[Contribution from the Aero-Space Division, Boeing Airplane Co.]

Derivatives of Triphenylphosphine and Triphenylphosphine Oxide

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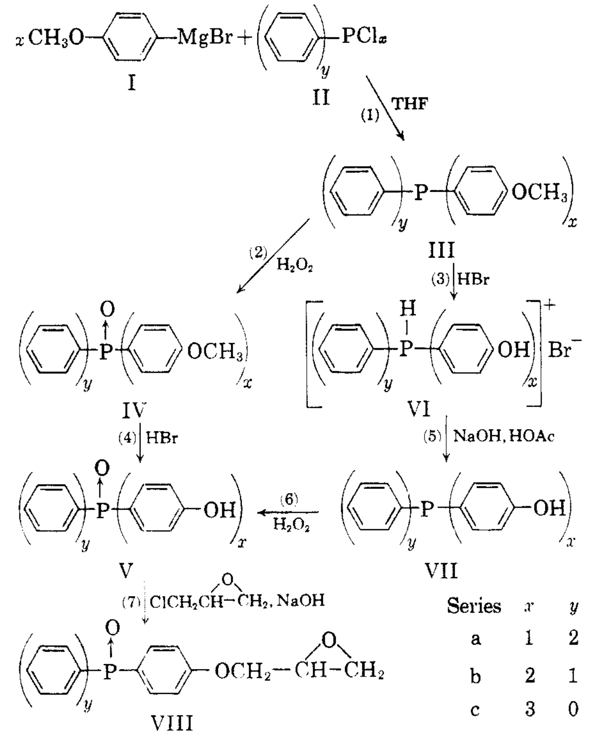
Received March 23, 1960

Synthesis of four monomers, *p*-styryldiphenylphosphine, *p*-glycidyloxyphenyldiphenylphosphine oxide, di(*p*-glycidyloxyphenyl)phenylphosphine oxide, and tri(*p*-glycidyloxyphenyl)phosphine oxide is described.

In view of the high thermal stability of triphenylphosphine oxide[1,2] we have undertaken the synthesis of a group of polymers containing this structure. In this paper we wish to describe the preparations and properties of a number of monomers required for this work.

The mono-, di-, and tri-*p*-hydroxy derivatives of triphenylphosphine and triphenylphosphine oxide were prepared as outlined below. Reactions of the hydroxyphenylphosphine oxides with epichlorohydrin yielded glycidyl ethers in which the triphenylphosphine oxide nucleus replaced the bisphenol A moiety of conventional epoxy resins. The Grignard synthesis of the mono-, di-, and tri-*p*-methoxy derivatives of triphenylphosphine went smoothly in tetrahydrofuran. Although the monofunctional product could be readily isolated by distillation, attempts to distill benzene extracts containing the di- and tri-functional compounds led to strongly exothermic decompositions beginning at about 225°. In large scale syntheses these became uncomfortably vigorous. Extraction with concentrated hydrochloric acid gave very satisfactory separations of products from accompanying tars and from *p,p'*-dimethoxybiphenyl, a principal by-product, and is therefore recommended in spite of its unpleasant features.



Series	x	y
a	1	2
b	2	1
c	3	0

Demethylation by hydrobromic acid (reaction 3) proceeded smoothly, with no sign of phosphorus-phenyl cleavage.[3] Because the free hydroxyphosphines were difficult or impossible to recrystallize, they were isolated and purified as their hydrobromic acid salts.

The hydrogen peroxide oxidations of the methoxyphosphines (reaction 2) and of the hydroxyphosphines (reaction 6) proceeded smoothly in excellent yields. The phosphine oxides were nicely crystalline solids. To obtain satisfactory analyses it was necessary to dry them very thoroughly, as they held traces of solvent tenaciously.

