Mechanism of the Thermal Decomposition of the Condensation Product of a Phosphonium Ylide with an Epoxide

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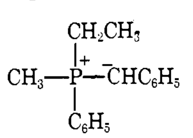
Abstract: The mechanism of the thermal decomposition of methylethylphenyl(1,3-diphenyl-3-hydroxypropyl)-phosphonium betaine (II) has been investigated by means of a C^{14} tracer study, a deuterium tracer study, a stereochemical study, and a study of cation effects. When lithium ion is coordinated with the negative oxygen atom of II, the major reaction gives rise to methylethylphenylphosphine (III) and benzylacetophenone (IV) by way of a 1,3-hydride shift as depicted in the transition state VIII. However, with sodium ion present in place of lithium ion, the major products are methylethylphenylphosphine oxide (V) plus a mixture of hydrocarbons. These products presumably arise by way of unstable intermediates of general type XI.

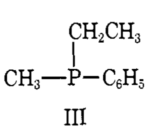
The reaction of methylethylphenylbenzylidenephosphorane (I), generated from methylethylphenylbenzylphosphonium iodide by the action of phenyllithium, with styrene oxide in ether solution has been reported[1] to give the lithium iodide adduct of methylethylphenyl-(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine (II). The adduct was found to undergo decomposition when refluxed in decalin suspension to give mainly methylethylphenylphosphine (III) and benzylacetophenone (IV); however, methylethylphenylphosphine oxide (V), *cis*- and *trans*-1,3-diphenylpropene, *trans*-1,2-diphenylcyclopropane (molar ratio of the hydrocarbons, 14:80:6, respectively), and 1,3-diphenylpropan-1-ol were also formed in relatively small amounts.[2]

Three mechanisms may be considered for the conversion of II to III and IV.[3-6] The first of these possibilities, one in which 2,4-diphenyloxetane (VI) is formed as an intermediate, has been eliminated from further consideration by means of a tracer study[3] in which the position marked by an asterisk in II was labeled with C^{14}. On degradation of the benzylacetophenone (IV) produced, none of the carbon-14 was found in the carbonyl group; all of it was found in the α-carbon of the benzyl group. Thus, the mechanism proceeding by way of VI, a symmetrical intermediate, is not operative.



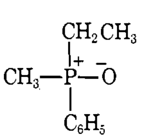
$CH_3—\overset{CH_2CH_3}{\underset{C_6H_5}{\overset{|+}{P}}}\bar{—}CHC_6H_5$

I



$CH_3—\overset{CH_2CH_3}{\underset{C_6H_5}{P}}$ wait

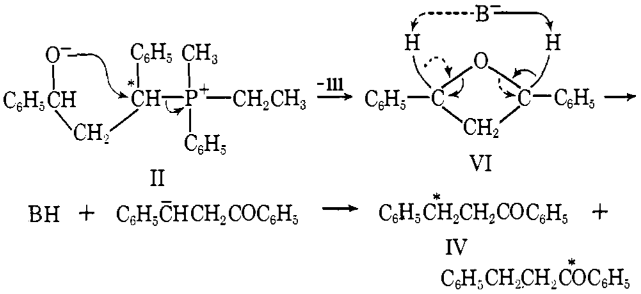
III



$CH_3—\overset{CH_2CH_3}{\underset{C_6H_5}{\overset{|+}{P}}}\bar{—}O$

V

The sequence of reactions undertaken to establish this conclusion was the following. (1) Methylethylphenylbenzyl-7-C^{14}-phosphonium iodide was prepared by reaction of methylethylphenylphosphine (III)[7] with benzyl-7-C^{14} iodide. (2) The labeled phosphonium iodide was converted to the corresponding ylide by the action of phenyllithium in ether. (3) Reaction of the ylide with styrene oxide gave the lithium iodide adduct of II as a precipitate. (4) Pyrolysis of a suspension of the adduct in decalin gave the mixture of products cited earlier. (5) The labeled benzylacetophenone (IV) which was isolated was converted to hydrocinnamanilide by the action of hydrogen azide and sulfuric acid. (6) Hydrolysis of the anilide gave hydrocinnamic acid. (7) A portion of the hydrocinnamic acid was subjected to the Schmidt reaction, and an assay of the carbon dioxide formed indicated that it did not contain the C^{14} label. (8) A second portion of the hydrocinnamic acid was oxidized by potassium permanganate to give benzoic acid. (9) The carbon dioxide obtained by a Schmidt reaction of the benzoic acid was found to contain all of the C^{14} label.



The two remaining mechanisms, each consistent with the results of the carbon-14 tracer experiment, will be discussed jointly in terms of a deuterium tracer experiment. These involve the conversion of II-*d* to III and IV-*d* either by way of a 1,2-diphenylcyclopropanol derivative (VII) as an intermediate or else by a direct 1,3-hydride transfer mechanism, the transition state of which is represented by VIII for the deuterium tracer reaction.

Although it is clear that the same deuterated product, IV-*d*, would be obtained from II-*d* by either mechanism, (B:⁻ could be a second molecule of II-*d* or else some other base, such as $C_6H_5C(-O^-)HCH_2C_6H_5$, known to

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[1] A. Blade-Font, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **84**, 677 (1962).

[2] Denney and Boskin had previously reported that the products of a similar reaction, that of carbethoxymethylenetriphenylphosphorane with styrene oxide, were triphenylphosphine oxide and ethyl *trans*-2-phenylcyclopropanecarboxylate: D. B. Denney and M. J. Boskin, *ibid.*, **81**, 6330 (1959).

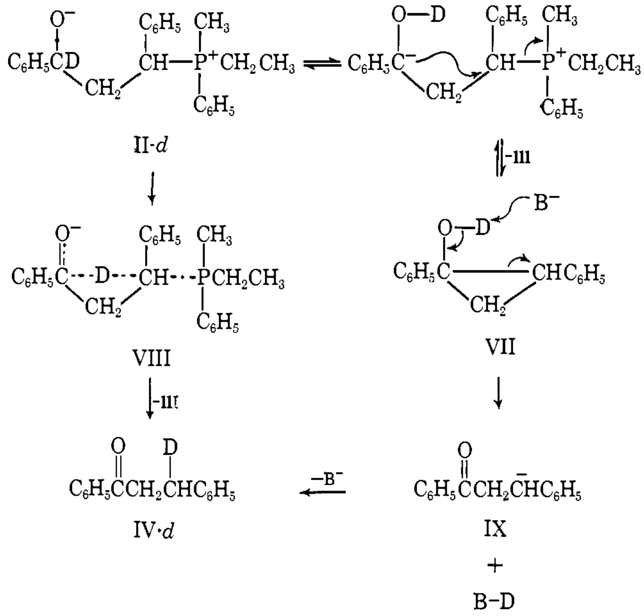
[3] W. E. McEwen and A. P. Wolf, *ibid.*, **84**, 676 (1962).

