Experimental Section

Synthesis. 2,3-Dimethylsulfolene was prepared essentially as previously described.[2] The crude product was purified by column chromatography (silicic acid, benzene eluent) rather than distillation, in order to avoid decomposition. Of several hydrogenation catalysts tried, platinum oxide (Adams) in ethyl acetate afforded the greatest stereoselectivity (ca. 95%) for the reduction to **1**. Refluxing a *t*-BuOK–*t*-BuOH solution of **1** for several hours followed by work-up yielded a mixture enriched in **2** (ratio 2:1 9:1). Isomer percentages were estimated from resolved NMR resonances in the methyl region ($CDCl_3$ solution).

Anal. (for enriched **1**). Calcd for $C_6H_{12}O_2S$: C, 48.64; H, 8.16. Found: C, 48.54; H, 8.25.

Thermolysis. As previously indicated, ca. 0.5-g portions of **1** or **2** were injected slowly via syringe into a heated reservoir (SiC chips at >500°) connected to a cold trap. Some refluxing was noted. Subsequently, the butenes were allowed to vaporize and were sampled by GLC [column, 15 ft of 25% $AgNO_3$–propylene glycol (1:2) on Chromosorb W, 25°]. Comparison was made to authentic 2-butenes. A minor, unidentified pyrolysate component was eluted shortly after (and overlapping) *trans*-butene. It has previously been asserted that sulfolane thermolysis affords 9–19% of "saturated hydrocarbon".[1] In the present case a complete analysis of product balance was not undertaken, since our interest only extended to alkene geometry.

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Registry No.—**1**, 54910-40-6; **2**, 54910-39-3; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2,3-dimethylsulfolene, 10033-87-1.

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Complete Resolution of *cis*-1-Benzyl-3-methyl-1-phenylphospholanium Iodide. Use of the Optically Active Salt in Stereochemical Studies

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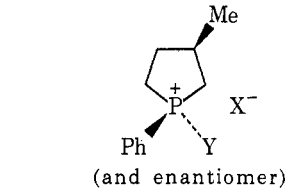
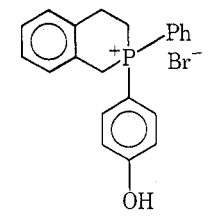
The literature records no total resolutions of heterocyclic phosphonium salts containing an asymmetric phosphorus atom. We report herein the first such instance, the complete resolution of racemic *cis*-1-benzyl-3-methyl-1-phenylphospholanium iodide (**1**) with the aid of silver (+)-10-camphorsulfonate. Compounds **2**,[1] **3**,[2] and **4**[3] have been partially resolved, although the resolution of **2** could not be reproduced and details of the resolution of **4** have not yet been disclosed. The spiro salt (**5**), which has been totally resolved, owes its optical activity to molecular dissymmetry rather than to an asymmetric phosphorus atom of the $R^1R^2R^3R^4P^+X^-$ type.[4]



(and enantiomer)
1, Y = CH_2Ph; X = I
6, Y = O^-; X = nil
7, Y = CH_2Ph; X = (+)-10-camphorsulfonate
8, Y = lone pair; X = nil
9, Y = CH_2Ph; X = Br
12, Y = OMe; X = PF_6



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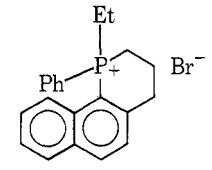
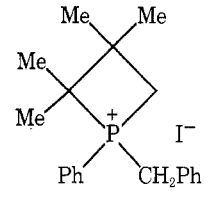


3



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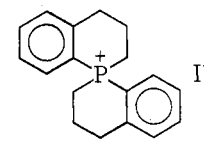
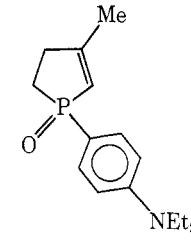
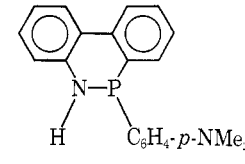