As di(*p*-hydroxyphenyl)phenylphosphine (VIIb) and tri(*p*-hydroxyphenyl)phosphine (VIIc) could not be recrystallized, samples of them were oxidized to the corresponding hydroxyphosphine oxides (Vb and Vc) to establish their identity and purity (reaction 6). The products, obtained in excellent yield, were identical with those prepared by demethylation of the appropriate methoxyphosphine oxides (reaction 4).

The preparation of *p*-vinylphenyldiphenylphosphine (XIII) was carried out by reactions 8–11, following Neville.[4] Attempts to prepare it directly from *p*-styrylmagnesium chloride and diphenylchlorophosphine (reaction 12) led to immediate polymerization instead.[5]

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

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(1) G. N. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, New York, 1950, page 98.

(2) J. W. Dale, I. B. Johns, *et al.*, *Synthesis of 1000°F. Stable Fluids*, paper presented at the Conference on High Temperature Polymer & Fluid Research sponsored by the Wright Air Development Center, May 26–28, 1959.

(3) L. M. Kindley and L. P. Glekas, *Synthesis of Thermally Stable Epoxide Resins for Dielectric Applications.* Quarterly Progress Report No. 5 to Wright Air Development Center, Contract AF 33(616)-5518, September 1959.

(4) R. G. Neville, *J. Org. Chem.*, **21**, 111 (1959).

(5) See J. R. Leebrick and H. E. Ramsden, *J. Org. Chem.*, **23**, 935 (1959) for the preparation of *p*-styrylmagnesium chloride, and A. E. Senear, R. G. Neville, and J. Wirth, *J. Org. Chem.*, **25**, 807 (1960) for a similar resinification reaction with a chlorosilane.

