ium may already be wholly or partially reduced to the rhenium(VI) state] probably experiences further reduction to a lower valent state which is the active form of the catalyst, since the analyses show a 6–7% increase in rhenium content of the catalyst after hydrogenation. Variability in the composition of the complex catalyst precludes any sound conjecture about its composition at this point.

The data for a representative listing of the hydrogenations carried out with this catalyst are presented in the accompanying table.

In general, the catalytic activity of rhenium(VII) oxide–tetrahydropyran complex in liquid phase hydrogenations is lower than that for the other rhenium catalysts studied heretofore[8]; however, the *pattern* of activity toward various reducible groups is entirely different from that noted for any other catalyst.

Most surprising are the relatively mild conditions required for the hydrogenation of most aromatic rings (no. 14, 17, 18, 19, 20, 21, 30, and 32) in comparison with the relatively strenuous conditions needed to reduce the nitro group which is usually so readily reduced (no. 22). The hope that this phenomenon would permit the as yet generally unobserved selective hydrogenation of aromatic rings without concomitant reduction of nitro groups in the same molecule was not realized, however (*cf.* no. 14 and 16, 30 and 31). Apparently, the presence of a nitro group in a molecule "poisons" the catalyst toward aromatic ring hydrogenation so that the latter function is not hydrogenated at all, and a given nitroarene suffers hydrogenation of the nitro group alone and then only under conditions more drastic than would be required to hydrogenate the aromatic function in the absence of the nitro group. Moreover, the complete inertness of the aminoarenes to further hydrogenation is illustrated by aniline (no. 24). The resistance of *m*-nitroacetophenone to reduction compared with acetophenone (no. 9, 10) also illustrates the adverse effect of the nitro group.

In contrast to aniline, phenol (no. 23) was relatively easily hydrogenated. The extreme inertness of naphthalene, biphenyl, and chlorobenzene in comparison to the other aromatic compounds is noteworthy (no. 25, 26, and 28 *vs.* 14, 17, 18, 19, 20, 21, 23, 30, and 32). The chlorine atom of chlorobenzene does not undergo hydrogenolysis even at 300°.

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[8] *Cf.* earlier papers in this series.

Phosphorus Compounds. III. Pyrolysis of Tertiary Phosphine Oxides[1-3]

WILLIAM J. BAILEY, WILLIAM M. MUIR,[4a] AND FRITZ MARKTSCHEFFEL[4b]

Department of Chemistry, University of Maryland, College Park, Maryland

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Pyrolytic study of a series of tertiary phosphine oxides has confirmed the high thermal stability of the carbon–phosphorus bond. Oxides containing alkyl groups with an available β-hydrogen atom apparently cleave by a cyclic mechanism to an olefin and a secondary phosphine oxide. The secondary oxides from the lower members of the series subsequently disproportionated into a secondary phosphine and a phosphinic acid. Oxides with no β-hydrogens were more stable than the preceding group at 600°, and, with the compounds examined, the phosphorus oxides all required temperatures approximately 300° above those required for similar decomposition of the corresponding amine oxides.

Since tertiary phosphine oxides appear to be one of the most stable groups of compounds in phosphorus chemistry, it was of interest to examine the thermal stability of some compounds in this class. This study was facilitated by the development in these laboratories of a general method for the preparation of a series of unsymmetrical tertiary phosphines.[1] The oxides were easily obtained by direct oxidation of the corresponding phosphines. For example, ethylmethylphenylphosphine was prepared in an over-all yield of 66% starting from phenyldichlorophosphine. Oxidation of this phosphine with hydrogen peroxide gave an 86% yield of the corresponding white crystalline phosphine oxide. The symmetrical phosphine oxides were prepared by the reactions of Grignards of alkyl halides with commercially available monosubstituted dichlorophosphines[5] or phosphorus trichloride,[6] or directly with phosphorus oxychloride.[7] It has been recorded[8] that the carbon–phosphorus bond in unsubstituted aromatic and aliphatic phosphonic acids [$RPO(OH)_2$] is both thermally and chemically stable, as might also be predicted for tertiary phosphine oxides. The carbon–phosphorus bond energy is 62 kcal.,[9] compared with 68 kcal. for carbon–silicon, 64 kcal. for carbon–carbon, and 57 kcal. for carbon–arsenic bonds.

