reddish crystalline solid. This substance was decolorized with Norit in methanol and crystallized to provide 3.0 g. (0.013 mole, 83.5%) of pale yellow needles of *o*-nitrodiphenylacetylene with m.p. 43–44°, $-C\equiv C-$ at 4.57, NO_2 at 6.55 and 7.50μ.

Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.34; H, 4.04; N, 6.28; mol. wt., 223. Found: C, 75.43; H, 4.36; N, 6.85; mol. wt., 217.

***p*-Carboxydiphenylacetylene.**—A mixture of 4.5 g. (0.0183 mole) of *p*-iodobenzoic acid, 3.0 g. (0.018 mole) of cuprous phenylacetylide and 100 ml. of pyridine warmed at 110° for 8 hr. yielded a brown crystalline solid. The substance was decolorized with Norit in methanol and recrystallized from chloroform–petroleum ether to give 3.4 g. (0.0153 mole, 85%) of white needles of *p*-carboxydiphenylacetylene having m.p. 221–222° (lit.[27] m.p. 220.5–221°), $-C\equiv C-$ at 4.55 μ.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.08; H, 4.51; mol. wt., 222. Found: C, 80.70; H, 4.71; mol. wt., 219.

***p*-Hydroxydiphenylacetylene.**—A mixture of 4.0 g. (0.018 mole) of *p*-iodophenol, 3.4 g. (0.0206 mole) of cuprous phenylacetylide, and 160 ml. of pyridine warmed at 125° for 8 hr. provided 3.4 g. of a reddish oil. The substance was decolorized with Norit in methanol and crystallized from petroleum ether to yield 2.9 g. (0.015 mole, 82%) of white needles of *p*-hydroxydiphenyl acetylene having m.p. 83–84°, $-C\equiv C-$ at 4.58, OH at 2.9–3.1 μ.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.60; H, 5.15. Found: C, 86.43; H, 5.03.

***p*-Aminodiphenylacetylene.**—A mixture of 5.35 g. (0.025 mole) of *p*-iodoaniline, 4.0 g. (0.024 mole) of cuprous phenylacetylide, and 100 ml. of pyridine warmed at 125° for 24 hr. upon work-up.[28] afforded a red oil. This substance was decolorized with Norit in methanol and recrystallized from chloroform–petroleum ether to yield 3.6 g. (0.0185 mole, 76%) of fine pale yellow needles of *p*-aminodiphenylacetylene. A further recrystallization gave 2.7 g. of white needles with m.p. 128–129° (lit.[29] m.p. 126–127°), $-C\equiv C-$ at 4.55, NH_2 at 2.95 and 3.05 μ.

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.05; H, 5.70; N, 7.25. Found: C, 87.02; H, 5.85; N, 7.14.

2-Phenylbenzofuran.—A mixture of 4.03 g. (0.0183 mole) of *o*-iodophenol, 3.0 g. (0.0184 mole) of cuprous phenylacetylide, and 100 ml. of pyridine warmed at 125° for 7 hr. provided 3.8 g. of a brown crystalline solid. The substance was decolorized with Norit in methanol and recrystallized from petroleum ether to yield 3.4 g. (0.0175 mole, 85%) of white platelets of 2-phenylbenzofuran having melting point and mixture melting point with an authentic sample of 120–121°. The infrared spectrum of the product was identical with that of an authentic sample.

This reaction was carried out in other solvents, but in no case did the yield exceed that in pyridine. The solvents[30] employed and the yields of of 2-phenylbenzofuran obtained were dimethyl sulfoxide, 79%; dimethylformanide, 81%; ethylene glycol, 70%; and acetic acid, 83%.

3-Phenylisocoumarin.—A mixture of 4.5 g. (0.204 mole) of *o*-iodobenzoic acid, 3.0 g. (0.0182 mole) of cuprous phenylacetylide, and 100 ml. of pyridine warmed at 125° for 6 hr. provided a tan solid which was recrystallized from methanol–water to yield 3.8 g. (0.0171 mole, 94%) of colorless 3-phenylisocoumarin with m.p. 90–91° (lit.[31] m.p. 91–92°), C=O at 5.70 μ.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.09; H, 4.50; mol. wt., 222. Found: C, 80.88; H, 4.69; mol. wt., 222.

2-Phenylindole.—A mixture of 4.0 g. (0.0175 mole) of *o*-iodoaniline, 3.0 g. (0.0182 mole) of cuprous phenylacetylide, and 100 ml. of pyridine at 125° for 8 hr. afforded a brownish solid. The substance was recrystallized from petroleum ether to yield 3.0 g. (0.0155 mole) of small white plates of 2-phenylindole having melting point and mixture melting point with an authentic sample of 189°. The infrared spectrum of the product was identical with an authentic sample.

2-*n*-Propylindole.—A mixture of 7.55 g. (0.0344 mole) of *o*-iodoaniline, 4.50 g. (0.0346 mole) of cuprous *n*-propylacetylide, and 100 ml. of pyridine was warmed at 125° for 6 hr. The work-up was like that described for *p*-methoxytolane except that the ether extracts were washed rapidly with cold very dilute (1%) hydrochloric acid followed immediately by the sodium bicarbonate and water washings. The dried (potassium carbonate) ether extracts upon concentration afforded 6 g. of a dark oil. This substance was fractionated through a small Vigreux column to yield 4.9 g. (0.0308 mole, 89%) of 2-*n*-propylindole having b.p. 93° (0.3 mm.). The material could not be induced to crytsallize.[32] The infrared spectrum of ths product was very similar to authentic 2-methylindole. The ultraviolet was characteristic of indoles, λ_{max} 219 and 260 mμ (weak, broad). A pine splint test was positive.