TABLE I

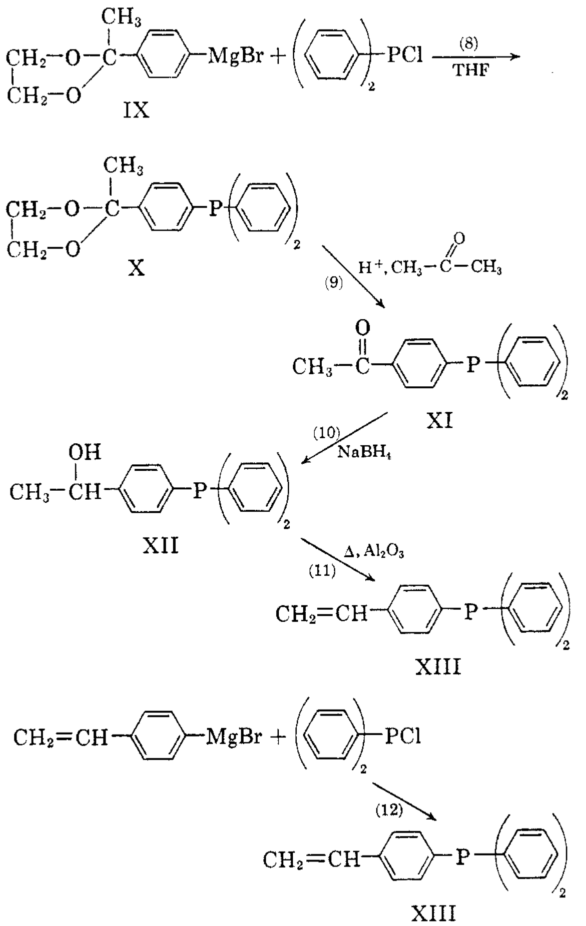
YIELDS, PHYSICAL PROPERTIES, ANALYSES

No.	Compound	Yield, %	M.P.[a]	Recry. Solvent	Calcd., %			Found, %			Comments
					C	H	P	C	H	P[b]	
IIIa	*p*-Methoxyphenyldiphenylphosphine	70	78–79	Methanol							Low melting form only analysed
			68–69	Methanol	78.07	5.86	10.60	78.14	5.90	10.88	See ref. 11
IIIb	Di(*p*-methoxyphenyl)phenylphosphine	75	89–90	Methanol	74.52	5.94	9.61	74.75	5.87	9.56	
IIIc	Tri(*p*-methoxyphenyl)phosphine	45	130–131	Methanol							Previously described, ref. 12
IVa	*p*-Methoxyphenyldiphenylphosphine oxide	93	117–118	Benzene-Pet. ether[d]	74.02	5.56	10.05	74.38	5.99	10.34	
IVb	Di(*p*-methoxyphenyl)phenylphosphine oxide	77	96–97	Benzene-Pet. ether[d]	70.99	5.66	9.16	71.21	5.93	9.06	
IVc	Tri(*p*-methoxyphenyl)phosphine oxide	90	143–144	Benzene	68.46	5.75	8.41	68.65	5.81	8.36	
VIa	*p*-Hydroxyphenyldiphenylphosphine hydrobromide	80	202–203	Methanol-HBr	60.19	4.49		60.26	4.58		Br, calcd. 22.25, found 22.03
VIb	Di(*p*-hydroxyphenyl)phosphine hydrobromide	70	220–221	Methanol-HBr	57.62	4.30		57.70	4.23		Br, calcd. 21.30, found 21.16
VIc	Tri(*p*-hydroxyphenyl)phosphine hydrobromide	70	227–228	Methanol-HBr	55.26	4.12	7.91	55.00	4.02	7.70	Br, calcd. 20.43, found 20.79
VIIa	*p*-Hydroxyphenyldiphenylphosphine	85	113–114	Benzene-Pet. ether[d]	77.65	5.43	11.13	77.97	4.84	10.88	Once recrystallized
			102.5–103.5	Benzene-Pet. ether[d]				77.43	5.23	[c]	After five recrystallizations
VIIb	Di(*p*-hydroxyphenyl)phenylphosphine	85	Oil								Yield based upon conversion to phosphine oxide
VIIc	Tri(*p*-hydroxyphenyl)phosphine	95	130–138								Could not be recrystallized
Va	*p*-Hydroxyphenyldiphenylphosphine oxide										
	(a) By oxidation	96	243–244	Methanol	73.45	5.14	10.53	73.20	5.00	10.66	
	(b) By hydrolysis	91									
Vb	Di(*p*-hydroxyphenyl)phenylphosphine oxide										
	(a) By oxidation	85	233–234	Methanol	69.68	4.87	9.98	69.45	4.95	9.81	
	(b) By hydrolysis	80									
Vc	Tri(*p*-hydroxyphenyl)phenylphosphine oxide										
	(a) By oxidation	95	273–275	Methanol	66.26	4.63	9.49	65.98	4.44	9.04	
	(b) By hydrolysis	95									
VIIIa	*p*-Glycidyloxyphenyldiphenylphosphine oxide		Oil								Epoxide equivalent, calcd. 350, found 453
VIIIb	Di(*p*-glycidyloxyphenyl)phenylphosphine oxide		Oil								Epoxide equivalent, calcd. 211, found 300
VIIIc	Tri(*p*-glycidyloxyphenyl)phosphine oxide		Oil								Epoxide equivalent, calcd. 165, found 210

TABLE I (*Continued*)

No.	Compound	Yield, %	M.P.[a]	Recry. Solvent	Calcd., % C	Calcd., % H	Calcd., % P	Found, % C	Found, % H	Found, % P[b]	Comments
X	2-Methyl-2-(4'-diphenylphosphinylphenyl)-1,3-dioxolane	71	73–74	Ethanol	75.84	6.08	8.89	76.15	6.24	9.32	Yield of oil, contaminated with XI
XI	*p*-Acetylphenyldiphenylphosphine	82	121–122	Acetone	78.93	5.63	10.18	78.90	5.96	10.24	Yield from oily intermediate (X)
XII	*p*-(1'-Hydroxyethyl)phenyldiphenylphosphine	99	Oil								
XIII	*p*-Styryldiphenylphosphine	38	75.0–75.5	Methanol	83.31	5.94	10.74	83.28	6.22	10.62	Yield based on acetyl compound (XI)

[a] Melting point of analytical sample. [b] Phosphorus analyses by Schöniger method, see K. Fleisher, *et al.*, *Anal. Chem.*, **30**, 152 (1958). [c] Formation of a precipitate following solution of the magnesium ammonium phosphate and fading of the titration end-point interfered with this phosphorus determination. [d] B.p. 30–60°.