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[1] Previous paper in this series, *J. Org. Chem.*, **25**, 1996 (1960).

[2] This work was done in fulfillment of a contract with the Army Chemical Corps.

[3] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 1961.

[4] (a) Chemical Corps Postdoctoral Fellow, 1960–1961; (b) Chemical Corps Postdoctoral Fellow, 1958–1959.

[5] G. M. Kosolapoff and R. F. Struck, *Proc. Chem. Soc.*, 351 (1960).

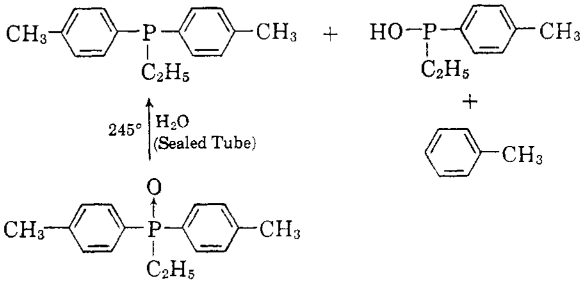
[6] W. C. Davies, P. L. Pearse, and W. J. Jones, *J. Chem. Soc.*, **135**, 1262 (1929).

[7] R. H. Pickard and J. Kenyon, *ibid.*, **89**, 262 (1906).

[8] L. D. Freedman and G. O. Doak. *Chem. Rev.*, **57**, 479 (1957).

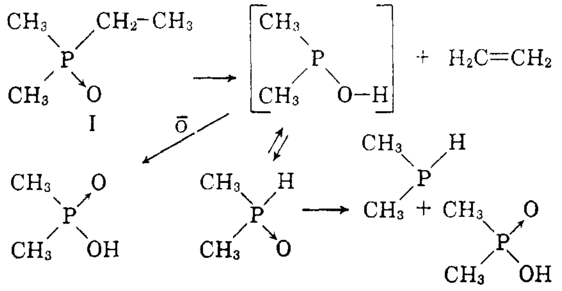
[9] M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

Although the carbon–phosphorus bond in these acids is normally stable, aromatic phosphoric acids containing strong electron-repelling groups in *ortho-* and *para-* positions to the phosphono group have a weakened C—P bond and are readily hydrolyzed under various experimental conditions. The low hydrolytic stability of *p*-methoxyphenylphosphonic acid is an example of this.[10] When the carbon–phosphorus bond in the tertiary alkyl- and alkylarylphosphine oxide series is considered, it is found that the bond shows strength comparable with that of carbon–carbon bonds. The bond may resist oxidation but will undergo cleavage under carefully chosen conditions. For instance, di(*p*-tolyl)ethylphosphine oxide heated at 245° with water in a sealed tube produced phosphines and phosphorus acids,[11] possibly as follows:

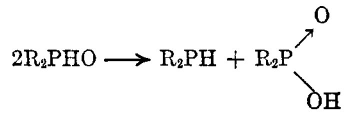


Although carbon–phosphorus bond cleavage has been recorded in the presence of base with a number of tertiary phosphine oxides,[12,13] no purely thermal scission is noted in the literature.

In the present investigation the tertiary phosphine oxides synthesized were chosen to represent various groups of oxides in an attempt to correlate thermal stability with β-hydrogen atom availability in the alkyl portion of the molecule. In general, wherever possible, scission produced an olefin or olefinic mixture accompained by a secondary phosphine oxide (which it was found possible to isolate only with the higher members of the series). With other oxides examined, the low molecular weight secondary oxide products were converted to phosphinic acids by atmospheric oxidation immediately on removal from the reaction vessels or by disproportionation.



