aqueous phase was drawn off.[5] The organic layer was washed numerous times with water and finally 1 *N* NaOH to remove most of the acetic anhydride. The solvent and most of the remaining acetic anhydride were removed on a rotary evaporator.

The resulting deep yellow oil was dissolved in 200 ml of pyridine and 100 ml of water was dropped in slowly while stirring in an ice bath.[6] After stirring for 10 min at room temperature, hexane–ethyl acetate (1:1) and water were introduced. The organic layer was separated and after washing with base, acid, and water, it was dried over magnesium sulfate and concentrated to give 41.2 g of a yellow solid. At this point the only contaminants remaining were the keto acetate **3** and a small amount of starting olefin **1**. Distillation afforded 27.9 g (48% yield) of dione **2**, bp 83–85° (0.1 mm), mp 42.5–43.5°;[7] the pot contained 12.3 g of essentially pure keto acetate **3**. Using methanolic potassium hydroxide the keto acetate was hydrolyzed to the α-hydroxy ketone which in the same reaction vessel, following the procedure of Blomquist and Goldstein,[8] was oxidized by cupric acetate to dione **2** in 90% yield (9.1 g) This raised the total isolated yield of α-diketone **2** to 37.0 g (63%).

Reaction 2 was also performed on a large scale and 42.1 g (0.300 mol) of 1-decene (**5**) was transformed to 22.7 g (36% isolated yield) of keto acetate **6**, mp 49–55°.[9] With the following exceptions the procedure was identical with that described for oxidation of **1**: 108 g of anhydrous potassium acetate[10] was added to the reaction mixture before permanganate addition; after permanganate addition, stirring was continued in the ice–salt bath for 5 hr.

The mechanism of these new transformations is currently under study and will be the subject of a later publication. However, we wish to point out several observations which bear on the synthetic utility of the reagent. Ketols **8** and **9** are readily oxidized by the MnO_4^-–Ac_2O reagent to the corresponding α-diketones. With the exception of the stilbenes, trans isomers are converted more efficiently to diketone than the cis isomers. This trend is especially apparent with the cyclododecenes where the yield of diketone from the trans isomer is greater than three times that from the cis isomer under identical conditions. When reaction I was quenched hydrolytically at an early stage (*ca.* $^1/_2$ hr) the α-hydroxy ketone **8** was present in amounts comparable to those of diketone **2** and keto acetate **3**. We found that under the standard reaction conditions primary alcohols are acetylated much faster than they are oxidized and are thus automatically protected, whereas with secondary alcohols the rate of oxidation to the ketone is comparable to the rate of acetylation.

Although the permanganate ion exhibits unique reactivity toward olefins, its usefulness in organic synthesis has been severely limited by solubility problems. Solubility is of less concern with the MnO_4^-–Ac_2O reagent since most organic substrates are soluble in acetic anhydride. However, some molecules, especially crystalline ones, are not soluble in acetic anhydride at the lower temperatures employed; in such cases (*e.g.*, *trans*-stilbene and ketols **8** and **9**) one can use dimethoxyethane (DME) as a diluent. A solution of the substrate in DME is added to the acetic anhydride. We found that one can replace as much as 50% of the acetic anhydride by DME without major decreases in the yield of diketone (Table I).

α-Diketones are valued as precursors of transition metal ligands, of acetylenes, and of heterocyclic compounds. Our new α-diketone synthesis makes this hitherto rare functional group much more readily accessible.

Caution! When working with more than 100 ml of acetic anhydride the instructions for cooling during the extraction must be heeded.[5]

Acknowledgment. We thank a Du Pont Fundamental Research Grant for providing financial support.

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(5) The extraction should be carried out quickly and the aqueous acetic anhydride phase should be washed down the sink; after warming to a certain point this layer hydrolyzes violently. In fact, if the extracting solvent and the bisulfite solution are not cooled to 0° vigorous hydrolysis may begin before the aqueous phase can be separated. This happened in an early experiment and the organic phase boiled right out of the separatory funnel. We have not had another accident of this type, since the cooling procedures now employed provide a good margin of safety. By contrast the smaller scale reactions (Table I) involving 30–60 ml of acetic anhydride never got out of control during the extraction even when room temperature water and extraction solvent were used.

(6) This serves to hydrolyze any remaining acetic anhydride as well as the mixed anhydrides of the diacid **4**.

(7) Lit. bp 99–101° (1.5 mm), mp 43°: C. W. N. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 2067 (1965).