Anal. Calcd. for $C_{11}H_{13}N$: C, 83.02; H, 8.18; N, 8.80. Found: C, 82.90; H, 8.18; N, 8.80.

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[27] K. Koch and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3443 (1953).

[28] The ether extracts were washed six times with water only.

[29] L. M. Litvinenko, *et. al.*, *Zh. Obshch. Khim.*, **28**, 2046 (1958); *Chem. Abstr.*, **53**, 2154*a* (1959).

[30] The work-up in these solvents was the same as that described for *p*-methoxytolane except that before ether extraction the solution was diluted with 400 ml. of water and the ether extracts were washed with water only.

[31] S. Gabriel, *Ber.*, **18**, 2445(1885).

[32] A melting point of 34° has been reported: A. Verley and J. Beduwe, *Bull. soc. chim. France*, **37**, 189 (1925).

Synthesis of Unsymmetrical Diarylphosphinous Chlorides and Their Conversion to Secondary Phosphine Oxides[1,2]

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The reduction with aluminum of six aryldiazonium fluoroborate–arylphosphonous dichloride reaction products (presumably $Ar_2PCl_2{}^+BF_4{}^-$) has produced diarylphosphinous chlorides in roughly 30–50% yield. This reaction offers a new route to unsymmetrical diarylphosphinous chlorides, which have remained relatively obscure up to the present study. It also was found that the phosphinous chlorides can be hydrolyzed on addition to water to produce diarylphosphine oxides in good yield and purity. Unsymmetrical diaryl phosphine oxides have not hitherto been available.

Recent reports from this laboratory[3] have described a new synthesis of arylphosphonous dichlorides, based on reactions 1 and 2. Reaction 1, conducted in dry solvents, was first observed by Doak and Freedman.[4] Structure I has been suggested,[5] but not established, for the product. This intermediate, which is not isolated, has been widely used[6] as a precursor of phosphonic acids which are formed on hydrolysis. The occurrence of reaction 2 was anticipated because of the resemblance of I to other structures capable of under-

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[1] A portion of this work was presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, and was the subject of a preliminary communication [L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **27**, 4120 (1962)]; taken from the Ph.D. dissertation of R. E. Montgomery, Duke University, 1963.

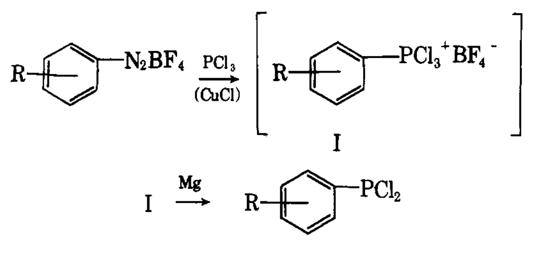
[2] Supported by Research Grant CY-5507 from the National Cancer Institute, Public Health Service.

[3] L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **82**, 3795 (1960); **83**, 4124 (1961).

[4] G. O. Doak and L. D. Freedman, *ibid.*, **73**, 5658 (1951).

[5] P. C. Crofts, *Quart. Rev.* (London), **12**, 341 (1958).

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

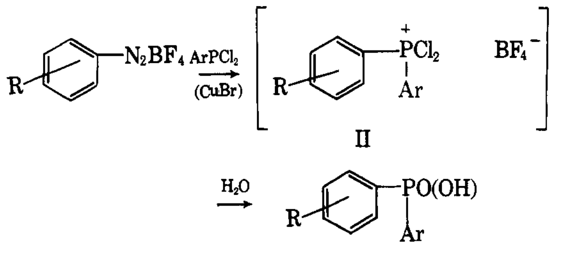


(1)

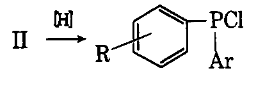
(2)

going reduction; a considerable body of information has been published recently on the reduction of compounds of general structure $[R_nPX_{4-n}^+][A^-]$, where $n = 1, 2$, or 3, to tricovalent compounds.[7]

Freedman and Doak[8] have also described the reaction of alkyl- and arylphosphonous dichlorides with aryldiazonium fluoroborates; the product II was used with-



out isolation as a source of phosphinic acids. Intermediate II, because of its resemblance to I, also appeared to us to be capable of reduction; in this case phosphinous chlorides would be the expected products. It is the purpose of this paper to describe the realization



III

of this reaction, and to demonstrate its value in synthesis of a variety of diarylphosphinous chlorides. The utilization of these products in the synthesis of diarylphosphine oxides will also be demonstrated.

Relatively little attention has been given in the past to the diarylphosphinous chlorides, except for the parent compound. Diphenylphosphinous chloride, now commercially available,[9] has been prepared by several methods. Kosolapoff[10] has summarized the older ones; three attractive new methods have since been described.[7b,11,12] Several symmetrically substituted diarylphosphinous chlorides also have been obtained by some of these methods. Unsymmetrically substituted compounds, only four of which are known,[10] are best prepared by reaction of a diarylmercury with an arylphosphonous dichloride.[13] None of the other known methods are likely to prove generally useful for the unsymmetrical cases, and a need for new synthetic methods is evident.

The reduction of six intermediates of structure II to diarylphosphinous chlorides has now been accomplished by stirring them with aluminum for several hours at 30–50°. The yields lie in the 30–50% range, but the synthesis nevertheless appears attractive as a means of obtaining a variety of unsymmetrical diarylphosphinous chlorides. It is particularly useful when an unsubstituted phenyl group is desired on phosphorus, because commercially available phenylphosphonous dichloride may then be used in reaction with a diazonium salt.