5



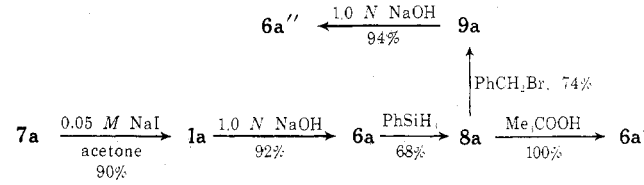
10



11

With the optically active phosphonium salts (**1**) available, we wished to verify earlier conclusions[5,6] that hydroxide cleavage of **1** occurs with complete retention of configuration at phosphorus. The NMR analyses leading to these conclusions were possibly subject to considerable error, although predominant retention had been rigorously proved. Within experimental error, the results shown in Scheme I are compatible with complete retention of configuration for base cleavage and phenylsilane reduction as previously reported.[5,6] This is true only if the oxide epimeric at phosphorus, produced by inversion of configuration at phosphorus, does not have a rotation comparable to that for the (+)

Scheme I[a]



Compd	Mp or bp, °C (mm)	$[\alpha]^{22}D$, deg (*c*)
7a	244–246	+28.09 ± 0.49 (2.980, EtOH)
1a	184.5–185.5	+2.16 ± 0.09 (15.57, $CDCl_3$)
6a	130 (0.5)	+23.52 ± 0.67 (7.590, $CDCl_3$)
8a	90 (0.5)	+22.18 ± 0.42 (6.710, MeOH)
6a′	132 (0.6)	+22.53 ± 0.59 (7.395, $CDCl_3$)
6a″	135 (0.6)	+22.59 ± 0.63 (6.505, $CDCl_3$)

[a] **9a** was not recrystallized prior to cleavage. *tert*-Butyl hydroperoxide oxidations of phosphines occur with retention of configuration: D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963). Phenylsilane has been found to reduce phosphine oxides with retention of configuration: K. L. Marsi, *J. Org. Chem.*, **39**, 265 (1974). Distillations were accomplished by use of a Kugelrohr.

enantiomer of **6**, since two chiral centers are present. However, the NMR spectra of both enantiomers, **1a** and **1b**, and **6a** gave no indication whatsoever of the presence of diastereomeric material.

Resolution was accomplished by treatment of the racemic bromide salt (**9**)[7] with silver (+)-10-camphorsulfonate and recrystallization of the diastereomeric salts utilizing a triangular scheme of recrystallization.[8] The head fraction was recrystallized to give **7a** of constant rotation and melting point (cf. Scheme I). **7a** was metathesized with sodium iodide in boiling acetone to provide **1a**, which was also recrystallized to constant rotation and melting point (cf. Scheme I). The tail fractions, enriched in **7b**, were combined and similarly converted to the optically impure iodide (**1b**), which was recrystallized from acetone to a constant rotation of $[\alpha]^{22}D$ $-2.14 \pm 0.11°$ (*c* 16.22, $CDCl_3$) and melting point of 184–185°. Because of the greater solubility of the racemic mixture in acetone, it was likewise possible to obtain optically pure **1a** as the less soluble fraction from mixtures of **1a** and **1b**, enriched in **1a**, by simple recrystallization from acetone.

Preparation of only one other simple five-membered ring phosphine oxide in optically active form has been reported previously. **10** was partially resolved with (+)-9-camphorsulfonic acid to afford the levorotatory isomer.[9]

Reduction of (+)-**6a** with phenylsilane yielded optically pure dextrorotatory phosphine **8a**. The optical purity of the phosphine is attested to by its conversion to the (+) oxides **6a′** and **6a″**, both of which showed, within experimental error, the same rotation as the dextrorotatory parent phosphine oxide **6a**. This is the first report of the preparation of an optically active saturated heterocyclic phosphine. It should be noted that two optically unstable isomers of the phosphorus heterocycle **11**[10] have been prepared by lithium aluminum hydride reduction of the corresponding optically active oxides, but that the activity of **11** may be due to molecular dissymmetry.[11] Optically active analogs of the oxides of **11** fail to undergo lithium aluminum hydride reduction to produce optically active phosphines[12] but fragment instead.