(8) A. T. Blomquist and A. Goldstein, "Organic Syntheses," Collect. Vol. 4, Wiley, New York, N. Y., 1963, p 838.

(9) Lit. mp 55°: K. L. Rinehart, C. L. Tarimu, and T. P. Culbertson, *J. Amer. Chem. Soc.*, 81, 5007 (1959).

(10) Anhydrous potassium acetate was found to have a beneficial effect on the yield of keto acetate from 1-alkenes.

(11) National Institutes of Health Predoctoral Fellow, 1969–1971.

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Received April 6, 1971

Peroxy Acid Oxidation of Phosphinothioates, a Reversal of Stereochemistry

Sir:

We wish to report that thiophosphoryl (P=S) compounds are rapidly, quantitatively, and stereospecifically converted to phosphoryl (P=O) compounds by organic peroxy acids under mild conditions. More strikingly, the stereochemistry at phosphorus can be either retained or inverted depending on the acidity of the system.

Several direct oxidations of thiophosphoryl groups have been reported, usually under vigorous conditions.[1] Despite the similarity of this conversion to the Wittig reaction of phosphorus ylides, little data on the mechanism or stereochemistry of this oxidation are available.[2–4]

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(1) For summaries, see L. Maier, *Top. Phosphorus Chem.*, 2, 43 (1965); K. Sasse, "Methoden der Organischen Chemie," (Houben-Weyl), Vol. XII/1, Georg Thieme Verlag, Stuttgart, 1963; Vol. XII/2, 1964.

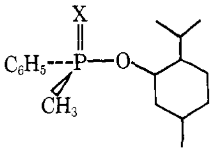
(2) L. Horner and H. Winkler (*Tetrahedron Lett.*, 175 (1964)) reported predominant retention on oxidation of a phosphine sulfide with permanganate in pyridine–water.

(3) S. Trippett, Heteroatom Symposium, London, Ontario, 1970, reported oxidation of *O*-methyl *tert*-butylphenylphosphinothioate with hydrogen peroxide in refluxing ethanol in which optical activity was maintained; the stereochemistry was not assigned.

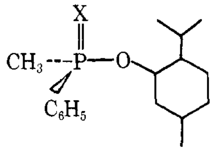
(4) J. Michalski, A. Okruszek, and W. Stec (*Chem. Commun.*, 1495 (1970)) recently reported oxidation of an *O,O*-dialkylphosphonothioate and a phosphine sulfide with nitric acid and with dinitrogen tetroxide. Assuming that optical rotations at 578 and 589 nm are proportional, the

The compounds used in this study were the menthyl methylphenylphosphinothioates **1** and **2**,[5,6] prepared as a 1:1 mixture from reaction of racemic methylphenylphosphinothiochloridate[7] with *l*-menthol. Crystallization from hexane or the neat oil afforded diastereomer **1**, mp 91–92°; $[\alpha]^{23}\mathrm{D}$ $-50.1°$ (*c* 4.6, benzene). The nmr spectrum (CCl_4) of **1** featured the *P*-methyl doublet at δ 1.87 and three *C*-methyl doublets in the region δ 0.70–1.02. The nmr spectrum (CCl_4) of a 30:70 mixture of **1** and **2** permitted assignment of a *P*-methyl doublet at δ 1.93 and a *C*-methyl doublet at δ 0.40 to isomer **2**.

The absolute configurations of **1** and **2** were determined by comparison of their nmr spectra with those of the corresponding phosphinates **3** and **4**. Lewis, Korpiun, and Mislow have established that a high-field chemical shift for a *C*-methyl group in one *l*-menthyl alkylphenylphosphinate epimer is characteristic of the *S* configuration at phosphorus.[8] The $(S)_\mathrm{P}$-phosphinate **4** also exhibits a lower chemical shift for the *P*-methyl group than does diastereomer **3**. On the basis of the striking similarity of their nmr spectra, the chiralities of **1** and **2** were equated with **3** and **4**, respectively.



1, X = S $(S)_\mathrm{P}$
3, X = O $(R)_\mathrm{P}$



2, X = S $(R)_\mathrm{P}$
4, X = O $(S)_\mathrm{P}$

The oxidations were carried out by adding 10% excess of 0.1 *M* peroxy acid in methylene chloride to a 0.5% solution of phosphinothioate in the same solvent at 0°. Iodometric titration established that 1.0 equiv of peroxy acid was consumed in each case. The yield of **3** + **4** was quantitative; the yield of colloidal sulfur was >90%. The extent and stereochemistry of the reaction were conveniently determined from the *P*-methyl signals in the nmr spectrum. The reaction was complete within 20 sec with no nmr signals other than starting material and products being detected.