Identification of the products as phosphinous chlorides was accomplished by elemental analysis and by converting them to diarylphosphinic acids (Table I). These acids were formed in high yield by potassium permanganate oxidation of the hydrolysis products of the chlorides. Phenyl(*m*-trifluoromethylphenyl)- and (*m*-chlorophenyl)(*p*-chlorophenyl)phosphinous chlorides have so far failed to give crystalline acids, but solid *p*-toluidine salts of these acids were readily obtained.

Aluminum[14] was the only reducing agent used in this work, although magnesium had been employed in the arylphosphonous dichloride synthesis.[3] It is now felt that aluminum is preferred for both syntheses; yields in the phosphonous dichloride synthesis, an example of which is described in Experimental, were slightly superior with aluminum, and product work-up was less difficult. One equivalent of aluminum was generally used, but only a portion, corresponding roughly to the yield of product, was consumed. Interestingly, in the phosphonous dichloride synthesis,[3] a full equivalent of magnesium is consumed. Since the yields of phosphonic acids by the Doak–Freedman method and of phosphonous dichlorides by either aluminum or magnesium reduction are roughly comparable, it appears that reactions causing consumption of magnesium beyond that required for reduction of the I present must not involve I or its reduction product. This was also indicated[3] by the failure of a 50% reduction in the amount of magnesium to show any effect on the yield. Garner and Tedeschi[15] have described the involvement of magnesium in a reaction with diphenylphosphinous chloride and tetrahydrofuran, and have also mentioned that a reaction occurs between magnesium, phenylphosphonous dichloride, and ethyl acetate. Conditions used in the reduction of I by magnesium apparently do not permit this reaction to occur to a significant extent.

Product isolation in the first two preparations was accomplished by the direct distillation of the reduction mixture, after removal of unreacted aluminum. The products (III, R = *p*-Cl or *p*-CN, Ar = C_6H_5) were obtained in satisfactory yield and purity, but the distillation was made difficult by the large solid residue developing in the still. An alternative procedure,

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[7] See, for example: (a) L. D. Quin and C. H. Rolston, *J. Org. Chem.*, **23**, 1693 (1958), and references cited therein; (b) C. Stuebe, W. M. LeSuer, and G. R. Norman, *J. Am. Chem. Soc.*, **77**, 3526 (1955); (c) I. P. Komkov, K. V. Karavanov, and S. Z. Ivin, *Zh. Obshch. Khim.*, **28**, 2963 (1958); (d) V. A. Ginsburg and A. I. Iakubovich, *ibid.*, **28**, 728 (1958); (e) G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960); (f) L. Horner, H. Hoffmann, and P. Beck, *Ber.*, **91**, 1583 (1958); (g) J. L. Ferron, *Can. J. Chem.*, **39**, 842 (1961); (h) M. I. Kabachnik and E. N. Tsvetkov, *Zh. Obshch. Khim.*, **31**, 684 (1961).

[8] L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **74**, 2884 (1952).

[9] Victor Chemical Division, Stauffer Chemical Co., Chicago, Ill.

[10] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Chap. 3.

[11] (a) A. E. Senear, *J. Org. Chem.*, **25**, 2001 (1960); (b) M. P. Brown and H. B. Silver, *Chem. Ind.* (London), 24 (1961).

[12] M. Sander, *Ber.*, **93**, 1220 (1960).

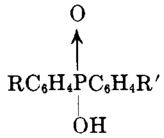
[13] See, for example, W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944).

[14] Success was experienced only with a granular form of aluminum; flake aluminum (Aluminum Co. of America Alflake 1) gave no reduction. Aluminum powder has not yet been tried.

[15] A. Y. Garner and A. A. Tedeschi, *J. Am. Chem. Soc.*, **84**, 4734 (1962).

TABLE I

PROPERTIES OF PHOSPHINIC ACIDS OR *p*-TOLUIDINE SALTS



$$RC_6H_4\overset{\overset{O}{\uparrow}}{\underset{OH}{|}}{P}C_6H_4R'$$

R	R′	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
			A. Phosphinic acids						
p-Cl	H	158.5–159.5[a]	$C_{12}H_{10}ClO_2P$[b]	57.05	56.96	3.99	3.97	12.26	12.24
p-COOH	H	258–260[c]	$C_{13}H_{11}O_4P$[d]	59.55	59.75	4.23	4.35	11.81	11.86
m-Cl	H	159–160[c,e]	$C_{12}H_{10}ClO_2P$	57.05	56.90	3.99	3.86	12.26	12.23
p-Br	H	173.5–174.5[c,f]							
			B. *p*-Toluidine salts of phosphinic acids						
m-CF$_3$	H	170–171[c]	$C_{20}H_{19}F_3NO_2P$	61.07	61.13	4.87	4.95	7.87	8.05
p-Cl	*m*-Cl	175 dec.[g]	$C_{19}H_{18}Cl_2NO_2P$	57.88	58.10	4.86	4.71	7.86	7.96

[a] Recrystallized from chloroform–carbon tetrachloride (1:4, v./v.), then aqueous ethanol. [b] Neut. equiv.: calcd., 252.6. found, 252.2. [c] Recrystallized from aqueous ethanol. [d] Neut. equiv.: calcd., 131.1. found, 132.1. [e] Lit.[8] m.p. 159–162°. [f] Lit.[13] m.p. 174.5°. [g] Recrystallized from 1-butanol–ether.

adopted in subsequent preparations, involved first the distillation of solvent from the reduction mixture, and then the subjection of the residue to extraction with an alkane (heptane or cyclohexane). The extract left little residue after distillation of the phosphinous chloride. Small amounts of the product of displacement of the diazonium group by chloride, as well as some unchanged arylphosphonous dichloride, were occasionally obtained in the distillations, but these compounds were readily separated from the higher boiling phosphinous chlorides.

