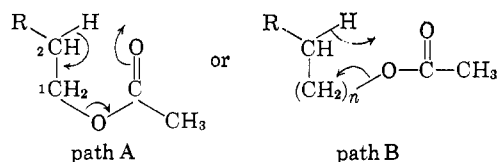
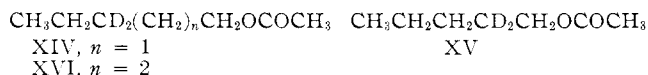


of hydrogen from the alkyl chain by the ether oxygen (path B)



*n*-Pentyl-2,2-*d*<sub>2</sub> acetate (XV), *n*-pentyl-3,3-*d*<sub>2</sub> acetate (XIV), and *n*-hexyl-4,4-*d*<sub>2</sub> acetate (XVI) were prepared by acetylation of the corresponding alcohols and their mass spectra determined (Fig. 1).



The results (Table III) indicate loss of hydrogen from C-2 to be 55% while hydrogen at C-3 is involved to 45%. In agreement with this, the spectrum of XVI indicates that the hydrogens at C-4 are not involved in the elimination of acetic acid. While the "1,2"-elimination would be predicted in analogy to the high specificity of this type of reaction and has been suggested previously,<sup>16</sup> the extent of 1,3-elimination and the complete retention of hydrogen at C-4 (in contrast to the alcohols themselves) is surprising. Path B must thus involve the formation—at least formally—of an alkylcyclopropane, *i.e.*, *n* = 2.

TABLE III  
ELIMINATION OF CH<sub>3</sub>COOD FROM DEUTERATED ALKYL  
ACETATES

Acetate	1,2-	1,3-	1,4-Elimination
<i>n</i> -Pentyl-2,2- <i>d</i> <sub>2</sub> (XIV), %	55(±3)		
<i>n</i> -Pentyl-3,3- <i>d</i> <sub>2</sub> (XV), %		45(±3)	
<i>n</i> -Hexyl-4,4- <i>d</i> <sub>2</sub> (XVI), %			0

The elimination of acetic acid from acetates leads always to an (M - 60)<sup>+</sup> ion rather than (CH<sub>3</sub>COOH)<sup>+</sup> and a peak at *m/e* 60 is thus not observed. Only if the acetic acid moiety abstracts in addition another hy-

(16) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

drogen (*i.e.*, transfer of a total of 2H to the CH<sub>3</sub>COO-group) is a species with a sufficiently stabilized positive charge obtained, namely an acetyloxonium ion, CH<sub>3</sub>CO<sub>2</sub>H<sub>2</sub><sup>+</sup> of mass 61. From the distribution of the peaks at *m/e* 61 and 62, one can conclude that the abstraction of the first hydrogen follows the same path as the elimination of acetic acid when leading to the (M - 60)<sup>+</sup> ion. The second hydrogen required for the formation of *m/e* 61 is neither removed from the same carbon atom as the first one (no significant peak at *m/e* 63) nor is it derived exclusively from C-4. Random abstraction is in best agreement with the mass spectrum of XV (Fig. 1).

This result is in qualitative agreement with earlier conclusions<sup>17</sup> concerning the elimination of CH<sub>3</sub>CO-OH<sub>2</sub><sup>+</sup> from *sec*-butyl-3,3-*d*<sub>2</sub> acetate. More recently, however, a selective transfer of one hydrogen at C-3, followed by a randomly selected hydrogen had been suggested.<sup>18</sup> These conclusions were based on the mass spectrum of *n*-butyl-3-*d*<sub>1</sub> acetate alone and without having available the derivative deuterated at C-2, which renders such an interpretation less reliable.

### Experimental

All mass spectra were determined with a CEC 21-103C mass spectrometer, equipped with a heated inlet system (170°). Ionizing voltage 70 e.v. Gas chromatographic separations were performed with either SE 30 or Apiezon L as a liquid phase.

The syntheses of the deuterated compounds is mentioned in principle in the theoretical part of this paper and follows conventional steps except that specifically deuterated reagents were used. Their more detailed description was omitted on suggestion of the referee. All products were identified by comparison of gas chromatographic retention times with that of authentic samples. Specimens for mass spectra were purified by gas chromatography.

**Acknowledgment.**—We are indebted to the Petroleum Research Fund of the American Chemical Society for financial support (Grant No. 625).

(17) F. W. McLafferty and M. C. Hamming, *Chem. Ind. (London)*, 1366 (1958).

(18) D. R. Black, W. H. McFadden, and J. W. Corse, Symposium on Mass Spectrometry, 11th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, Calif., May, 1963.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITIES OF KANSAS, LAWRENCE, KAN., AND MASSACHUSETTS, AMHERST, MASS.]

## Mechanisms of Substitution Reactions at Phosphorus. X. The Wittig Reaction and the Decomposition of Quaternary Phosphonium Hydroxides

BY WILLIAM E. McEWEN,<sup>1</sup> KARL F. KUMLI, ARTURO BLADE-FONT, MURRAY ZANGER, AND CALVIN A. VANDERWERF<sup>2</sup>

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An optically active, noncyclic quaternary phosphonium salt in which the phosphorus atom is the sole center of asymmetry has been prepared. This compound, methylethylphenylbenzylphosphonium iodide (I), undergoes a stereospecific reaction with sodium hydroxide to produce toluene and methylethylphenylphosphine oxide (VII). Arguments and experimental data are presented to show that the phosphorus atom undergoes inversion of configuration in this reaction. Also, the choice of possible mechanisms is reduced to a small number by the stereochemical and kinetic data. The Wittig reaction, with benzaldehyde, of the ylid derived from optically active I has also been found to be stereospecific, and arguments are advanced as to why this reaction should take place with retention of configuration of the phosphorus atom.

In previous communications we have reported: (1) the successful resolution of methylethylphenyl-

benzylphosphonium iodide (I),<sup>3</sup> (2) the stereospecific reaction of this salt with sodium hydroxide to give methylethylphenylphosphine oxide (VII) and toluene,<sup>4</sup>

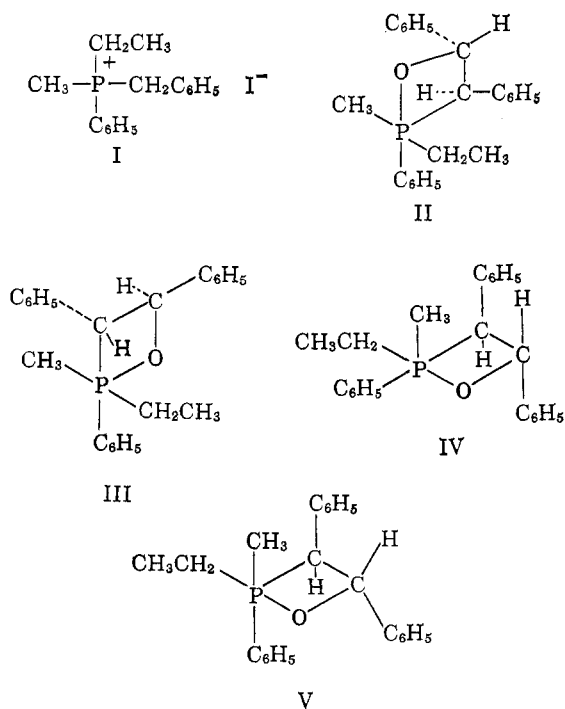
(1) Department of Chemistry, University of Massachusetts, Amherst, Mass.