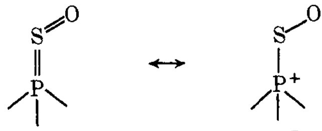
The stereochemical course of the oxidation showed a surprising dependence on the nature of the peroxy acid. Oxidation of **1** with *m*-chloroperoxybenzoic acid proceeded with a high degree of retention at phosphorus, but oxidation with peroxytrifluoroacetic acid occurred with predominant inversion! Variation of solvent (benzene, acetonitrile, *tert*-butyl alcohol), temperature (−75°), or reaction time had no significant effect on the stereochemical outcome of *m*-chloroperoxybenzoic acid reactions. But the ratio of **3**:**4** changed dramatically when the oxidation was run in the presence of stronger acids. The data summarized in Table I indicate that the stereochemistry is a sensitive function of the acidity of the reaction medium.[9]

Table I. Oxidation of **1**[c]

Reagent	Added acid	% **3**[b]	% **4**[b]
CF_3CO_3H	*a*	21	79
m-$ClC_6H_4CO_3H$		97	3
m-$ClC_6H_4CO_3H$	0.02 *M* CF_3CO_2H	65	35
m-$ClC_6H_4CO_3H$	0.07 *M* CF_3CO_2H	11	89
m-$ClC_6H_4CO_3H$	0.07 *M* $CHCl_2CO_2H$	63	37

[a] The reagent contains *ca.* 0.2 *M* CF_3CO_2H. [b] Average of two or more determinations; ±2%. [c] Comparable stereospecificities were obtained from mixtures enriched in **2**.

The variation in stereochemistry requires at least two distinct mechanisms in the reaction of phosphinothioates with peroxy acids.[10] The sulfur atom must play a key role in both mechanisms, since **4** was unaffected after 5 days at 25° under any of the reaction conditions.[11] By analogy with the oxidation of thiocarbonyl groups to sulfines,[12] the *S*-oxide **5** is a plausible intermediate in the retention reaction.[13] Closure to a three-membered ring and concomitant or successive loss of sulfur would produce **3**.[14]



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Nucleophilic attack of peroxy acid on protonated **1** followed by loss of proton, sulfur, and carboxylic acid would provide the most direct route to **4**.[14] Detailed interpretation of the mechanisms of this reaction and the origin of the novel reversal of stereochemistry must await further studies which are in progress.

Acknowledgment. Support of this work by the Research Corporation and the Research Foundation of the State University of New York is gratefully acknowledged.

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nitric acid oxidation of the phosphine sulfide can be calculated to have proceeded with *ca.* 85% net inversion while the N_2O_4 reaction gave 0–7% net retention. Some unspecified inversion was obtained with N_2O_4 in trifluoroacetic acid.

(5) Satisfactory analyses and mass spectra were obtained for **1** and a 1:1 mixture of **1** and **2**; we thank Mr. Peter Cacciotti for an initial preparation of **1**.

(6) For a review of the utility of menthyl esters in organophosphorus stereochemistry, see G. Zon and K. Mislow, *Fortschr. Chem. Forsch.*, in press.

(7) L. Maier, *Chem. Ber.*, **94**, 3051 (1961).

(8) R. A. Lewis, O. Korpiun, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4847 (1968).

(9) Peroxytrifluoroacetic acid is not formed from *m*-chloroperoxybenzoic acid and trifluoroacetic acid in CH_2Cl_2. We thank Mr. James Carnahan for assistance in this determination by ^{19}F nmr.

(10) This trend may be rather general for thiophosphoryl oxidation; *cf.* ref 4.

(11) Thiophosphoryl compounds are less basic and less susceptible to nucleophilic displacements than phosphoryl compounds: P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967); J. Ketelaar, H. Gersmann, and K. Koopmans, *Recl. Trav. Chim. Pays-Bas*, 71, 1253 (1952).

(12) B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 3453 (1967), and earlier papers. Interestingly, the sulfines lose sulfur on photolysis to produce carbonyl groups.

(13) Expansion of the sulfur valence shell has been suggested to explain the retention of configuration observed in reduction of phosphine sulfides with hexachlorodisilane: G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7023 (1969).

(14) Pseudorotation of pentacoordinate intermediates should be relatively slow since methyl and phenyl groups would prefer to remain equatorial.

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Received March 20, 1971