We believe that these reactions ilustrate the synthetic potential of the stabilized phosphoramidate radicals in pyrrolidine synthesis. At present, we are thoroughly studying these and related reactions, and further applications of these results to the synthesis of heterocyclic natural products are under investigation and will be reported in due course.

Acknowledgment. Part of this work was supported by the Investigation Programme of the Comisión Asesora de Investigación Científica y Técnica. J.I.C. expresses his gratitude to the Excmo Cabildo Insular de La Palma for a fellowship.

Registry No. **1a**, 87509-76-0; **1b**, 87509-77-1; **1c**, 87509-78-2; **2a**, 87509-79-3; **2b**, 87509-80-6; **2c**, 87509-81-7; **2d**, 87509-82-8; **3**, 87509-83-9; **4**, 87509-84-0; **5a**, 87509-85-1; **5b**, 87509-86-2; **6**, 87509-87-3; 6β-amino-5α-cholestan-3β-ol, 87509-88-4; diethyl phosphorochloridate, 814-49-3; 3β-hydroxy-20(*S*)-aminopregn-5-ene, 5035-10-9; diphenyl phosphorochloridate, 2524-64-3.

Supplementary Material Available: IR, ^{1}H NMR, and mass spectral data for **1a–c**, **2a–c**, **3**, **4**, **5a,b**, and **6**. (5 pages). Ordering information is given on any current masthead page.

(21) Compound **2b**: mp 123–126 °C (*n*-pentane); $[\alpha]_D$ −24° ($CHCl_3$); IR ($CHCl_3$) ν_{max} 1725, 1590, 1490, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.27, 3.11 (2 H, AB, J = 11 Hz, C-19 H), 3.78 (1 H, m, $W_{1/2}$ = 10 Hz, C-6α H); MS, m/e (assignment, relative intensity) 675.4086 (M^+, $C_{41}H_{58}NO_5P$, 10), 352.1129 ($C_{20}H_{19}NO_3P$, 100). Compound **2c**: mp 137–141 °C (MeOH); $[\alpha]_D$ −13° ($CHCl_3$); IR ($CHCl_3$) ν_{max} 1720, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.06 (2 H, br s, C-19 H), 3.61 (1 H, m, $W_{1/2}$ = 10 Hz, C-6α H); MS, m/e (assignment, relative intensity) 703 (M^+, 2), 440.1675 ($C_{24}H_{27}NO_5P$, 100). Catalytic hydrogenation[20] over PtO_2 of **2c** followed by acid treatment [HCl(dil), pH 4, 25°C, 0.5 h] and subsequent neutralization (NaOH aqueous) afforded **2d**: 70% yield; IR ($CHCl_3$) ν_{max} 3400, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70 (3 H, s, C-18 H), 3.00 (2 H, br s, C-19 H), 3.45 (1 H, m, $W_{1/2}$ = 10 Hz, C-6α H); MS, m/e 443.3755 (M^+, $C_{29}H_{49}NO_2$).

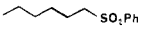
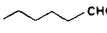
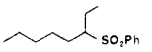
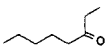
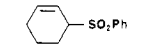
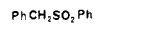
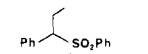
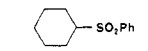
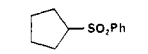
Carmen Betancor, José I. Concepción
Rosendo Hernández, José A. Salazar
Ernesto Suárez*
Instituto de Productos Naturales Orgánicos, CSIC and Departamento de Química Orgánica
Universidad La Laguna
La Laguna, Tenerife, Spain
Received July 28, 1983

A Novel Oxidative Desulfonylation. Facile Conversion of Sulfones to Aldehydes or Ketones

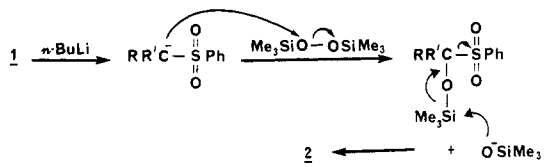
Summary: Alkyl, allylic, benzylic, and cycloalkyl sulfones can be converted to aldehydes or ketones in good-to-excellent yields by treatment with *n*-BuLi followed by $Me_3SiOOSiMe_3$. Preparation of ^{18}O-labeled carbonyl compounds with $Me_3Si^{18}O^{18}OSiMe_3$ was also successful.

