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A New and Efficient Conversion of Olefins into Thiiranes Using Diethoxyoxophosphoranesulfenyl Chloride

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ABSTRACT

An expedient synthesis of thiiranes is described that involves electrophilic addition of diethoxyoxophosphoranesulfenyl chloride to alkenes followed by fluoride anion promoted conversion of the intermediate adducts into thiiranes. © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8***: 429–433, 1997*

INTRODUCTION

Thiiranes are a class of cyclic sulfides that are currently attracting much interest [1]. Among several different approaches to thiiranes synthesis, the generation of a thiolate anion in the *β*-position to a leaving group is the most widely used. Thiol esters [2], thiol phosphates [3], disulfides [4], sulfenamides [5], and thiocyanates [6] have been used as sources of the thiolate ion, while mesylates [2], tosylates [2], phosphates and thio-phosphates [3], phosphonium derivatives [7], and halogens [4,6] have been used as suitable leaving groups.

Most of the methods based on this approach to thiirane synthesis require harsh conditions or special starting materials. Very often, accurate control of reaction conditions is necessary to avoid extensive decomposition (polymerisation) of the thiiranes product [1].

In this article, we describe a simple and efficient route to thiiranes **7** making use of diethoxyoxophosphoranesulfenyl chloride $(EtO)_2P(O)SCl$ **1** that behaves as a strong S-electrophile. Sulfenyl halides of type **1** (Scheme 1) play an important role in organophosphorus-sulfur chemistry [8] and more recently in general organic synthesis [9]. They can readily be obtained from a common starting material, such as diethylphosphorothioic acid **2,** which can undergo O-silylation to give the ester **3,** and **3** is, in turn, transformed into the sulfenyl chloride **1** by the action of sulfuryl chloride. These reactions proceed with almost quantitative yields and can be performed as one-flask procedures [10].

Sulfenyl chloride **1** is a pale yellow liquid that can be stored at room temperature without decomposition in solvents such as dichloromethane and tetrahydrofuran. One of the most useful properties of compound **1** is its ability to undergo facile regio- and stereoselective addition to alkenes and other un-

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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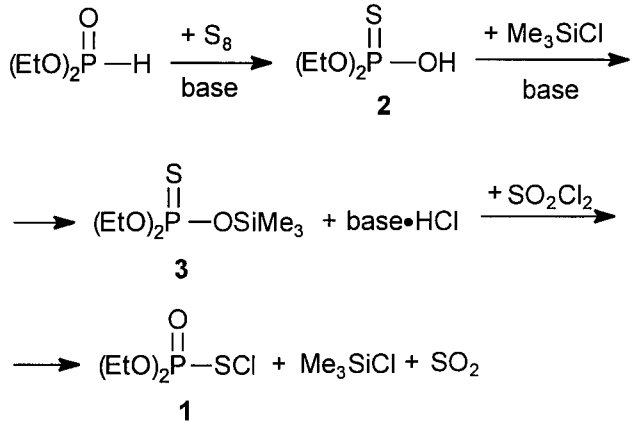
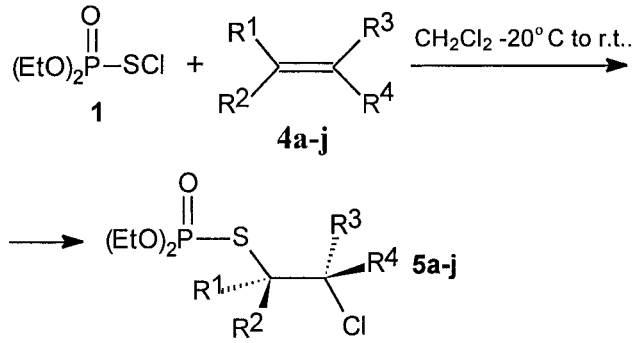
saturated systems [9a,b,11]. The sulfenyl chloride **1** reacts with aliphatic alkenes in dichloromethane to give high yields of the corresponding adducts **5**, which can be purified by column chromatography. ^{1}H and ^{31}P NMR data are in agreement with the structures **5** (Scheme 2).

