aromatic-stacking distance and some 0.25 Å shorter than the corresponding intraorbital distance in C_{16}-hexaquinacene (**6**). Perpendiculars drawn from the midpoints of the three double bonds intersect on the threefold axis at a distance of 2.07 Å from each bond.

The He I photoelectron (PE) spectrum of triene **2** shown in Figure 1 exhibits a relatively broad band near 8 eV and a smaller one near 9.5 eV in the ratio 3:1. The PE bands were assigned both by empirical correlation with similar molecules and by comparing the sequence of bands with the results of semiempirical MINDO/3 calculations. The results, given in Table I, reveal a split between the $e(\pi)$ and $a_1'(\pi)$ bands of 0.3 eV, indicating a relatively small interaction between the π fragments. This result can be understood by considering the distance between the termini of the π fragments in **2** (2.60 Å) in comparison with the distances and band splits reported for **4** (2.46 Å;[4] 0.6 eV[10]), **5** (2.53 Å;[5] 0.4 eV[11]), and **6** (2.85 Å;[3] 0.47 eV[3]).

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Registry No. 2, 91266-48-7; **7**, 80427-20-9; **8**, 91266-49-8; **9**, 91266-50-1; **10**, 91266-51-2; **10** (diketone), 91266-52-3; **11**, 91266-53-4; **12**, 91266-54-5.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles and torsion angles, and observed and calculated structure factors for the X-ray analysis (14 pages). Ordering information is given on any current masthead page.

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Determination of Enantiomeric Purities of Alcohols and Amines by a ^{31}P NMR Technique

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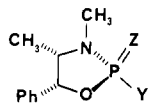
Techniques that do not rely on optical rotation have been developed for the determination of enantiomer excesses (ee's) of various classes of compounds.[1-5] Several convenient and reasonably accurate methods utilize NMR to distinguish between diastereomeric adducts or complexes in solution. This has been accomplished through the use of chiral solvents,[3] chiral shift reagents,[4] and the preparation of diastereomeric derivatives.[5] In order to accurately determine enantiomeric purity by the use of chiral derivatizing reagents in conjunction with NMR several criteria must be met: (1) The reagents must be available in enantiomerically pure form. (2) The substrate and the reagent must react to produce the required adducts in quantitative yield, and the adducts should not be subjected to purification techniques which could lead to enrichment of one diastereomer. (3) In the process of adduct formation perturbations at chiral centers should not occur or should occur with complete stereospecificity. (4) The difference in chemical shifts between selected groups in the two diastereomeric adducts should be great enough to allow for accurate integration.

Since ^{31}P NMR chemical shifts occur over a wide range (ca. 400 ppm) and peaks appear as singlets (in the usual decoupled spectra), it appeared to us that chiral phosphorus compounds might be well suited as chiral derivatizing reagents for NMR analysis of enantiomeric excesses.[6] Two of the more readily obtainable classes of compounds enantiomerically pure at phosphorus are the 2-halo-1,3,2-oxazaphospholidine 2-sulfides and 2-oxides derived from the condensation of the appropriate phosphorus halides and enantiomerically pure amino alcohols.[7] The 1,3,2-oxazaphospholidine 2-sulfides and 2-oxides derived from *l*-ephedrine are readily obtained in enantiomerically pure form and have received considerable attention as substrates for physical organic studies.[8] Substitution of halide in these systems is known to proceed with complete retention of configuration at phosphorus.[9]

Compounds **1** and **2** were prepared by reaction of *l*-ephedrine



1 Z=S, Y=Cl 2 Z=O, Y=Cl
3 Z=S, Y=NHR* 4 Z=O, Y=NHR*
5 Z=S, Y=OR* 6 Z=O, Y=OR*

with thiophosphoryl trichloride and phosphoryl trichloride according to the procedure of Cooper, Harrison, Hall, and Inch.[9b] The major isomer (shown) prevailed over the minor one (epimeric at phosphorus) by a ratio of 8:1 in the case of Z = S and 11:1 in the case of Z = O. In both cases, recrystallization led to optically pure material in approximately 60% yield.

Compounds **1** and **2** were treated with a series of chiral amines and alcohols to provide, in essentially quantitative yields, the amide (**3** and **4**) and ester (**5** and **6**) derivatives, respectively, as diastereomeric mixtures. Although both series of derivatives were suitable for quantitation of ee's of the substrates, the thio derivatives, in general, had superior ^{31}P chemical shift differences and, in addition, were more responsive to supplemental quantitation by HPLC. For these reasons this preliminary account will focus on reagent **1**.