(2) President, Hope College, Holland, Mich.

(3) K. F. Kumli, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 248 (1959).

(3) the stereospecific Wittig reaction with benzaldehyde of the ylid derived from this salt to produce methylethylphenylphosphine oxide (VII) plus stilbene (predominantly the *trans* isomer),<sup>5</sup> and (4) the demonstration that the reaction of the phosphonium chloride with sodium hydroxide is third order showing a first-order dependence on the concentration of the methylethylphenylbenzylphosphonium cation and a second-order dependence on the concentration of hydroxide ion.<sup>6</sup> These data and certain supporting arguments lead to the conclusions that (1) the Wittig reaction takes place with retention of the configuration of the phosphorus atom, (2) a pentacovalent intermediate is formed in the phosphonium hydroxide decomposition reaction, and (3) the configuration of the phosphorus atom is inverted in the latter reaction.

First of all, an argument will be developed which indicates that the Wittig reaction of optically active methylethylphenylbenzylidenephosphorane with benzaldehyde should take place with retention of the configuration of the phosphorus atom. It is not known with certainty whether an unstable intermediate in which the phosphorus atom is pentacovalent is formed in the Wittig reaction.<sup>7</sup> However, even if such a species is best described as a transition state, the stereochemical arguments will not be changed. Four conceivable types of unstable intermediates (or transition states) are depicted in structures II, III, IV, and V.



In any of the unstable intermediates of types II, III, and IV there is no new type of angular strain about any of the bonds. The internal angles of the four-membered ring are  $90^\circ$ , and, in II and III, the bonds between phosphorus and the atoms which occupy the basal positions of the trigonal bipyramid are  $120^\circ$ .

In IV, the bonds between phosphorus and the atoms which occupy the basal positions of the square pyramid are the normal  $90^\circ$ . In a structure of the type V, however, there is great angular strain. The internal angles of the four-membered ring cannot be  $90^\circ$  if the bonds from phosphorus to the atoms occupying the basal positions of the trigonal bipyramid are the normal  $120^\circ$ , and *vice versa*. There would be so much angular strain in a structure such as V that it is very unlikely that such a type of intermediate would be formed. *These considerations are of profound importance with respect to the stereochemistry of the reaction.* On the basis of the arguments of Haake and Westheimer,<sup>8</sup> intermediates (or transition species) of the types of II, III, and IV would collapse to give the products of the Wittig reaction with retention of the configuration of the phosphorus atom. An intermediate of type V, if it could be formed in the first place, would collapse to give the products of the Wittig reaction with inversion of the configuration of the phosphorus atom. However, the angular strain described above inhibits formation of intermediates of type V. Thus the only intermediates (or transition species) which can readily be formed are those of types II, III, and/or IV, all of which lead to retention of configuration of the phosphorus atom in the formation of methylethylphenylphosphine oxide (VII) and stilbene (96% *trans* isomer). The fact that the stilbene produced is predominantly the *trans* isomer is readily explained on the basis that the bulky phenyl groups preferentially occupy *trans* positions about the four-membered rings of intermediates of types II, III, and IV.

The argument that the action of sodium hydroxide on optically active methylethylphenylbenzylphosphonium iodide (I) gives methylethylphenylphosphine oxide (VII) with inversion of the configuration of the phosphorus atom may be developed as follows. Since dextrorotatory I gives levorotatory VII in the reaction with sodium hydroxide but dextrorotatory VII in the Wittig reaction, and since the arguments cited above indicate that the Wittig reaction takes place with retention of the configuration of the phosphorus atom, it follows that the phosphonium hydroxide decomposition occurs with inversion of the configuration of the phosphorus atom.

Evidence supplied by other workers<sup>9,10</sup> also indicates that the phosphonium hydroxide decomposition reaction leads to inversion of the configuration of the phosphorus atom. Using our method<sup>3</sup> of resolution, Horner, *et al.*, resolved methyl-*n*-propylphenylbenzylphosphonium iodide. Cathodic reduction of the optically active salt gave toluene and optically active methyl-*n*-propylphenylphosphine,<sup>9</sup> and later work<sup>10</sup> showed that the reduction took place with retention of the configuration of the phosphorus atom. Oxidation of the phosphine with hydrogen peroxide produced one enantiomorph of methyl-*n*-propylphenylphosphine oxide. The other enantiomorph was produced when the same methyl-*n*-propylphenylbenzylphosphonium iodide was treated with sodium hydroxide. Since it is a reasonable assumption that the oxidation of the optically active phosphine with hydrogen peroxide pro-

(4) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **81**, 3805 (1959).

(5) A. Blade Font, C. A. VanderWerf, and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

(6) M. Zanger, C. A. VanderWerf, and W. E. McEwen, *ibid.*, **81**, 3805 (1959).

(7) A. J. Speziale and D. E. Bissing, *ibid.*, **85**, 1888 (1963).

(8) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

(9) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman, and P. Beck, *Tetrahedron Letters*, 161 (1961).

(10) L. Horner, H. Fuchs, H. Winkler, and A. Rapp, *ibid.*, 965 (1963).

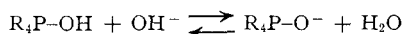
ceeded with retention of configuration of the phosphorus atom, it follows that the phosphonium hydroxide decomposition reaction took place with inversion of the configuration of the phosphorus atom.