II. The spectra were determined using potassium bromide pellets, and measured in a Perkin-Elmer Model 12 single beam spectrophotometer with sodium chloride optics.

EXPERIMENTAL[6]

Diphenylchlorophosphine (IIa).[7] In a 5-l. flask attached to a 2-foot, unwrapped Vigreux column were mixed 4650 g. (26.0 moles) of phenyldichlorophosphine[8] (IIb) and 175 g. of anhydrous aluminum chloride. The mixture was heated so that phosphorus trichloride distilled off the top of the column at 85–95° as it was formed by redistribution. After 20 hr. 700 ml. (8.0 moles) had been collected. The pot residue was distilled *in vacuo* through a fractionating column to yield 1015 ml. (7.5 moles) of unchanged phenyldichlorophosphine, b.p. 90–95°/1 mm., followed by 1624 g. (7.35 moles) of diphenylchlorophosphine, b.p. 145–147°/1 mm., (79%, based on consumed starting material).[9]

p-Methoxyphenyldiphenylphosphine (IIIa). To the Grignard reagent prepared from 112 g. (0.60 moles) of *p*-bromoanisole in 250 ml. of tetrahydrofuran was added a solution

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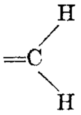
(6) All melting points were measured in glass capillaries immersed in a heated silicone bath, and are uncorrected.

(7) Although this compound has been described frequently [see reference 1, page 55, also F. G. Mann and I. T. Miller, *J. Chem. Soc.*, 4453 (1952) and B. A. Arbuzov and N. P. Grechlin, *Zhur Obschei Khim.*, **20**, 107 (1950); cf. *Chem. Abstr.*, **44**, 5832 (1950)], this method is presented as it conveniently furnishes a good yield with easily available starting material.

(8) Available from Victor Chemical Co., Chicago Heights, Ill.

TABLE II

INFRARED SPECTRA, CM.$^{-1}$

Compound	Phenyl, Monosubstituted	Phenyl p-Substituted	C—O, Ether or Phenolic	P—O	P—C_6H_5	—CH_3 bend	Aromatic C=C	OH Region	Comments
IIIa	696, 746	833	1247		1424	1451	1494, 1566, 1590		p-Substitution and methyl bending bands increase in intensity on going from mono- to trifunctional
IIIb	697, 753	831	1247		1429	1449	1494, 1566, 1592		
IIIc		831	1247		1437	1451	1494, 1566, 1590		
IVa	704, 728	838	1259	1174–1178	1426	1451	1499, 1563, 1596		
IVb	704, 726	831	1259	1175	1434	1455	1499, 1570, 1600		
IVc		805	1252	1176	1439	1455	1449, 1566, 1596		
VIa	683, 738	843	1117, 1294		1432		1497, 1577, 1600	3021	P-H at 2257
VIb	683, 746	846	1118, 1283		1424		1494, 1576, 1600	3067	P-H at 2328
VIc		830	1115, 1283		1424		1494, 1576, 1600	3130, 3257	P-H at 2358
VIIa	697, 743	833	1093, 1217		1426		1494, 1582, 1596	3280	
VIIb	697, 746	826	1093, 1245		1429		1503, 1582, 1604	3280	
VIIc		830	1115, 1247		1429		1497, 1583, 1604	3416	
Va	692, 729	836	1117, 1285	1158–1166	1429		1499, 1574, 1600	3021	
Vb	694, 728	831	1120, 1276	1156	1432		1497, 1586, 1604	3106	
Vc		831	1118, 1276	1171	1426		1997, 1582, 1604	3179	
VIIIa	709, 754	831	1026, 1258	1183	1437		1500, 1570, 1596	3390	Oxirane bands at 863, 919, 1163
VIIIb	700, 754	833	1026, 1255	1176	1434		1497, 1570, 1592	3205	Oxirane bands at 865, 919, 1163
VIIIc		831	1024, 1255	1176	1429		1503, 1574, 1596	3257	Oxirane bands at 863, 916, 1160
X	697, 746	831	1255		1429		1476, 1590		Ketal doublet at 1041, 1071
XI	697, 746	826	1265		1424		1476, 1592		C=O strong at 1680
XII	696, 746	830	1082		1426		1476, 1586	3311	Variable band at 2392[a]
XIII	696, 750	838			1426		1478, 1590		C=C at 1628,  at 919