The thermal decomposition of dimethylethylphosphine oxide between 330° and 670° produced ethylene and an unstable secondary phosphine oxide.[14] The liquid pyrolysate containing dimethylphosphine oxide from this reaction presented an interesting problem. The clear yellow liquid inflamed spontaneously on exposure to the air. Infrared examination showed the presence of both P—H and P—OH bonds, and dimethyl phosphinic acid[15] was present in the original pyrolysate along with odoriferous dimethylphosphine, although atmospheric oxidation would increase the amount of acid present. Increased acidity of the reaction mixture (pH ~ 1) over the aqueous solution of the starting material (pH ~ 5) also was noted. The disproportionation is as follows:

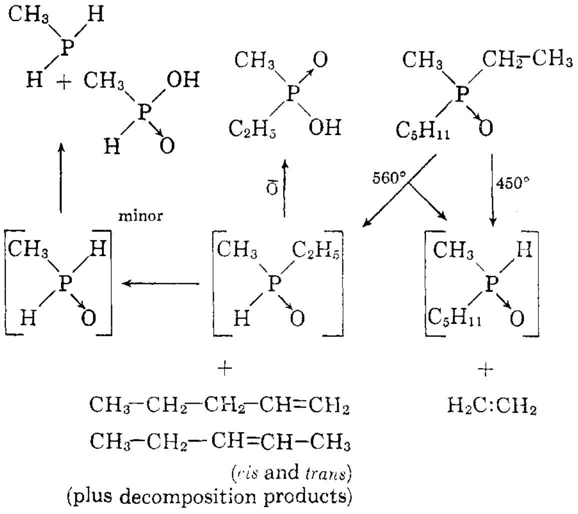


$$2R_2PHO \longrightarrow R_2PH + R_2P(\rightarrow O)OH$$

A thermal disproportionation similar to the one suggested for secondary phosphine oxides has been recorded for phosphonous acids which yield a primary phosphine and a phosphonic acid at moderate temperatures[16]:

$$3RP(OH)_2 \longrightarrow RPH_2 + 2RPO(OH)_2$$

Methylethylpentylphosphine oxide also liberated ethylene between 350° and 450°, but at 560° all the possible pentenes were present, together with ethylene and pentene decomposition products, such as butenes and propylene. The reaction scheme appears to be as follows:



The other unsymmetrical phosphine oxide examined, methylethylphenylphosphine oxide, de-

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[10] V. L. Bell and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 4901 (1953).

[11] P. W. Morgan and B. C. Herr, *ibid.*, **74**, 4526 (1952).

[12] L. Horner, H. Hoffmann, and H. G. Wippel, *Ber.*, **91**, 64 (1958).

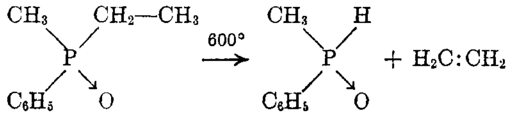
[13] K. D. Berlin and G. D. Butler, *Chem. Rev.*, **60**, 251 (1960).

[14] The secondary oxide structure (P—H bond) appears more probable than the phosphinous acid (P—OH bond) [see B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957)].

[15] Phosphorus acid nomenclature listed in Nomenclature Report, *J. Chem. Soc.*, 5122 (1952).

[16] A. Michaelis, *Ann.*, **181**, 265 (1876).

composed in a simpler manner but was much more thermostable, yielding ethylene only at higher temperatures:

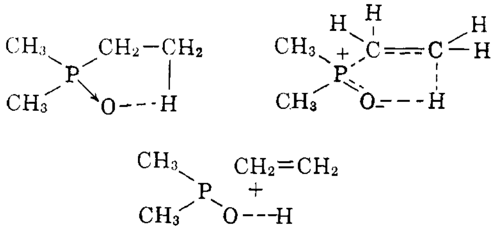


The secondary phosphine oxide produced by this reaction was characterized by oxidation and hydrolysis to a phenylphosphinic acid, C_6H_5-$P(OH)_2$. In an investigation of symmetrical phosphine oxides containing available β-hydrogen atoms, triethylphosphine oxide liberated ethylene. The reaction products again showed the tendency to inflame spontaneously and also smelled strongly of phosphine. The source of diethylphosphinic acid is doubtful—namely, arising from disproportionation or oxidation of the unstable diethylphosphine oxide. Tri-*n*-butylphosphine oxide, also with available β-hydrogen atoms, produced a butene mixture and a rather unstable secondary phosphine oxide, contaminated with the oxidation product, dibutylphosphinic acid, and a small amount of elemental phosphorus. At the highest temperature employed (650°) butene isomers also appeared, perhaps from rearrangement by acidic reaction products in a fashion similar to production of olefin isomers during ester pyrolysis.[17] The two most stable phosphine oxides were the trimethyl and triphenyl compounds, which showed virtually no decomposition to 700°. Since these oxides have no available β-hydrogens, they cannot eliminate via a cyclic intermediate. Relative stabilities (microfurnace) are shown in Table I.

TABLE I

Compound $R_1R_2R_3 \rightarrow O$	Temp. for 50% decomposition, ° C.
Trimethyl	Stable to 700
Triphenyl	Slight discoloration at 690
Ethylmethylphenyl	665
Dimethylethyl	525
Triethyl	510
Ethylmethylpentyl	490
Tri-*n*-butyl	490

A parallel study of the thermal decomposition of unsymmetrical tertiary amine oxides by earlier investigators[18] demonstrated that these compounds produced olefins by an intramolecular elimination which followed a predominantly *cis*- steric course. Pyrolysis of unsymmetrical amine oxides at temperatures to 150° yielded an almost statistical distribution of olefins with a small preference over the statistical ratio for the most highly substituted olefin (Saytzeff rule). In contrast, during the present work the phosphine oxides showed greatly increased thermal stability over the corresponding amine oxides and the general stability of the C—P bond was of the same order as that of the C—C bond during ester pyrolysis.[19] By analogy with the mechanism proposed for the decomposition of amine oxides[20-22] a cyclic five-membered transition state might be written. If the decomposition did involve such a cyclic process, one would expect that a higher temperature would be required to promote the cleavage since the transition state would be on the path to a high energy trivalent phosphorus compound as an unstable intermediate. However, until evidence concerning the *cis*- nature of the elimination has been obtained, one can only speculate about the mechanism.



This work indicates that the pyrolysis of tertiary phosphine oxides is an excellent method for the synthesis of high molecular weight secondary phosphine oxides and suggests the use of the tertiary oxides in the design of thermally stable materials.

Experimental[23]

Except where noted, phosphines, phosphine solutions, secondary phosphine oxides, and Grignard reagents were handled under nitrogen from which traces of oxygen were removed by an acidic chromic sulfate solution over a zinc-mercury couple.[24] Each phosphine oxide was pyrolyzed initially on a micro scale between 300° and 650° at 50° intervals under helium in a microfurnace which was connected directly to a gas chromatography unit. Later, under optimum conditions, each oxide was pyrolyzed on a larger scale at the several temperatures noted through a vertical Vycor tube packed with small sections of Vycor tubing, as described previously.[25] The tube was externally heated by a furnace and flushed continuously with a slow stream of oxygen-free nitrogen. The pyrolysates were collected at the reactor base in a side-inlet flask which was cooled in an acetone–Dry Ice mixture. Olefins in the exit gases were trapped in an ice-cooled bromine–carbon tetrachloride trap to which a small amount of aluminum was added (caution!).

Dimethylethylphosphine Oxide (I)—While a solution of methylmagnesium iodide [prepared from 14.4. g. (0.6 g.-

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[17] W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

[18] A. C. Cope, N. A. LaBel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).

[19] W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

[20] A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949).