On the basis of evidence presently available, it is not possible to propose a single definitive mechanism for the phosphonium hydroxide decomposition reaction. However, it is possible to limit the possible mechanisms to a relatively small number. In the first place, the demonstration of a third-order rate law for the reaction<sup>11</sup> indicates that two hydroxide ions and one phosphonium cation are involved during or prior to the rate-determining step of the reaction. To us, it seems that the most reasonable interpretation of this result is that the mechanism consists of the following steps<sup>12</sup>:

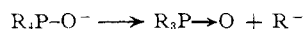
(1) Fast, reversible addition of hydroxide ion to the phosphorus atom of the quaternary phosphonium salt



(2) Fast, reversible formation of the conjugate base of the intermediate in which the phosphorus is pentacovalent



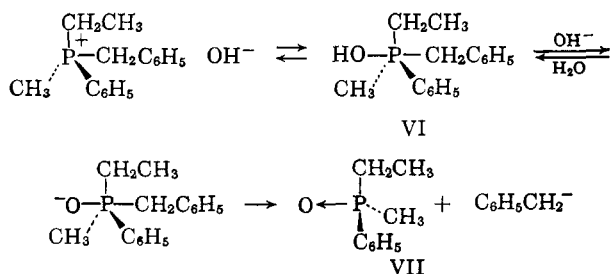
(3) Rate-determining formation of the phosphine oxide and a carbanion



(4) Fast conversion of the carbanion to the appropriate hydrocarbon by the action of water (the solvent)



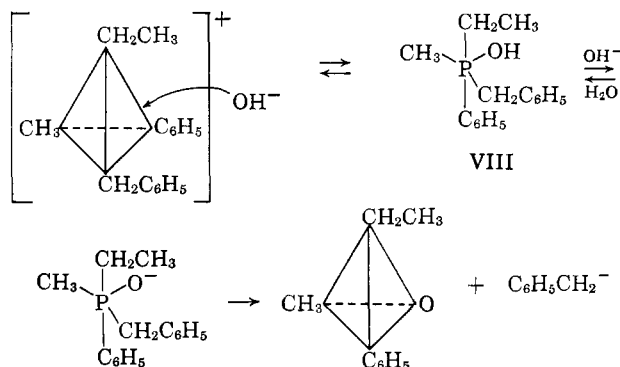
As applied to optically active methylethylphenylbenzylphosphonium iodide (I), there appears to be no reason why addition of the hydroxide ion to the phosphorus atom should not occur at every face of the tetrahedral cation, thus giving four diastereoisomeric intermediates of the trigonal bipyramidal type in which the phosphorus has the  $sp^3d$  configuration. Also, each of these diastereoisomers should give a small equilibrium concentration of its conjugate base. However, in step 3 the resonance-stabilized benzyl anion would be formed at a much faster rate than the methyl, ethyl, or phenyl anion, and, consequently, the over-all reaction gives essentially exclusively toluene and methylethylphenylphosphine oxide (VII). The stereochemical course of the reaction can thus be pictured as shown in the accompanying equations.



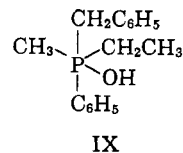
(11) H. Hoffman has provided confirmation of our<sup>6</sup> prior demonstration that the decomposition of quaternary phosphonium hydroxides is a third-order reaction: H. Hoffman, *Ann.*, **634**, 1 (1960).

(12) Conceivable variations of this general mechanism are (a) synchronous attack of the second hydroxide ion and departure of the benzyl anion and (b) the formation of an unstable intermediate with two hydroxide ions bonded to phosphorus (tetragonal bipyramidal structure).

The pathway by which an intermediate (VI) is formed in which the attacking base,  $OH^-$ , and the departing base,  $C_6H_5CH_2^-$ , occupy the apical positions of a trigonal bipyramid is not the only one which can lead to inversion of configuration of the phosphorus atom. It is possible that hydroxide ion could attack an edge of the tetrahedral cation to give an intermediate of type VIII in which the attacking base,  $OH^-$ , and the departing base,  $C_6H_5CH_2^-$ , occupy basal positions of a trigonal bipyramid. Collapse of an intermediate of type VIII would also result in inversion of the configuration of the phosphorus atom.<sup>13</sup>



A persuasive but not completely rigorous argument can be invoked against the operation of the inversion mechanism involving basal attack of  $OH^-$  and basal departure of  $C_6H_5CH_2^-$ . If  $OH^-$  can attack an edge of the tetrahedral phosphonium cation, then intermediates of type IX can also be formed. In this case there is basal attack of  $OH^-$  and apical departure of  $C_6H_5CH_2^-$ . Such a pathway, according to Haake and Westheimer,<sup>13</sup> might be expected to lead to retention of the configuration of the phosphorus atom. Thus a large degree of racemization in the formation of the phosphine oxide VII would be anticipated if there were any major tendency for hydroxide ion to attack the edges rather than the faces of the tetrahedral phosphonium cation. Since the phosphonium hydroxide decomposition reaction is 100% stereospecific, within the limits of our measurements of optical rotation, it seems likely that the products are being formed by way of intermediate VI.



The resolution of methylethylphenylbenzylphosphonium iodide (I) represented the first successful resolution of a noncyclic quaternary phosphonium salt in which the phosphorus atom is the sole center of asymmetry. Numerous previous failures<sup>14</sup> in attempts to resolve such salts led Mann<sup>15</sup> to propose a hypothesis to explain the results. He suggested that quaternary phosphonium salts undergo reversible dissociation in solution and that the tertiary phosphine so formed undergoes rapid racemization by a vibration

(13) See ref. 8 and also J. R. Cox, Jr., W. E. Wall, and F. H. Westheimer, *Chem. Ind. (London)*, 929 (1959).

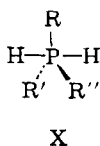
(14) A list of references has been provided in a previous communication.<sup>3</sup>

(15) F. G. Mann, *J. Chem. Soc.*, 65 (1945).

mechanism. Since three different groups<sup>9,16,17</sup> have demonstrated that asymmetric phosphines possess a good degree of optical stability, and since we have found that optically active I undergoes no racemization whatsoever when allowed to stand in solution for a month or more, it is clear that Mann's rationalization is untenable. It should also be pointed out, however, that Holliman and Mann,<sup>18</sup> proceeding through the *d*-camphorsulfonate, were on one occasion able to isolate pure crystalline dextrorotatory 2-phenyl-2-*p*-hydroxyphenyl-1,2,3,4-tetrahydroisophosphinolinium bromide, but later they were unable to repeat this work. More recently, Hart and Mann<sup>19</sup> accomplished the resolution of P-spirobis-1,2,3,4-tetrahydrophosphinolinium iodide into its dextro and levo isomers *via* the *d,l*-phosphonium 1-methoxyacetate. Mann made no comment in the later papers<sup>18,19</sup> about the hypothesis he had proposed earlier.<sup>15</sup>

It is of interest that the ylid, methylethylphenylbenzylidenephosphorane, derived from optically active I is optically stable at room temperature, at least for a few hours. When optically active I is converted to the ylid by the action of phenyllithium, then the ylid reconverted to I by the action of water, there is no change in the rotation of the recovered salt.

Some time ago<sup>16</sup> we reported that lithium aluminum hydride reduction of optically active I, even when effected at 0° in ethylene glycol dimethyl ether, gave racemic methylethylphenylphosphine. Since various workers<sup>9,16,17</sup> have shown that asymmetric tertiary phosphines are optically stable at room temperature, it is clear that the production of racemic methylethylphenylphosphine from optically active I is an integral part of the mechanism of the reduction. Campbell and Way<sup>20</sup> have also reported formation of a racemic phosphine by lithium aluminum hydride reduction of an optically active phosphine oxide. In view of these results, it appears possible that *meso*-phosphoranes of type X might be formed at some stage of such reduction reactions.<sup>21</sup> We are presently attempting to elucidate the detailed mechanism of such reactions.



