B. 2,4-Diphenyl-1-butene (III).—The compound that was eluted in 22 min. on the fluorosilicone column gave the following spectra. Infrared (film): μ 3.28 (shoulder), 3.32 (w), 3.42 (w), 3.50 (shoulder), 6.14 (m), 6.24 (w), 6.67 (w), 6.86 (m), 9.30 (w), 9.70 (w), 11.16 (m), 12.87 (m), 13.40 (m), 14.35 (s); n.m.r. (CCl_4): τ 2.85 and 2.93 (10), 4.84 (doublet, 1, J = 2 c.p.s.), 5.05 (partially resolved doublet, 1), 7.31 (singlet, 4).

C. *trans*-1,3-Diphenyl-2-butene (V).—The compound that was eluted in 32 min. on the fluorosilicone column gave the following spectra. Infrared (film) μ 3.28 (shoulder), 3.30 (w), 3.43 (w), 6.25 (w), 6.68 (m), 6.87 (m), 7.25 (w), 9.32 (w), 9.47 (w), 9.71 (w), 13.25 (s), 13.50 (shoulder), 14.40 (s); n.m.r. (CCl_4): τ 2.85 (multiplet, 10), 4.08 (triplet, 1), 6.50 (doublet, 2), 7.88 (singlet, 3); ultraviolet (95% ethanol): 245 mμ (ϵ 8250), 273 mμ (ϵ 3750 sh).

2,4-Diphenyl-1-butene (III) (Wittig Synthesis[11]).—A suspension of triphenylmethylphosphonium bromide (Beacon Chemical Industries) (1.43 g., 0.004 mole) in a solution of 0.320 g. (0.005 mole) of *n*-butyllithium in 25 ml. of ether was stirred at 25° under nitrogen for 2 hr. To the solution which was effected during this period, was added 0.84 g. (0.004 mole) of β-phenylpropiophenone (II); stirring was continued at 25° for another 0.5 hr. Dry tetrahydrofuran (50 ml.) was added, the ether removed by distillation, and the solution was refluxed for 4 hr. The tetrahydrofuran was distilled at 20 mm., and the residue was triturated with six 40-ml. portions of pentane. Removal of the pentane left 0.68 g. of a colorless oil. Chromatography on the fluorosilicone column at 190° and 40 ml. min. gave a major peak at 9 min. and a small peak (starting ketone, 5% of the major peak) at 21 min. The infrared and n.m.r. spectra of the compound represented by the major peak were identical with those obtained from component no. 3 of the "styrene dimer fraction," and from the second fraction of the chromatographed olefinic dehydration mixture.

Anal. Calcd. for $C_{16}H_{16}$ (208.29): C, 92.26; H, 7.74. Found: C, 92.38; H, 8.03.

Oxidation of Component No. 1.—To a solution of 10 mg. of component no. 1 in 0.5 ml. of glacial acetic acid held at 70°, was added, portionwise, 50 mg. of chromic anhydride over a period of 45 min. The mixture was cooled and extracted with ether which then was washed with 10% sodium hydroxide solution, dried, and evaporated. The residue in 0.2 ml. of hexane was placed on an alumina column (Merck, acid-washed, 0.5 g. in a 4-mm. tube) and eluted with hexane. The hexane solution was concentrated to 0.2 ml., cooled to −30°, and filtered. A 4-mg. crop of crystals was obtained, m.p. 70–73° (lit.,[7] m.p. for β-phenylpropiophenone 73°). Admixture with an authentic sample (II) did not depress the melting point; infrared (melt): 5.92 μ (C=O).

Oxidation of Component No. 3.—A 2% aqueous solution of potassium permanganate was added dropwise over a period of 2 hr. to 10 mg. of component 3 on a steam bath until the permanganate color persisted. The mixture was extracted with ether, and the ether solution was dried and evaporated. The residue was treated with 2,4-dinitrophenylhydrazine. Three recrystallizations of the product from ethanol-water gave the 2,4-dinitrophenylhydrazine, m.p. 162–164.5°, whose identity was proved by mixed melting point with an authentic sample of β-phenylpropiophenone 2,4-dinitrophenylhydrazone and by comparison of the infrared spectra.