[4] I. Tomoskozi, *Tetrahedron*, **19**, 1969 (1963).

[5] S. Trippett, *Quart. Rev.* (London), **17**, 427 (1963).

[6] J. Wolfe and W. E. McEwen, *J. Am. Chem. Soc.*, **89**, 3374 (1967).

[7] W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, **25**, 1996 (1960).



be present in trace amounts[8]), it is also obvious that the mechanism involving VII as an intermediate would lead to dilution of deuterium content in the product, IV-*d*, if a suitable Brønsted acid containing ordinary hydrogen were added to II-*d* prior to the decomposition step.[9] Also, deuterium would undoubtedly be found α to the carbonyl group of IV if the anion IX were formed as an intermediate.[10]

Benzaldehyde-*d*, prepared by the reaction of 1-benzoyl-1,2-dihydroquinaldonitrile with D_2SO_4, was converted to styrene-α-*d* oxide by the method of Corey and Chaykovsky[11] and converted to II-*d* as described previously. The sample of IV-*d* obtained by the decomposition of II-*d* was converted to hydrocinnamanilide by reaction with hydrogen azide and sulfuric acid, and the anilide was then hydrolyzed to give hydrocinnamic acid, the mass spectrum of which has been analyzed, at least to some extent.[12] Finally, the decomposition of II-*d* was carried out in the presence of 1 equiv of triphenylcarbinol, and IV-*d* was isolated and converted to hydrocinnamic acid as described above. The most pertinent mass spectral data of the various samples of hydrocinnamic acid are given in Table I.[13] Within the limits of experimental error, the mass spectra of hydrocinnamic acid derived from samples of IV-*d*, produced from II-*d* either in the presence or absence of triphenylcarbinol, were identical. It was also apparent that no deuterium was present in the $-CH_2CO_2H$ portion of the hydrocinnamic acid derived from IV-*d* by observation of the *m/e* peaks at 59 (attributable to $^+CH_2CO_2H$) and at 60 (attributable to $^+CH_2CO_2H$ containing a normal abundance of C^{13}). Thus, the conclusion can be reached that benzylacetophenone (IV) and methylethylphenylphosphine (III) arise from II by way of a direct 1,3-hydride transfer mechanism (transition state VIII in the case of the deuterated compound).

Table I. Mass Spectral Data of Hydrocinnamic Acid and of Hydrocinnamic-β-*d* Acid

	m/e	$I \pm 0.6$	Ratio of *I* values
Hydrocinnamic acid	151	4.0	4.0/32.0 = 0.16
	150	32.0	
Hydrocinnamic-β-*d* acid derived from IIb from experiment without $(C_6H_5)COH$ present	151	16.5	16.5/33.8 = 0.490
	150	33.8	
	92	58.2	58.2/146.5 = 0.400
	91	146.5	
Hydrocinnamic-β-*d* acid derived from IIb from experiment with $(C_6H_5)_3COH$ present	151	12.5	12.5/23.5 = 0.530
	150	23.5	
	92	35.8	35.8/81.5 = 0.439
	91	81.5	

Trippett[5] has raised the question as to whether a cation effect might be operative in the decomposition of II. This has now been explored. Methylethylphenylbenzylidenephosphorane (I) was prepared from methylethylphenylbenzylphosphonium iodide by the action of phenylsodium in ether solution. This was treated with styrene oxide to give II and sodium iodide. The ether was evaporated, decalin added to the residue, and the mixture heated. No benzylacetophenone (IV) and methylethylphenylphosphine (III) were produced. The products of the reaction were methylethylphenylphosphine oxide (V) and the mixture of hydrocarbons mentioned previously. These results can be explained on the basis that, in the lithium iodide adduct of II, the presence of a strong and largely covalent bond between lithium and oxygen decreases the nucleophilicity of the oxygen to a sufficient extent that it does not readily attack the positive phosphorus atom, the key step in the production of the phosphine oxide and hydrocarbon mixture.[1,3,14]

The nature of the nonreacting groups bonded to phosphorus is also of importance in determining the major reaction pathway in the thermal decomposition of an ylide–epoxide condensation product. For example, decomposition of the lithium iodide adduct of triphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine (X), obtained by treatment of triphenylbenzylphosphonium chloride with phenyllithium and subsequent condensation of the resulting ylide with styrene oxide, gave triphenylphosphine oxide (80% yield), triphenylphosphine (8%), benzylacetophenone (0.3%), 1,3-diphenylpropan-1-ol (1.5%), a mixture of *cis*-1,3-diphenylpropene, the *trans* isomer, and *trans*-1,2-diphenylcyclopropane (50% yield, molar ratio 30:65:5), and an unidentified keto alcohol. With this system, in spite of the presence of lithium ion, the major

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[8] *trans*-Stilbene is isolated in very small amounts when the hydrocarbon fraction of the reaction mixture is chromatographed on alumina. The lithium salt of phenylbenzylcarbinol, the dehydration of the conjugate acid of which affords the olefin, arises by reaction of phenyllithium with styrene oxide.

[9] Hydrogen–deuterium exchange between alcohol functional groups has been found to attain equilibrium in less than 2 min at elevated temperatures: H. Kwart, L. P. Kuhn, and E. L. Banister, *J. Am. Chem. Soc.*, 76, 5998 (1954).

[10] The conversion of $C_6H_5C(=O)CH_2C^-HC_6H_5$ to $C_6H_5C(=O)C^-HCH_2C_6H_5$ would be expected to occur rapidly.

[11] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

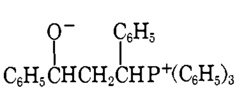
[12] "Mass Spectral Data," Dow Chemical Co., Midland, Mich., 1963.

[13] The *m/e* peak at 91 (attributable to $C_6H_5CH_2^+$) is the principal one in the mass spectrum of hydrocinnamic acid. The peak at 150 is that of the molecular ion $[C_6H_5CH_2CH_2CO_2H]^+$. The peaks at 92 and 151, derived from deuterated hydrocinnamic acid, are attributable mainly to $C_6H_5CHD^+$ and $[C_6H_5CHDCH_2CO_2H]^+$, respectively, although there are also minor contributions to these peaks arising from small concentrations of naturally occurring C^{13} in the samples.

[14] E. Zbiral, *Monatsh.*, **94**, 78 (1963).