The determination of the order of reaction of I with sodium hydroxide was a part of a larger study of the kinetics of phosphonium hydroxide decomposition reactions, particularly as applied to substituted tetra-benzylphosphonium salts. The details<sup>22,23</sup> of these studies will be published in a subsequent paper.

The resolution of methylethylphenyl-*p*-tolylphosphonium iodide and its stereospecific reaction with sodium hydroxide is described in the Experimental

section. Also, a new and convenient synthesis of tertiary phosphines having three different groups bonded to phosphorus, by reaction of phenyldichlorophosphine with a mixture of two Grignard reagents, is described.

### Experimental<sup>24</sup>

**Ethylbenzylphenylphosphine.**—Solutions of 0.50 mole of ethylmagnesium bromide and 0.50 mole of benzylmagnesium chloride, the former in 500 ml. and the latter in 700 ml. of anhydrous ether, were prepared in the usual manner and mixed. To the mixed Grignard reagents was added dropwise with stirring over the course of 1.5 hr. a solution of 0.50 mole of phenyldichlorophosphine in 500 ml. of ether. The mixture was then refluxed, with stirring, for 1 hr. In the latter stages of the reaction, the mixture became very thick if insufficient quantities of ether were present, and mechanical stirring became difficult. The reaction mixture was hydrolyzed by the dropwise addition of about 200 ml. of water. Addition of water was stopped when solid material precipitated as a gummy mass, and the ether layer became clear. The ether layer was removed by decantation and dried over anhydrous magnesium sulfate. Evaporation of the ether, after removal of the drying agent by filtration, gave about 100 ml. of yellow oil. The oil was distilled *in vacuo*, and the following fractions were collected: (1) 19.0 g. (24.5%) of diethylphenylphosphine, b.p. 85–90° (5 mm.); (reported<sup>25</sup> b.p. 156–160° (10 mm.)); (2) 47.0 g. (41%) of ethylphenylbenzylphosphine, b.p. 145–150° (5 mm.); (reported<sup>25</sup> b.p. 156–160° (10 mm.)); and (3) 27.5 g. (18%) of dibenzylphenylphosphine oxide,<sup>26</sup> m.p. 173–174° (reported<sup>25</sup> m.p. 173–174°).

**Racemic Methylethylphenylbenzylphosphonium Iodide (I).**—To a solution of 14.2 g. (0.10 mole) of methyl iodide in 250 ml. of anhydrous ether was added 22.8 g. (0.10 mole) of ethylphenylbenzylphosphine. The mixture was allowed to stand at 4° for 16 hr. There was obtained 33.1 g. (90%) of methylethylphenylbenzylphosphonium iodide, m.p. 166–167° (reported<sup>25</sup> m.p. 167–168°). On some occasions the compound precipitated from ether as a white semisolid mass, which crystallized readily when the sample was placed under hot ethyl acetate and the flask scratched. The salt can be crystallized from methanol, water, or acetone. A very pure sample had a m.p. of 170–171°.

**(+)-Methylethylphenylbenzylphosphonium D(-)-Dibenzoylhydrogentartrate.**—A solution of 62.0 g. (0.167 mole) of racemic I in 335 ml. of absolute methanol was added to a stirred slurry of 98.0 g. (approximately 0.20 mole) of silver D(-)-dibenzoylhydrogentartrate<sup>27</sup> in 335 ml. of methanol. The suspension was refluxed gently for 1 hr. with vigorous mechanical stirring. The mixture was filtered to remove silver iodide. The solvent was removed from the filtrate by distillation under reduced pressure and the residue treated with hot 1-propanol. The insoluble ammonium D(-)-dibenzoylhydrogentartrate (an impurity present in the silver D(-)-dibenzoylhydrogentartrate)<sup>27</sup> was removed by filtration, and a mixture of diastereoisomers crystallized from the hot filtrate as it cooled. Ten successive recrystallizations from absolute 1-propanol gave 16.0 g. of pure (+)-methylethylphenylbenzylphosphonium D(-)-dibenzoylhydrogentartrate, m.p. 139–140°,  $[\alpha]_D^{25} -57^\circ$  (*c* 2.560 in methanol).

(24) Analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All reactions in which ylids or tertiary phosphines were either products or reagents were carried out in an atmosphere of pure nitrogen.

(25) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

(26) Although all operations cited above were carried out as much as possible in a nitrogen atmosphere, sufficient oxygen reaches the products in the various transfer operations to oxidize dibenzylphenylphosphine to the oxide. This is actually advantageous, as it permits more facile separation of products by distillation. It is not known why dibenzylphenylphosphine is oxidized by air more rapidly than the other two phosphines produced in the reaction.

(27) D. M. Coyne, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **78**, 3061 (1956). In most cases the silver dibenzoylhydrogentartrate was found to contain 10–15% of ammonium dibenzoylhydrogentartrate, m.p. 193–194° dec. However, the ammonium salt did not interfere in the resolution because, owing to its extreme insolubility in hot 1-propanol, it could easily be separated from the desired diastereoisomers. Allowance for the impurity was made in calculating the amount of silver salt (plus a 10–20% excess) required in its reaction with racemic I. A fairly pure sample of silver D(-)-dibenzoylhydrogentartrate had a m.p. of 170–172° dec,  $[\alpha]_D^{25} -98^\circ$  (*c* 0.865 in 1 N  $\text{NH}_4\text{OH}$ ).

(16) W. E. McEwen, C. A. VanderWerf, A. Blade-Font, C. B. Parisek, G. Keldsen, D. C. Velez, D. P. Young, K. Kumli, and G. Axelrad, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3–8, 1961, p. 96Q.

(17) I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 5034 (1960).

(18) F. H. Holliman and F. G. Mann, *ibid.*, 1634 (1947).

(19) F. A. Hart and F. G. Mann, *ibid.*, 4107 (1955).

(20) I. G. M. Campbell and J. K. Way, *ibid.*, 2133 (1961).

(21) Cf. C. B. Parisek, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **82**, 5503 (1960).

(22) M. Zanger, Ph.D. Dissertation, University of Kansas, 1959.

(23) G. Axelrad, Ph.D. Dissertation, University of Kansas, 1960.

*Anal.* Calcd. for  $C_{34}H_{33}O_8P$ : C, 68.00; H, 5.54; P, 5.17. Found: C, 68.21; H, 5.73; P, 5.48.

The diastereoisomeric salts from the mother liquors were recovered and converted to the iodide I. This material was subsequently used for the isolation of (–)-I.