Acknowledgment.—The work described is part of a broad study of styrene dimerization by Dr. F. R. Mayo who furnished the fraction described. The authors are indebted to Mr. Norman Bhacca of Varian Associates for the 100-Mc. n.m.r. spectrum, and to Dr. S. A. Fuqua of Stanford Research Institute for many helpful discussions of n.m.r. spectra. The n.m.r. and mass spectra were run at Stanford Research Institute by Mr. W. R. Anderson, Jr., and Mrs. L. Peters, respectively.

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The Metalation of Methyl(disubstituted)phosphine Oxides and Their Subsequent Reactions

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A series of phosphine oxides containing an additional carboxy, hydroxy, carbonyl, or phosphinyl group was prepared by reaction of the lithium metalated methyl(disubstituted)phosphine oxide with the appropriate reagent. The physical data and the infrared frequencies of the main functional groups are reported.

Bis(disubstituted phosphinyl)methanes, $R_2P(O)CH_2P(O)R_2$, appear to be more effective extractants for various metal ions than the monophosphine oxides.[1] It was found desirable to study the effect of substitution of other functional groups for one of the phosphinyl groups on the extractability of metal ions.

Use was made of the acidic nature of the hydrogen atom of a methylene group adjacent to the P—O group of a phosphine oxide to introduce functional groups such as carboxy, hydroxy, and carbonyl into the molecule.[2-6] Di-*n*-hexylmethylphosphine oxide and methyldiphenylphosphine oxide were first metalated with *n*-butyllithium and the resulting intermediate was treated with the various types of compounds listed below to give the indicated product. The method also can be used to prepare bis(disubstituted phosphinyl)methanes (equation 5).

$$R_2P(O)CH_2Li + CO_2 \longrightarrow \xrightarrow{H^+} R_2P(O)CH_2CO_2H \quad (1)$$

$$R_2P(O)CH_2Li + R'CHO \longrightarrow \xrightarrow{H^+} R_2P(O)CH_2C(OH)HR' \quad (2)$$

$$R_2P(O)CH_2Li + R_2'CO \longrightarrow \xrightarrow{H^+} R_2P(O)CH_2C(OH)R_2' \quad (3)$$

$$R_2P(O)CH_2Li + R'CO_2Et \longrightarrow R_2P(O)CH_2C(O)R' \quad (4)$$

$$R_2P(O)CH_2Li + R_2'P(O)Cl \longrightarrow R_2P(O)CH_2P(O)R_2' \quad (5)$$

Although the lithium salts of the methyl(disubstituted)phosphine oxides were not isolated, they were formed in at least 60–70% yield as indicated by the recovery of the carboxymethyl(disubstituted)phosphine oxides.

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TABLE I

PREPARATION AND PROPERTIES OF SOME PHOSPHINE OXIDES

Compound	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
1. $(C_6H_{13})_2P(O)CH_2CO_2H$	67				60.84	60.82	10.57	10.80	11.21	11.11
2. $(C_6H_5)_2P(O)CH_2CO_2Na$	63				59.58	59.61	4.29	4.38	10.98	11.25
3. $(C_6H_5)_2P(O)CH_2CO_2H$[a,b]				145–146						
4. $(C_6H_{13})_2P(O)CH_2CO_2CH_3$	50	168	0.3		62.04	61.61	10.76	10.81	10.67	10.90
5. $(C_6H_{13})_2P(O)CH_2C(OH)(C_2H_5)_2$	46	158–168	.1		67.88	67.82	12.34	12.22	9.71	9.70
6. $(C_6H_5)_2P(O)CH_2C(OH)(C_2H_5)_2$	61			114–116	71.50	71.55	7.67	7.72	10.24	10.15
7. $(C_6H_{13})_2P(O)CH_2C(OH)(C_6H_5)_2$	49			82–83	75.33	75.76	9.48	9.57	7.47	7.39
8. $(C_6H_5)_2P(O)CH_2C(OH)(C_6H_5)_2$	81			192–193	78.37	78.84	5.82	5.85	7.77	7.75
9. $(C_6H_{13})_2P(O)CH_2CH(OH)(C_6H_5)$	50	220	.15		70.97	71.29	10.42	10.48	9.15	9.11
10. $(C_6H_{13})_2P(O)CH{=}CH(C_6H_5)$	10	205–210	.15		74.96	75.08	10.38	10.45	9.67	9.56
11. $(C_6H_5)_2P(O)CH_2CH(OH)(C_6H_5)$	31			141–142	74.75	74.70	5.65	5.94	9.61	9.69
12. $(C_6H_{13})_2P(O)CH_2C(OH)(C_6H_5)CH_3$	51	207	.18	83–84	71.55	71.50	10.59	10.76	8.79	8.92
13. $(C_6H_{13})_2P(O)CH_2CH(OH)CH_3$	44	165–170	.20		65.18	65.10	12.03	11.84	11.21	11.01
14. $(C_6H_{13})_2P(O)CH_2CH(OH)C_3H_7$	33	175	.25		67.03	67.25	12.25	12.22	10.18	9.97
15. $(C_6H_5)_2P(O)CH_2P(O)(C_8H_{17})_2$	25			96–97	71.28	71.00	9.50	9.48	12.68	12.66
16. $(C_6H_{13})_2P(O)CH_2C(O)CH_3$	30	137–144	.10		65.66	65.47	11.39	11.44	11.29	11.32
17. $(C_6H_{13})_2P(O)CH_2C(O)C_6H_5$	33	182–187	.05		71.39	71.28	9.89	9.74	9.21	9.27
18. $(C_6H_5)_2P(O)CH_2C(O)C_6H_5$[c]	40			139–140	74.97	74.99	5.35	5.43	9.67	9.61
19. $(C_6H_{13})_2P(O)CH_2P(O)(C_6H_{13})_2$[d]	35	225–235	.23							
20. $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)_2$[e]	25			178–180						