One substituted phenylphosphonous dichloride (*p*-chloro) was placed in reaction with a diazonium salt (*m*-chlorophenyl). The reaction gave a modest yield (28%) of (*m*-chlorophenyl)(*p*-chlorophenyl)phosphinous chloride. This result suggests that numerous diarylphosphinous chlorides with both rings bearing substituents are potentially available with this new synthesis. Such compounds have not been reported previously.

One failure of the method has been experienced. The reaction mixture of phenylphosphonous dichloride with *p*-nitrophenyldiazonium fluoroborate[8] consumed about one-half of an equivalent of aluminum, but, on work-up of the mixture by the extraction method, no diarylphosphinous chloride was obtained. Hydrolysis of the reaction mixture to convert any phosphinous chloride retained therein to the *sec*-phosphine oxide (*vide infra*), followed by extraction, also failed to give the desired product. Several attempts to prepare nitrophenylphosphonous dichlorides also have been unsuccessful,[16] and we must conclude that the reaction conditions (or isolation procedures) as presently employed are not applicable to compounds bearing a nitro substituent.

Phosphinous chlorides are readily reactive to nucleophiles, but surprisingly their reaction with water has been little studied. Perhaps this is due to early reports suggesting extensive disproportionation to occur during hydrolysis.[17] It was not until 1959 that simple

$$2Ar_2PCl \xrightarrow{H_2O} Ar_2PH + Ar_2PO(OH)$$

displacement of chlorine was demonstrated, and phosphine oxides were obtained. This was accomplished by refluxing a solution of the chloride in wet benzene,[18a]

$$Ar_2PCl \xrightarrow{H_2O} [Ar_2POH] \longrightarrow Ar_2P(O)H$$

or at room temperature in wet carbon tetrachloride.[18b] In the diaryl family, this reaction has only been used to prepare diphenylphosphine oxide.[19] With a new, versatile path now open to substituted diarylphosphinous chlorides, further development of the hydrolysis reaction as a preparative method for *sec*-phosphine oxides was undertaken. These oxides are of comparatively recent recognition as a class[20]; the meager knowledge of their chemistry has been reviewed.[21] Only symmetrical diarylphosphine oxides are known at present; methods used in their preparation[22–24] are unlikely to provide unsymmetrical oxides.

It has been found that hydrolysis of the phosphinous chlorides to phosphine oxides can be accomplished by simply adding them to water at room temperature. The reaction was slow and little heat was evolved. Ether extracts of the heterogeneous mixture gave oils which were shown to be largely the desired phosphine oxides by the formation with chloral hydrate of crystalline adducts,[24] $Ar_2P(O)CH(OH)CCl_3$ (Table II). Attempts to purify two of the oils by distillation at low pressure were unsuccessful and resulted only in disproportionation, as might be expected.[25]

The infrared spectra of some of the oils suggested an impurity of the diarylphosphinic acid to be present. After removal of this impurity with sodium bicarbonate solution, three of the oils (Table III) readily crystallized while a fourth crystallized on chilling a pentane solu-

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[16] L. D. Quin, J. S. Humphrey, Jr., and R. E. Montgomery, unpublished work.

[17] Ref. 10, p. 52.

[18] (a) R. C. Miller, *J. Org. Chem.*, **24**, 2013 (1959); (b) G. I. Derkach and A. V. Kirsanov, *Zh. Obshch. Khim.*, **29**, 1815 (1959). This reaction is presumed to proceed through the phosphinous acid (in brackets), which then rearranges.

[19] A. Frank, *J. Org. Chem.*, **24**, 966 (1959), has obtained phosphine oxides by hydrolysis of polymethylbenzene-phosphorus trichloride-aluminum chloride reaction mixtures; presumably phosphinous chlorides, or complexes thereof, were the species hydrolyzed.

[20] R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952).

[21] K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

[22] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

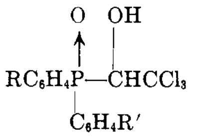
[23] J. L. Willans, *Chem. Ind.* (London), 235 (1957).

[24] M. M. Rauhut and H. A. Currier, *J. Org. Chem.*, **26**, 4626 (1961).

[25] Ref. 10, p. 12.

TABLE II

CHLORAL ADDUCTS OF DIARYLPHOSPHINE OXIDES



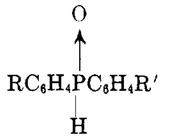
$$\mathrm{RC_6H_4}\underset{\underset{\mathrm{C_6H_4R'}}{|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\text{—}\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}\mathrm{HCCl_3}$$

R	R'	M.p., °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
H	H	171.5–172.5	73[a]	$C_{14}H_{12}Cl_3O_2P$	48.10	48.35	3.46	3.52	8.86	8.95
H	*p*-Br	176–178	70[a]	$C_{14}H_{11}BrCl_3O_2P$	39.24	39.45[b]	2.59	2.66[b]	7.23	7.17
H	*p*-Cl	167.5–168.5	68[a]	$C_{14}H_{11}Cl_4O_2P$	43.78	44.01	2.89	2.91	8.07	7.94
H	*m*-Cl	171–173	59[a]	$C_{14}H_{11}Cl_4O_2P$	43.78	43.77	2.89	2.93	8.07	7.94
p-Cl	*m*-Cl	163–164	83[c]	$C_{14}H_{10}Cl_5O_2P$	40.18	40.21	2.41	2.46	7.40	7.58

[a] Based on phosphinous chloride. Adduct recrystallized from aqueous ethanol. [b] Analysis on unrecrystallized product gave C, 39.45; H, 2.64. [c] Based on diarylphosphine oxide. Adduct recrystallized from aqueous ethanol, then chloroform–carbon tetrachloride.