(+)-Methylethylphenylbenzylphosphonium Iodide ((+)-I).—The 16.0 g. (0.0267 mole) of (+)-methylethylphenylbenzylphosphonium D(–)-dibenzoylhydrogentartrate cited above was treated with 4.0 g. (0.0276 mole) of ammonium iodide in 200 ml. of hot methanol. The solution was evaporated to dryness and the residue extracted several times with boiling acetone (in which ammonium dibenzoylhydrogentartrate is insoluble). Concentration of the acetone extracts and cooling afforded 9.30 g. (0.0251 mole, 97%) of optically pure (+)-I, m.p. 166–168°,  $[\alpha]^{25}_D +25.0 \pm 1.0$  (c 2.815 in methanol).

*Anal.* Calcd. for  $C_{16}H_{20}PI$ : C, 51.90; H, 5.44; P, 8.37; I, 34.28. Found: C, 52.06; H, 5.34; P, 8.12; I, 34.38.

(–)-Methylethylphenylbenzylphosphonium L(+)-Dibenzoylhydrogentartrate.—The same procedure described for the attainment of (+)-methylethylphenylbenzylphosphonium D(–)-dibenzoylhydrogentartrate yielded, from 82.0 g. (0.221 mole) of racemic I and 142 g. (about 0.13 mole) of silver L(+)-dibenzoylhydrogentartrate,<sup>28</sup> 22.5 g. of pure (–)-methylethylphenylbenzylphosphonium L(+)-dibenzoylhydrogentartrate, m.p. 137–138° dec.,  $[\alpha]^{25}_D +57$  (c 2.875 in methanol).<sup>29</sup>

*Anal.* Calcd. for  $C_{34}H_{33}O_8P$ : C, 68.00; H, 5.54; P, 5.17. Found: C, 68.19; H, 5.64; P, 5.07.

(–)-Methylethylphenylbenzylphosphonium Iodide ((–)-I). The (–)-methylethylphenylbenzylphosphonium L(+)-dibenzoylhydrogentartrate (22.5 g., 0.0375 mole) was converted to the iodide by reaction with 5.70 g. (0.0393 mole) of ammonium iodide and the optically active salt isolated in exactly the same manner as described for (+)-I. From the acetone extracts, 12.10 g. (0.0327 mole, 87%) of (–)-I, m.p. 167–168°,  $[\alpha]^{25}_D -24.5 \pm 1.0$  (c 2.625 in methanol), was isolated.<sup>30</sup>

*Anal.* Calcd. for  $C_{16}H_{20}PI$ : C, 51.90; H, 5.44; P, 8.37; I, 34.28. Found: C, 52.11; H, 5.63; P, 8.13; I, 34.35.

**Wittig Reaction of Racemic I with Benzaldehyde.**—To a stirred suspension of 7.40 g. (0.020 mole) of racemic I in 100 ml. of anhydrous ether was added 68 ml. of a 0.370 *N* (0.0252 mole) ethereal solution of phenyllithium.<sup>31</sup> To the orange-red solution was added dropwise a solution of 2.52 g. (0.0238 mole) of benzaldehyde in 25 ml. of ether. Decolorization of the solution took place immediately, and a colorless precipitate of methylethylphenylphosphine oxide–lithium iodide adduct appeared. The mixture was stirred for 12 hr. at room temperature, then filtered and the hygroscopic precipitate washed several times with ether. The solid was dissolved in 15 ml. of water, the aqueous solution washed with ether, and potassium hydroxide pellets were dissolved in the aqueous solution until a yellow oil separated. The oil was extracted into benzene, the benzene solution dried over sodium hydroxide pellets, filtered, and the benzene evaporated. Vacuum distillation of the residue yielded 2.66 g. (79%) of methylethylphenylphosphine oxide (VII), m.p. 52–56° (reported<sup>32</sup>

m.p. 50°). Samples of VII having a m.p. as high as 56–58° were obtained on several occasions.

*Anal.* Calcd. for  $C_9H_{13}PO$ : C, 64.30; H, 7.79; P, 18.41. Found: C, 64.30; H, 7.98; P, 18.16.

The ether filtrate was washed with water, 40% sodium bisulfite solution, and water once again. After having been dried over anhydrous magnesium sulfate, the solution was distilled to remove the solvent and the residue treated with methanol to give 3.13 g. (87%) of *trans*-stilbene, m.p. 122–124°, also in admixture with authentic material. The methanol was evaporated from the filtrate and the residual oil chromatographed on Grade I alumina,<sup>33</sup> petroleum ether of b.p. 35–60° being used as solvent and eluent. There was obtained 0.145 g. (4.0%) of crude *cis*-stilbene,  $n^{20}_D$  1.6162 (reported<sup>34</sup>  $n^{20}_D$  1.6083), also identified by its infrared spectrum and the fact that it was isomerized to *trans*-stilbene when boiled in acetic acid solution containing a trace of hydrobromic acid. A small amount of *trans*-stilbene and 70 mg. of crude benzyl benzoate were next eluted from the column.

**Reaction of (+)-Methylethylphenylbenzylidenephosphorane with Benzaldehyde.**—The Wittig reaction of the phosphinemethylene, formed from (+)-I by the action of phenyllithium, with benzaldehyde was carried out in exactly the same manner as described for racemic I, the same amounts of starting material being used. There was obtained *trans*-stilbene (3.04 g., 84%), *cis*-stilbene (0.175 g., 5%), and crude (+)-methylethylphenylphosphine oxide, m.p. 46–50°, b.p. 109–112° (0.15 mm.) (2.95 g., 88%). The phosphine oxide contained some *trans*-stilbene, which was removed by dissolving the phosphine oxide in water and extracting the insoluble olefin into petroleum ether of b.p. 35–60°. Repetition of the isolation procedure for the phosphine oxide gave 2.35 g. (70%) of pure material, m.p. 46–50°,  $[\alpha]^{25}_D +21.5 \pm 1.0$  (c 2.128 in water); reported<sup>36</sup> m.p. 50°,  $[\alpha]^{25}_D +22.8$  (c 2.184 in water). The infrared spectrum of the (+)-phosphine oxide, taken in chloroform solution, was identical with that of the racemic material.

*Anal.* Calcd. for  $C_9H_{13}PO$ : C, 64.30; H, 7.79; P, 18.41. Found: C, 64.54; H, 7.91; P, 18.22.

**Reaction of (–)-Methylethylphenylbenzylidenephosphorane with Benzaldehyde.**—The procedure cited above gave, from 5.55 g. (0.015 mole) of (–)-I, 0.0204 mole of phenyllithium, and 2.0 g. (0.0188 mole) of benzaldehyde, the following products: 2.25 g. (82%) of *trans*-stilbene, 0.15 g. (6%) of *cis*-stilbene, and 2.20 g. (87%) of crude (–)-methylethylphenylphosphine oxide, m.p. 46–51°, b.p. 95–105° (0.15 mm.). Purification of the phosphine oxide in the manner described for the (+)-isomer gave (–)-methylethylphenylphosphine oxide (1.72 g., 68%), m.p. 47–51°,  $[\alpha]^{25}_D -21.0 \pm 1.0$  (c 2.238 in water).