A useful property of the phosphoryl group is its affinity toward strong P-nucleophiles such as the fluoride anion. When the adduct **5** is allowed to react with tetrabutylammonium fluoride (TBAF) at room temperature in dichloromethane solution, the thiolate anion **6** is formed.



SCHEME 1



a) $R^1 = R^3 = H$, R^2, $R^4 = (CH_2)_3$
b) $R^1 = R^3 = H$, R^2, $R^4 = (CH_2)_4$
c) $R^1 = R^2 = R^3 = H$, $R^4 = (CH_2)_2CH_3$
d) $R^1 = R^2 = R^3 = H$, $R^4 = (CH_2)_3CH_3$
e) $R^1 = R^2 = R^3 = H$, $R^4 = (CH_2)_4CH_3$
f) $R^1 = R^2 = R^3 = H$, $R^4 = (CH_2)_5CH_3$
g) $R^1 = R^2 = R^3 = H$, $R^4 = (CH_2)_{13}CH_3$
h) $R^1 = R^2 = R^3 = H$, $R^4 = C(CH_3)_3$
i) $R^1 = R^4 = H$, $R^2 = CH_3$, $R^3 = (CH_2)_2CH_3$
j) $R^1 = H$, $R^2 = R^3 = R^4 = CH_3$

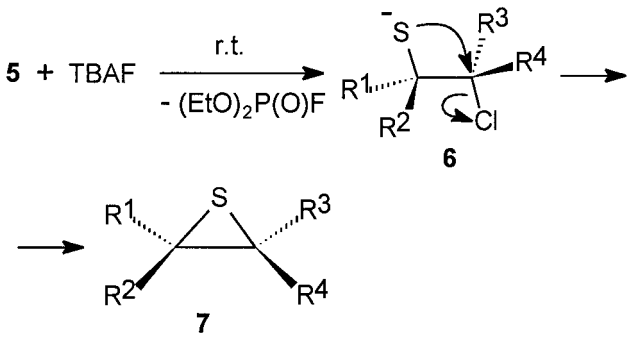
SCHEME 2

The intermediate thiolate anion **6** undergoes spontaneous cyclization to the desired thiirane structure **7** with retention of the alkene configuration. Chloride anion has proved to be a sufficiently good leaving group to allow fast cyclization. Diethoxyphosphorofluoridate and side products can readily be separated by column silica-gel chromatography. It is noteworthy that there is no need to isolate the intermediate adducts **5**, and the best results are obtained when conversion of the alkenes to the thiiranes is performed as a one-flask procedure. According to ^{1}H NMR data, formation of thiiranes **7** is almost quantitative in most cases. Relatively low yields of isolated thiiranes **7a, 7g,** and **7j,** after the chromatography procedure, are due to their partial decomposition to the corresponding unsaturated systems. The structures and configurations of thiiranes were determined on the basis of ^{1}H NMR data.

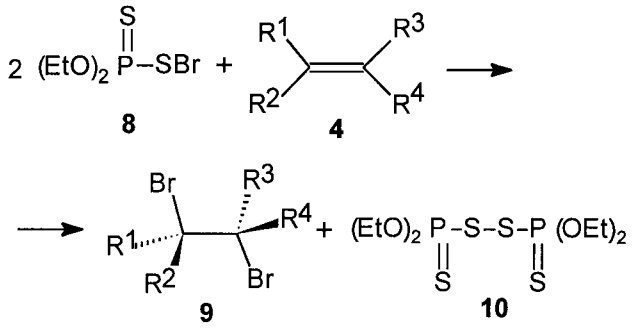
This synthesis is superior to that recently published by us [3a]. Our previous synthesis was based on diethoxythioxaphosphoranesufenyl bromide $(EtO)_2P(O)SBr$ **8.** Although this compound can readily be prepared from diethylphosphorodithioic acid $(EtO)_2P(S)SH$ by reaction with elemental bromine [12], its stability is much lower than that of diethoxyoxophosphoranesulfenyl chloride **1.** Also, sulfenyl bromide **8** reacts with alkenes to give a considerable amount of side products (alkane dibromides **9** and disulfide **10**) together with addition products of the type **5** [13].