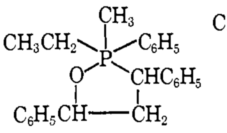
products are the phosphine oxide and mixture of hydrocarbons. The difference in behavior between II and X can best be explained on the basis that, owing to the inductive electron-releasing effect of the methyl and ethyl groups bonded to the phosphorus atom of II, there would be less tendency for an intermediate of type XI to be formed than would be the analogous case if three electron-withdrawing phenyl groups were bonded to phosphorus, as in X.

It is also of interest to consider why, on pyrolysis of both II and X, only relatively small amounts of cyclopropane derivatives are formed, whereas this represents the major reaction pathway in the systems studied by Denney and Boskin.[2] This difference is readily rationalized by consideration of the type of intermediate that is the immediate precursor to the cyclopropane. In the case of XII, formed by dissociation of XI, only an α-phenyl group is available to help stabilize the anionic center. However, in Denney's compounds, the much more efficient anion stabilizing group, a carbethoxyl group, is available. Thus, XI has little tendency to dissociate to form XII, which then can produce the phosphine oxide plus the cyclopropane. The adducts derived from carbethoxymethylenephosphorane and various epoxides, on the other hand, can readily form intermediates analogous to XII and thus give rise to cyclopropane derivatives in high yields.[2]

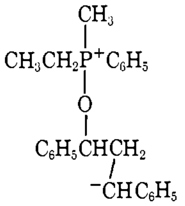


$C_6H_5\overset{O^-}{\overset{|}{C}}HCH_2\overset{C_6H_5}{\overset{|}{C}}HP^+(C_6H_5)_3$

X



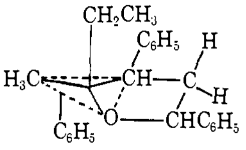
XI



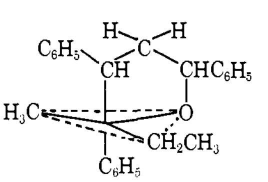
XII

Having optically active methylethylphenylbenzylphosphonium iodide available,[15,16] we also investigated the stereochemistry, with respect to the phosphorus atom, of this type of reaction. When the sequence of operations cited previously was carried out with (+)-methylethylphenylbenzylphosphonium iodide in place of the racemic salt, the methylethylphenylphosphine oxide (V) produced was dextrorotatory, $[\alpha]^{25}\text{D}$ $+12.5°$ (c 4.735, methanol), whereas the methylethylphenylphosphine (III) was racemic. With levorotatory phosphonium salt as starting material, the methylethylphenylphosphine oxide produced was levorotatory, $[\alpha]^{25}\text{D}$ $-11.3°$ (c 2.115, methanol), and the methylethylphenylphosphine again was racemic. Thus, on the basis of these results and data reported previously,[16-18] it can be concluded that the phosphorus atom of optically active methylethylphenylbenzylphosphonium iodide undergoes about 50% net inversion of configuration in that part of the over-all reaction which leads to the phosphine oxide.

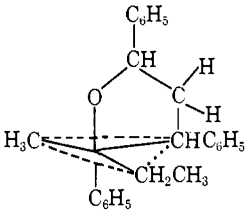
An attractive interpretation of this stereochemical result is that inversion of the configuration of the phosphorus atom occurs when methylethylphenylphosphine oxide (V) and the isomeric 1,3-diphenylpropenes are formed from II by way of one or more of the three possible unstable intermediates (or transition states) of the type XIII in which both the attacking and departing groups occupy basal positions of the trigonal bipyramid; retention of configuration results when the unstable intermediate has the type of geometry shown in XIV, XV, or XVI, these being but a few of many possibilities.[16,19,20] Unlike the situation which pertains when optically active I is treated with benzaldehyde in a conventional Wittig reaction,[16] none of the unstable intermediates (types XIII–XVI in the epoxide reaction) have prohibitive angle strain. Thus, reactions take place with both retention and inversion of the configuration of the phosphorus atom.



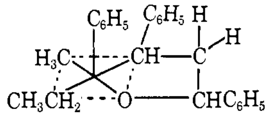
XIII



XIV



XV



XVI

Inasmuch as the amount of *trans*-1,2-diphenylcyclopropane formed in the reaction was but a very small fraction of the product mixture, the amount of methylethylphenylphosphine oxide (V) formed in conjunction with the cyclopropane derivative was also small. On the basis of Denney's mechanism,[2] it is conceivable that the phosphorus atom might be inverted, might retain the same configuration, or undergo both stereochemical transformations by competitive paths. In fact, one or more of the many possible intermediates exemplified by XIII, XIV, XV, or XVI should be involved in one of the steps of Denney's mechanism.

As shown above, methylethylphenylphosphine and benzylacetophenone arise from II by way of the transition state VIII. The fact that the phosphine is racemic is undoubtedly the result of thermal racemization of the initially optically active phosphine (presumably formed with retention of the configuration of the phosphorus atom) at the reaction temperature of 190–200°.[21,22]

Two detailed mechanisms may be considered for the conversion of XI (actually, one or more of the stereoisomers of types XIII–XVI) to methylethylphenylphosphine oxide (V) and a mixture of *cis*- and *trans*-1,3-diphenylpropene. In one of these mechanisms, a strong base, B^-, present in solution removes a proton from the methylene group of the 1,3-diphenyl-1-propyloxyphosphorane ring with formation of V plus the conjugate base (XVII) of 1,3-diphenylpropene. If this

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

(16) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *ibid.*, **86**, 2378 (1964).

(17) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

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

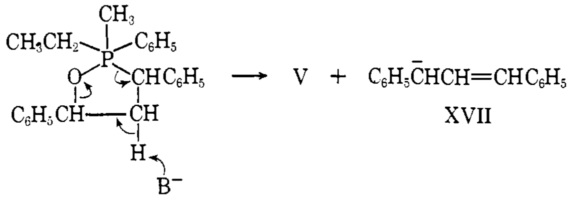
(19) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

(20) W. E. McEwen, *Topics Phosphorus Chem.*, **2**, 1 (1965).

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

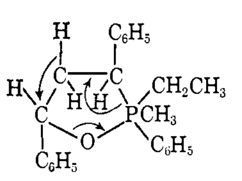
(22) D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, and C. A. VanderWerf, *ibid.*, 359 (1963).

mechanism were operative, the same ratio of *cis*- to *trans*-1,3-diphenylpropene should be formed regardless of whether the lithium iodide adduct of methylethylphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine (II) or of triphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine (X) is subjected to decomposition, provided that each compound is treated in the same manner. Actually, the ratio of *cis*- to *trans*-1,3-diphenylpropene is distinctly different in the two cases, and this provides a strong argument against a mechanism involving XVII as an intermediate.