Sir: The sulfone group is widely employed in organic synthesis.[1] However, this functional group must usually be removed after transformations have been completed. It has been proven that desulfonylation of sulfones to give carbonyl compounds can occur under basic conditions if an oxygen atom is located at the α position.[2] Recently, Little reported an elegant oxidative desulfonylation method to convert sulfones directly to ketones.[3] However, a 3-fold excess of the comparatively expensive oxidant, molybdenum peroxide (MoO_5·Py·HMPA)), is required. We report herein a general method for the conversion of sulfones to aldehydes or ketones using the readily available reagent bis(trimethylsilyl)perioxide[4] (BTSP). This method is also useful for the direct preparation of ^{18}O-labeled carbonyl compounds.

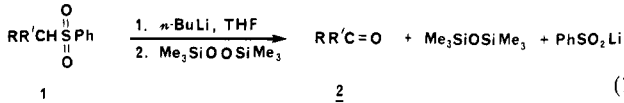
Table I. Conversion of Sulfones to Aldehydes or Ketones with BTSP

entry	sulfone	aldehyde or ketone[12]	yield, %
1			81
2			76
3			66
4			91
5			80
6			90
7			83

Scheme I



Removal of an α proton of phenylsulfone **1** with *n*-BuLi in tetrahydrofuran (THF) at −78 °C provides a bright yellow solution of the corresponding phenylsulfonyl carbanion. After 15 min, a slight excess of BTSP is injected to produce a reddish brown solution, which is then stirred overnight. A white precipitate appears, indicating the formation of the lithium salt of benzenesulfinic acid. After workup, aldehydes or ketones are obtained in good-to-excellent yields (see eq 1 and Table I.) This method has



(1)

been successful with some alkyl, allylic, benzylic, and cycloalkyl sulfones. For more hindered systems, such as cyclohexyl phenyl sulfone, refluxing is required to complete the reaction.

The mechanism of this two-step, one-pot reaction is illustrated in Scheme I. Owing to the low energy of O–O bonds and the high energy of O–Si bonds,[5] the trimethylsiloxyl anion (Me_3SiO^-) can behave as both an efficient leaving group and a back-attacking moiety.

In addition to requiring only simple manipulations and giving respectable yields, the method allows easy removal of byproducts.[6] It is therefore an attractive procedure for use in organic synthesis.

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Preparation of the starting material (1) begins with the corresponding bromide, RR'CHBr. Reaction of the Grignard reagent, RR'CHMgBr, with phenyl disulfide[7] followed by oxidation of the resulting phenyl thioether with *t*-BuOOH in the presence of a catalytic amount of $Mo(CO)_6$[8] provides the desired sulfone, generally in excellent overall yield.

By taking advantage of the fact that one oxygen atom of BTSP becomes the carbonyl oxygen of the product, it is possible to label an oxygen at a specific position in situ if the appropriate sulfone is used. Following the procedure reported by Davies et al.,[4] $H_2{}^{18}O_2$[9] was converted to $Me_3Si^{18}O^{18}OSiMe_3$, which was used directly for oxidative desulfonylation without further purification.[10] Thus, benzyl phenyl sulfone and cyclohexyl phenyl sulfone were converted to benzaldehyde-^{18}O and cyclohexanone-^{18}O, respectively. The labeled products were purified by Kugelrohr distillation. Their IR and mass spectra are identical with those of samples prepared by ^{18}O exchange of benzaldehyde and cyclohexanone with ^{18}O-enriched water under acidic conditions.

