256 mg of benzyl bromide (1.5 mmol) were dissolved in 10 mL of dry THF. The solution was poured into 30 mL of a 0.1 M solution of SmI_2 in THF (3 mmol). This solution was stirred for a few minutes while decoloration occurred, 129 mg of trimethylacetaldehyde (1.5 mmol), dissolved in 5 mL of dry THF, was poured into the preceding solution. Continued stirring for 2 h at room temperature lead, after hydrolysis and workup,[18] to a crude product, which was analyzed by GLC and ^1H NMR. 1-Phenyl-2-nonanone was present in 74% yield.

Stoichiometric Meerwein–Ponndorf Reaction with a Magnesium Alkoxide. A 40-mL sample of a 0.2 M solution of iodomagnesium alkoxide (*n*-BuCH(OMgI)-*t*-Bu) was prepared according to the Grignard procedure (1.84 g of butyl iodide (10 mmol), excess magnesium, 688 mg of pivalaldehyde (8 mmol) in 40 mL of ether). Ten milliliters of this solution (2 mmol), separated from the excess of magnesium, was allowed to react with 256 mg of octanal (2 mmol) for 24 h at 45 °C. After hydrolysis and ether extraction, the crude product was analyzed by GLC (Carbowax 20M, 160 °C). 2,2-Dimethyl-3-heptanol and 2,2-dimethyl-3-heptanone could be detected in 70% and 7% yield, respectively.

Stoichiometric Meerwein–Ponndorf Reaction with a Samarium Alkoxide. A 254-mg sample of iodine (1 mmol) dissolved in 5 mL of THF was added to 20 mL of a 0.1 M SmI_2 solution in THF (2 mmol) under nitrogen at room temperature. Decoloration occurred immediately; 10 mL of the preceding iodomagnesium alkoxide solution (2 mmol) was then added. A 256-mg sample of octanal (2 mmol) dissolved in 5 mL of THF was then allowed to react with the solution of samarium alkoxide for 24 h at 45 °C. After hydrolysis and ether extraction, the crude product was analyzed by GLC (Carbowax 20M, 160 °C). 2,2-Dimethyl-3-heptanol could be detected in 10% yield and 2,2-dimethyl-3-heptanone was obtained in 78% yield.

Preparation of Catalyst 1. Octanal (128 mg, 1 mmol) and benzyl bromide (171 mg, 2 mmol) dissolved in 5 mL of THF were added under nitrogen to 20 mL of 0.1 M SmI_2 in THF (2 mmol) at room temperature. After stirring for 3 min, the typical blue color of SmI_2 disappeared and a yellow precipitate formed.

Preparation of Catalyst 2. Samarium diiodide in 0.1 N THF solution (20 mL, 2 mmol) was added to a 5-mL THF solution of di-*tert*-butyl peroxide (146 mg, 1 mmol). Decoloration from deep blue green to yellow occurred after stirring for 15 min at room temperature. A light yellow solution was obtained.[24]

Titrations of THF Solution of Catalyst 2. Titration with 0.1 N aqueous HCl and titration with iodine in toluene were performed as previously described.[25] The latter showed that the solution has no reducing power (neither from the presence of divalent samarium nor from C–Sm bonds). The former showed that O–Sm bonds are present. The concentration is 0.08 M; it is confirmed by titration of Sm with EDTA at pH 5.5 (and xylenol orange as indicator) and titration of iodides by potentiometry in the presence of silver nitrate ($2I^-$/Sm). These combinated titrations agree with the "*t*-$BuOSmI_2$, *n*THF" formula for the species present in solution. The complete structure in solution remains unknown.

Preparation of Catalyst 3. The same procedure as for catalyst 2 was followed, using ytterbium diiodide instead of samarium diiodide. The same titrations led to the "*t*-$BuOYbI_2$, *n*THF" formula. The concentration was 0.04 M.