XVII

The second possible mechanism for formation of V plus *cis*- and *trans*-1,3-diphenylpropene from XI consists of a synchronous elimination of V and a 1,2-hydride shift, as shown in the transition species XVIII. We consider this to be the actual mechanism operative.



XVIII

In a control experiment, 1,2-diphenylcyclopropane was recovered unchanged when added to II and then subjected to the decomposition described previously. Thus, *cis*- and *trans*-1,3-diphenylpropene do not arise by pyrolysis of the cyclopropane. Zbiral[14] has provided evidence that *cis*- and *trans*-1,3-diphenylpropene do not arise by isomerization of styrene oxide to phenylacetaldehyde followed by a Wittig reaction of the aldehyde with triphenylbenzylidenephosphorane.[23]

The proof of structure of the lithium iodide adduct of II consisted mainly of its reaction with sodium hydroxide solution to give 1,3-diphenylpropan-1-ol, methylethylphenylphosphine oxide (V), and lithium iodide. Additional support for the structure of the adduct is provided by other experiments which are described in the Experimental Section.

Experimental Section

Reaction of Styrene Oxide with Methylethylphenylbenzylidenephosphorane (I). *dl*-Methylethylphenylbenzylphosphonium iodide was prepared as described previously.[16] To a suspension of 5.50 g (0.0149 mole) of the finely pulverized salt in 200 ml of anhydrous ether was added dropwise with mechanical stirring a solution of 0.02 mole of phenyllithium in 25 ml of ether-benzene (90% ether, 10% benzene), the mixture being maintained in a nitrogen atmosphere. To the resulting orange solution was added a solution of 3.0 g (0.025 mole) of styrene oxide in 10 ml of anhydrous ether, and the mixture was stirred at room temperature for 14 hr. Ether was removed from the thick, white suspension which had formed by distillation, and 75 ml of anhydrous decalin was added to the solid residue. The mixture was refluxed for 3 hr with stirring.

The reaction mixture was cooled, 200 ml of anhydrous ether was added, and the ether-decalin solution was separated from a yellow solid which had formed by decantation. To the ether-decalin solution, dried over anhydrous sodium sulfate, was added a large excess of methyl iodide, and the solution was stirred at 0° for 2 days. A colorless, crystalline solid which had precipitated was collected by filtration and amounted to 1.55–2.65 g (35–60%) of dimethylethylphenylphosphonium iodide, mp 147–148° (lit.[24] mp 137°).

Anal. Calcd for $C_{10}H_{16}PI$: C, 40.84; H, 5.48; P, 10.53; I, 43.15. Found: C, 40.71; H, 5.29; P, 10.64; I, 43.18.

The solvents were removed from the organic phase by distillation *in vacuo*. The residual yellow oil was then distilled to give 1.8–2.7 ml of colorless distillate, bp 105–147° (0.55 mm). This was mixed with 10 ml of 1 *N* hydrochloric acid and extracted with Skelly F solvent. The organic layer was washed with water, dried over anhydrous sodium sulfate, and filtered and the solvent removed by distillation. The residual oil was dissolved in 30 ml of absolute ethanol, and 1.5 g of Girard "T" reagent plus 2.85 ml of acetic acid were added. The solution was refluxed for 2 hr and cooled, a solution of 1.8 g of sodium hydroxide in 200 ml of water added, and the mixture stirred for 10 min. The solution was extracted with ether, and the aqueous layer was acidified with hydrochloric acid. The acid solution was heated to its boiling point and then cooled. There was obtained 1.16–1.66 g (37–53%) of benzylacetophenone, mp 72–73°, as a crystalline product. A mixture melting point test with an authentic[25] sample of the ketones showed no depression, and the infrared spectra of the two samples were identical.

The ether extract of the alkaline solution was distilled to remove the solvent, and a solution of the residue in petroleum ether of bp 35–60° was chromatographed on grade II[26] alumina. Elution with the same solvent gave 0.26–0.41 g (9–14% based on an average molecular formula of $C_{15}H_{14}$) of a hydrocarbon mixture, $n^{20}\mathrm{D}$ 1.5960–1.6023. Further elution with petroleum ether gave about 50 mg of *trans*-stilbene, and final elution with ethyl ether afforded 0.19–0.38 g (6–12%) of 1,3-diphenylpropan-1-ol. The latter product was identified by comparison of its infrared spectrum with that of an authentic sample of the alcohol and by preparation of the *p*-nitrobenzoate ester, mp 91–92°, also in admixture with an authentic[27] sample of the ester.

Vapor phase chromatography of the hydrocarbon fraction was carried out on a Beckman GC-2 gas chromatograph, the column being constructed of 0.25 × 0.030 in. Revere Dryseal copper tube, 2.5 m long and packed with 60–80 mesh acid-treated Celite containing 35 wt % Niax Triol LHT-42 (polypropylene glycol manufactured by Union Carbide Corp.), packing density 0.3 g/in. Helium was the carrier gas, and, with the column maintained at 240°, a cell current of 300 ma and an inlet pressure of 25 psi were used. Peak areas were measured by means of a planimeter, and the method of internal normalization was applied. The hydrocarbon mixture consisted of *cis*-1,3-diphenylpropene, *trans*-1,3-diphenylpropene, and *trans*-1,2-diphenylcyclopropane in a molar ratio of 14:80:6. Decalin, naphthalene, biphenyl, and *cis*-stilbene were also present, these by-products constituting 15–25% of the total mixture. Catalytic hydrogenation of the hydrocarbon mixture at atmospheric pressure and room temprature over Adams' catalyst gave a new mixture in which 1,3-diphenylpropane was identified and found to be present to the extent of 82–84% and *trans*-1,2-diphenylcyclopropane to the extent of 4–5% by glpc analysis. The remainder of the hydrogenated material consisted of the same by-products found in the nonhydrogenated mixture plus bibenzyl, which resulted from the reduction of stilbene. In a control experiment it was found that a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane remained unchanged under the conditions of the catalytic hydrogenation cited above. The retention times (minutes) of the various compounds were as follows: biphenyl, 7.18; bibenzyl, 10.5; *cis*-stilbene, 10.5; *cis*-1,2-diphenylcyclopropane, 13.6; 1,3-diphenylpropane, 15.2; *cis*-1,3-diphenylpropene, 16.4; *trans*-1,2-diphenylcyclopropane, 19.1; *trans*-stilbene, 21.6; *trans*-1,3-diphenylpropene, 21.6; and 1,3-diphenylpropan-1-ol, 40.6.