[a] This band, absent in some preparations and very strong when treatment of the reaction mixture with acid was omitted, was attributed to residual B—H structures in the oily product. Its presence or absence did not materially affect the subsequent dehydration of the carbinol.

of 90 g. (0.40 mole) of diphenylchlorophosphine in 50 ml. of tetrahydrofuran.[10] The mixture was refluxed 1 hr. and poured over ice-hydrochloric acid. The product was extracted into benzene, washed, dried, and distilled to yield 97 g. of yellow oil, b.p. 195–225°/5 mm. Trituration with methanol caused the oil to crystallize, and recrystallization from 1 l. of methanol gave 82 g. (70%) of colorless crystals, m.p. 78–79°.[11]

Di(p-methoxyphenyl)phenylphosphine (IIIb). A mixture of 3.0 moles of p-methoxyphenylmagnesium bromide and 1.25 moles of phenyldichlorophosphine in 3 l. of tetrahydrofuran

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(9) CAUTION: At the end of the distillation a waxy yellow solid collected in the still head. While hot, both this material and the still pot residue would ignite on contact with air. After cooling, air could be carefully admitted, and these materials rinsed out with acetone.

(10) Substitution of p-chloroanisole (Ansul Chemical Co.) gave comparable yields, and the Grignard formed readily in tetrahydrofuran. Tetrahydrofuran was preferred to ether, as it held complexes of the reaction products in solution, greatly facilitating working up the products.

(11) In our first preparation a metastable crystalline form, m.p. 68–69°, was isolated, recrystallized, and analysed. Both forms gave quantitative yields of p-methoxyphenyldiphenylphosphine oxide (IVa) upon oxidation, and had identical infrared spectra. The lower melting form yielded the higher melting one when seeded with the latter during recrystallization.

was refluxed 3 hr., poured over ice, and acidified with hydrochloric acid. After standing overnight to allow the tetrahydrofuran to evaporate, the product was taken up in benzene, washed with water, and extracted with four 1-l. portions of concd. hydrochloric acid. The acid extracts were cautiously neutralized with concd. ammonia giving an oil which solidified on cooling. The solid was filtered, washed, dried, and recrystallized from 2 l. of methanol to yield 271 g. (75%) of colorless crystals, m.p. 85–90°. Upon a second crystallization the melting point became 89–90°.

Tri(p-methoxyphenyl)phosphine (IIIc).[12] This compound was prepared in 45% yield by treating in tetrahydrofuran 6.0 moles of *p*-methoxyphenylmagnesium bromide[10] with 1.8 moles of phosphorus trichloride, and isolating the product by the procedure described above for the dimethoxy compound.

Mono-, di-, and tri-p-methoxy derivatives of triphenylphosphine oxide (IVa, b, c). To the methoxyphosphine suspended in 4–8 volumes of acetone was slowly added enough 10% hydrogen peroxide to furnish 1.1 moles of the latter per mole of phosphine.[13] During the vigorous exothermic reaction the solids dissolved. The acetone was allowed to evaporate, and the products taken up in benzene, washed peroxide free with ferrous ammonium sulfate solution, and dried. Evaporation of the benzene left the phosphine oxides as readily crystallizable oils. The mono- and trimethoxy compounds recrystallized easily. To avoid oiling out the dimethoxy derivative, careful addition of petroleum ether (b.p. 30–60°) to a dilute benzene solution at room temperature, followed by refrigeration was necessary; the yield was lowered by recrystallization losses.

