Experimental[15]

Preparation of Diethyl Propionylphosphonate.—The following general procedure was followed in the preparation of all esters and the corresponding 2,4-DNP derivatives. To triethyl phosphite (35.9 g., 0.216 mole), stirred in a 100-ml. round-bottom flask under anhydrous conditions and under nitrogen, was added dropwise 20.0 g. (0.216 mole) of distilled propionyl chloride.[16] An exothermic reaction (temperature maintained below 50°) resulted during which bubbles of a gas were evolved. The mixture was allowed to stand for 1 day under nitrogen and was then vacuum distilled to give 36.0 g. (85.7%) of a colorless liquid. The 2,4-DNP was prepared by adding a few drops of the dialkyl acylphosphonate to about 10 ml. of a stock solution of 2,4-dinitrophenylhydrazine and filtering the crystals which formed in the solution after standing a few minutes. Recrystallization from methanol gave a yellow, fibrous mass of crystals, m.p. 93–94°.

Acknowledgment.—The senior author acknowledges partial support by the Research Foundation, Oklahoma State University.

[15] All melting points are corrected; all boiling points are uncorrected. The infrared spectra were obtained on a Beckman IR-5 as films on sodium chloride cells. The n.m.r. spectra were obtained on a Varian A-60 instrument with carbon tetrachloride as the solvent. Tetramethylsilane was used as an internal standard. We gratefully acknowledge the gift from Stauffer Chemical Co., Victor Chemical Division, of samples of the various phosphites needed in this work. Analyses were performed by Galbraith Laboratories. Copies of spectra may be obtained from the senior author.

[16] The acid halides were purchased or prepared by standard procedures and were distilled prior to use.

A Convenient Synthesis of Esters of Diphenylphosphinic Acid. III[1,2]

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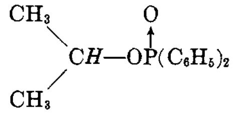
Phosphinates are a somewhat rare class of organophosphorus esters which have been prepared by a variety of methods none of which has been systematic in approach.[4] Recently, it was demonstrated that diazo alkanes can be employed with a phosphorus acid to give good yields of esters.[5,6] Phosphonites are not useful precursors since aryl halides are not effective in promoting a Michaelis–Arbuzov rearrangement.[7]

We now report several new phosphinates of the type $(C_6H_5)_2P(O)OR$ which were synthesized by a general procedure involving a classic reaction between diphenylphosphinic chloride and the corresponding alcohol in the presence of triethylamine in ether. After a short time at reflux, the mixture was filtered and the resulting organic solvent was evaporated to give a solid. A slight excess of the alcohol removed all of the acid chloride which, *via* hydrolysis, could lead to diphenylphosphinic acid—a difficult contaminant to remove. The method is superior both with respect to simplicity of isolation of relatively pure products and yields of esters. An exception, *t*-butyl diphenylphosphinate, was obtained from condensation of potassium *t*-butoxide with diphenylphosphinic chloride since the regular procedure gave only complex mixtures. A list of the esters is found in Table I.

As expected infrared analyses revealed absorption by the phosphoryl group near 8.2 μ while the P–O–C groups displayed peaks from 9.6 to 10.85 μ.[8,9] In addition the P-phenyl band was observed at 6.93 μ. Examination of the esters by n.m.r. showed complex multiplets, particularly for the α-protons, due to H^1–P^{31} coupling. With isopropyl diphenylphosphinate, a symmetrical eight-line pattern was visible (each line was split again) for the tertiary hydrogen. This possibly may occur from overlap of two heptets, one appearing as a result of $CH–CH_3$ coupling and the other from $H–P^{31}$ coupling assuming the J_{CH-CH_3} and $J_{CH-P^{31}}$ constants were close in value. It has been demonstrated that $J_{CH_2-P^{31}}$ and $J_{CH_2-CH_3}$ are equal or nearly so in triethyl phosphite and give rise to a symmetrical five-line grouping without further splitting.[10,11] Additional n.m.r. data is provided in Table II.



Experimental[12]

The following procedure is typical of that used for the preparation of the title compounds.

Cyclohexyl Diphenylphosphinate.—To a mixture of 40.04 g. (0.40 mole) of cyclohexanol and 50.57 g. (0.50 mole) of triethylamine in 350 ml. of anhydrous ether under nitrogen was added 78.80 g. (0.33 mole) of diphenylphosphinic chloride[13] in 100 ml. of anhydrous ether with rapid stirring over a period of 0.5 hr. The reaction mixture was heated at reflux for 1 hr. After filtering the hydrochloride salt,[14] the mixture was concentrated to give a solid which, upon recrystallization from benzene–heptane, gave 78.47 g. (78.5%) of cyclohexyl diphenylphosphinate.