In later studies, the same separations were carried out on a Wilkens Auto-Prep gas chromatograph at a column temperature of 230–240°, a 20-ft column packed with silicone rubber being used. *cis*-1,3-Diphenylpropene, *trans*-1,3-diphenylpropene, and *trans*-1,2-diphenylcyclopropane were found to be present in a

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[23] Zbiral[14] reported that reaction of styrene oxide with triphenylbenzylidenephosphorane gave almost exclusively *cis*-1,3-diphenylpropene, a result which does not agree with our findings. However, Zbiral did not provide details about the reaction conditions he employed.

(24) A. Michaelis, *Ann.*, **181**, 265 (1876).

(25) C. W. Shoppee, *J. Chem. Soc.*, 2567 (1928).

(26) H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941).

(27) P. Pfeiffer, E. Kalckbrenner, W. Kunze, and K. Levin, *J. Prakt. Chem.*, **119**, 109 (1928).

molar ratio of 13:80:8. The by-products cited above were also detected. The retention times (minutes) for the major components were as follows: biphenyl, 2.12; *cis*-stilbene, 2.83; *cis*-1,3-diphenylpropene, 3.89; *trans*-1,2-diphenylcyclopropane, 5.06; *trans*-1,3-diphenylpropene, 6.01; and *trans*-stilbene, 8.74.

The original yellow solid remaining after decantation of the decalin–ether solution consisted of an adduct of methylethylphenylphosphine oxide with lithium iodide. This solid material was dissolved in 20 ml of water, the solution extracted with ether, the aqueous layer filtered and treated with potassium hydroxide pellets until a yellow oil separated from the aqueous solution. The oil was extracted with benzene and the extract dried over potassium hydroxide pellets. Distillation of the benzene at atmospheric pressure and then of the residue *in vacuo* gave 0.33–0.73 g (13–29%) of methylethylphenylphosphine oxide (V), mp 52–57°. Its infrared spectrum, taken in chloroform solution, was identical with that of an authentic[16] sample of the oxide.

As indicated by the numbers given above, the yields of products were erratic from one experiment to another. However, high yields of benzylacetophenone and methylethylphenylphosphine were always accompanied by low yields of methylethylphenylphosphine oxide plus the various hydrocarbons, and *vice versa*.

Control Reaction with 1,2-Diphenylcyclopropane Added to the Reaction Mixture. When a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane was added to the reaction mixture prior to the period of refluxing in decalin, the mixture then being worked up as described above, not less than 80% of the 1,2-diphenylcyclopropane was recovered unchanged. Thus, no significant fraction of the isomeric 1,3-diphenylpropenes arose by pyrolysis of the cyclopropane derivatives.

Characterization of the Lithium Iodide Adduct of Methylethylphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium Betaine (II). The thick white suspension which resulted when styrene oxide was added to an ether solution of methylethylphenylbenzylidenephosphorane (which also contained lithium iodide since the ylide was prepared by treatment of methylethylphenylbenzylphosphonium iodide with phenyllithium) was filtered. The following experiments were carried out with the hygroscopic precipitate.

1. A sample of the solid was heated on the steam bath for 3 hr in aqueous methanolic potassium hydroxide solution. Methanol was removed *in vacuo*, and the aqueous residue was extracted with ether. From the ether layer, 1,3-diphenylpropan-1-ol was obtained in 65% yield. From the aqueous layer, after the usual work-up, methylethylphenylphosphine oxide was obtained in 54% yield.

2. A sample of the precipitate was added to water and then extracted with chloroform. Removal of the solvent by distillation gave a hygroscopic solid, mp 50–60° (changed to a glass but did not melt completely until the bath temperature reached 80°). The infrared spectrum of the crude methylethylphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine, taken in chloroform solution, was similar to that of methylethylphenylbenzylphosphonium iodide, the only striking difference being the presence of a broad band in the hydroxyl region of the spectrum of the new compound. The compound could not be recrystallized.

3. Treatment of the solid with *p*-nitrobenzoyl chloride in pyridine or chloroform solution gave a solid of mp 70–80° dec. Chromatography on Woelm neutral alumina (grade I) and elution with chloroform–methanol yielded a yellow solid, mp 65–69° dec. The infrared spectrum of this material, taken in chloroform solution, showed the presence of the ester carbonyl function (band at 5.80 μ).

Reaction of Methylethylphenylbenzylphosphonium Iodide with Phenylsodium and Subsequently with Styrene Oxide. This reaction was carried out in precisely the same manner as that described previously, except that a solution of phenylsodium in toluene, prepared by the method of Gilman,[28] was used in place of phenyllithium to convert methylethylphenylbenzylphosphonium iodide to the ylide. After reaction with styrene oxide, pyrolysis of the residue in decalin, and the usual work-up, the only products isolated were methylethylphenylphosphine oxide, *cis*-1,3-diphenylpropene, *trans*-1,3-diphenylpropene, and *trans*-1,2-diphenylcyclopropane, the latter three compounds in the molar ratio 1:85:14, respectively. No methylethylphenylphosphine and benzylacetophenone were produced in this reaction. Small amounts of the usual by-products, *trans*-stilbene, 1,3-diphenylpropan-1-ol, biphenyl, and *cis*-stilbene, were detected.

Reaction of Triphenylbenzylidenephosphorane with Styrene Oxide. This reaction was carried out in the same manner as that described for the methylethylphenylbenzylidenephosphorane case. The products were triphenylphosphine oxide (70–80% yield), mp 152–154°, which precipitated when the solid residue remaining after decantation of the decalin–ether solution was added to water, triphenylmethylphosphonium iodide (8%), obtained by addition of methyl iodide to the decalin–ether solution, *cis*-1,3-diphenylpropene, *trans*-1,3-diphenylpropene, and *trans*-1,2-diphenylcyclopropane (molar ratio 30:65:5, respectively), the total hydrocarbon fraction being obtained in 40–55% yield, 1,3-diphenylpropan-1-ol (1.5%) and the usual by-products (*cis*-stilbene, *trans*-stilbene, tetralin, naphthalene, and biphenyl), and benzylacetophenone (0.3%). Distillation of the oily residue remaining after evaporation of the ether–decalin solution gave 0.70 g of an unknown keto alcohol, bp 140–180° (0.2 mm), this fraction distilling after the hydrocarbon mixture, bp 93–115° (0.15 mm), had been collected. Redistillation of the unknown compound gave 0.50 g of light yellow, viscous liquid, $n^{20}\text{D}$ 1.6009. Its infrared spectrum, taken in chloroform solution, showed bands characteristic of an OH group at 2.68 and 2.81 μ and a strong band at 5.6 μ, characteristic of a strained ring carbonyl group.

Anal. Found: C, 86.79, 86.50; H, 6.68, 7.02.