For the preparation of amides from chiral primary amines, the following procedure was employed: Halide **1** (1 mmol) was dissolved in 5 mL of tetrahydrofuran and triethylamine (1.5 mmol) was added. The amine of interest (1.00 mmol) was added, and the mixture was stirred at room temperature for 24 h and than at 65 °C for 24 h. The reaction mixture was poured into diethyl ether and water. The organic layer was separated, dried over sodium sulfate, and concentrated. The diastereomeric amides were analyzed without further purification. For the preparation of the esters from chiral primary and secondary alcohols the following procedure was used: The chiral alcohol (1 mmol) was dissolved in diethyl ether (10 mL), the solution was cooled to 0 °C and treated with 1 equiv of butyllithium in hexane. Reagent **1** (1 mmol) was added, and the reaction mixture was refluxed for 15–20 h. The workup was accomplished in the same manner as described above for the amides.

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(7) Several optically pure 2-oxazolidones prepared from amino alcohols have been used as chiral derivatizing agents (Pirkle, W. H.; Simmons, K. A. *J. Org. Chem.* **1983**, *48*, 2520).
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Table I. Addition of *dl* Amines and Alcohols to Reagent **1**

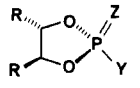
dl compd	^{31}P $\Delta\delta$ (ppm)	integration of low-field diastereomer	integration of high-field diastereomer	α (HPLC)	adduct recovery, %
1-phenylethylamine	0.175	50	50	1.35	99.5
sec-butylamine	0.628	49.6	50.4	1.14	98
1,3-dimethylbutylamine	0.843	48.9	51.1	1.20	97
1-methyl-2-phenoxyethylamine	0.347	50.5	49.5	1.00	100
1-phenyl-1-propanol	0.111	49.5	50.5	1.18	97
2-octanol	0.307	50.1	49.9	1.22	99.5
2-methyl-2-butanol	0.167	50.3	49.7	1.08	96.5
4-methyl-2-pentanol	0.301	49.8	50.2	1.17	97

Table II. Addition of Optically Active Alcohols and Amines to **1**

substrate	% ee by weight	% ee by rotation	% ee by ^{31}P NMR	% ee by HPLC	adduct recovery, %
l-menthol		100	100		96
l-borneol		16.3	16		98.5
(+)-2-octanol	19.7	20	21	20.0	99.5
	49.6	50.1	51	51.5	99.5
	80.3	80.0	81	80.1	99.5
		100	100		97.5
(-)-1-phenyl-ethylamine	32	32	32		98
	48	48	50		99
	70.5	70.5	70.4		99
		95.8	95.7		99

Table I illustrates the technique using a series of racemic amines and alcohols. Table II summarizes data obtained from optically active substrates and compares the ee's determined by weight (dilution of optically pure sample with *dl* sample), by rotation, by ^{31}P NMR,[10] and by HPLC on a silica gel column with hexane/ethyl acetate.

In addition to compounds **1** and **2** shown above, a number of other chiral phosphorus reagents have been examined including the reagents derived from ephedrine but epimeric at phosphorus and the correspsonding reagents derived from pseudo-ephedrine. A number of compounds, **7**, derived from chiral diols, including



7

2,3-butanediol,[11] 1,2-diphenylethanediol, and 1,1'-bi-2-naphthol have been prepared. In this latter series, the phosphorus center is not a chiral unit, and the stereochemistry of the displacement reactions at phosphorus is irrelevant. These reagents tend to be quite reactive. The reagents prepared from 2,3-butanediol and 1,2-diphenylethanediol provided adducts that do not exhibit ^{31}P chemical shift differences comparable to compounds in which the phosphorus atom is chiral, e.g., **3** and **4**;[11] HPLC separations are also less. Side reactions apparently involving ring opening were observed with the use of the reagent (Z = S) prepared from 1,1'-bi-2-naphthol.

Acknowledgment. This work was supported by grant CHE-83 06594 from the National Science Foundation with assistance from the Lubrizol Foundation (fellowship for RCE) and the Monsanto Agricultural Produts Co.