A typical procedure for the conversion of sulfones to unlabeled aldehydes or ketones is as follows. A THF solution (4.4 mL) of benzyl phenyl sulfone (0.501 g) was placed in a dried reaction flask under a nitrogen atmosphere and cooled to −78 °C. After *n*-BuLi (1.00 mL, 2.6 M in hexane) was injected into the reaction vessel, the bright yellow solution was stirred for 15 min. Neat BTSP (0.465 g) was added and the color changed to reddish brown. After the solution was stirred at room temperature overnight, it was poured into ice-cold, saturated aqueous $NaHCO_3$ solution and extracted twice with fresh ether. The combined organic extracts were dried ($MgSO_4$) and condensed under reduced pressure. The residue was chromatographed on a silica gel column, eluting with 20% EtOAc/hexanes, to provide pure benzaldehyde (0.208 g, 91%).[12]

Acknowledgment. This project was supported in part by BRSG Grant SO7 RR7041, awarded by the Biomedical Research Support Grant Program, Division of Research Resource, National Institutes of Health. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank R. Gibbs for his assistance with preliminary studies.

Registry No. 1 (R = H; R¹ = *n*-C_5H_{11}), 16823-63-5; 1 (R = C_2H_5; R¹ = *n*-C_5H_{11}), 87413-31-8; 1 (R = R¹ = CH=CH·$(CH_2)_3$), 87413-32-9; 1 (R = H; R¹ = Ph), 3112-88-7; 1 (R = C_2H_5; R¹ = Ph), 87413-33-0; 1 (R = R¹ = $(CH_2)_5$), 6947-57-5; 1 (R = R¹ = $(CH_2)_4$), 14633-46-6; 2 (R = H; R¹ = *n*-C_5H_{11}), 66-25-1; 2 (R = C_2H_5; R¹ = *n*-C_5H_{11}), 106-68-3; 2 (R = R¹ = CH=CH·$(CH_2)_3$), 930-68-7; 2 (R = H; R¹ = Ph), 100-52-7; 2 (R = C_2H_5; R¹ = Ph), 93-55-0; 2 (R = R¹ = $(CH_2)_5$), 108-94-1; 2 (R = R¹ = $(CH_2)_4$), 120-92-3; BTSP, 5796-98-5; $Me_3Si^{18}O^{18}OSiMe_3$, 87413-34-1; benzaldehyde-^{18}O, 55076-26-1; cyclohexanone-^{18}O, 73007-69-9; 1-bromohexane, 111-25-1; 3-bromooctane, 999-64-4; 3-bromocyclohexene, 1521-51-3; benzyl bromide, 100-39-0; α-ethylbenzyl bromide, 2114-36-5; cyclohexyl bromide, 108-85-0; cyclopentyl bromide, 137-43-9; phenyl disulfide, 882-33-7.

Jih Ru Hwu
Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland 21218
Received August 12, 1983

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(12) Idenfified by chromatographic as well as IR, NMR, and mass spectral comparison with an authentic specimen.

Total Synthesis of 1α,25(*R*)-Dihydroxy Vitamin D_3 26,23(*S*)-Lactone (Calcitriol Lactone), a Natural Metabolite of Vitamin D_3

Summary: The total synthesis of 1α,25(*R*)-dihydroxy vitamin D_3 26,23(*S*)-lactone (calcitriol lactone) and the 23*R*,25*S* diastereomer via a convergent approach utilizing an ene reaction for C20 and C23 functionalization and the HPLC comparison to the natural metabolite are described.

Sir: The isolation and characterization of a new vitamin D_3 metabolite, termed 1α,25(*R*)-dihydroxy vitamin D_3 26,23(*S*)-lactone (calcitriol lactone, **1a**), has been reported recently.[1,2] Due to the importance of the vitamin D_3 dependent endocrine system in humans and animals[3] and the unknown biological function of this new metabolite, we were interested in obtaining sufficient material for structure verification and biological evaluation. While several partial syntheses of the related metabolite 25-(*R*)-hydroxy vitamin D_3 26,23(*S*)-lactone (calcidiol lactone, **1b**) have been reported[4] and could potentially be used to form **1a**, we have applied our recently published total synthesis in the preparation of this metabolite.[5] With this, we extend the generality of the convergent total synthetic approach to 1α-hydroxy vitamin D_3 metabolites[5] as well as further explore the introduction of steroidal side-chain functionality via the ene reaction.[5,6] At the time we embarked on this project, the C23, 25 configurations of **1a**

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