p-Hydroxyphenyldiphenylphosphine hydrobromide (VIa). Fifty-nine grams (0.2 mole) of *p*-methoxyphenyldiphenylphosphine (IIIa) and 150 ml. of 48% hydrobromic acid were refluxed under nitrogen 4 hr. A 6.5-ml. sample (65%) of methyl bromide collected in a cold trap attached to the condenser top. On chilling 61.8 g. (80%) of crystalline product, m.p. 200–203°, came out of solution. Recrystallization from 160 ml. of methanol and 10 ml. of hydrobromic acid gave 55.1 g. (71%) of colorless crystals, m.p. 202.5–203.5° dec.

Di-(p-hydroxyphenyl)phenylphosphine hydrobromide (VIb) *and tri(p-hydroxyphenyl)phosphine hydrobromide* (VIc). These compounds were prepared in the same fashion as the mono functional analog, in yields of 70% following recrystallization.

p-Hydroxyphenyldiphenylphosphine (VIIa). The phosphine hydrobromide (VIa) prepared above was dissolved in 500 ml. of 3% sodium hydroxide solution. The free phosphine, precipitated by the slow addition of acetic acid, came down as an oil and then solidified. After 4 days *in vacuo* it melted over a wide range, 87–112°, and weighed 40.4 g. (theory is 36.7 g.). It was dissolved in 200 ml. of benzene and refluxed. By means of a Dean Stark trap 4.5 ml. of water was removed. After addition of 200 ml. of petroleum ether (b.p. 30–60°) to the dried benzene solution, chilling caused 31.3 g. (85%) of crystalline product, m.p. 110–112° to form. This represents an over-all yield of 60% from *p*-methoxyphenyldiphenylphosphine.

During the course of several recrystallizations from benzene-petroleum ether (b.p. 30–60°) the melting point of the hydroxyphenylphosphine dropped to 102.5–103.5°, and then remained constant. The infrared spectrum was unaltered during this change, and was in agreement with the proposed structure. Both forms were reconverted quantitatively to *p*-hydroxyphenyldiphenylphosphine hydrobromide (VIa) on recrystallization from methanol–hydrobromic acid, and yielded *p*-hydroxyphenyldiphenylphosphine oxide (Va) on oxidation.

Di(p-hydroxyphenyl)phenylphosphine (VIIb) *and tri(p-hydroxyphenyl)phosphine* (VIIc). The phosphine hydrobromides were converted to the free bases by solution in sodium hydroxide and precipitation with acetic acid. The dihydroxy compound was a noncrystallizable oil. The trifunctional product yielded a taffy-like precipitate which gradually solidified. After grinding with water, washing salt-free, and drying, it melted at 130–138°. Attempted recrystallization led to oils. The high yields, 85% and 95%, of the di- and trihydroxy phosphine oxides, obtained by oxidation (see below), confirm the compositions of these products.

p-Hydroxyphenyldiphenylphosphine oxide (Va). a. *By hydrolysis.* A suspension of 70.4 g. (0.23 mole) of *p*-methoxyphenyldiphenylphosphine oxide (IVa) in 250 ml. of 48% hydrobromic acid was refluxed 3.5 hr. Twelve milliliters (97%) of methyl bromide was isolated. After cooling, the acid phase was discarded, and the oily residue dissolved in dilute sodium hydroxide and precipitated with acetic acid. Recrystallization of the tan powder from 500 ml. of methanol gave 82.7 g. (91%) of crystals, m.p. 237–239°.

b. *By oxidation.* Addition of a slight excess of 10% hydrogen peroxide to a solution of *p*-(hydroxyphenyl)diphenylphosphine in six volumes of acetone produced a vigorous reaction. As the acetone evaporated a product, identical with the hydrolysis product above, crystallized out in 96% yield.