Participation of the side reaction shown in Scheme 4 depends on the structures of both of the substrates, and, in the case of sulfenyl chloride **1,** it is marginal. Consequently, in the case of the sulfenyl bromide, it is necessary to purify the intermediate adducts **5.**

To summarize, we have demonstrated that a great variety of thiiranes **7** can readily be prepared via electrophilic addition of sulfenyl chloride **1** to alkenes, with subsequent fluoride anion promoted conversion of the adducts **5** into the thiiranes **7.**



SCHEME 3



SCHEME 4

EXPERIMENTAL

All experiments were carried out under a dry argon atmosphere. ^{31}P and ^{1}H NMR spectra were recorded on a Bruker 300MSL instrument at 81.014 MHz, *J* values being given in Hz.

Materials

Solvents and commercial reagents were purified and dried by conventional methods. Diethoxyoxophosphoranesulfenyl chloride **1** was prepared using the method described in the literature [10].

Preparation of Adducts **5a–j.** *General Procedure*

A solution of freshly prepared diethoxyoxophosphoranesulfenyl chloride **1** (0.01 mol) in dichloromethane (20 mL) was added dropwise to a stirred solution of the corresponding alkene **4** (0.01 mol) in dichloromethane (20 mL) at −20°C. Stirring was continued at room temperature for an additional 20 minutes. The yellow color disappeared. Then the solvent was removed under reduced pressure to give the crude adduct **5,** which was purified by column chromatography on silica gel with hexane/benzene (5:1) as eluent.

S-(2-Chlorocyclopentane)-O,O-diethylthiophosphate **5a**

From cyclopentene, 2.454 g (90%) of **5a** was prepared as a colorless liquid; δ_P ($CDCl_3$) 25.58; δ_H ($CDCl_3$) 1.37 (6H, t, J = 7.1, $C\underline{H}_3CH_2O$), 1.72–2.00 (4H, m, $C\underline{H}_2$), 2.21–2.52 (2H, m, $C\underline{H}_2$), 3.59–3.75 (1H, m, CHS), 4.02–4.20 (1H, m, CHCl), 4.10–4.35 (4H, m, CH_2O).

S-(2-Chlorocyclohexane)-O,O-diethylthiophosphate **5b**

From cyclohexene, 2.667 g (93%) of **5b** was prepared as a colorless liquid; δ_P ($CDCl_3$) 26.52; δ_H ($CDCl_3$) 1.34 (6H, td, J_1 = 7.06, $J_2 < 1$, $C\underline{H}_3CH_2O$), 1.41–1.54 (2H, m, $C\underline{H}_2$), 1.56–1.81 (4H, m, $C\underline{H}_2$), 2.19–2.44 (2H, m, $C\underline{H}_2$), 3.32–3.49 (1H, m, CHCl), 4.03–4.09 (1H, m, CHS), 4.09–4.27 (4H, m, CH_2O).

S-(2-Chloropentane)-O,O-diethylthiophosphate **5c**

From pentene-1, 2.528 g (92%) of **5c** was prepared as a colorless liquid; δ_P ($CDCl_3$) 26.56; δ_H ($CDCl_3$) 0.86 (3H, t, J = 6.5, $C\underline{H}_3CH_2$), 1.33(6H, td, J_1 = 7.1, $J_2 <$ 1, $C\underline{H}_3CH_2O$), 1.33–1.94 (4H, m, $C\underline{H}_2$), 3.36–3.52 (1H, m, CHCl), 3.62–3.91 (2H, m, CH_2S), 4.04–4.23 (4H, m, CH_2O).