We have recently shown that alkoxyphospholanium salts (**12**) experience nucleophilic displacement at phosphorus to yield a mixture of oxides of inverted and retained configuration at phosphorus.[13] This observation leads us to believe that the preparation of optically pure phospholane oxides such as **6** by Mislow's method,[14] so useful for the synthesis of optically active acyclic phosphine oxides, would probably not be successful. Our resolution thus provides ready access to both optically isomeric phospholane oxides and phospholanes useful for stereochemical studies. The optically active phosphines may have additional value in the preparation of chiral phosphine–metal complexes.[15]

Experimental Section

(+)-1-Benzyl-3-methyl-1-phenylphospholanium Camphorsulfonate (7a). To 80.52 g of **9**[6] dissolved in 500 ml of ethanol was added 78.24 g of silver (+)-10-camphorsulfonate. Silver bromide was removed by filtration and the filtrate was further clarified by filtration through diatomaceous earth. The filtrate was evaporated to dryness and the residue was redissolved in a minimum amount of hot ethanol to which ethyl acetate was added dropwise to the cloud point. Triangular recrystallization,[8] carried out in this manner, gave a head fraction of constant melting point and rotation (cf. Scheme I).

Anal. Calcd for $C_{28}H_{37}O_4PS$: C, 67.18; H, 7.45. Found: C, 66.91; H, 7.40.

(+)-1-Benzyl-3-methyl-1-phenylphospholanium Iodide (1a). To 61 ml of 0.05 *M* sodium iodide in acetone was added 1.542 g of optically pure **7** and the mixture was stirred under gentle reflux for 45 min. Precipitated sodium camphorsulfonate was recovered in quantitative yield by filtration of the cooled reaction mixture. Crude **1a**, obtained after evaporation of the filtrate, was recrystallized from acetone to constant rotation and melting point (cf. Scheme I).

Anal. Calcd for $C_{18}H_{22}IP$: C, 54.56; H, 5.60. Found: C, 54.61; H, 5.55; S, 0.00.

It was discovered that head fractions of optically impure camphorsulfonate (**7a**) could be similarly converted to the optically impure iodide (**1a**) and the iodide conveniently recrystallized from acetone to the optically pure dextrorotatory form. Likewise, tail fractions concentrated in the more soluble diastereomeric camphorsulfonate, when treated as described above, produced the optically pure levorotatory isomer of mp 184.0–185.0°, $[\alpha]^{22}D$ $-2.14 \pm 0.11°$ (*c* 16.220, $CDCl_3$).

Anal. Calcd for $C_{18}H_{22}IP$: C, 54.56; H, 5.60. Found: C, 54.44; H, 5.76.

Hydroxide Cleavage of 1a and Recovery of Product. The procedure followed was essentially as described elsewhere for the racemic bromide salt.[6]

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Registry No.—(±)-**1**, 54964-37-3; **1a**, 54964-38-4; **1b**, 54932-22-8; **6a**, 54932-23-9; **7a**, 54932-25-1; **7b**, 54932-27-3; **8a**, 54932-28-4; **9**, 54932-29-5; silver (+)-10-camphorsulfonate, 20520-61-0.

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Hydrogenation of Unsaturated Carboxylic Acids with Alkanes by Aluminum Chloride Catalysis

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In the course of a previous study[1] of the Friedel–Crafts reactions of some unsaturated carboxylic acids on benzene, we observed the presence of an unexpected saturated ketone **4**, which could possibly arise from the reaction of the saturated counterpart **2** of the starting material **1** (Scheme I, pathway a). An alternative route (Scheme I, pathway b) was of course possible.[2] The finding that even a poor hydride donor like 4,4-dimethyltetralone, one of the reaction products, was able to perform the hydrogenation of **1** in the presence of aluminum chloride led us to investigate better hydrogen donors for the reduction, also in view of the great practical importance of the hydrogenation of fatty acids.

Alkanes were the obvious first choice. It should be mentioned that hydrogen transfer to unsaturated carboxylic acids was reported previously only in the particular case of