Benzylacetophenone (IV) was prepared by catalytic hydrogenation of benzalacetophenone. Recrystallization from ethanol gave colorless crystals, mp 71–72° (lit.[25] mp 72–73°); semicarbazone, mp 144–145° (lit.[25] mp 144°).

1,3-Diphenylpropan-1-ol was prepared by reduction of benzylacetophenone with lithium aluminum hydride in ether solution. It was obtained as a yellow, dense oil, $n^{20}\text{D}$ 1.5722 (lit.[27] $n^{20}\text{D}$ 1.5724); *p*-nitrobenzoate ester, mp 91.5–92.5° (lit.[27] mp 89–90°).

***trans*-1,3-Diphenylpropene** was prepared by the method of Stoermer and Thier.[29] The product was light yellow in color, mp 12–16° (lit.[29] 15–16°), bp 104–106° (0.20 mm) (lit.[29] bp 178–179° (14 mm)), $n^{20}\text{D}$ 1.6001 (lit.[30] $n^{20}\text{D}$ 1.6000); dibromide, mp 108–110° (lit.[29] mp 109°). Actually, glpc analysis showed this compound to be a mixture of *trans*-1,3-diphenylpropene (95.5%), *cis*-1,3-diphenylpropene (3.6%), and traces of solvents (0.9%).

1,3-Diphenylpropane. Catalytic hydrogenation of *trans*-1,3-diphenylpropene at atmospheric pressure gave 1,3-diphenylpropane, bp 95–97° (0.20 mm) (lit.[29] bp 166–168° (16 mm)), $n^{20}\text{D}$ 1.5600 (lit.[30] $n^{20}\text{D}$ 1.5594). Nitration with fuming nitric acid afforded the yellow tetranitro derivative, mp 162–165° (lit.[31] mp 162–164°).

1,2-Diphenylcyclopropane. A mixture of *cis*- and *trans*-1,2-diphenylcyclopropane was prepared by the method of Knipmeyer.[32] The product, bp 105–120° (1.1 mm) (lit.[32] bp 122–126° (2 mm)), $n^{20}\text{D}$ 1.5955, was found by glpc analysis to contain 64% of the *trans* isomer, 22.5% of the *cis* isomer, and 13.5% of an unknown impurity.

Reaction of Optically Active Methylethylphenylbenzylidenephosphorane with Styrene Oxide. The reaction was carried out with optically active methylethylphenylbenzylidenephosphorane (I) prepared from 5.0 g (0.0135 mole) of (+)-methylethylphenylbenzylphosphonium iodide,[16] 0.021 mole of phenyllithium, and 3.0 g (0.025 mole) of styrene oxide in exactly the same manner as described for the reaction of the racemic phosphorane. The isolation procedures were also identical except that benzyl chloride instead of methyl iodide was used to trap methylethylphenylphosphine (III). The yields and products were as follows: (a) 9.5% hydrocarbons (containing 26% of the usual by-products and 74% of a mixture of *cis*-1,3-diphenylpropene, *trans*-1,3-diphenylpropene, and *trans*-1,2-diphenylcyclopropane in a molar ratio of 14.2:78.4:7.4, respectively); (b) 48.8% racemic methylethylphenylphosphine (III) isolated as the racemic methylethylphenylbenzylphosphonium chloride,[16] mp 138–140°; (c) 12.5% of 1,3-diphenylpropan-1-ol; (d) 22.2 % of benzylacetophenone; (e) 12.3% of methylethylphenylphosphine oxide (V), $[\alpha]^{25}\text{D}$ +12.5° (*c* 4.735, methanol).

Almost identical results were obtained when (−)-methylethylphenylbenzylphosphonium iodide was used as a starting material. (−)-Methylethylphenylphosphine oxide, $[\alpha]^{25}\text{D}$ −11.3° (*c* 2.115, methanol), was obtained in 13.2% yield.

Benzaldehyde-*d*. To a solution of 10 g (0.385 mole) of 1-benzoyl-1,2-dihydroquinaldonitrile,[33] mp 153–154°, in 100 ml of anhy-

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(28) H. Gilman, H. A. Pacevitz, and O. Baine, *J. Am. Chem. Soc.*, **62**, 1514 (1940).

(29) R. Stoermer and C. Thier, *Ber.*, 58, 2607 (1925).

(30) K. J. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, 73, 4766 (1951).

(31) A. Michaelis and A. Fleming, *Ber.*, **34**, 1291 (1901).

(32) H. E. Knipmeyer, Ph.D. Thesis, University of Illinois, 1956.

(33) A. Reissert, *Ber.*, **38**, 1603 (1905).

drous methylene chloride was added dropwise with rapid stirring over a 10-min period 1.5 ml of concentrated D_2SO_4, the reaction mixture being maintained at 33–35° in a nitrogen atmosphere. The concentrated D_2SO_4 has been prepared from γ-sulfur trioxide (Sulfan "B", Allied Chemical Corp.) and D_2O essentially by the method of Herber.[34] Stirring was continued for 12 hr, and a viscous red oil gradually precipitated. The excess D_2SO_4 was neutralized by the careful addition of 100 ml of saturated sodium bicarbonate solution. The methylene chloride layer was separated from the aqueous layer, and the methylene chloride was removed by distillation. The residue was dissolved in 50 ml of hot 95% ethanol, cooled, and filtered to remove unreacted 1-benzoyl-1,2-dihydroquinaldonitrile which had crystallized, and the filtrate distilled. After removal of the ethanol, a dark red oil remained. Vacuum distillation of this material afforded 2.19 g (53%) of benzaldehyde-*d*, bp 25–33° (0.4 mm). A total amount of 156 g of benzaldehyde-*d* was accumulated by this procedure. This material was redistilled twice and then stored in a nitrogen atmosphere in a vessel designed to prohibit oxidation of the benzaldehyde-*d* by atmospheric oxygen. The compound was shown to be pure by glpc analysis, and it remained uncontaminated throughout the course of this research.

Styrene-*α-d* Oxide. This compound, bp 23° (0.23 mm), was prepared by reaction of benzaldehyde-*d* with dimethylsulfonium methylide in dimethyl sulfoxide–tetrahydrofuran (3.3:1 parts by volume) essentially according to the procedure of Corey and Chaykovsky.[35] A total of 30.60 g of redistilled styrene-*α-d* oxide was accumulated and shown to be pure by glpc analysis.

Hydrolysis of Styrene-*α-d* Oxide. A 3.0-g (0.025 mole) sample of styrene-*α-d* oxide was suspended in 50 ml of distilled water and refluxed for 12 hr. The resulting aqueous solution was concentrated nearly to dryness, and a residual yellow oil was taken up in ether. The ether solution was dried over anhydrous magnesium sulfate. After concentration of the solution, 2.1 g (61%) of 1-phenylethylene-1-*d* glycol, mp 65.5–66.5°, crystallized.