S-(2-Chlorohexane)-O,O-diethylthiophosphate **5d**

From hexene-1, 2.743 g (95%) of **5d** was prepared as a colorless liquid; δ_P ($CDCl_3$) 26.67; δ_H ($CDCl_3$) 0.91 (3H, t, J = 6.8, $C\underline{H}_3CH_2$), 1.24–1.42 (6H, m, $C\underline{H}_3CH_2O$), 1.42–2.00 (6H, m, $C\underline{H}_2$), 3.36–3.57 (1H, m, CHCl), 3.62–3.96 (2H, m, CH_2S), 4.03–4.33 (4H, m, CH_2O).

S-(2-Chloroheptane)-O,O-diethylthiophosphate **5e**

From heptene-1, 2.907 g (96%) of **5e** was prepared as a colorless liquid; δ_P ($CDCl_3$) 26.53; δ_H ($CDCl_3$) 0.88 (3H, t, J = 6.8, $C\underline{H}_3CH_2$), 1.27–1.39 (6H, m, $C\underline{H}_3CH_2O$), 1.42–2.05 (8H, m, $C\underline{H}_2$), 3.32–3.62 (1H, m, CHCl), 3.65–3.96 (2H, m, CH_2S), 4.06–4.37 (4H, m, CH_2O).

S-(2-Chlorooctane)-O,O-diethylthiophosphate **5f**

From octene-1, 3.105 g (98%) of **5f** was prepared as a colorless liquid; δ_P ($CDCl_3$) 26.60; δ_H ($CDCl_3$) 0.87 (3H, t, J = 6.5, $C\underline{H}_3CH_2$), 1.20–1.32 (8H, m, $C\underline{H}_2$), 1.59 (6H, t, J = 6.0, $C\underline{H}_3CH_2O$), 1.43–1.73 (2H, m, $C\underline{H}_2CHCl$), 3.36–3.55 (1H, m, CHCl), 3.67–3.94 (2H, m, CH_2S), 4.04–4.29 (4H, m, CH_2O).

S-(2-Chlorohexadecane)-O,O-diethylthiophosphate **5g**

From hexadecene-1, 4.039 g (94%) of **5g** was prepared as a white crystalline solid; δ_P ($CDCl_3$) 26.55; δ_H ($CDCl_3$) 0.87 (3H, t, J = 6.6, $C\underline{H}_3CH_2$), 1.39 (6H, t, J = 6.8, $C\underline{H}_3CH_2O$), 1.15–2.05 (26H, m, $C\underline{H}_2$), 3.36–3.64 (1H, m, CHCl), 3.64–3.97 (2H, m, CH_2S), 4.02–4.27 (4H, m, CH_2O).

S-(2-Chloro-3,3-dimethylbutane)-O,O-diethylthiophosphate **5h**

From 3,3- dimethylbutene-1, 2.369 g (92%) of **5h** was prepared as a colorless liquid; δ_P ($CDCl_3$) 27.36; δ_H ($CDCl_3$) 1.05 (9H, s, C$\underline{H}_3$C), 1.30 (6H, td, J_1 = 7.1, J_2 = 0.8, C$\underline{H}_3$CH_2O), 3.34–3.48 (1H, m, CHCl), 3.69 (1H, dd, J = 11.9, 6.6, CHHS), 3.87–3.95 (1H, m, CHHS), 4.00–4.25 (4H, m, CH_2O).

