

REACTIONS OF OPTICALLY ACTIVE METHYL-*n*-BUTYLBENZYLPHOSPHINE

WITH CYCLOHEXENE EPISULFIDE AND WITH SULFUR

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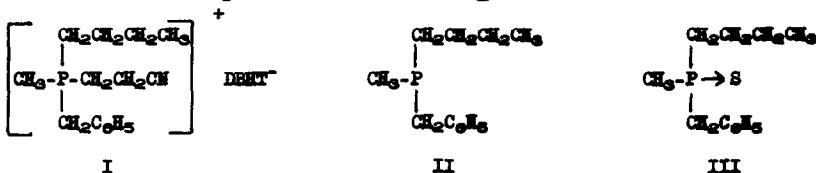
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The isolation of optically active phosphines has recently been reported by three different groups (1,2,5). Our method (1) consisted of the preparation and resolution of the methyl-*L*-cyanoethyl-*n*-butylbenzylphosphonium D(-) and L(+)-dibenzoylhydrogentartrates (I) and subsequent decomposition of these salts by the action (4) of sodium methoxide in refluxing methanol to produce both enantiomorphs of methyl-*n*-butylbenzylphosphine (II). The purest samples of the phosphines (II) exhibited $[\alpha]_D^{27}$ values of $+24 \pm 2^\circ$ and $-28 \pm 2^\circ$, respectively (c , 2.9 in benzene). However, the samples used in the reactions described below had specific rotations of $11 \pm 2^\circ$.



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The optically active phosphines were converted to the optically active methyl-*n*-butylbenzylphosphine sulfides (III) by reactions with three different sources of sulfur. The results are summarized in Table 1.

TABLE 1

Reactions of Optically Active Methyl-*n*-butylbenzylphosphine (II)
with Various Sources of Sulfur

Methyl- <i>n</i> -butylbenzyl- phosphine [α] _D ²⁷ = 11.2°	Source of Sulfur	Methyl- <i>n</i> -butylbenzyl- phosphine sulfide, [α] _D ²⁷
(+)	Cyclohexene sulfide	+7.2 ± 1.2
(-)	Cyclohexene sulfide	-6.1
(+)	Monatomic Sulfur	+7.1
(+)	Octatomic Sulfur	+6.9
(-)	Octatomic Sulfur	-7.1

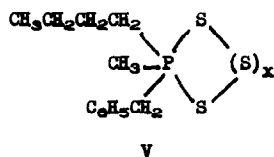
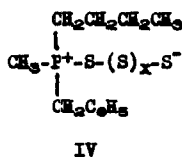
The mechanism of the reaction of *cis*- and *trans*-2-butene episulfide with triphenylphosphine has been shown by Denney and Boskin (5) to be stereospecific with respect to formation of the olefins. Thus, the *cis*-episulfide gave triphenylphosphine sulfide and pure *cis*-2-butene, and the *trans*-episulfide gave the pure *trans*-2-butene. These and other data provided by Denney and Boskin are consistent with a mechanism involving synchronous formation of the phosphine sulfide and olefin by direct nucleophilic displacement of the phosphine on the sulfur atom of the episulfide. This mechanism would be consistent with the formation of (+) and (-) - III with retention of configuration of the phosphorus atom. Also, reaction of optically active II with monatomic sulfur (6) would be expected to give III with retention of configuration of the phosphorus.

The kinetics of the reaction of triphenylphosphine with octatomic sulfur has been studied by Bartlett and Meguerian (6). The results were consistent with a mechanism in which the rate-determining step of the reaction is attack

of the phosphine on a sulfur atom of the eight-membered sulfur ring to give a dipolar intermediate in which the phosphorus bears a formal positive charge and the terminal sulfur atom of the S_8 open chain a formal negative charge. This dipolar intermediate is then degraded, by attack of additional triphenylphosphine molecules, into triphenylphosphine sulfide and new dipolar intermediates with successively shorter sulfur chains bonded to phosphorus.