[21] A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

[22] D. J. Cram and J. E. McCarty, *ibid.*, **76**, 5740 (1954).

[23] The authors are grateful to Dr. Franz Kasler for the microanalyses, and to Mr. S. Hirsch for preparing the dimethylsulfolane gas chromatography column. The infrared spectra were determined on a Beckman IR-4 infrared spectrometer on liquids, melts, or Nujol mulls for solids. Melting points are uncorrected.

[24] H. W. Stone and D. N. Hume, *Ind. Eng. Chem., Anal. Ed.*, **11**, 598 (1939).

[25] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

atom) of magnesium and 85 g. (0.6 mole) of methyl iodide in 500 ml. of anhydrous ether] was cooled in an ice bath, 40.0 g. (0.3 mole) of freshly distilled ethyldichlorophosphine, b.p. 108–110° (Army Chemical Center, Maryland), was added with stirring over a 90-min. period. After the mixture had been stirred for an additional hour, it was slowly hydrolyzed with 100 ml. of water and 200 ml. of a saturated ammonium chloride solution. The layers were separated and the aqueous layer was repeatedly extracted with ether and benzene. Treatment of the combined organic extracts with 50 ml. of 30% hydrogen peroxide in 50 ml. of acetone gave, after being heated under reflux for 2 hr. and then treated with platinum, 15.2 g. (47%) of the highly hygroscopic dimethylethylphosphine oxide, m.p. 75–76° (sealed tube; reported[26] m.p. 73–75°).

Pyrolysis of Dimethylethylphosphine Oxide (I).—With the technique outlined for micropyrolysis, the oxide I was decomposed under helium betweeen 330° and 650° at 50° intervals. Chromatographic analysis indicated that only ethylene and the secondary oxide were produced. By melting the compound with a heat lamp and an electrically heated dropping funnel with a pressure-equalizing side arm, 14.0 g. (0.13 mole) of I was pyrolyzed at 530°. The oxide was added (0.3 g. per minute) to the pyrolysis tube while a steady stream of nitrogen flowed through the system and out *via* the bromine–carbon tetrachloride trap. The pyrolysate (10.4 g.) warmed to room temperature appeared to evolve a gas (dimethylphosphine has b.p. 25°)[27] and a strong phosphine odor was apparent; the liquid pyrolysate also tended to inflame spontaneously. The olefin trap contained only one product, ethylene dibromide (determined by chromatographic analysis), corresponding to a 58% yield of ethylene. The first fraction of the liquid reaction products gave an infrared spectrum with strong absorption at 2315–2320 cm.$^{-1}$ and at 1140–1145 cm.$^{-1}$, corresponding to frequencies suggested earlier for P—H and P—O bonds, respectively, in secondary dialkylphosphine oxides.[28] The strongly acid liquid pyrolysate (pH $\sim$ 1.0) was fractionated under reduced pressure and gave approximately 2 g. of a clear liquid, b.p. 74–116° (0.2 mm.), and 6 g. of a liquid, b.p. 121–163° (0.2 mm.); both fractions gave white needles on standing over phosphorus pentoxide in an evacuated desiccator. Fraction 1 was identified by its infrared spectrum as dimethylphosphinic acid, m.p. 65–68° (sealed tube; reported m.p. 70°)[29]; a mixed melting point determination with a pure sample of dimethylethylphosphine oxide became liquid around 35°. The acid also gave a precipitate, presumably the silver salt of dimethylphosphinic acid, from aqueous ethanol when treated with silver hydroxide. Fraction 2 was shown to be unchanged starting material, m.p. 72–73°, by mixed melting point determination and infrared analysis.

Ethylmethylpentylphosphine Oxide (II).—This phosphine oxide II was prepared by reduction of 182 g. (0.5 mole) of benzylethylmethylpentylphosphonium iodide (III) with 20 g. (0.5 mole) of lithium aluminum hydride, followed by oxidation of the resulting crude ethylmethylpentylphosphine with hydrogen peroxide to give 67 g. (83%) of II, b.p. 88–91° (0.5 mm.), n^{25}D 1.4541. The product was a hygroscopic colorless liquid.