TABLE III

DIARYLPHOSPHINE OXIDES



$$\mathrm{RC_6H_4}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{C_6H_4R'}$$

IV

Compound	R	R'	M.p., °C.	Yield,[a] %	Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
IV A	H	H	51–53[b]	79	$C_{12}H_{11}OP$	70.95	71.19	5.45	5.39	15.11	15.20
IV B	*p*-Cl	H	48–50	70	$C_{12}H_{10}ClOP$	60.90	60.98	4.26	4.42	13.09	13.05
IV C	*p*-Br	H	53–55	72	$C_{12}H_{10}BrOP$	51.27	51.51[c]	3.59	3.62[c]	11.02	10.79[c]
IV D	*m*-Cl	H	35–36.5	71	$C_{12}H_{10}ClOP$	60.90	60.82[d]	4.26	4.27[d]	13.09	13.20[d]
IV E	*p*-CN	H	*e*	33	$C_{13}H_{10}NOP$	68.74	68.54	4.44	4.45	13.64	13.35
IV F	*m*-CF_3	H	*e*	95	$C_{13}H_{10}F_3OP$	57.79	57.58	3.73	3.83	11.46	11.47
IV G	*p*-Cl	*m*-Cl	*e*	72	$C_{12}H_9Cl_2OP$	53.16	53.05	3.35	3.31	11.43	11.16

[a] Crude product. [b] Lit.[24] m.p. 53–56°. [c] Analysis prior to recrystallization gave C, 51.35; H, 3.68; P, 10.99. [d] Obtained on noncrystalline sample. [e] Obtained as oils.

tion. The others have not yet been obtained in crystalline form. One of the crystallized oxides gave an acceptable analysis even before recrystallization; this suggested that the three oxides that failed to crystallize might still be analytically pure, and this proved to be the case. The infrared spectra of all oxides were consistent with the assigned structures. Weak but sharp absorption peaks for P–H occurred at 2265–2300 cm.$^{-1}$ while for P–O strong absorption at 1190–1205 cm.$^{-1}$ was noted. It is evident, then, that the hydrolysis proceeds smoothly to give easily recovered high purity diarylphosphine oxides. With the exception of one low value (33%, possibly due to use of an old sample of chloride), the yields ranged from 70 to 95% in single experiments.

Experimental

General.—Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting and boiling points are uncorrected. All operations involving the preparation or manipulation of phosphinous chlorides were conducted in a nitrogen atmosphere.

Except for *p*-aminobenzonitrile, all amines were Eastman research grade; only *m*-chloroaniline was further purified (by distillation). Practical *p*-aminobenzonitrile was purified by passage in 95% ethanol solution through a short Norit column, followed by crystallization from a hot water–ethanol medium. Diazonium fluoroborates were prepared by procedure IIA of Roe,[26] and were dried overnight *in vacuo* over phosphorus pentoxide. Solvents were dried over phosphorus pentoxide and then distilled. Phenylphosphonus dichloride was used as received from Eastman. Aluminum (Baker and Adamson, 8–10 mesh) was activated shortly before use by shaking with 1% sodium hydroxide for a few minutes, and then washing with water, and finally acetone.

***p*-Chlorophenylphosphonous Dichloride.**—A modification of the method of Quin and Humphrey[3] was used. To the reaction mixture from *p*-chlorophenyldiazonium fluoroborate (145 g., 0.64 mole), phosphorus trichloride (89 g., 0.65 mole), and cuprous bromide (1.2 g.) in 640 ml. of ethyl acetate was added slowly 15.5 g. (0.57 g.-atom) of aluminum. The mildly exothermic reaction was controlled at 35–40°. After several hours, the liquid was removed from residual aluminum by decantation, and phosphorus oxychloride (100 g.) was added to it to destroy any complex of aluminum salts with the product.[27] Solvent was removed by distillation, leaving a thin syrup. This was continuously extracted for 5 hr. with cyclohexane. The extract was distilled *in vacuo;* 53.7 g. of product (0.252 mole, 39.4%) was collected at 86–90° (1.4–2.8 mm.). On repetition of the preparation, the yield was 39.6%.

(*p*-Chlorophenyl)phenylphosphinous Chloride.—To a suspension in a 5-l. flask of 136 g. (0.60 mole) of *p*-chlorophenyldiazonium fluoroborate and 5 g. of cuprous bromide in 600 ml. of isopropyl acetate was added 128 g. (0.60 mole) of phenylphosphonous dichloride. No reaction was noted after 20 min.; the mixture was then heated gently, whereupon vigorous gas evolution and foaming occurred. The temperature was held below 35° during the reaction period. At the completion of the reaction, a clear amber solution resulted. Aluminum (10.8 g., 0.4 g.-atom) was then added, and the mixture was stirred vigorously at 40–50° for 30 min. and then at room temperature for 2 days (probably excessive). The pale yellow liquid was decanted from residual aluminum, treated with 92 g. of phosphorus oxychloride, and distilled at reduced pressure. The main fraction, b.p. 125–130° (0.28–0.33 mm.), was collected as product (52 g., 0.21 mole, 34%). A large amount of solid remained in the still. The product was redistilled through an 8-in. Vigreux column; b.p. 134–135° (0.80 mm.) was observed.