[a] Calcd.: equiv. wt., 260. Found: equiv. wt., 259. [b] Reported[11] m.p. 142–144°. [c] Reported[13] m.p. 140–140.5°. [d] Reported[10] b.p. 218–223° at 0.2 mm. [e] Reported[10] m.p. 180–182°.

The β-hydroxyphosphine oxides, as opposed to the α-hydroxyphosphine oxides which decompose into starting material when heated to their melting points or when dried at 100°,[7] are thermally stable. Di-*n*-hexyl(2-hydroxy-2-phenylethyl)phosphine oxide, however, partially dehydrates upon distillation. Distillation also causes the carboxymethyl(disubstituted)phosphine oxides to decarboxylate.

The infrared data would seem to indicate that the β-hydroxyphosphine oxides are intramolecularly hydrogen bonded as are the α-hydroxyphosphine oxides.[8] The hydroxy band is shifted an average of only 70 cm.$^{-1}$ on going from solid or liquid state into solution in carbon tetrachloride (1% by weight) and further dilution produced no further shift.

Initial studies by reversed-phase chromatography indicate that several of these compounds may possess desirable characteristics as extractants for metal ions. A systematic study of their properties as extractants will be made in the future.

Experimental

Methyldiphenylphosphine Oxide[9] and Di-*n*-hexylmethylphosphine Oxide.[10]—Most of di-*n*-hexylmethylphosphine oxide used in the following experiments was obtained as a by-product from the synthesis of bis(di-*n*-hexylphosphinyl)methane,[10] but can be prepared in 70% yield by the synthesis listed below. One mole of diethyl hydrogen phosphite was added to 3 moles of the Grignard reagent (*n*-hexyl or phenyl) at such a rate to maintain steady reflux. The mixture was refluxed for an additional 3 hr., at which time a mole of methyl bromide dissolved in anhydrous ether was added. The mixture was refluxed overnight, hydrolyzed, and the phases separated. Di-*n*-hexylmethylphosphine oxide was obtained in 70% yield upon distillation of the organic phase, b.p. 130–135° at 0.2 mm. Methyldiphenylphosphine oxide[9] was obtained upon evaporation of the aqueous phase (pH 6) after removal of the magnesium hydroxide by filtration or centrifugation (pH 12). The methyldiphenylphosphine oxide separated as an oil and was extracted into hot benzene from which it crystallized on cooling. A 50% yield was obtained, m.p. 108–109°.

Lithium Salts of Di-*n*-hexylmethylphosphine Oxide (I) and Methyldiphenylphosphine Oxide (II).—*n*-Butyllithium (0.1 mole) dissolved in hexane was added to 0.1 mole of methyl(disubstituted)phosphine oxide dissolved in 300 ml. of anhydrous ether in a 500-ml. three-necked flask equipped with stirrer, dropping funnel, and reflux condenser. The mixture was refluxed for 4 hr. and used in the reactions below. An inert atmosphere was maintained throughout the reactions.