Di(p-hydroxyphenyl)phenylphosphine oxide (Vb) *and tri(p-hydroxyphenyl)phosphine oxide* (Vc). Hydrogen peroxide oxidation of the oily difunctional phenol (VIIb) produced the phosphine oxide in 85% yield, based on the hydrogen bromide salt precursor of the free base. Hydrobromic acid demethylation of di(*p*-methoxyphenyl)phenylphosphine oxide (IVb) gave the same product in 80% yield. Similarly tri(*p*-hydroxyphenyl)phosphine oxide was prepared in 95% yield both by oxidation of crude tri(*p*-hydroxyphenyl)-phosphine and by demethylation of tri(*p*-methoxyphenyl)-phosphine oxide.

Mono-, di-, and tri(p-glycidyloxy)triphenylphosphine oxide (VIIIa, b, c). Following the reactions of epichlorohydrin with the hydroxyphenylphosphine oxides as described by Lee and Neville for bisphenol A,[14] the products were taken up in benzene, and washed salt free. Solvent stripping *in vacuo* left viscous oils. The epoxide equivalents shown in Table I indicate that some opening of the epoxide ring had occurred during reaction. The products could be converted to tough, strong, adherent resins by reaction with such typical epoxy curing agents as amines, acid anhydrides, and boron trifluoride.

2-Methyl-2-(4′-diphenylphosphinylphenyl)-1,3-dioxolane (X). To the Grignard reagent from 529 g. (2.18 moles) of 2-(4′-bromophenyl)-2-methyl-1,3-dioxolane (IX)[4] and 58 g. (2.40 moles) of magnesium in 1.5 l. of tetrahydrofuran was added slowly a solution of 386 g. (1.75 moles) of diphenylchlorophosphine in 0.5 l. of tetrahydrofuran. After refluxing 1.5 hr. the solution was poured over cracked ice and the product extracted into benzene. Emulsification made this a tedious procedure. After drying, the benzene solution was distilled to yield a crystalline fraction, b.p. 120–130°/25 mm. (probably 2-phenyl-2-methyl-1,3-dioxolane), and a product-containing fraction, b.p. 200–300°/3.5 mm., weighing 423 g. (71%), mainly distilling at 235–255°/3.5 mm.

Trituration with 300 ml. of ethanol caused the oil to crystallize. The crystals, m.p. 63–70°, were shown by infrared spectroscopy to consist mainly of ketal (X), with some ketone (XI) as impurity, probably formed by hydrolysis during work-up. Although ketone-free ketal, m.p. 73–74° could be prepared by ethanol recrystallization, this product was converted directly to the ketone without purification.

p-Acetylphenyldiphenylphosphine (XI). The crude crystalline product from the previous reaction was dissolved in 2 l.

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(12) F. G. Mann and E. Chaplin, *J. Chem. Soc.*, 527 (1937).

(13) R. Letsinger, J. Nazy, and A. Hussey, *J. Org. Chem.*, **23,** 1806 (1958).

(14) H. Lee and K. Neville, *Epoxy Resins.* McGraw-Hill Book Co., Inc., New York, 1957.

of acetone containing 10 g. of *p*-toluenesulfonic acid. Following 3 hr. of reflux the solution was neutralized with methanolic sodium hydroxide solution and, after filtering out sodium *p*-toluenesulfonate, concentrated to 800 ml. On chilling 220 g. of product, m.p. 117–119°, crystallized.