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Anal. Calcd. for $C_{12}H_9Cl_2P$: C, 56.50; H, 3.56; Cl, 27.80; P, 12.14. Found: C, 56.15; H, 3.84; Cl, 27.57; P, 12.11.

(*p*-Cyanophenyl)phenylphosphinous Chloride.—Phenylphosphonous dichloride (60 g., 0.33 mole) was added to 72 g. (0.33 mole) of *p*-cyanophenyldiazonium fluoroborate and 2.4 g. of cuprous bromide in 300 ml. of isopropyl acetate. Reaction commenced after about 20 min. The temperature was then moderated at 20–40°. Aluminum (8.0 g., 0.30 g.-atom) was added to the red slurry, and the mixture was stirred at 40–50° for 2 hr. A clear, dark amber solution resulted. Liquid was decanted from residual aluminum and was treated with 51 g. of phosphorus oxychloride. The mixture was distilled *in vacuo*. Following low boiling material, a fraction (5 g.) was obtained at 60–70° (2 mm.) which consisted of a mixture of solid and liquid. The solid (m.p. 96°), after removal from the liquid (probably phenylphosphonous dichloride), was not affected by water. It was not further investigated, but is believed to be *p*-chlorobenzonitrile, m.p. 96°. The main fraction of 39 g. (0.16 mole, 47%) was obtained over the range 158° (0.7 mm.) to 195° (3.1 mm.). Pressure control was made difficult during this period by some decomposition of the large solid residue in the still. On redistillation, b.p. 162° (0.20 mm.) was observed.

Anal. Calcd. for $C_{13}H_9ClNP$: C, 63.56; H, 3.69; Cl, 14.43; P, 12.61. Found: C, 63.21; H, 3.51; Cl, 14.25; P, 12.77.

(*m*-Chlorophenyl)phenylphosphinous Chloride.—*m*-Chlorophenyldiazonium fluoroborate (107 g., 0.50 mole) and cuprous bromide (3.5 g.) were suspended in 500 ml. of ethyl acetate and treated with 90 g. (0.50 mole) of phenylphosphonous dichloride. The reaction did not start in 2 hr. Additional catalyst (0.5 g.) was then added, initiating the reaction. After 2.5 hr., gas evolution had ceased, and a thin red slurry resulted. To this was added 20 g. (0.74 g.-atom) of aluminum, and the mixture heated to 74° and then stirred at room temperature overnight. A clear green solution was obtained. The solution was decanted from unchanged aluminum (15 g., 0.56 g.-atom), treated with 44 g. of phosphorus oxychloride, and distilled until b.p. 82° was reached. The viscous residue was then continuously extracted with cyclohexane for 4 hr. Solvent was stripped from the extract, and the residue was subjected to distillation at 2–3 mm. A forerun (4 g.) was collected at 57–75° (1.6–3.1 mm.), but no further distillation could be effected without excessive fume production. The pressure was then reduced further, and distillation occurred smoothly at 107–125° (0.087–0.14 mm.). This distillate was combined with the forerun; on redistillation, there were obtained a 3.4-g. fraction of b.p. 42–57° (1.9 mm.), 19.7 g. (0.11 mole) of phenylphosphonous dichloride at 60–70° (1.8–2.1 mm.), and then 42 g. (0.16 mole) of the phosphinous chloride at 123–125° (0.27 mm.). The yield of phosphinous chloride based on phenylphosphonous dichloride charged was 33% and on phenylphosphonous dichloride consumed was 42%.

Anal. Calcd. for $C_{12}H_9Cl_2P$: C, 56.50; H, 3.56; P, 12.14. Found: C, 56.26; H, 3.48; P, 12.29.

Phenyl(*m*-trifluoromethylphenyl)phosphinous Chloride.—Upon addition of 70 g. (0.39 mole) of phenylphosphonous dichloride to a slurry of 120 g. (0.46 mole) of *m*-trifluoromethylphenyldiazonium fluoroborate and 3.0 g. of cuprous bromide in 600 ml. of isopropyl acetate, a vigorous reaction occurred, and some of the flask contents was ejected through the condenser. The reaction temperature exceeded 50° even during application of an ice bath. Upon completion of the reaction, aluminum (10 g., 0.37 g.-atom) was added. The reduction was mildly exothermic; it was allowed to proceed overnight at room temperature. Phosphorus oxychloride (61 g.) was added, causing the formation of a small amount of gelatinous precipitate. Filtration of the solid was difficult, and the entire mixture was then distilled to b.p. 84°. The viscous residue was continuously extracted with cyclohexane for 8 hr. Distillation gave 5.4 g. (0.030 mole) of phenylphosphonous dichloride at 47° (0.2 mm.), and a product fraction of 28.3 g. (0.098 mole), b.p. 92–98° (0.2–0.3 mm.). A portion on redistillation had b.p. 95° (0.3 mm.). The yield based on phenylphosphonous dichloride charged was 25% and on the dichloride consumed was 27%. The yields are not adjusted for the loss of some of the reaction mixture in the first step.

Anal. Calcd. for $C_{13}H_9ClF_3P$: C, 54.09; H, 3.14; P, 10.73. Found: C, 54.05; H, 3.51; P, 10.77.

