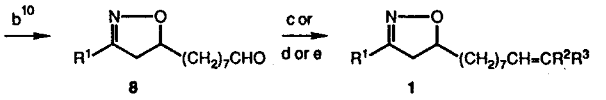

Reagents: (a) NaOCl, Et_3N, CH_2Cl_2 (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78°C (c) *n*-BuLi, Ph_3P^+-CHR^2R^3 X^- (X= Br or I), THF for **1a-1c**, **1f**, **1g**, and **1l** (d) NaH, $(MeO)_2P(=O)CH_2CO_2Me$, THF for **1d** and **1j** (e) $Ph_3P=CMeCO_2Me$, CH_2Cl_2 for **1e**

as follows.

6. Isoxazolines **2** required for these studies were prepared from oximes **5** ($R^1=C_5H_{11}$ or *i*-Pr) with 1,4-cyclohexadiene by employing the Lee's (3+2) cycloaddition method.[9]
7. Only saturated analogue of **3a** was isolated by the use of boric acid, other reaction conditions being same. When the amount of Lindlar catalyst was reduced to half, a 2 : 1 mixture of **3a** and its saturated derivative was obtained after 27h of reaction.
8. The presence of the other diastereomer was not detected by a 200 MHz NMR spectrometer.
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Synthesis of 1-Chlorovinyl Sulfoxides from Diethyl Chloro(phenylsulfinyl)methanephosphonate

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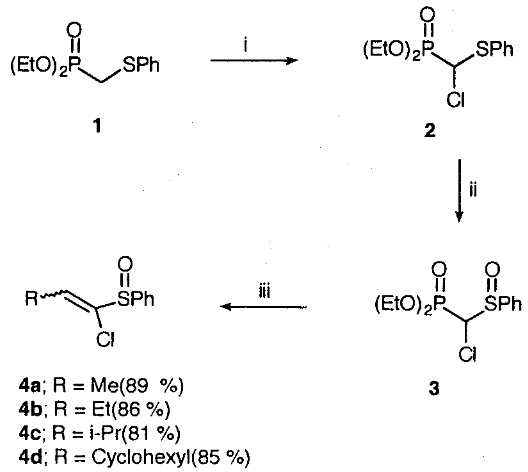
A recent report concerning the Horner-Wittig reaction of [(1-chloro) sulfinylmethyl] diphenylphosphine oxide for the preparation of 1-chlorovinyl sulfoxide **4** prompts us to disclose our own synthetic process.[1] Vinyl sulfoxides are intermediates of great synthetic potential as Michael acceptors,[2] diennophiles,[3] and Pummerer reaction substrates.[4]

In contrast with the report by van der Gen and co-workers,[1] however, we found a new synthetic method of the 1-chlorovinyl sulfoxides **4** by the oxidation of chloro(phenylthio)methanephosphonate **2** followed by the Horner-Wadsworth-Emmones (HWE) reaction of phosphonate **3** with aldehydes in the presence of lithium diisopropyl amide (LDA).

We approached the synthesis of compound such as **4** as follows. Oxidation of chloro(phenylthio)methanephosphonate **2** with *m*-chloroperbenzoic acid (*m*-CPBA) in chloroform furnished the sulfoxide **3** in 84% yield (Scheme 1).[5] This reaction was complete in 1 h at 0 ℃ and then over-night at room temperature. The sulfoxide **3** was obtained as mixtures of two diastereomers in a ratio of 2.5 : 1 determined by ^1H NMR.[5] Chloro phosphonate **2** as the starting material was obtained by performing the chlorination of phenylthiomethanephosphonate **1** with N-chlorosuccinimide (NCS) in 98% yield.[6]



4a; R = Me(89 %)
4b; R = Et(86 %)
4c; R = i-Pr(81 %)
4d; R = Cyclohexyl(85 %)

Scheme 1. *Reagents and conditions*: i, NCS, CCl_4, 4h, 25 ℃; ii, *m*-CPBA, $CHCl_3$, 1h, 0 ℃, then over-night, room temperature; iii, LDA, THF, −78 ℃, RCHO.