The ethanolic mother liquor from the ketal preparation was evaporated, and the residual oil treated with acetone and *p*-toluenesulfonic acid as described above to give an additional 35 g. of ketone. By concentration of the combined acetone mother liquors 48 g. of impure ketone was obtained, making the overall yield of ketone (XI) 58%, based upon the original diphenylchlorophosphine.

p-(1'-Hydroxyethyl)phenyldiphenylphosphine (XII). To a suspension of 254 g. (0.84 mole) of *p*-acetylphenyldiphenylphosphine (XI) in 1.2 l. of methanol was slowly added a solution of 32 g. (0.84 mole) of sodium borohydride in 0.5 l. of methanol. Mild cooling was needed to keep the temperature below 30°. After standing overnight 150 ml. of glacial acetic acid and 200 ml. of water were added. Four hours later 1.5 l. of water was added and the product was taken up in benzene and washed with dilute hydrochloric acid, dilute base, and water. Removal *in vacuo* of the benzene left 254 g. (99%) of a very viscous oil which resisted crystallization. The infrared spectrum (Table II) confirmed its structure.

p-Styryldiphenylphosphine (XIII). Over a 4-hr. period a solution of 253 g. (0.83 mole) of the carbinol (XII) in 250 ml. of toluene was dropped into a 40 cm. × 25 mm. column filled with 7–10 mesh activated alumina. The column was heated to 400°, with an exit pressure of 2–5 mm. and an inlet pressure of 15–20 mm. The tendency of the product to crystallize in the condenser below the column caused some difficulty.

From the Dry Ice trap protecting the vacuum pump approximately one-third of the toluene and 8 ml. (53%) of water were isolated. Addition of 500 ml. of methanol to the toluene solution of the product caused 46.2 gm. of white crystals, m.p. 74–76°, to form. By removing all the solvent *in vacuo* from the mother liquor, and treating the oily residue with methanol, an additional 34.1 g. of product was obtained, giving a total yield of 38%.

Acknowledgment. We wish to thank Dr. Murray Taylor of this laboratory for the microanalyses reported, and Mr. Harry Goldberg and Miss Carolyn Aldrich for measurements of infrared spectra.

SEATTLE, WASH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

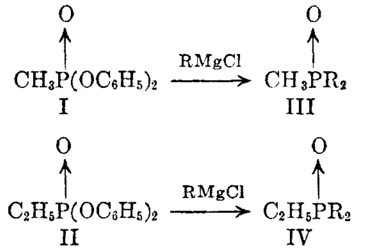
The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. VII. Phosphorus-Containing Dienes[1]

K. DARRELL BERLIN[2] AND GEORGE B. BUTLER

Received May 9, 1960

Two unsymmetrical trialkylphosphine oxides, dimethallylmethylphosphine oxide and dimethallylethylphosphine oxide, have been synthesized. Polymerization of these monomers was initiated with α,α'-azobisisobutyronitrile and afforded soluble polymers. An intrinsic viscosity determination on a sample of poly(dimethallylmethylphosphine oxide) indicates it is of low molecular weight. Conversions to polymer are low for both oxides, and it is suggested that the presence of a large number of active hydrogen substituents may cause excessive degradative chain transfer.

The formation of linear polymers, *via* cyclic polymerization, from certain unsaturated, tertiary phosphine oxides has been reported from two independent studies.[3,4] Extension of this idea to include unsymmetrical trialkylphosphine oxides prompted this investigation. Dimethallylmethylphosphine oxide(III) and dimethallylethylphosphine oxide(II) were synthesized by treatment of the appropriate phosphonate with an excess of the methallyl Grignard reagent under forcing conditions. The yields approximated 50% in both cases. Preparation of diphenylmethylphosphonate (I)



$$\underset{\text{I}}{\mathrm{CH_3\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2}} \xrightarrow{\text{RMgCl}} \underset{\text{III}}{\mathrm{CH_3\overset{\overset{O}{\uparrow}}{P}R_2}}$$

$$\underset{\text{II}}{\mathrm{C_2H_5\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2}} \xrightarrow{\text{RMgCl}} \underset{\text{IV}}{\mathrm{C_2H_5\overset{\overset{O}{\uparrow}}{P}R_2}}$$

R = Methallyl

was by the method recorded in the literature.[5] The scheme below afforded diphenyl ethylphosphonate (II)[6,7] in an overall yield of 36%.

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract Number AF 33(616)-5616, Part I. Reproduction in whole or in part is permitted for any purpose of the United States government.

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