(*p*-Bromophenyl)phenylphosphinous Chloride.—Phenylphosphonous dichloride (111 g., 0.62 mole) was dropped into a suspension of *p*-bromophenyldiazonium fluoroborate (167 g., 0.62 mole) and 5.0 g. of cuprous bromide in 600 ml. of ethyl acetate. A vigorous reaction occurred after 1 hr.; it was moderated with an ice bath. Aluminum (13 g., 0.48 g.-atom) was added; 9.5 g. remained unchanged after 22 hr. of stirring at room temperature and then refluxing for 1.5 hr. Phosphorus oxychloride (92 g.) was added, and solvent was then stripped off. The viscous residue was continuously extracted overnight with cyclohexane. Attempted distillation of the extract at 0.65 mm. gave only a forerun (30 g., b.p. 40–47°), and failed to give the desired product before excessive decomposition commenced. Distillation at a lower pressure was successful, however, and there was obtained 51 g. (0.168 mole) at 115–127° (0.034–0.080 mm.), which upon redistillation had b.p. 127° (0.19 m.m); lit.[13] b.p. 203–204° (11 mm.). On redistillation of the forerun from the first distillation, there was obtained at 112–128° (3.7 mm.) a distillate comprised of 3 g. of a solid (not identified) in admixture with 26 g. (0.15 mole) of phenylphosphonous dichloride. The yield of phosphinous chloride was 27% on phenylphosphonous dichloride charged and 35% on the dichloride consumed.

Anal. Calcd. for $C_{12}H_9BrClP$: P, 10.34. Found: P, 10.40.

(*m*-Chlorophenyl)(*p*-chlorophenyl)phosphinous Chloride.—To a mixture of 62 g. (0.27 mole) of *m*-chlorophenyldiazonium fluoroborate, 2.4 g. of cuprous bromide, and 300 ml. of ethyl acetate was added 45 g. (0.21 mole) of *p*-chlorophenylphosphonous dichloride. Reaction commenced after 2.5 hr. and was controlled at about 30–35°. When gas evolution was complete, 12.3 g. (0.455 g.-atom) of aluminum was added to the red slurry. A strongly exothermic reaction occurred and cooling was required to control the temperature at 40°. After 12 hr., unchanged aluminum (9.7 g., 0.36 g.-atom) was removed from the green solution and 45 g. of phosphorus oxychloride was added. Solvent was stripped as usual but the residue was too viscous for effective continuous extraction. It was thinned with ethyl acetate and then extracted several times with *n*-heptane. Distillation of the extract gave three fractions: (A) 3 g., b.p. 68–80° (25 mm.), which after washing with water and 1% sodium bicarbonate solution had b.p. 68–71° (24 mm.) and gave an infrared spectrum identical with that from known *m*-dichlorobenzene; (B) 8.4 g. (0.039 mole), b.p. 77° (0.60 mm.), of unchanged *p*-chlorophenylphosphonous dichloride; (C) 14.4 g. (0.050 mole), b.p. 140–146° (0.40–0.42 mm.), of the desired phosphinous chloride. Redistillation of a portion of fraction C gave b.p. 125° (0.07 mm.). The yields, on charged and consumed phosphonous dichloride, respectively, were 24% and 28%.

Anal. Calcd. for $C_{12}H_8Cl_3P$: C, 49.78; H, 2.79; P, 10.70. Found: C, 49.74; H, 2.74; P, 10.82.

Conversion of Phosphinous Chlorides to Phosphinic Acids.—The following general procedure was used. The phosphinous chloride (1–2 g.) was dropped into 10 ml. of cold water; the mixture was stirred for several minutes, and then treated with 10 ml. of 10% sodium hydroxide. Solid potassium permanganate was added until a definite purple color persisted. The mixture was heated on a steam bath for 20 min.; enough ethanol was then added to discharge the purple color. The mixture was filtered, and the colorless filtrate was made acidic with concentrated hydrochloric acid. The phosphinic acid was precipitated in 90–95% yield. Two phosphinic acids (see Table I) were obtained as oils on precipitation and resisted attempts to induce crystallization. These acids were dissolved in ether and this solution added to a solution of *p*-toluidine in ether. Precipitates of the salts formed almost immediately and were readily recrystallized. In the treatment of (*p*-cyanophenyl)phenylphosphinous chloride, hydrolysis of the cyano group was also performed; this was accomplished by refluxing the basic mixture for 1 hr. after oxidation was complete. No attempt was made to isolate the intermediate (*p*-cyanophenyl)phenylphosphinic acid. Melting points and analytical data for all compounds are given in Table I.

Chloral Adducts of Diarylphosphine Oxides.—The following general procedure was used. The phosphinous chloride (0.01 mole) was added over a period of 10 min., with stirring, to 15 ml. of water. The mixture was stirred without temperature control for 2–4 hr. and then extracted with three 20-ml. portions of ether. The ether layer was dried briefly with magnesium sulfate and then evaporated. The clear oil was taken up in 10 ml. of isopropyl alcohol and mixed with a solution of 2.0 g. of chloral hydrate in 5 ml. of isopropyl alcohol. After heating on a steam bath for a few minutes, precipitation of the adduct commenced. After 1 hr., the semisolid mass was mixed with 50 ml. of ether, chilled, and filtered. The products were recrystallized from aqueous ethanol. Further data are provided in Table II. In the case of phenyl(*m*-trifluoromethylphenyl)phosphine oxide and of (*p*-cyanophenyl)phenylphosphine oxide, no adduct precipitated, and removal of solvent left an oil that failed to crystallize.