Reaction of 1-Phenylethylene-1-*d* Glycol with Periodic Acid. To a cold, stirred solution of 2.1 g (0.015 mole) of 1-phenylethylene-1-*d* glycol in 21 ml of 10% acetic acid maintained under an atmosphere of nitrogen was added over a 5-min period a solution of 2.9 g (0.015 mole) of periodic acid in 21 ml of water. The reaction mixture was then maintained at 40° for 4 hr. The solution was extracted with ether, the ether solution stirred with a saturated solution of sodium thiosulfate for 1 hr, washed with a saturated solution of sodium bicarbonate, and dried over anhydrous magnesium sulfate, and the ether distilled. Distillation of the residual oil *in vacuo* afforded 0.924 g (57%) of benzaldehyde-*d*.

Mass Spectral Data of Benzaldehyde-*d*. Mass spectra were taken on a Hitachi-Perkin-Elmer mass spectrometer, Model Rmu-6A, with an electromagnet input of 2 kv and an acceleration field of 1–5 kv. In Table II are mass spectral data taken under identical conditions for ordinary benzaldehyde (A), benzaldehyde-*d* obtained by treatment of 1-benzoyl-1,2-dihydroquinaldonitrile with D_2SO_4 (B), and benzaldehyde-*d* obtained by hydrolysis and subsequent cleavage of styrene-*α-d* oxide (C). These data indicate clearly that there was no loss in deuterium content in the conversion of benzaldehyde-*d* to styrene-*α-d* oxide by the procedure of Corey and Chaykovsky.[35]

Reaction of Methylethylphenylbenzylidenephosphorane (I) with Styrene-*α-d* Oxide. The reaction was carried out as described previously, and benzyl-*α-d*-acetophenone was isolated in the usual manner.

Schmidt Reaction of Benzyl-*α-d*-acetophenone. To a stirred solution of 1.60 g (0.0076 mole) of benzyl-*α-d*-acetophenone and 4.8 ml of concentrated sulfuric acid in 14 ml of glacial acetic acid maintained at 60° was added 1.04 g (0.016 mole) of sodium azide in small portions over a 1-hr period. The mixture was maintained at 60–70° with stirring for another 2 hr, then poured onto ice. The excess sulfuric acid was neutralized by the careful addition of solid sodium bicarbonate, and the colorless, crystalline product which had formed was collected by filtration. The solid material was dissolved in 30 ml of ethanol containing 6.6 ml of glacial acetic acid, and 4.4 g of Girard "T" reagent was added. The solution was refluxed for 2 hr, then poured into a solution of 4.2 g of sodium hydroxide in 56 ml of water. The basic solution was extracted with ether, the ether solution dried over anhydrous magnesium sulfate, and the ether distilled. The yellow semisolid residue was crystallized from absolute ethanol to give 0.73 g of hydrocinnam-*β-d*-anilide, mp 96–97° (lit.[36] mp 97°). An additional 0.57 g of hydrocinnam-*β-d*-anilide was obtained from the ethanol mother liquor.

Table II

Benzaldehyde	*m/e*[a]	*I* ± 0.6	Ratio of *I* values
A	107	4.0	$\frac{4.0}{41.5} = 0.096$
	106	34.0	
	77	41.5	
	30	0	
	29	13.0	
B	107	13.0	$\frac{13.0}{30.0} = 0.434$
	106	13.5	
	77	30.0	
	30	3.0	
	29	3.0	
C	107	15.0	$\frac{15.0}{33.5} = 0.447$
	106	16.0	
	77	33.5	
	30	3.0	
	29	3.0	

[a] The *m/e* peak at 107 is due primarily to $[C_6H_5CDO]^+$, that at 106 to $[C_6H_5CHO]^+$, that at 77 to $C_6H_5^+$, that at 30 to CDO^+, and that at 29 to CHO^+. It is apparent that the benzaldehyde obtained by the reaction of 1-benzoyl-1,2-dihydroquinaldonitrile with the concentrated D_2SO_4 prepared by the method of Herber[33] contained about 50% benzaldehyde-*d* and 50% ordinary benzaldehyde.

Hydrolysis of Hydrocinnam-*β-d*-anilide. A suspension of 1.30 g (0.0058 mole) of hydrocinnam-*β-d*-anilide in 60 ml of water containing 7 ml of concentrated hydrochloric acid was refluxed for 1.5 hr. An additional 32 ml of concentrated hydrochloric acid was added and the mixture refluxed for another 0.75 hr. When the solution was cooled to room temperature, an oil separated. This was taken up in ether, the ether solution dried over anhydrous magnesium sulfate, and the ether distilled. The residue was recrystallized from Skelly F solvent to give 0.51 g (0.0034 mole) of hydrocinnamic-*β-d* acid, mp 47–48° (lit.[37] mp 48°).

Decomposition of Methylethylphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium Betaine (II) in the Presence of Triphenylcarbinol. The preparation of methylethylphenylbenzylidenephosphorane (I) by the reaction of 5.5 g (0.0149 mole) of methylethylphenylbenzylphosphonium iodide with 0.02 mole of phenyllithium was carried out as previously described. After addition of 3.0 g (0.025 mole) of styrene-*α-d* oxide and precipitation of the adduct of lithium iodide and methylethylphenyl(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine, 3.38 g (0.015 mole) of triphenylcarbinol was added to the reaction mixture. The decomposition reaction in refluxing decalin and the work-up of the reaction mixture were carried out as described previously. Also, the benzyl-*α-d*-acetophenone isolated was converted to hydrocinnamic-*β-d* acid as described above.

Mass Spectral Data of Hydrocinnamic-*β-d* Acid. Most of the pertinent data have been given in Table I and in the Discussion. It should also be pointed out that the assignment of the location of all of the deuterium present in the samples of hydrocinnamic acid described above was made by means of mass spectrometry. It was found that, within the limits of experimental error, the mass spectra of the samples of deuterated hydrocinnamic acid obtained from the experiments both with and without triphenylcarbinol present were identical. A comparison of the *m/e* peak at 59 (due to $^+CH_2CO_2H$) and the *m/e* peak at 60 (due to $^+CH_2CO_2H$ containing the normal abundance of C^{13} and/or $^+CHDCO_2H$) in the mass spectra of ordinary hydrocinnamic acid and the two samples of deuterated hydrocinnamic acid obtained as described above showed that no deuterium was present in the CH_2CO_2H moiety. In an analogous manner, it was demonstrated that no deuterium was present in the phenyl ring of either of the two samples of deuterated hydrocinnamic acid by observation of the constancy of the *m/e* peaks at 77, 78, and 79 of the respective mass spectra of these samples and of ordinary hydrocinnamic acid. The peak at 77 is attributable to a contribution from the $C_6H_5^+$ ion, that at 78 to

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(34) R. H. Herber, "Inorganic Isotope Syntheses," W. A. Benjamin, Inc., New York, N. Y., 1962, p 45.