S-(2-Chloroheptane)-O,O-diethylthiophosphate **5i**

From *trans* heptene-2, 2.029 g (95%) of **5i** was prepared as a colorless liquid; δ_P ($CDCl_3$) 27.19 δ_H ($CDCl_3$) 0.87 (3H, t, J = 5.8, C$\underline{H}_3$CH_2), 1.32 (6H, td, J_1 = 7, J_2 = 2, C$\underline{H}_3$CH_2O), 1.54 (3H, d, J = 6.72, C$\underline{H}_3$CH), 1.20–1.82 (6H, m, C$\underline{H}_2$), 3.31–3.47 (1H, m, -CH-), 4.07–4.24 (4H, m, CH_2O), 4.26–4.39 (1H, m, -CH-).

S-(3-Chloro-3-methylbutane)-O,O-diethylthiophosphate **5j**

From 3-methylbutene-2, 1.429 g (91%) of **5j** was prepared as a colorless liquid; δ_P ($CDCl_3$) 27.63; δ_H ($CDCl_3$) 1.29 (6H, t, J = 7.06, C$\underline{H}_3$CH_2O), 1.56 (3H, d, J = 6.9, C$\underline{H}_3$CHS), 1.63 (3H, s C$\underline{H}_3$CCl), 1.65 (3H, s C$\underline{H}_3$CCl), 3.45–3.56 (1H, m, CHS), 4.00–4.19 (4H, m, CH_2O).

Preparation of Thiiranes **7a–j.** *General Procedure*

To a solution of adduct **5** (0.01 mol) in dichloromethane (20 mL) was added dropwise with stirring a solution of tetrabutylammonium fluoride trihydrate (0.01 mol) in tetrahydrofuran (10 mL) at −78°C. Stirring was continued at room temperature for 3 hours. The reaction mixture was diluted with diethyl ether (20 mL), washed with saturated ammonium chloride (3 × 20 mL), and dried over magnesium sulfate. The solvents were removed under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (20:1) as eluent.

One-Pot Preparation of Thiirane **7a–j.** *General Procedure*

To a solution of freshly prepared diethoxyoxophosphoranesulfenyl chloride **1** (0.01 mol) in dichloromethane (20 mL) was added dropwise with stirring a solution of the corresponding alkene **4** (0.01 mol) in dichloromethane (20 mL) at −20°C. Stirring was continued at room temperature for 20 minutes. Then the solvent was removed under reduced pressure. To the crude adduct dissolved in dichloromethane (20 mL) was added dropwise with stirring a solution of tetrabutyloammonium fluoride trihydrate (0.01 mol) in tetrahydrofuran (10 mL) at −78°C. Then stirring was continued at room temperature for an additional 3 hours. The reaction mixture was diluted with diethyl ether (20 mL), washed with saturated ammonium chloride (3 × 20 mL), and dried over magnesium sulfate. The solvents were removed under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (20:1) as eluent.

6-Thia-bicyclo [3.1.0] Hexane **7a** *(Cyclopenteneepisulfide) [5,15]*

From **5a,** 0.350 g (35%) of **7a** was prepared as a colorless liquid, bp 68° (10 mm); δ_H ($CDCl_3$), 1.49–1.70 (2H, m, C$\underline{H}_2$), 1.74–1.91 (4H, m, C$\underline{H}_2$), 3.18–3.25 (2H, m, CHS); NMR yield 95%.

7-Thia-bicyclo [3.1.0] Heptane (Cyclohexeneepisulfide) **7b** *[5,15]*

From **5b,** 0.742 g (65%) of **7b** was prepared as a colorless liquid, bp 44°/6 mm; δ_H ($CDCl_3$), 0.84–0.97 (2H, m, C$\underline{H}_2$), 1.42–1.65 (2H, m, C$\underline{H}_2$), 2.09–2.26 (4H, m, C$\underline{H}_2$CHS), 3.19–3.25 (2H, m, CHS); NMR yield 95%.