Anal. Calcd. for $C_8H_{19}PO$: C, 59.3; H, 11.8. Found: C, 59.6; H, 11.9.

Pyrolysis of Ethylmethylpentylphosphine Oxide (II).—Micropyrolysis at the temperatures listed below gave the following information. (*Trans*- isomers were eliminated from the chromatography column before the *cis*- isomers with each olefin analyzed when the stationary phase was dimethylsulfolane.[30] A mixture of phosphinic acids also was observed when the products were analyzed on a 10% Apiezon N-on-Chromosorb column.)

Temp., °C.	Olefin yield, %	Composition, % Ethylene[a]	1-Pentene	2-Pentene *Trans*	*Cis*	Others
410	16	83	17	..	..	..
450	36	67	22	6	5	..
500	54	33	27	27	11	2
565	67	24	23	28	21	4

[a] Preferential elimination of ethylene over some higher olefins also has been observed in pyrolytic elimination from mixed tertiary alkylamine oxides.

In a typical full-scale pyrolysis, 20 g. (0.12 mole) of II was pyrolyzed at 570° in the Vycor reactor under nitrogen to give 14.7 g. of a clear brown liquid which smelled of phosphine and contained traces of yellow phosphorus in suspension. When it was exposed to the air, the liquid fumed strongly and tended to inflame. The olefin trap showed a weight gain of *ca.* 2 g. but was not readily reproducible and was not used for quantitative work, since only ethylene appeared to be trapped quantitatively. The pentenes condensed in the liquid pyrolysate and were recovered. After cautious oxidation, the liquid pyrolysate was distilled into three fractions. Fraction 1, 3 ml., b.p. 28–47° (757 mm.), decolorized bromine instantly and was shown to be a mixture of pentenes by chromatographic and infrared analyses. Fraction 2, 5.5 g. of clear liquid, b.p. 81–125° (0.7 mm.), was apparently a mixture of phosphinic acids and a trace of unchanged II. Three compounds were present, II and possibly methylphosphonic acid, $CH_3PH(OH)_2$ and ethylmethylphosphinic acid, $C_2H_5P(CH_3)O(OH)$, derived from oxidation of the unstable primary $[CH_3P(O)H_2]$ and secondary $[CH_3PH(O)C_2H_5]$ oxides, respectively, both apparently too unstable to air oxidation to be isolated under the conditions employed.[31] Fraction 3, 3.5 g. of yellow liquid, b.p. 130–165° (0.4 mm.), n^{25}D 1.4511, was slightly impure unchanged II and there was approximately 1 g. of a high boiling residue from the distillation.

Ethylmethylphenylphosphine Oxide (IV).—Reduction of 210 g. (0.65 mole) of benzylethylmethylphenylphosphonium bromide (V) with 25 g. (0.65 mole) of lithium aluminum hydride in 1000 ml. of tetrahydrofuran was followed by hydrolysis with 1500 ml. of a 5% sodium potassium tartrate solution. After the aqueous layer was extracted several times with ether, the organic extracts were combined. After most of the tetrahydrofuran was removed by distillation, the resulting phosphine was oxidized with 150 ml. of 30% hydrogen peroxide in 150 ml. of acetone by heating under reflux in air for 2 hr. Destruction of the excess peroxide (with electrolytically deposited platinum on platinum from platinum chloride solution) gave the oxide IV in solution. The layers were separated and the aqueous layer was flash distilled to yield a yellow oil (impure IV) which was added to the organic layer. Fractional distillation of the organic solution gave 94 g. (86%) of impure oxide, b.p. 96–107° (0.4 mm.). Analytically pure material was obtained as white hygroscopic crystals, m.p. 52°,[1] by recrystallization from alcohol.