***t*-Butyl Diphenylphosphinate.**—To a rapidly stirred solution of potassium *t*-butoxide, prepared from 11.73 g. (0.3 g.-atom) of potassium and 300 ml. of anhydrous *t*-butyl alcohol, was added, under nitrogen, 43.13 g. (0.18 mole) of diphenylphosphinic chloride in 100 ml. of benzene over a period of 0.5 hr. The mixture

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[1] We gratefully acknowledge support by the Air Force Office of Scientific Research, Grant AF AFOSR-132-65.

[2] Preceding papers in the series: (a) K. D. Berlin, T. H. Austin, and K. L. Stone, *J. Am. Chem. Soc.*, **86**, 1787 (1964); and (b) K. D. Berlin and M. Nagabhushanam, *Chem. Ind.* (London), 974 (1964).

[3] Postdoctorate, 1963–1965.

[4] The meager data on the subject has been covered in a review; see K. Sasse, "Methoden der organischen Chemie," Vol. 12, Part 1, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1963.

[5] K. Issleib and H. M. Möbius, *Ber.*, **94**, 102 (1961).

[6] B. E. Smith and A. Burger, *J. Am. Chem. Soc.*, **75**, 5891 (1953).

[7] A review is available: E. R. De Sombre and R. G. Harvey, "Topics in Phosphorus Chemistry," M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964.

[8] K. L. Paciorek, *Inorg. Chem.*, **3**, 96 (1964).

[9] L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961).

[10] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

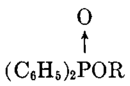
[11] See J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963), ref. 95.

[12] All melting points are corrected and all boiling points are uncorrected. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Beckman IR 5 spectrophotometer. A Varian Model A-60 high-resolution spectrometer fitted with a field-sensing stabilizer "Super Stabilizer" was used to determine the n.m.r. spectra.

[13] This compound was prepared from oxidation of diphenylphosphinous chloride which was obtained from Stauffer Chemical Co., Victor Chemical Division. We express our thanks to W. D. Ebert and E. L. Kubiak for generous samples of this material.

[14] An alternative procedure of using a slight excess of diphenylphosphinic chloride was attempted. This necessitated a wash with sodium bicarbonate at the end of the heating period to remove diphenylphosphinic acid and to destroy the amine salt. However, yields of the esters approximated those obtained by the method given. In the cases of **7** and **8**, phenol and α-naphthol, respectively, were contaminants and could be removed by sodium hydroxide without saponifying **7** or **8**.

TABLE I


$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OR$

Compd.	R	Yield, %	M.p. or b.p., °C. (mm.)	λ_{max}, μ P–O–C	λ_{max}, μ P→O	Calcd., % C	Calcd., % H	Calcd., % P	Found, % C	Found, % H	Found, % P
1[2a]	CH_3	92.5	178 (2.4)[a]	9.6	8.1						
2	$(CH_3)_2CH$[b]	60.2	97–99	10.1	8.2						
3	$(CH_3)_3C$	80.1	111–112	10.2	8.2	70.06	6.98	11.29	70.28	6.94	11.34
4	C_6H_{11}	78.5	120–121	10.1	8.2	71.98	7.05	10.31	71.86	6.80	10.36
5	*trans*-4-$(CH_3)_3CC_6H_{10}$[c]	72.0	132–133	9.9	8.2	74.15	8.15	8.70	73.94	8.18	8.71
6	$CH_2{=}CHCH_2$	75.0	162–165 (5)	9.8, 10.05[d]	8.15	69.77	5.81	12.02	69.65	5.72	12.03
7	C_6H_5[e]	97.9	135–136	10.85[f]	8.2						
8	α-$C_{10}H_7$	92.7	122–124	10.95[f]	8.1	76.74	4.98	9.00	76.45	4.91	9.10

[a] This crystalline solid liquifies upon standing in air with no essential change in its infrared spectrum. [b] A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **42,** 395 (1910); *Chem. Zentr.*, **81** (II), 453 (1910). [c] The *trans* isomer is tentatively assigned for this compound in analogy with the corresponding acetates; see R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80,** 6098 (1958). It was observed that the broad peaks for H-1 in the *trans* alcohol and acetate had half-widths of 22 c.p.s. while the *cis* isomer and its acetate had a sharp signal with a half-width of 7 c.p.s. In **5**, H-1 appeared as a broad signal centered at δ 4.3 with a half-width of 22 c.p.s. at the following settings on a near-saturated solution in $CDCl_3$: filter band width, 4; radio frequency field, 0.2; sweep time, 250 sec.; sweep width, 500; spectrum amplitude, 1.6. [d] Two bands of equal intensity. [e] A. Michaelis and A. Link, *Ann.*, **207,** 193 (1881). [f] See ref. 8 and 9.