Carboxymethyldi-*n*-hexylphosphine Oxide and Carboxymethyldiphenylphosphine Oxide.—The lithium salt, I or II, was poured with stirring onto a slurry of Dry Ice and ether. The ether was evaporated and the residue was dissolved in dilute base. This solution was acidified and the carboxymethyldi-*n*-hexylphosphine oxide was purified by reextracting into ether. The purification process was repeated a second time and gave almost complete removal of the unreacted starting material. Carboxymethyldiphenylphosphine oxide, upon acidification, separated into a third phase. The desired phase was separated and the sodium salt precipitated by the addition of a small amount of concentrated aqueous sodium hydroxide. The sodium salt was recrystallized from acetone. Acidification of the sodium salt with dilute hydrochloric acid gave the acid.[11]

Di-*n*-hexyl(methoxycarbonylmethyl)phosphine Oxide.—Carboxymethyldi-*n*-hexylphosphine oxide was esterified using methyl alcohol in the usual manner. Sapon. equiv.—calcd.: 290.4; found: 289.1.

β-Hydroxyphosphine Oxides.—The appropriate ketone or aldehyde (0.1 mole) dissolved in 50 ml. of anhydrous ether was added to the lithium salt, I or II. The mixture was refluxed for 4 hr., cooled, and hydrolyzed with 3% hydrochloric acid. The phases were separated and the ether phase was washed with two small portions of water. The ether was evaporated and the residue was either recrystallized or vacuum distilled.

(2-Ethyl-2-hydroxybutyl)di-*n*-hexylphosphine oxide and (2-ethyl-2-hydroxybutyl)diphenylphosphine oxide were prepared by the reaction of 3-pentanone with I and II, respectively. The aryl compound was recrystallized from ether.

Di-*n*-hexyl(2-hydroxy-2,2-diphenylethyl)phosphine oxide and (2-hydroxy-2,2-diphenylethyl)diphenylphosphine oxide were prepared by the reaction of benzophenone and I and II, respectively. After removal of the unchanged di-*n*-hexylmethylphosphine oxide by vacuum distillation, the hexyl compound was re-

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crystallized from petroleum ether (b.p. 65–110°). The tetraphenyl compound precipitated from the reaction mixture upon hydrolysis. It was filtered and recrystallized from benzene.

Di-*n*-hexyl(2-hydroxy-2-phenylethyl)phosphine oxide and 2-(hydroxy-2-phenylethyl)diphenylphosphine oxide were prepared by the reaction of benzaldehyde and I and II, respectively. The *n*-hexyl compound dehydrated upon distillation giving di-*n*-hexylstyrylphosphine oxide. If the ether solution is extracted with base prior to distillation, the dehydration product is held to approximately 10% of the total yield. The aryl compound was purified by recrystallization from benzene.

Di-*n*-hexyl (2-hydroxy-2-phenylpropyl)phosphine oxide, di-*n*-hexyl(2-hydroxy-*n*-propyl)phosphine oxide, and di-*n*-hexyl-(2-hydroxy-*n*-pentyl)phosphine oxide were prepared by the reaction of I with acetophenone, acetaldehyde, and butyraldehyde, respectively.

The disubstituted phosphinyl chlorides used in the following preparations were prepared by the method of Kosolapoff.[12]

Bis(di-*n*-hexylphosphinyl)methane[10] was prepared by the reaction of di-*n*-hexylphosphinyl chloride, b.p. 160–163° at 1 mm., and I. The reaction mixture was refluxed for 4 hr., hydrolyzed, extracted with 5% sodium hydroxide and water, and vacuum distilled.

Bis(diphenylphosphinyl)methane[10] was prepared by the reaction of diphenylphosphinyl chloride and II. The product is very insoluble in the reaction media and precipitated as a sticky residue at the bottom of the flask. The liquid was decanted from the residue which was then dissolved in hot benzene from which it crystallized on cooling.