*Anal.* Calcd. for  $C_9H_{13}PO$ : C, 64.30; H, 7.79. Found: C, 64.02; H, 7.97.

**Optical Stability of Methylethylphenylbenzylidenephosphorane.**—A suspension of 1.00 g. of (+)-I in 25 ml. of anhydrous ether was treated with an excess of phenyllithium and the orange-red solution allowed to stand in a nitrogen atmosphere for 1 hr. Addition of a saturated solution of water in ether caused immediate decolorization of the solution, and 0.85 g. of I precipitated, m.p. 162–167°,  $[\alpha]^{25}_D +26.0 \pm 1.0$  (c 2.820 in methanol).

**Reaction of Racemic I with Sodium Hydroxide.**—The reaction of racemic I with sodium hydroxide was carried out in a closed system connected to a gas buret to determined whether any methane or ethane was produced. To 200 ml. of 1 *M* sodium hydroxide solution was added 37.00 g. (0.10 mole) of racemic I, and the resulting solution was heated on the steam bath for 16 hr. There was no evidence of any gas evolution (other than that attributable to the partial pressure of toluene). A hydrocarbon layer which had formed was separated from the aqueous layer, dried over anhydrous magnesium sulfate, and subjected to vapor phase chromatography. Only one peak was observed, and this appeared at the same retention time observed for pure toluene. Not a trace of benzene was detected. (Control experiments showed that as little as 0.1% of benzene would have easily been detected had it been present.) The yield of toluene was 8.70 g. (95%).

**Reaction of (–)-Methylethylphenylbenzylphosphonium Iodide (I) with Sodium Hydroxide.**—To a solution of 2.80 g. (0.0076 mole) of (–)-I,  $[\alpha]^{25}_D -23.8 \pm 1.0$ , in 50 ml. of methanol was added 10 ml. of 10 *M* aqueous sodium hydroxide solution. The

(28) A fairly pure sample had a m.p. of 176–179° dec.,  $[\alpha]^{25}_D +103$  (c 0.865 in 1 *N*  $NH_4OH$ ).

(29) The mixture of diastereoisomeric phosphonium L(+)-dibenzoylhydrogentartrates was found to be more soluble in absolute 1-propanol than the mixture of phosphonium D(–)-dibenzoylhydrogentartrates. Thus, whereas about 20% solutions (hot) were used for initial crystallization of the D(–)-dibenzoylhydrogentartrates, about 25–30% solutions were used for the L(+)-dibenzoylhydrogentartrates. In each case, the hot absolute 1-propanol solution was allowed to deposit crystals very slowly in a hot water bath or in a thermos bottle before being refrigerated. Quick cooling provided only poor separation of the diastereoisomers. Seed crystals were most helpful in promoting a good separation.

(30) There is some evidence for the existence of dimorphic forms of optically active I. When first crystallized from acetone, as described in the resolution procedure, (+)-I had a m.p. 166–168°, unchanged after several recrystallizations from water. Subsequent recrystallization of this material from acetone afforded material, m.p. 159–160°. This salt, when recrystallized from water several times, melted again at 167–168°. No change in optical rotation was observed during these manipulations. In our previous communication,<sup>2</sup> we reported m.p.'s of 159–160° and 158–159° for (+)-I and (–)-I, respectively.

(31) The phenyllithium solution was added portionwise to the suspension of phosphonium salt until a clear, orange-red solution resulted. More than the theoretical amount of phenyllithium was required to effect complete conversion of the phosphonium salt into the ylid. Freshly prepared I underwent reaction with phenyllithium and dissolved much faster than material kept several weeks prior to use.

(32) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911).

(33) H. Brockmann and H. Schodder, *ibid.*, **74**, 73 (1941).

(34) K. N. Campbell and M. J. O'Connor, *J. Am. Chem. Soc.*, **61**, 2897 (1939).

mixture was heated on the steam bath for 16 hr., then evaporated to dryness and the residue placed in a vacuum sublimator. Distillation *in vacuo* gave 1.06 g. (89%) of methylethylphenylphosphine oxide (VII), m.p. 47–48°,  $[\alpha]_D^{25} + 22.4 \pm 1.0^\circ$  (*c* 2.184 in water).

**Reaction of (+)-I with Sodium Hydroxide.**—Treatment of (+)-I in the same manner as described for (–)-I gave (–)-VII, m.p. 48–49°,  $[\alpha]_D^{25} - 22.8 \pm 1.0^\circ$  (*c* 2.168 in water).

**Kinetics of Reaction of Methylethylphenylbenzylphosphonium Chloride with Sodium Hydroxide.**—In each determination an aqueous solution was prepared which was 0.0882 *N* with respect to methylethylphenylbenzylphosphonium chloride<sup>35</sup> and 1.11 *N* with respect to potassium chloride. A test tube with a thin-walled bulb blown in the end of the tube, containing 10.00 ml. of a 0.7396 *N* solution of sodium hydroxide, was suspended in a reaction vessel containing 90.00 ml. of the phosphonium chloride-potassium chloride solution, and the entire apparatus was allowed to equilibrate in a constant temperature bath maintained at 99.4°. When sufficient time had elapsed, a glass rod was used to break the bottom of the test tube. A magnetic stirrer was used to mix the reagents, and, after the punctured test tube had been removed, a 10.00-ml. aliquot was removed and the reaction essentially quenched by addition to 5 ml. of cold water. The sample was titrated with standard hydrochloric acid, the end point being determined by use of brom thymol blue as indicator. Similar aliquots were taken after suitable intervals and treated in the same manner. The initial amounts of phosphonium salt and base corresponded to 0.0794 *N* each; *i.e.*,  $(R_4P^+) = (OH^-)$ . After the two initial solutions had been mixed, the potassium chloride concentration was 1.00 *N*.

In a second set of rate determinations, 80.00 ml. of a 0.0992 *N* solution of phosphonium salt and 20.00 ml. of 0.7936 *N* sodium hydroxide were employed, with the mixed solutions also being 1.00 *N* in potassium chloride. The initial concentrations of phosphonium salt and base at the time of mixing corresponded to 0.0794 and 0.1588 *N*, respectively; *i.e.*,  $2(R_4P^+) = (OH^-)$ .

Third-order rate constants were determined graphically in the usual way. A total of four kinetic determinations were made, the first two with  $(R_4P^+) = (OH^-)$  and the other two with  $2(R_4P^+) = (OH^-)$ . The average specific rate constant, *av.*  $k_3 = 7.90 \pm 0.24$  l.<sup>2</sup>/moles<sup>2</sup>·hr. The data were completely inconsistent with a second-order reaction.<sup>36</sup>

**Ethylphenyl-*p*-tolylphosphine.**—To a mixture of 0.50 mole of ethylmagnesium bromide and 0.50 mole of *p*-tolylmagnesium bromide contained in 1500 ml. of ether was added dropwise over a period of 1.5 hr. a solution of 0.50 mole of phenyldichlorophosphine in 500 ml. of ether. The mixture was then refluxed for 1 hr. and hydrolyzed by dropwise addition of about 200 ml. of water. The addition of water was stopped when a gummy precipitate formed. The clear, yellow ether solution was decanted from the precipitate and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, distillation of the ether left, as a residue, about 100 ml. of yellow oil. This was distilled *in vacuo* and the following fractions collected: (1) 19 g. of diethylphenylphosphine, b.p. 87–92° (5 mm.); (2) 52 g. (44.7%) of ethylphenyl-*p*-tolylphosphine, b.p. 138–145° (5 mm.); and (3) 24 g. of phenyldi-*p*-tolylphosphine, m.p. 56–58° (reported<sup>37</sup> m.p. 57°).