Since the reaction of optically active methyl-n-butylbenzylphosphine (II) with octatomic sulfur gives the phosphine sulfide III having the same rotation as the samples produced by reaction of II with cyclohexene episulfide and monatomic sulfur, respectively, and on the basis of the arguments cited above that the latter reactions proceed with retention of the configuration of the phosphorus atom, it may be concluded that the reaction of optically active II with octatomic sulfur also proceeds with retention of configuration of the phosphorus atom. This result is of theoretical interest because it indicates that the dipolar intermediates of type IV do not exist in equilibrium with cyclic tautomers of type V. If such cyclic tautomers had been formed, it is highly probable that the phosphine sulfide III eventually produced would have been largely or completely racemic. This follows from the arguments of Westheimer and Haake (7) regarding the stereochemistry of nucleophilic displacements on phosphorus and from our demonstration (8) of such principles as applied to the formation of intermediate cyclic derivatives in which phosphorus is pentacovalent. Specifically, in the hypothetical equilibrium among species of types IV and V, a cycle $IV \rightarrow V \rightarrow IV$ would cause inversion of the configuration of the phosphorus if it attained, in V, the trigonal bipyramidal configuration by basal attack of the negatively charged sulfur atom of IV, and if there were subsequent basal departure of the sulfur at the other end of the chain. In like manner, inversion of the configuration of phosphorus would result by apical attack and apical departure of sulfur (a distinct possibility with a large sulfur chain). On the

contrary, apical attack and basal departure of sulfur, or *vice versa*, would lead to retention of configuration of the phosphorus, as would any transformations by way of a cyclic intermediate of type V in which the square pyramidal configuration of phosphorus is involved. All of these possible pathways for the cycle IV → V → IV would probably be important if the equilibria among species of types IV and V were operative, and this would cause the phosphine sulfide III eventually formed to be largely racemic. The fact that reaction of optically active II with octatomic sulfur takes place with retention of configuration of the phosphorus atom therefore provides a strong argument that no equilibration among species of types IV and V occurs in these reactions.



The synthesis of racemic methyl-β-cyanoethyl-n-butylbenzylphosphonium iodide was accomplished by two different approaches. The first was a suitable modification of the procedure developed by Grayson, Keough and Johnson (4) for the synthesis of asymmetrically substituted phosphonium salts. The second method made use of an appropriate application of the procedure of Bailey, Buckler and Marktscheffel (9,10) to prepare racemic methyl-n-butylbenzylphosphine (II) from n-butyldichlorophosphine (11) as the principal starting material. In a new application of the familiar cyanoethylation reaction, II was treated with equivalent amounts of acrylonitrile and ammonium iodide in acetonitrile solution to give methyl-β-cyanoethyl-n-butylbenzylphosphonium iodide in 83% yield. The resolution of this salt was effected by the procedure of Kumli, VanderWerf and McEwen (12). The diastereoisomeric dibenzoyl-hydrogen tartrate salts were crystallized many times from absolute 1-propanol and exhibited the following properties: (+)-methyl-β-cyanoethyl-n-butyl-

benzylphosphonium D(-)-dibenzoylhydrogen tartrate, m.p. 127.0-127.8° (dec.), $[\alpha]_D^{27}$ -69° (c, 2.072 in methanol); (-)-methyl- β -cyanoethyl-n-butylbenzylphosphonium L(+)-dibenzoylhydrogen tartrate, m.p. 128.9-129.1° (dec.), $[\alpha]_D^{27}$ + 67° (c, 2.002 in methanol). When either of these salts was heated under reflux for two hours with a seven-fold excess of sodium methoxide in absolute methanol, water added, the methanol removed by distillation and the residue extracted with benzene, all of these operations being carried out in a nitrogen atmosphere, optically active II was found in the benzene solution. The reactions of optically active II with the various sources of sulfur listed in Table 1 were carried out in benzene solution. The concentration of the phosphine was determined by treatment of an aliquot with ethyl iodide and collection of the ethiodide salt. Satisfactory analyses were obtained for all new compounds reported in this communication.

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