The HWE reaction of **3** with aldehydes at −78 ℃ led largely to the formation of the 1-chlorovinyl sulfoxides **4** (Scheme 1). The desired compounds were obtained as the mixture of E and Z isomers.[7] The ratio of Z to E isomers of vinyl sulfoxides **4** was determined with the chemical shifts of the vinylic protons such as 3 : 1 in **4a**, 2 : 1 in **4b**, 1.7 : 1 in **4c**, and 1 : 1 in **4d**.

The typical experimental procedure for the preparation of **4** is as follows. A solution of lithium diisopropylamide in tetrahydrofran (THF) was prepared under nitrogen by adding of 1.6 M n-butyllithium (1 mL) in hexane to a solution of diisopropylamide (0.15 g, 1.5 mmol) in THF (10 mL) at −78 ℃ and in 30 min a solution of diethyl chloro(phenylsulfinyl)methanephosphonate **3** (0.31 g, 1 mmol) in THF (3 mL) was added dropwise for 10 min. The reaction mixture was stirred at −78 ℃ for 30 min and cyclohexanecarboxaldehyde (0.01 g, 1 mmol) was added. The mixture was stirred until the starting material was disappeared, treated with water (10 mL), extracted with ether (2×10 mL), dried with magnesium sulfate, and concentrated. The crude product was chromatographed on silica gel using ethyl acetate : n-hexane=1 : 3 to give 1-chloro-1-phenylsulfinyl-2-cyclohexylethene **4d**.

In conclusion, the reaction described here represents a new one-step procedure[8] for the conversion of aldehydes to homologous 1-chlorovinyl sulfoxides using the HWE reaction of diethyl chloro(phenylsulfinyl) methane phosphonate **3**.

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5. To a solution of diethyl chloro(phenylthio)methanephosphonate (0.02 mol) **2** in chloroform (30 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (4.2 g, 0.02 mol) in chloroform (30 mL) at 0 ℃. The mixture was stirred at 0 ℃ for 1 hr and then allowed to stand overnight at room temperature. The insoluble materials were filtered off, and the filtrate was washed with 10% aqueous sodium carbonate solution (3×10 mL), water (10 mL), and brine (10 mL), dried, filtered, and concentrated. The residue was chromatographed on silica gel using ethyl acetate : hexane=1 : 1 to give the sulfoxide **3**. Selected data for **3**: mp 51-53 ℃. ^{1}H NMR ($CDCl_3$) δ 1.34 (m, 6H, OCH_2CH_3), 4.27 (m, 4H, OCH_2CH_3), 4.47 (d, 1H, CHCl, $J_{PH}=11.48$ Hz, major diastereomer) and 4.74 (d, 1H, CHCl, $J_{PH}=10.05$ Hz, minor diastereomer), 7.51-7.82 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 16.18, 64.80, 70.64 (d, $J_{PC}=150.0$ Hz), 124.83 (126.51), 129.04 (128.57), 131.92 (132.49), 140.84 (140.00). ^{31}P NMR ($CDCl_3$) δ 11.97 and 11.07. IR($CDCl_3$) 1274 (P=O, s), 1047 (S=O, vs) cm^{-1}. MS m/e=65 (26.2), 93 (30.5), 125 (100), 157 (29.1), 159 (8.7), 310 (3.9, M), 312 (1.3, M+2).
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7. Selected data for **4a**: ^{1}H NMR ($CDCl_3$) δ Z: 1.82 (d, 3H, $J=6.91$ Hz), 6.76 (q, 1H), 7.38-7.60 (m, 5H), E: 2.16 (d, 3H, $J=7.48$ Hz), 6.36 (q, 1H), 7.42-7.63 (m, 5H). IR($CDCl_3$) 1055 (S=O, vs) cm^{-1}.
Selected data for **4b**: ^{1}H NMR ($CDCl_3$) δ Z: 1.10 (t, 3H), 2.36 (qn, 2H), 6.80 (t, 1H, $J=7.25$ Hz), 7.49-7.79 (m, 5H), E: 1.20 (t, 3H), 2.86 (dm, 2H), 6.34 (t, 1H, $J=8.10$ Hz), 7.51-7.71 (m, 5H). IR($CDCl_3$) 1056 (S=O, vs) cm^{-1}.
Selected data for **4c**: ^{1}H NMR ($CDCl_3$) δ Z: 1.07 (d, 6H), 2.82 (m, 1H), 6.61 (d, 1H, $J=9.20$ Hz), 7.47-7.66 (m, 5H), E: 1.11 (dd, 6H), 3.35 (m, 1H), 6.10 (d, 1H, $J=10.80$ Hz), 7.45-7.60 (m, 5H). IR($CDCl_3$) 1056 (S=O, vs) cm^{-1}.
Selected data for **4d**: ^{1}H NMR ($CDCl_3$) δ Z: 1.21 (brs, 11H), 6.59 (d, 1H, $J=9.38$ Hz), 7.42-7.62 (m, 5H), E: 1.67 (brs, 11H), 6.13 (d, 1H, $J=10.66$ Hz), 7.38-7.60 (m, 5H). IR ($CDCl_3$) 1056 (S=O, vs) cm^{-1}.
8. Synthesis of **4** in a three steps from aldehydes, see: T. Satoh, Y. Hayashi, and K. Yamakawa, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1866.