Registry No. 1 (Z = S, Y = Cl), 57651-34-0; **1** (Z = S, Y = (*R*)-1-Phenylethylamino), 91279-05-9; **1** (Z = S, Y = (*S*)-1-phenylethylamino), 66007-24-7; **1** (Z = S, Y = (*R*)-*sec*-butylamino), 91228-05-6; **1** (Z = S, Y = (*S*)-*sec*-butylamino), 91279-06-0; **1** (Z = S, Y = (*R*)-1,3-dimethylbutylamino), 91228-06-7; **1** (Z = S, Y = (*S*)-1,3-dimethylbutylamino), 91279-07-1; **1** (Z = S, Y = (*R*)-1-methyl-2-phenoxyethylamino), 91228-07-8; **1** (Z = S, Y = (*S*)-1-methyl-2-phenoxyethylamino), 91279-08-2; **1** (Z = S, Y = (*R*)-1-phenyl-1-propyloxy), 91228-08-9; **1** (Z = S, Y = (*S*)-1-phenyl-1-propyloxy), 91279-09-3; **1** (Z = S, Y = (*R*)-2-octyloxy), 91237-75-1; **1** (Z = S, Y = (*S*)-2-octyloxy), 91279-88-8; **1** (Z = S, Y = (*R*-3-methyl-2-butanol), 91228-09-0; **1** (Z = S, Y = (*S*-3-methyl-2-butanol), 91279-10-6; **1** (Z = S, Y = (*R*)-4-methyl-2-pentyloxy), 91228-10-3; **1** (Z = S, Y = (*S*)-4-methyl-2-pentyloxy), 91279-11-7; **1** (Z = S, Y = Cl) l-menthol adduct, 91228-11-4; **1** (Z = S, Y = Cl) l-borneol adduct, 91228-12-5; *dl*-1-phenylethylamine, 618-36-0; *dl-sec*-butylamine, 33966-50-6; *dl*-1,3-dimethylbutylamine, 54548-48-0; *dl*-1-methyl-2-phenoxyethylamine, 65236-31-9; *dl*-1-phenyl-1-propanol, 613-86-5; *dl*-2-octanol, 4128-31-8; *dl*-3-methyl-2-butanol, 70116-68-6; *dl*-4-methyl-2-pentanol, 20281-88-3; *l*-menthol, 2216-51-5; *l*-borneol, 464-43-7; (+)-2-octanol, 6169-06-8; (-)-1-phenylethylamine, 2627-86-3.

(10) ^{31}P NMR spectra were obtained on a Nicolet NT-300 operating at 121.47 MHz. The spectra were taken in deuterochloroform and reported downfield from external 85% phosphoric acid. The spectra were gated proton decoupled with a delay time of 60 s between pulse sequences (16K data points, 12-20 scans, 90° pulse, 16 μs). Representative chemical shifts: **1** δ 75.90; **2** δ 21.79; derivatives of 1-phenylethylamine and **1** δ 78.51, 78.34; derivatives of 1-phenylethylamine and **2** δ 23.45, 23.42; derivatives of 2-octanol and **1** δ 82.70, 82.39; derivatives of 2-octanol and **2** δ 19.80, 19.76.

(11) After submission of this manuscript a paper appeared that describes the use of **7** (R = Me) as a chiral derivatizing agent for primary and secondary alcohols (Anderson, R. C.; Shapiro, M. J. *J. Org. Chem.* **1984**, *49*, 1304). In accordance with our observations, the authors found **7** to be quite reactive (reaction time with alcohols in the presence of triethylamine and 4-(dimethylamino)pyridine suggested in 15 min). The shift differences found when using **7** are often quite small, e.g., Anderson and Shapiro report that the derivatives of **7** (R = Me) and 2-butanol exhibit $\Delta\delta$ 0.0056 (C_6D_6) whereas the corresponding derivatives of **1** exhibit $\Delta\delta$ 0.200 ($CDCl_3$).

Thianthrene 5-Oxide as Mechanistic Probe in Oxygen-Transfer Reactions: The Case of Carbonyl Oxides vs. Dioxiranes

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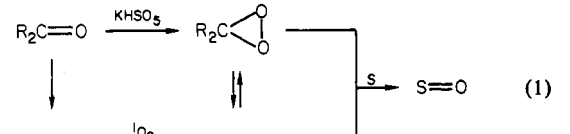
One of the persisting challenging problems concerns the differentiation between carbonyl oxides and dioxiranes (eq 1).[1]



(1)

Despite intensive work, conflicting evidence has accumulated regarding the electrophilic vs. nucleophilic nature of these oxygen-transfer agents. Indeed, the primordial mechanistic question must be raised whether carbonyl oxides and dioxiranes are chemically differentiable species.

The abundant literature[1] reveals that a stringent mechanistic differentiation by employing identical substitution patterns in these

† Undergraduate research participant, spring 1984.

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