Preparation of Catalyst 4. Cerium powder (1.614 g, 11.5 mmol), iodine (1.463 g, 5.74 mmol), and 2-propanol (345 mg, 5.74 mmol) were mixed in 72 mL of dry THF. After stirring for 2 h, a yellow solution was obtained and excess metal settled out. Titrations lead to the "CeI_2O-*i*-Pr, *n*THF" formula. The concentration was 0.08 M.

General Procedure for Oppenauer Oxidations. Samarium diiodide, *tert*-butoxide (0.08 M in THF, 2 mL, 0.16 mmol), alcohol (1.6 mmol), and oxidant (1.6*n* mmol; *n* is the number of equivalents of oxidant) were dissolved in 10 mL of dry THF. The mixture was heated at 65 °C for 24 h or less (see Table I). Excess 0.1 N HCl was then added. Organic products were extracted twice with ether; the organic layer was then washed with brine, 0.1 N $Na_2S_2O_3$ solution, and brine. After drying over $MgSO_4$, ether, THF, and other volatile products (e.g., *t*-BuOH from the catalyst, acetone or 2-propanol, butanone or butanol, ...) were removed. The remaining material was purified by flash chromatography in order to remove the excess of oxidant and the corresponding alcohol produced by the reaction (this is the case when 2-furaldehyde was used as oxidant).

General Procedure for Meerwein–Ponndorf Reductions. The same procedure was followed, using 2 mL of *t*-$BuOSmI_2$ (0.08 M in THF, 0.16 mmol), 1.6 mmol of ketone or aldehyde, and 384 mg of 2-propanol (6.4 mmol).

Trichloro-2,2,2-acetaldehyde octyl hemiacetal: NMR ($CDCl_3$) δ 0.90 (t, J = 6 Hz, 3 H), 1.10–1.75 (m, 12 H), 3.50 (m, disappears after D_2O addition, 1 H), 4.35 (t, J = 7 Hz, 2 H), 5.0 (s, 1 H); mass spectrum (70 eV), m/e (relative intensity) 261 (0.6, M^+ – OH), 259 (1.1, M^+ – OH), 119 (31.9), 117 (27.7), 96 (20.1), 95 (22.0), 84 (38.6), 82 (63.4), 63 (33.6), 61 (71.4), 60 (23.2), 49 (40.5), 48 (21.8), 47 (100), 36 (31.5).

Trichloro-2,2,2-acetaldehyde benzyl hemiacetal: NMR ($CDCl_3$) δ 4.25 (m, disappears after D_2O addition, 1 H), 4.95 (s, 1 H), 5.35 (s, 2 H), 7.40 (s, 5 H); mass spectrum (70 eV), m/e (relative intensity) 256 (0.3, M^+), 254 (0.7, M^+), 119 (1.5), 117 (1.2), 107 (3.3), 91 (100), 77 (9.9), 65 (17.0), 51 (11.6), 39 (11.7).

Isopropyl 3-phenyl-2-propenyl ether: NMR ($CDCl_3$) δ 1.15 (d, J = 6 Hz, 6 H), 3.30–3.80 (m, 1 H), 4.00–4.25 (m, 2 H), 6.10–6.70 (m, 2 H), 7.10–7.50 (m, 5 H); mass spectrum (70 eV), m/e (relative intensity) 176 (38.6, M^+), 134 (46.3), 118 (9.3), 105 (100), 92 (94.7).

Isopropyl 2-cyclohexenyl ether: mass spectrum (70 eV), m/e (relative intensity) 140 (2.2, M^+), 112 (4.8), 98 (100), 81 (65.7), 70 (96.2), 55 (14.6), 43 (27).

Meerwein–Ponndorf Equilibration Reactions between 2-Octanol and 2-Octanone. Five milliliters of *t*-$BuOSmI_2$ (0.08 M in THF, 0.4 mmol), 520 mg of 2-octanol (4 mmol), and 288 mg of 2-butanone (4 mmol) were mixed at room temperature under nitrogen. The general procedure led to a crude product, which was analyzed by GLC (capillary column, OV1, 15 m, 55 °C) and ^1H NMR. 2-Octanol (t = 105 s) and 2-octanone (t = 89 s) may be separated under these GLC conditions. The product ratio was determined from the respective peak areas, using a calibration curve. The result was 2-octanone/2-octanol = 0.95.