(35) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(36) D. Bigiavi and M. Marri, *Gazz. Chim. Ital.*, **54**, 99 (1924).

(37) E. Erlenmeyer, *Ann.*, **137**, 327 (1866).

$C_6H_6^+$ or $C_6H_4D^+$, and that at 79 to $C_5H_5(2C^{13})^+$ or $C_6H_6(1C^{13})^+$ or $C_6H_5D^+$. The deuterium in the two deuterated samples of hydrocinnamic acid cited above is therefore present solely at the benzylic position.

Methylethylphenylbenzyl-7-C^{14}-phosphonium Iodide. To 25 ml of tetrahydrofuran, distilled from lithium aluminum hydride after first having been treated with sodium hydroxide pellets, was added 2.59 g of inactive methylethylphenylbenzylphosphonium iodide.[16] A nitrogen atmosphere was maintained over the stirred mixture as 0.50 g of lithium aluminum hydride was added, and the new mixture was stirred and refluxed for 4 hr. Most of the tetrahydrofuran was removed by distillation, and 20 ml of 20% sodium potassium tartrate solution was added to the residue. The mixture was extracted with two 50-ml portions of ether. The ether solution of methylethylphenylphosphine (III) was dried briefly over anhydrous magnesium sulfate, and then a solution of 1.53 g of benzyl-7-C^{14} iodide having a specific activity of 39.1 mμcuries/mg of C in 15 ml of ether was added. The solution was allowed to stand overnight in the refrigerator, and then 0.8516 g of crude methylethylphenylbenzyl-7-C^{14}-phosphonium iodide which had crystallized was collected by filtration. This salt was contaminated with methylethylphenylphosphine oxide which had resulted by partial air oxidation of methylethylphenylphosphine during the manipulations cited above, even though the mixture had been protected by a nitrogen atmosphere as much as possible during the various operations. Therefore, the crude salt was added to 8.8255 g of inactive methylethylphenylbenzylphosphonium iodide and recrystallized several times from acetone containing about 5% of methanol. The melting point of the completely purified salt was 170–171° (lit.[16] mp 170–171°).

Anal. Found activity for $C_{16}H_{20}PI$: 1.38 mμcuries/mg of C.

Reaction of Methylethylphenylbenzylidene-7-C^{14}-phosphorane with Styrene Oxide. By the usual procedure, 7.0964 g of methylethylphenylbenzyl-7-C^{14}-phosphonium iodide was converted to the ylide and condensed with styrene oxide. Pyrolysis of the adduct in decalin and the work-up described previously afforded 1.16 g of crude, labeled benzylacetophenone. After several recrystallizations from ethanol, 0.4591 g of pure material, mp 71–72°, was obtained. This was diluted to 4.7700 g with inactive benzylacetophenone and recrystallized again from ethanol to give 3.1687 g of the ketone.

Anal. Calcd activity for $C_{15}H_{14}O$: 0.142 mμcurie/mg of C. Found: 0.145 mμcurie/mg of C.

Schmidt Reaction of the Active Benzylacetophenone. This was carried out as described previously, and, from 2.9490 g of the labeled ketone, there was obtained 0.2661 g of highly purified, active hydrocinnamanilide, mp 96–97°.

Anal. Calcd activity for $C_{15}H_{15}NO$: 0.142 mμcurie/mg of C. Found: 0.139 mμcurie/mg of C.

Hydrolysis and Degradation of Active Hydrocinnamanilide. This was carried out as described previously on the 0.2661 g of the active anilide, and there was obtained 0.18 g of crude, active hydrocinnamic acid. Several recrystallizations from hexane afforded 0.0321 g of pure acid, mp 47–48°. This was diluted to 4.3815 g with inactive hydrocinnamic acid and crystallized again from hexane.

A portion of the active hydrocinnamic acid was subjected to the Schmidt reaction, and the carbon dioxide which was collected was found to be inactive.

A 1.000-g portion of the active hydrocinnamic acid was added to 50 ml of 0.1 *M* sodium hydroxide solution containing 4.75 g of potassium permanganate, and the mixture was heated at a bath temperature of 130° for 4.5 hr until the purple color had faded. The mixture was acidified with sulfuric acid, 1 ml of ethanol was added, and the mixture heated on the steam bath for 2 hr. A small amount of sodium bisulfite was then added to complete the reduction of the manganese dioxide present. The clear solution, when cooled in an ice bath, gave 0.70 g of benzoic acid. This was recrystallized from distilled water to give pure, active acid of mp 121–122°. A portion of this acid was subjected to the Schmidt reaction and the carbon dioxide which was evolved was collected.

Anal. Calcd activity for CO_2: 0.0156 mμcurie/mg of C. Found: 0.0150 mμcurie/mg of C.

Acknowledgment. This work was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the fund. It was also supported in part by the U. S. Atomic Energy Commission. The authors also wish to thank Dr. David R. Christman for the radioanalyses, Miss C. Redvanly for carrying out the Schmidt reactions of the radioactive carboxylic acids, and Dr. Irving S. Fagerson for help with the mass spectral analyses.

Mechanism of the Chromic Acid Oxidation of Ketones[1,2]

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Abstract: The chromic acid oxidation of isobutyrophenone in acetic acid and of 2-chlorocyclohexanone in water undergoes, with increasing concentration of chromic acid, a change from first- to zero-order dependence in the oxidant. The limiting rate is close to the rate of enolization as determined by bromination measurements. This demonstrates that the oxidation of ketones proceeds through the enol intermediates. No direct oxidation of the keto form could be observed.

In a previous paper[4] we offered proof that the main intermediate in the oxidation of cyclohexanone is 2-hydroxycyclohexanone. This study is concerned with the mechanism of its formation.

In an oxidation reaction a ketone can react with the oxidant either directly or in its enol form. Direct oxidations, demonstrated by an oxidation rate exceeding the rate of enolization, have been found for cobaltic[5,6] and ceric[6,7] salts and for manganic sulfate[6] as oxidants. All of them undergo a one-electron reduction, and the reactions seem to have a free-radical mechanism.

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(1) This work was supported by the Petroleum Research Fund administered by the American Chemical Society by Grant No. 1524-A4. The support is gratefully acknowledged.

(2) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965. Preliminary communication: J. Roček and A. Riehl, *J. Am. Chem. Soc.*, **88**, 4749 (1966).

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