Pyrolysis of Ethylmethylphenylphosphine Oxide (IV).—Micropyrolysis above 470° of IV produced ethylene and methylphenylphosphine oxide. Decomposition of 10 g. (0.068 mole) of the oxide at 680° under nitrogen produced a weight increase of approximately 1 g. (> 50% decomposition) in the olefin trap; ethylene dibromide was the only product detected in this trap (chromatographic analysis). The pyrolysate (6.7 g.) was a yellow liquid with a strong phosphine odor. Some carbon deposits were noted in the reactor. When the pyrolysate was allowed to stand over phosphorus pentoxide in a vacuum desiccator, white crystals of un-

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(26) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

(27) A. W. Hofmann, *Ber.*, **4**, 605 (1871).

(28) C. D. Miller, R. C. Miller, and W. J. Rogers, *J. Am. Chem. Soc.*, **80**, 1562 (1958).

(29) A. W. Hofmann, *Ber.*, **5**, 104 (1872).

(30) E. M. Fredericks and F. R. Brooks, *Anal. Chem.*, **28**, 297 (1956).

(31) A. W. Frank, *J. Org. Chem.*, **24**, 966 (1959).

changed IV, m.p. 47–49°, formed. After these crystals were removed by filtration, the residual liquid was added to the aqueous washings (15 ml.) from the reactor and the mixture was heated under reflux for several hours. Afterwards, most of the water was removed and crystals appeared, not of the expected methylphenylphosphinic acid (VI), Ph—P—CH_3(O)(OH), m.p. 134°[32] [from oxidation of secondary methylphenylphosphine oxide, Ph—P—H—(CH_3)(O)], but phenylphosphonic acid (VII), Ph—P—O$(OH)_2$, m.p. 158–159° (reported[33] m.p. 161–162°), confirmed by infrared. Compound VII probably was produced by hydrolysis of VI.

Anal. Calcd. for $C_6H_7O_3P$: C, 45.6; H, 4.4. Found: C, 45.4; H, 4.1.

Triethylphosphine Oxide (VIII).—By the method of Pickard and Kenyon,[7] 77 g. (0.5 mole) of phosphorus oxychloride was treated with 200 g. (1.5 moles) of ethylmagnesium bromide to give 38 g. (57%) of very hygroscopic VIII, m.p. 42–44° (reported[34] m.p. 44°).

Pyrolysis of Triethylphosphine Oxide (VIII).—Micropyrolysis of this oxide liberated only ethylene between 370° and 650° and the unstable secondary phosphine oxide. Pyrolysis of 20 g. (0.15 mole) of VIII at 580° gave a fuming yellow liquid (12.8 g.) which was extremely inflammable. The olefin trap gained *ca.* 3 g. with ethylene dibromide as the only product. Cautious oxidation of the liquid pyrolysate was followed by addition of 20 ml. of water. The solution was heated under reflux for 2 hr. After the water was removed, fractional distillation gave small amounts of impure ethylphosphonic acid, $C_2H_5PO(OH)_2$, m.p. 53–55° (reported[35] m.p. 61–62°), but the main product was diethylphosphinic acid, a clear liquid, b.p. 110–127° (0.4 mm.), from oxidation of the unstable pyrolysis product, diethylphosphine oxide. The phosphinic acid was confirmed by infrared analysis and formation of a silver salt from silver hydroxide. There also was obtained approximately 2 g. of unchanged VIII.

Tri-*n*-butylphosphine Oxide (IX).—While a stream of air was passed through the liquid, 100 g. (0.46 mole) of tri-*n*-butylphosphine[36] was oxidized quantitatively to IX by reflux at its boiling point (~295°). Pure IX was a hygroscopic white crystalline substance, m.p. 61.6–62.5°.