**Methylethylphenyl-*p*-tolylphosphonium Iodide.**—To a solution of 14.2 g. (0.1 mole) of methyl iodide in 250 ml. of ether was added 22.8 g. (0.1 mole) of ethylphenyl-*p*-tolylphosphine, and the mixture was allowed to stand at 4° for 16 hr. At the end of this time, 35.0 g. (94.6%) of methylethylphenyl-*p*-tolylphosphonium iodide, m.p. 167–168°, was collected by filtration. Previously reported m.p.'s were inexplicably low: *viz.*, 138°<sup>37</sup> and 150°.<sup>38</sup>

*Anal.* Calcd. for  $C_{16}H_{20}PI$ : C, 51.90; H, 5.39; P, 8.38; I, 34.35. Found: C, 51.73; H, 5.47; P, 8.28; I, 34.32.

**Resolution of Methylethylphenyl-*p*-tolylphosphonium Iodide.**—Treatment of 37.0 g. (0.05 mole) of methylethylphenyl-*p*-tolylphosphonium iodide with a 10–15% excess of silver *D*(–)-dibenzoylhydrogentartrate in methanol afforded 34.8 g. (53%) of the desired mixture of diastereoisomers. Seven successive recrystallizations of this material from absolute 1-propanol caused no change in rotation,  $[\alpha]_D^{25} - 70.0 \pm 1.0^\circ$  (*c* 1.120 in

methanol). However, the m.p. changed from 127–128° dec. to 143–144° dec.

*Anal.* Calcd. for  $C_{34}H_{38}O_8P$ : C, 68.00; H, 5.54; P, 5.17. Found: C, 67.94; H, 5.70; P, 5.27.

Treatment of 4.28 g. of this pure diastereoisomer with ammonium iodide in methanol by the same procedure used for the preparation of (+)-I gave 2.30 g. of methylethylphenyl-*p*-tolylphosphonium iodide, m.p. 187–188°,  $[\alpha]_D^{25} 0.00 \pm 1.00^\circ$  (in methanol).

*Anal.* Calcd. for  $C_{16}H_{20}PI$ : C, 51.90; H, 5.39; P, 8.38; I, 34.35. Found: C, 51.19; H, 5.31; P, 8.42; I, 34.45.

The mother liquors from the recrystallizations of the phosphonium *D*(–)-dibenzoylhydrogentartrate were evaporated to dryness, and the residue was treated with ammonium iodide in methanol. The methylethylphenyl-*p*-tolylphosphonium iodide so recovered was converted to the *L*(+)-dibenzoylhydrogentartrate, m.p. 132–133°, 24.3 g. being obtained. Seven recrystallizations from absolute 1-propanol gave 3.70 g. of the pure diastereoisomer, m.p. 142–143°.

*Anal.* Calcd. for  $C_{34}H_{38}O_8P$ : C, 68.00; H, 5.54; P, 5.17. Found: C, 68.36; H, 5.63; P, 5.26.

This was reconverted in the usual manner to the iodide salt, m.p. 185–186°,  $[\alpha]_D^{25} 0.00 \pm 1.00^\circ$ .

*Anal.* Calcd. for  $C_{16}H_{20}PI$ : C, 51.90; H, 5.39; P, 8.38; I, 34.35. Found: C, 51.98; H, 5.46; P, 8.60; I, 34.34.

When 0.50 g. of the isomer, m.p. 187–188°, and 0.500 g. of the isomer, m.p. 185–186°, were dissolved in 10 ml. of methanol and recrystallized, racemic methylethylphenyl-*p*-tolylphosphonium iodide, m.p. 167–168°, was obtained.

**Reaction of Racemic Methylethylphenyl-*p*-tolylphosphonium Iodide with Sodium Hydroxide.**—Treatment of 18.5 g. (0.05 mole) of methylethylphenyl-*p*-tolylphosphonium iodide with 100 ml. of 2.0 *N* sodium hydroxide solution in the same manner as described for the corresponding reaction of I gave 3.60 g. of a hydrocarbon mixture which was analyzed by vapor phase chromatography. This analysis indicated that benzene had been produced in 56.4% yield and toluene in 30.4% yield. There was no evidence for formation of either methane or ethane.

**Reaction with Sodium Hydroxide of the Active Methylethylphenyl-*p*-tolylphosphonium Iodide from the *D*(–)-Dibenzoylhydrogentartrate.**—Treatment of 6.3 g. of methylethylphenyl-*p*-tolylphosphonium iodide, m.p. 185–186°, with sodium hydroxide solution gave, after 16 hr. of refluxing, 1.86 g. (68%) of a mixture of methylethylphenylphosphine oxide and methylethyl-*p*-tolylphosphine oxide. The rotation of this mixture was taken. The mixture of phosphine oxides was then treated with an excess of dilute potassium permanganate solution for a period of 24 hr. in order to oxidize the *p*-tolyl group to a *p*-carboxyphenyl group. Extraction of the alkaline solution with benzene, distillation of the solvent, and sublimation of the residue gave 0.175 g. of pure methylethylphenylphosphine oxide, m.p. 48–49°,  $[\alpha]_D^{25} + 22.5 \pm 1.0^\circ$  (in water).

*Anal.* Calcd. for  $C_9H_{13}PO$ : C, 64.30; H, 7.79; P, 18.46. Found: C, 64.22; H, 7.79; P, 18.35.

From the ratio of benzene to toluene produced, the observed rotation of the mixture of phosphine oxides and the known specific rotation of methylethylphenylphosphine oxide, it can be calculated that the specific rotation of the methylethyl-*p*-tolylphosphine oxide produced in this reaction was about  $-18.5^\circ$  in aqueous solution at 25°.

**Lithium Aluminum Hydride Reduction of (+)-I.**—To a suspension of 3.70 g. (0.01 mole) of (+)-I in 25 ml. of anhydrous ethylene glycol dimethyl ether was added 0.245 g. (0.007 mole) of lithium aluminum hydride. The mixture was stirred at 0° for 1 hr.; then the solvent was evaporated *in vacuo* at the same temperature. After addition of 25 ml. of cold ethyl ether, the mixture was hydrolyzed by addition of 20% sodium tartrate solution. The ether layer was removed and checked for optical activity. No rotation was observed. To the cold ether solution was added 1.0 g. of benzyl chloride. The solution was allowed to stand at 0° for 16 hr. An oily precipitate which had formed was treated with a solution of 1.5 g. of sodium iodide in acetone. There was obtained 2.5 g. of racemic I, m.p. 166–167°.