Attempted Distillation of Diphenylphosphine Oxide.—Two grams of diphenylphosphine oxide was subjected to distillation at 10^{-3} mm. A distillate (0.9 g.) was received over the range 115–121°. Solid residue remained in the still. The analysis for the distillate suggested it to be impure diphenylphosphine, and not diphenylphosphine oxide.

Anal. Calcd. for $C_{12}H_{11}P$: C, 77.41; H, 5.96; P, 16.64. Found: C, 76.23; H, 5.74; P, 16.23.

Preparation of Diarylphosphine Oxides.—The ether extract of a hydrolysis mixture prepared as described in the chloral adduct reaction was extracted with two 30-ml. portions of 5% sodium bicarbonate. Small amounts of phosphinic acid generally precipitated on acidification of the aqueous layer. The ether layer was washed once with 20 ml. of water and then dried with magnesium sulfate for 30 min. Removal of ether on a rotary evaporator left an oil, which was then further freed of volatiles by evacuation at 1 mm. overnight. Compounds IVA–C (see Table III) solidified completely in 1–2 days, and were recrystallized from pentane by slow cooling of a saturated solution to about −50°. Compound IVD on one occasion crystallized on similar treatment of the oil, but later attempts to repeat this crystallization failed. Compounds IVE–G could not be made to crystallize, and were analyzed without purification. The oxides were quite hygroscopic. Yield and analytical data for all compounds appear in Table III. The infrared spectra for compounds IVA–C were taken on potassium bromide pellets; other spectra were taken on the oils. All showed peaks at 2265–2300 cm.$^{-1}$ (weak, sharp) for P–H and at 1190–1205 cm.$^{-1}$ (strong) for $P \rightarrow O$. Since compounds IVE–F could not be crystallized, further details on prominent features of their spectra are offered.[28]

IVE, 2990(w), 2300(w), 2200(m), 1430(m), 1380(m), 1200(s), 1120(s), 945(s), 830(m), 750(m), 708(m), 693(m); IVF, 2990(w), 2285(w), 1430(m, shoulder 1410), 1320(s), 1195(s, shoulder 1165), 1120(s), 1070(m), 945(m), 805(m), 745(m), 695(m); IVG, 3000(w), 2290(w), 1575(m, shoulder 1555), 1475(m, shoulder 1460), 1395(m, shoulder 1380), 1190(s), 1140(s), 1085(s), 943(m), 820(m), 790(m), 750(s), 683(m).

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(28) Longer wave numbers are accurate to no more than about ±5 cm.$^{-1}$; spectra were taken with a Perkin-Elmer Model 137 spectrophotometer. Abbreviations: w, weak; m, medium; s, strong.

Diene Structure and Diels–Alder Reactivity

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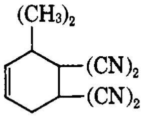
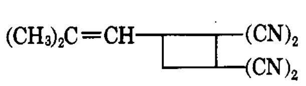
Adducts from tetracyanoethylene and a variety of dienes, including several *cis*-pentadienes, have been prepared and relative reactivities examined.

Diels–Alder reactions between maleic anhydride and dienes which contain a *cis*-methyl substituent on the terminal carbon of the diene system have been reported in a number of instances,[1–3] but in general such reactions are limited due to low reactivity and the enhancement of side reactions such as polymerization.[4] The current investigation was undertaken to determine the usefulness of the more potent dienophile, tetracyanoethylene[5] (TCNE), toward these less reactive dienes. A preliminary communication[6] has reported the simultaneous formation from 4-methyl-1,3-pentadiene of the Diels–Alder adduct, 3,3-dimethyl-4,4,5,5-tetracyanocyclohexene (I), and the four-membered ring adduct, 3-(2-methyl-1-propenyl)-1,1,2,2-tetracyanocyclobutane (II).



I



II

Results

Good yields of adducts have indeed been obtained from the dienes examined with the exception of *cis*-1,3-pentadiene by allowing excess diene to react with TCNE in tetrahydrofuran solution at room temperature. As with the more reactive *trans* isomers, a deep brown to red-brown color is developed immediately when the *cis* dienes are added to the reagent and adducts may be isolated in high yield by evaporation of the solution when the color has faded (Table I). In the case of 1,3-cyclohexadiene, the reaction is over within minutes, as is the case with the *trans* dienes examined. For 4-methyl-1,3-pentadiene, 3-methyl-*cis*-1,3-pentadiene, and *cis,trans*-2,4-hexadiene, two to three days at room temperature are required before color fading is complete. In the case of *cis*-1,3-pentadiene, significant color fading did not occur even on prolonged heating, and unreacted TCNE was recovered, although occasionally an apparently polymeric material having the right composition for a 1:1 adduct was obtained. Spectral properties of the adducts were consistent with the structures expected for a normal Diels–Alder reaction (analogous to I) in all cases except 4-methyl-1,3-pentadiene.[6] Attempts to favor cyclobutane formation for other dienes by use of the more polar solvent, nitromethane, led only to the same products obtained in tetrahydrofuran.

Relative reactivity toward TCNE was determined for these dienes and for a selection of more reactive compounds in an attempt to gain more insight into the nature of the process. Semiquantitative values were obtained from visual estimates of the rate of disappearance of the characteristic color and more precise values for dienes of comparable reactivity by competition experiments. Calculated second-order rate constants are listed in Table I. In view of the strong tendency for complex formation, it is possible that significant absolute error is involved in the assumption of second-order kinetics,[7,8] but relatively little relative error is expected from this source. For comparison,

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