Propylthiirane **7c**

From **5c,** 0.6029 g (59%) of **7c** was prepared as a colorless liquid, bp 42°/4 mm; δ_H ($CDCl_3$) 0.89 (3H, t, J = 6.7, C$\underline{H}_3$CH_2), 1.23–1.85 (4H, m, C$\underline{H}_2$), 2.13 (1H, d, J = 5.7, CHHS), 2.49 (1H, d, J = 6.3, CHHS), 2.81–2.93 (1H, m, CHS); NMR yield 93%.

Butylthiirane **7d** *[14]*

From **5d,** 0.9762 g (84%) of **7d** was prepared as a colorless liquid, bp 58°/5 mm; δ_H ($CDCl_3$) 0.91 (3H, t, J = 7.1, C$\underline{H}_3$CH_2), 1.15–1.85(6H, m, C$\underline{H}_2$), 2.14 (1H, d, J = 5.9, CHHS), 2.49 (1H, d, J = 6.35, CHHS), 2.84–2.90 (1H, m, CHS).

Pentylhiirane **7e** *[15]*

From **5e,** 1.016 g (78%) of **7e** was prepared as a colorless liquid, bp 48°/0.2 mm; δ_H ($CDCl_3$) 0.89 (3H, t, J = 6.3, C$\underline{H}_3$CH_2), 1.12–1.39 (6H, m, C$\underline{H}_2$), 1.41–1.63 (2H, m, C$\underline{H}_2$), 2.14 (1H, d, J = 5.8, C$\underline{H}$HS), 2.49 (1H, d, J = 6.3, CH$\underline{H}$S), 3.84–3.91 (1H, m, CHS).

Hexylthiirane **7f** *[15]*

From **5f,** 1.082 g (75%) of **7f** was prepared as a colorless liquid, bp 47°/0.06 mm; δ_H ($CDCl_3$) 0.92 (3H, t,

J = 6.5, C$\underline{H}_3$CH$_2$), 1.18–1.59 (10H, m, CH$_2$), 2.18 (1H, d, J = 5.6, CHHS), 2.53 (1H, d, J = 6.5, CHHS), 3.77–3.89 (1H, m, CHS).

Tetradecylthiirane **7g**

From **5g,** 1.052 g (41%) of **7g** was prepared as a white crystalline solid; δ_H ($CDCl_3$) 0.88 (3H, t, J = 6.8, C$\underline{H}_3$CH$_2$), 1.20–1.63 (26H, m, CH$_2$), 2.13–2.17 (1H, m, CHHS), 2.48–2.52 (1H, m, CHHS), 2.84–2.91 (1H, m, CHS); NMR yield 90%.

tert-Butylthiirane **7h** *[16]*

From **5h,** 0.9530 g (82%) of **7h** was prepared as a colorless liquid, bp 62°/0.1 mm, δ_H ($CDCl_3$) 0.96 (9H, s C$\underline{H}_3$), 2.19 (1H, dd, J = 6.1, 1.33, CHHS), 2.33 (1H, dd, J = 6.6, 1.33, CHHS), 2.87 (1H, t, J = 6.4, CHS).

trans-2-Butyl-3-methylthiirane **7i**

From **5i,** 0.8726 g (67%) of **7i** was prepared as a colorless liquid, bp 58°/0.07 mm; δ_H ($CDCl_3$) 0.91 (3H, t, J = 7.2, C$\underline{H}_3$CH$_2$), 1.49 (3H, d, J = 5.5, C$\underline{H}_3$CH), 1.24–1.82 (6H, m, CH$_2$), 2.56–2.68 (2H, m, CHS).

2,2,3-Trimethylthiirane **7j** *[17]*

From **5j,** 0.5314 g (52%) of **7j** was prepared as a colorless liquid, bp 45°/40 mm; δ_H ($CDCl_3$) 2.18 (3H, s, C$\underline{H}_3$C), 2.25 (3H, s, C$\underline{H}_3$C), 2.96 (3H, d, J = 7.2, C$\underline{H}_3$CH), 3.09 (1H, qt, J_1 = 7.2, J_2 = 1, CHS); NMR yield 95%.

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