[(Di-*n*-octylphosphinyl)(diphenylphosphinyl)]methane was prepared by the reaction of di-*n*-octylphosphinyl chloride, b.p. 190° at 0.1 mm., and II. The reaction mixture, after having been refluxed for 4 hr., was hydrolyzed with 3% hydrochloric acid, the layers were separated, and the organic layer was extracted with 5% sodium hydroxide and water several times to remove the methyldiphenylphosphine oxide and di-*n*-octylphosphinic acid. Purification was by recrystallization from petroleum ether (b.p. 65–110°).

Di-*n*-hexylphenacylphosphine oxide and acetonyldi-*n*-hexylphosphine oxide were prepared by the reaction of I with ethyl benzoate and ethyl acetate, respectively. The phenacyl compound was isolated and purified by recrystallization from ether–petroleum ether (b.p. 30–60°) at −80° or vacuum distillation and the acetonyl compound was vacuum distilled.

TABLE II

PHOSPHORYL, HYDROXYL, AND CARBONYL FREQUENCIES OF SOME PHOSPHINE OXIDES

Compound	P—O, cm.$^{-1}$ Solid or liquid	P—O, cm.$^{-1}$ 1% solution in CCl_4	OH, cm.$^{-1}$ Solid or liquid	OH, cm.$^{-1}$ 1% solution in CCl_4	C═O, cm.$^{-1}$ Solid or liquid
1[a]	1110		2500		1715
2	1186				1612 and 1360
3	1170				1715
4	1162				1135
5	1142	1168	3330	3430	
6	1163	1182	3420	3470	
7	1133	1150	3260	3330	
8	1162	1177	3380	3380	
9	1147	1150	3230	3280	
10	1159				
11	1174	1185	3270	3440	
12	1143	1168	3300	3380	
13	1142	1157	3280	3330	
14	1142	1157	3280	3380	
15	1186				
16	1170				1710
17	1173				1680
18	1177				1670
19	1164				
20	1190				
21[b]	1150				
22[c]	1168				

[a] See Table I. [b] Di-*n*-hexylmethylphosphine oxide. [c] Methyldiphenylphosphine oxide.

Phenacyldiphenylphosphine oxide[13] was prepared by treating ethyl benzoate and II. It was recrystallized from acetone.

Physical properties, yields, and analytical data for the compounds prepared are compiled in Table I. Those features of the infrared spectra used in confirming assigned structures are listed in Table II. The spectra described here were obtained with a Perkin–Elmer Model 21 double beam instrument. Liquid samples and low melting solids were scanned as capillary films while the higher melting solid samples were scanned as potassium bromide pellets. The hydroxy-containing phosphine oxides were also scanned in 1% by weight solution of carbon tetrachloride.

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Synthesis of Nitro-olefins from Olefin Dinitrogen Tetroxide Adducts[1]

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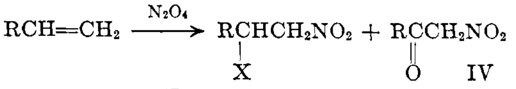
A convenient synthesis has been developed for the direct conversion of 1-octadecene into 1-nitro-1-octadecene and of cyclooctene into 1-nitrocyclooctene in 80% and 95% yields, respectively. The reaction involves addition of the olefin and oxygen to an ethereal solution of dinitrogen tetroxide and subsequent elimination of nitrous and nitric acids from the adducts with triethylamine. Elimination reactions of the independently synthesized intermediates of the addition were studied with several bases. The dependence of the product composition on the amount of oxygen used in the dinitrogen tetroxide–olefin reaction was investigated by quantitative infrared analysis, and the relative rates of elimination were determined. The results led to a nitro-olefin synthesis from a 1-olefin making isolation of any intermediate unnecessary.

Addition of pure dinitrogen tetroxide and oxygen to 1-olefins in ether or ester-type solvents has been shown[2–4] to give dinitro, I, nitro nitrite, II, nitro nitrate, III, and nitro ketone, IV, compounds as the major products.



$$RCH{=}CH_2 \xrightarrow{N_2O_4} \underset{X}{RCHCH_2NO_2} + \underset{O}{\overset{}{RCCH_2NO_2}} \quad IV$$

(I. X = NO_2)
(II. X = ONO)
(III. X = ONO_2)

Oxygen is responsible for the formation of III[2] and IV[3,4]; both are formed at the expense of I. The unstable nitro nitrite, II, is isolated as nitro alcohol V

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