A second experiment starting from 5 mL of *t*-$BuOSmI_2$ (0.08 M, 0.4 mmol), 512 mg of 2-octanone (4 mmol), and 296 mg of 2-butanol (4 mmol) led to the following ratio: 2-octanone/2-octanol = 0.94.

^1H NMR spectra are in agreement with these results. Integration of singlet (δ 2.1 (s, 3 H)) for 2-octanone and multiplet (δ 3.7 (m, 1 H)) for 2-octanol lead to the same values for the preceding ratios.

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Registry No. *t*-$BuOYbI_2$, 89890-10-8; SmI_2, 32248-43-4; (*n*-BuCH(OMgI)*t*-Bu), 89890-08-4; *t*-$BuOSmI_2$, 89890-09-5; octanal, 124-13-0; benzyl bromide, 100-39-0; trimethylacetaldehyde, 630-19-3; 1-phenyl-2-nonanone, 32508-90-0; butyl iodide, 542-69-8; 2,2-dimethyl-3-heptanol, 19549-70-3; 2,2-dimethyl-3-heptanone, 19078-97-8; di-*tert*-butyl peroxide, 110-05-4; ytterbium diiodide, 19357-86-9; cerium, 7440-45-1; iodine, 7553-56-2; 2-propanol, 67-63-0; trichloro-2,2,2-acetaldehyde octyl hemiacetal, 37964-93-5; trichloro-2,2,2-acetaldehyde benzyl hemiacetal, 37964-99-1; iso-

propyl 3-phenyl-2-propenyl ether, 13645-20-0; isopropyl 2-cyclohexenyl ether, 4982-24-5; 2-octanol, 123-96-6; 2-octanone, 111-13-7; 2-methylbenzyl alcohol, 98-85-1; 1-octanol, 111-87-5; 2,2-diphenylpropanol, 75-84-3; benzyl alcohol, 100-51-6; 4-*tert*-butylbenzyl alcohol, 877-65-6; 2-cyclohexen-1-ol, 822-67-3; *cis*-carveol, 1197-06-4; geraniol, 106-24-1; cholesterol, 57-88-5; 2-butanone, 78-93-3; propionaldehyde, 123-38-6; 2-furaldehyde, 98-01-1; trichloroacetaldehyde, 75-87-6; acetone, 67-64-1; cyclohexanone, 108-94-1; acetophenone, 98-86-2; 2,2-diphenylpropionaldehyde, 22875-82-7; benzaldehyde, 100-52-7; 4-*tert*-butylbenzaldehyde, 939-97-9; 2-cyclohexen-1-one, 930-68-7; carvone, 99-49-0; (*E*)-citral, 141-27-5; (*Z*)-citral, 106-26-3; 4-cholesten-3-one, 601-57-0; *p*-nitrobenzaldehyde, 555-16-8; *p*-anisaldehyde, 123-11-5; ethyl pyruvate, 617-35-6; cinnamaldehyde, 104-55-2; *p*-nitrobenzyl alcohol, 619-73-8; 4-methoxybenzyl alcohol, 105-13-5; ethyl lactate, 97-64-3; cinnamyl alcohol, 104-54-1; octanoic acid, 124-07-2; *p*-anisic acid, 100-09-4; dicyclohexenyl ether, 15129-33-6; myrcene, 123-35-3; limonene, 138-86-3; ocimene, 502-99-8.