TABLE II

CHEMICAL SHIFT PARAMETERS FOR DIPHENYL ALKYLPHOSPHINATES[a]

Compd.	$-CH_3$	$>CH_2$	$H-C<$	Aryl-H
1	3.70 d[b]			7.25–8.20 m
2	1.28 d[c]		4.64 o	7.28–8.25 m
3	1.45 s			7.25–8.05 m
4		1.57 m	4.45 m	7.28–8.25 m
5	0.75 s	1.53 m	4.38 m	7.20–8.12 m
6[d]		4.40 m[e]		7.20–8.05 m
7				6.97–8.28 m
8				7.08–8.45 m

[a] Given in δ-values downfield from internal TMS. Except for **6** in which deuteriochloroform was the solvent, all other determinations were made in methylene chloride as solvent. Multiplicity of signals: d, doublet; s, singlet; m, multiplet; o, octet. [b] J_{P-H} = 11.0 c.p.s. [c] J = 6.0 c.p.s. [d] Multiplets as expected for the alkyl group are observed centered at δ 5.12, 5.39, and 6.0 which is similar to the pattern given by alkyl alcohol (see NMR Spectra Catalog I, Varian Associates, Palo Alto, Calif., 1962, spectrum 34). [e] This is the CH_2 group attached to the oxygen atom.

was heated at reflux for 1.5 hr. and, after washing with 15% aqueous ammonium chloride solution, was dried over magnesium sulfate and concentrated. A solid was isolated which was recrystallized from benzene–heptane; yield 40.05 g. (80.1%).

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Reactions of Diethyl N-Alkoxyphosphoramidate Anions with Carbon Dioxide and Carbon Disulfide

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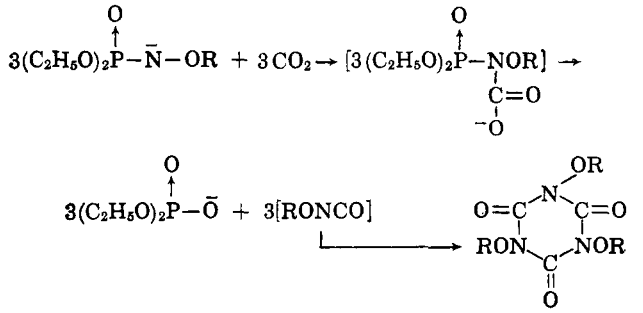
For over 60 years chemical investigators have tried, unsuccessfully, to synthesize N-alkoxyisocyanic acids, RONCO.[1] It seemed possible to us that these novel compounds might be made by the interaction of sodium diethyl N-alkoxyphosphoramidates and carbon dioxide. Wadsworth and Emmons have reported that sodium diethyl N-alkylphosphoramidates and carbon dioxide produce alkyl isocyanates.[2]

Wadsworth and Emmons[2] reported the preparation of diethyl N-methoxyphosphoramide. By utilization of a similar synthesis diethyl N-ethoxyphosphoramide has now been made. However, reaction of carbon dioxide with sodium diethyl N-alkoxyphosphoramidates did not yield N-alkoxyisocyanates but their trimers, 1,3,5-trialkoxyisocyanuric acids, $(RONCO)_3$.

1,3,5-Tribenzyloxyisocyanuric acid and several substituted benzyl derivatives have been made by McKay, *et al.*,[1c] by the treatment of the corresponding benzyloxyamine hydrochlorides with phosgene followed by treatment of the resulting intermediate with triethylamine.

It seems rather probable that the N-alkoxyisocyanic acids were formed first in the reaction between carbon dioxide and sodium diethyl N-alkoxyphosphoramidates and that the monomer then polymerized in the presence of the anions present. Trimerization of isocyanates is well known.[3]

Both 1,3,5-trimethoxy- and 1,3,5-triethoxyisocyanuric acid were relatively stable, crystalline compounds.



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(1) (a) L. W. Jones, *Am. Chem. J.*, **20,** 1 (1898); (b) L. W. Jones and L. Neuffer, *J. Am. Chem. Soc.*, **39,** 652 (1917); (c) A. F. McKay, D. L. Garmaise, G. Y. Paris, and S. Gelblum, *Can. J. Chem.*, **31,** 343 (1960).

(2) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **84,** 1316 (1962); *J. Org. Chem.*, **29,** 2816 (1964).

(3) (a) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IB, Elsevier Publishing Co., New York, N. Y., 1952, p. 939; (b) V. E. Shashoua, W. Sweeney, and R. F. Tietz, *J. Am. Chem. Soc.*, **82,** 866 (1960).