New Method of Generating Trifluoroperoxyacetic acid for the Baeyer-Villiger Reaction

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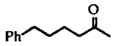
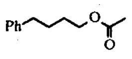
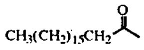
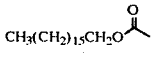
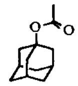
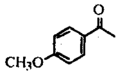
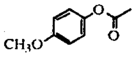
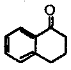
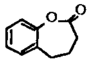
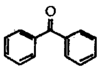
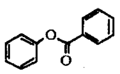
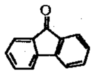
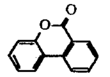
The Baeyer-Villiger oxidation of ketones to esters is of considerable synthetic use and has been performed with a variety of organic peroxy acids in those cases where the ketone is alicyclic, aralkyl or aromatic.[1] However, ketones, especially of the type RCH_2COCH_2R', do not readily undergo oxidation to the corresponding esters with conventional reagents such as perbenzoic, substituted perbenzoic, peroxyacetic, and Caro's acid. It has been reported that trifluoroperoxyacetic acid (TFPAA) has been shown to be an effective reagent for this type of reaction.[2,3] Reactions with this reagent are rapid and clean, giving high yields of product, though it is often necessary to add a buffer such as disodium hydrogen phosphate.[4] Despite its powerful reactivity and usefulness, 85% or higher hydrogen peroxide, of which the grade is now not widely available, is employed in most TFPAA oxidations. Few alternatives, including the use of urea-hydrogen peroxide complex, have been studied to overcome this problem.[5]

Table 1. Oxidation of ketones to esters with sodium percarbonate and TFAA

Entry	Substrate	Product	Time (hr)	%Yield[a]
1			2	84(94)[b]
2			2	96
3			1.5	96
4			0.67	72(82)[b]
5			2.5	87
6			5	67(99)[b]
7			20	56(98)[b]

[a] all yields are isolated ones. [b] Yields in the parentheses are based upon recovered starting materials.

Here, we report an alternative way of generating TFPAA, which uses sodium percarbonate and trifluoroacetic anhydride (TFAA). Sodium percarbonate is a safe and versatile oxidizing agent, which is commercially available and cheap.[6] In fact, Sodium percarbonate in acidic media showed that the Baeyer-Villiger oxidation was effective for cyclic ketones. But simple alicyclic ketones were not suitable substrates under this condition and deactivated ketones required long reaction times.[7] In our condition, TFAA is added to sodium percarbonate in dichloromethane at room temperature to generate TFPAA *in situ* and an extra buffering agent is not necessary due to the sodium carbonate contained in the reagent.[8]