Pyrolysis of Tri-*n*-butylphosphine Oxide (IX).—Oxide IX yielded only 1-butene when pyrolyzed on the micro scale at temperatures to 550°. Above this temperature, small amounts of isomers appeared along with secondary di-*n*-butylphosphine oxide (X). Decomposition of 20 g. (0.09 mole) of IX at 560° produced *ca.* 4 g. weight increase in the olefin trap (chromatographic analysis showed the presence of only brominated butenes) and 12 g. of brown liquid pyrolysate, smelling of phosphine and fuming in air. Fractional distillation of the pyrolysate gave traces of butylphosphonic acid (XI) [$C_4H_9PO(OH)_2$], dibutylphosphinic acid (XII) [$(C_4H_9)_2PO(OH)$] and 7 g. of slightly impure di-*n*-butylphosphine oxide (XIII), m.p. 64–65° (reported[37] m.p. 66°). The oxide XIII was characterized by oxidation to dibutylphosphinic acid (XII), m.p. 67° (reported[38] m.p. 70–71°).

Trimethylphosphine Oxide (XIV).—Oxide XIV was prepared in a 38% yield from molar amounts of phosphorus oxychloride and the methyl Grignard, as described previously.[7] The pure product was a very hygroscopic white crystalline solid, m.p. 140–142°.

Pyrolysis of Trimethylphosphine Oxide (XIV).—Decomposition of oxide XIV on the micro scale between 350° and 700° produced no detectable breakdown. On a larger scale, 20 g. of the material passed through the reactor at 700° unchanged and was recovered as white crystals with only a small loss (2 to 3 g.) by hold-up in the reactor.

Triphenylphosphine Oxide (XV).—Oxidation of 100 g. (0.36 mole) of triphenylphosphine gave an almost quantitative yield of XV, m.p. 152–153°, when the reaction was carried out with heating under reflux for several hours in the presence of excess dilute nitric acid.

Pyrolysis of Triphenylphosphine Oxide (XV).—The oxide XV showed no decomposition in the microreactor to 700°, but slight discoloration was noted when it was pyrolyzed at 690° in the Vycor reactor under nitrogen. It was recovered as a pale yellow crystalline material, m.p. 150–152°.

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(32) W. J. Pope and C. S. Gibson, *J. Chem. Soc.*, 740 (1912).

(33) A. D. F. Toy, *J. Am. Chem. Soc.*, **70**, 186 (1948).

(34) J. N. Collie and F. Reynolds, *J. Chem. Soc.*, 367 (1915).

(35) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 1180 (1945).

(36) The authors are grateful to Food Machinery and Chemical Corp. for a generous supply of this compound.

(37) M. M. Rauhut, I. Hechenbleikner, H. A. Currier, and V. P. Wystrach, *J. Am. Chem. Soc.*, **80**, 6690 (1958).

(38) G. M. Kosolapoff, *ibid.*, **71**, 369 (1949).

The Migratory Group in the Jacobsen Rearrangement[1]

ELLIOT N. MARVELL AND DANIEL WEBB

Chemistry Department, Oregon State University, Corvallis, Oregon

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1,2,4,5-Tetraethylbenzene-α-C^{14} has been submitted to the Jacobsen rearrangement and the product degraded. The ethyl group has been shown thus to migrate without rearrangement.

The Jacobsen rearrangement,[2] known since early in the 1880's[3] has evoked some interest in the fascinating art of mechanistic speculation,[4] but not any great amount of experimental confirmation. About twenty years ago Arnold and Barnes[5] presented some evidence on the basis of which they proposed the following mechanism. Since Smith and Lo tried unsuccessfully[6] to verify one possible consequence of this mechanism the subject

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(1) Taken in part from a thesis submitted by Daniel Webb in partial fulfillment of the requirements for the M.S. degree, Oregon State University, September 1960. The authors are happy to acknowledge generous financial assistance by the Sigma Xi-RESA research fund and the general research grants of Oregon State University.

(2) For a general review see L. I. Smith, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 370.

(3) (a) J. Herzig, *Ber.*, **14**, 1205 (1881); (b) O. Jacobsen, *ibid.*, **19**, 1209 (1886).

(4) *Cf.*, for example, E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 257–259; and L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, pp. 665–667.

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