Similar results were observed when tetrahydrofuran was used as solvent in place of ethylene glycol dimethyl ether. Analysis by v.p.c. of the hydrocarbon fraction of the reaction mixture revealed that it contained only toluene.

**Other Examples of the Mixed Grignard Synthesis of Tertiary Phosphines.**—Ethylphenyl-*n*-hexylphosphine, b.p. 120–124° (1 mm.), was obtained in 40% yield by reaction of 1 mole of phenyl-

(35) Prepared by reaction of methylethylphenylphosphine with benzyl chloride in xylene (mixture of isomers) solution at reflux temperature.

(36) See ref. 22 for complete data.

(37) A. Michaelis, *Ann.*, **315**, 58 (1901).

(38) E. Wedekind, *Ber.*, **45**, 2933 (1912).

dichlorophosphine with 1 mole each of a mixture of ethylmagnesium bromide and *n*-hexylmagnesium bromide. The racemic phosphine was readily separated from the other phosphines produced, *viz.*, diethylphenylphosphine, b.p. 72–78° (1 mm.), and di-*n*-hexylphenylphosphine, b.p. 162–166° (1 mm.), by fractional distillation.

Although a mixture of tertiary phosphines was produced by reaction of phenyldichlorophosphine with ethylmagnesium and isobutylmagnesium bromides, the components could not be separated easily by fractional distillation.

Reaction of phenyldichlorophosphine with a mixture of  $\alpha$ -naphthylmagnesium bromide and *p*-tolylmagnesium bromide gave a predominant amount of phenyl-di- $\alpha$ -naphthylphosphine, m.p. 208°.

*Anal.* Calcd. for  $C_{26}H_{18}P$ : C, 86.2; H, 5.28; P, 8.60. Found: C, 85.9; H, 5.56; P, 8.61.

**Ethylphenyl-*n*-hexylbenzylphosphonium Bromide.**—Treatment of 2.22 g. (0.01 mole) of ethylphenyl-*n*-hexylphosphine with an excess of benzyl bromide at room temperature for 16 hr. gave an oily product which was washed with ether and crystallized from

acetone. There was obtained 3.50 g. (89%) of ethylphenyl-*n*-hexylbenzylphosphonium bromide, m.p. 121–122°.

*Anal.* Calcd. for  $C_{21}H_{30}PBr$ : C, 64.2; H, 7.64; P, 7.88; Br, 20.3. Found: C, 64.4; H, 7.82; P, 7.99; Br, 20.3.

**Di-*n*-hexylphenylbenzylphosphonium bromide** was obtained from di-*n*-hexylphenylphosphine and benzyl bromide in the same manner as described for ethylphenyl-*n*-hexylbenzylphosphonium bromide. The di-*n*-hexylphenylbenzylphosphonium bromide had m.p. 134–135° after crystallization from acetone.

*Anal.* Calcd. for  $C_{28}H_{38}PBr$ : C, 66.9; H, 8.46; P, 6.90; Br, 17.8. Found: C, 67.1; H, 8.68; P, 6.99; Br, 17.9.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, N. Y.]

## The Effects of Solvent and Structure on the Low Intensity ( $n \rightarrow \pi^*$ ) Electronic Transition of Carboxylate Esters

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The effects of alkyl substitution, conformation, and solvent polarity on the low intensity electronic transition of saturated carboxylate esters have been investigated. All the observed effects are in keeping with identification of the weak band as an  $n \rightarrow \pi^*$  transition. Moderate shifts to longer wave length were observed with methyl substitution either on the carbon adjacent to the carbonyl group or on the carbon adjacent to the ether oxygen. Evidence is presented indicating that the former is due to inductive effects while the latter is probably of steric origin. The solvent sensitivities of the spectra indicated that the ester carbonyl group interacts with solvent in the same way, and to approximately the same degree, as the carbonyl group in aliphatic ketones. The *s-cis* conformation was found to have its absorption maximum located at longer wave lengths than that of *s-trans*.

### Introduction

While the  $n \rightarrow \pi^*$  transition of the carbonyl group in aldehydes and ketones is well known and reasonably well understood,<sup>1</sup> the corresponding transition in compounds in which a heteroatom is bonded directly to the carbonyl group has received little attention. The gross effects of attaching a group bearing lone-pair electrons to the carbonyl group are easily predicted.<sup>2</sup> Such groups most commonly met with are  $-NR_2$ ,  $-OR$ , or halogen, although certain others (*e.g.*,  $-SR$ ,  $-SCN$ ,  $-N_3$ , etc.) may be expected to bring about the same effects. An approximate energy level diagram for the ester carbonyl system is presented in Fig. 1.

As shown in Fig. 1, interaction of the nonbonding electrons on the heteroatom with the  $\pi$ -orbitals of the carbonyl group raises the energy of the antibonding  $\pi$ -orbital ( $\pi^*$ ) and splits the bonding  $\pi$ -orbital into two new orbitals,  $\pi_1$  and  $\pi_2$ ,<sup>2</sup> the latter being essentially a nonbonding orbital located mainly on the heteroatom. The two transitions of lowest energy should be  $n \rightarrow \pi_3^*$  and  $\pi_2 \rightarrow \pi_3^*$ , as shown.

These two transitions will frequently be very close in energy, and, depending on the hetero substituent, either may appear at longer wave length. Acyl chlorides are examples where the  $n \rightarrow \pi_3^*$  band is clearly the lowest energy transition (near 235  $m\mu$ ),<sup>3</sup>

and the fairly intense band near 230  $m\mu$  in the spectrum of thiol esters<sup>4</sup> is almost surely an example of the  $\pi_2 \rightarrow \pi_3^*$  transition appearing at longest wave length. In the case of carboxylic acids and esters, it is well known<sup>1-3</sup> that a weak absorption band occurs near 210  $m\mu$ , and this is commonly regarded as the "forbidden"  $n \rightarrow \pi^*$  transition, analogous to that observed in ketones and aldehydes. Recently, evidence based on rotatory dispersion and circular dichroism data and, to a certain extent, direct observation has been presented that indicated the existence of  $n \rightarrow \pi^*$  transitions near 250  $m\mu$  in  $\alpha,\beta$ -unsaturated acids.<sup>5</sup> Distinct absorption maxima corresponding to this transition have also been observed in the spectra of acrylate esters.<sup>6</sup>

In the present study the effects of molecular structure and solvent on the low intensity transition of saturated carboxylate esters have been examined. These effects have been thoroughly studied in the case of aldehydes and ketones.<sup>1,7</sup> In particular, three effects were

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