Efficient Synthesis of 2-Methyl-1-cyclopentene-1-carboxylic Acid

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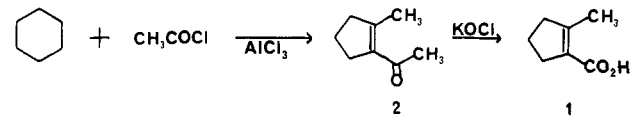
The utility of 2-methyl-1-cyclopentene-1-carboxylic acid (**1**) as a synthetic intermediate in our research efforts[1] as well as the efforts of other research groups[2] led us to develop a short, economical synthesis of this material. Previous syntheses[2,3] proved unsuitable for routine preparation of **1** in large quantities. A synthetic approach involving organocuprate addition to derivatives of 2-carbomethoxycyclopentanone reported previously by one of us[3d] and by Weiler and Sum[3e] appears to be quite sensitive to the purity of reagents and reaction scale.

The current approach was based on the recognition that a haloform-type oxidation of the known 1-acetyl-2-methylcyclopentene (**2**) should give the desired acid. The acetyl derivative **2** can be synthesized in a variety of ways. One common approach[4] utilizes an aldol cyclization of 2,7-octanedione,[5] but we have found that direct acetylation of cyclohexane provides an experimentally simple procedure that avoids the use of expensive starting materials or sensitive organometallic reagents. The conditions used for the acetylation reaction are a modification of the method reported by Tabushi.[9,10] It was found that treatment of the crude product with methanolic KOH prior to distillation gave material that did not discolor upon standing.

The haloform oxidation makes use of potassium hypochlorite formed by reaction of commercial calcium hypochlorite (Olin HTH) with potassium hydroxide and potassium carbonate.[11] Excess hypochlorite was destroyed by addition of sodium bisulfite, neutral materials were removed by ether extraction, and acid **1** was isolated by extraction after acidification to a Congo Red endpoint.[12]



2 **1**

Experimental Secton

1-Acetyl-2-methylcyclopentene (2). Aluminum trichloride (200 g, 1.5 mol) was added to 1 L of chloroform. Acetyl chloride (117.7 g, 1.5 mol) was added, and the mixture was stirred for 10 min, at which time cyclohexane (126.2 g, 1.5 mol) was added. The mixture was heated at reflux for 2 h, and then allowed to stir at room temperature for 2 days. The mixture was poured onto ice/HCl and the layers were separated. The aqueous layer was washed with CH_2Cl_2, and the combined organic layers were concentrated by rotary evaporation. The resulting material was dissolved in approximately 500 mL of methanol, 50 g of KOH was added, and the mixture was stirred overnight. The methanol was removed by rotary evaporation, and then the residue was dissolved in ether and washed with water and 10% NaOH. The ether layer was dried over $MgSO_4$, concentrated, and distilled (85–95 °C/27 torr) to yield 69.03 g (0.556 mol, 37% yield) of **2**: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.6–2.0 (m, 2 H), 2.1–2.2 (m, allylic CH_3), 2.23 ($COCH_3$), 2.3–2.8 (m, 4 H); ^{13}C ($CDCl_3$, 50.31 MHz) δ 16.8 (CH_3), 21.5 (C-4), 30.3 ($COCCH_3$), 34.4 and 41.2 (C-3 and C-5), 135.8 (C-1), 154.1 (C-2), 198.3 (CO).

2-Methyl-1-cyclopentene-1-carboxylic Acid (1). Commercial calcium hypochlorite (Olin HTH, 65% CaOCl, 35 g) was suspended in 140 mL of H_2O in a 250-mL Erlenmeyer flask. A solution of KOH (7 g, 0.125 mol) and K_2CO_3 (24.5 g, 0.177 mol) in 70 mL of H_2O was added. The flask was stoppered and shaken until the initial gelatinous precipitate liquefied. The potassium hypochlorite solution (containing approximately 0.14 mol of KOCl) was then filtered to remove the precipitated calcium salts and the filter cake was rinsed with 30 mL of water.

The resulting solution of potassium hypochlorite was cooled to 0 °C, and ketone **2** (10 g, 80.5 mmol) was added dropwise under

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(12) It is important that the solution be made strongly acidic before extraction or the isolated yield is drastically reduced.

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