

was purified by vacuum distillation and then converted to the corresponding diazonium fluoroborate by Roe's procedure IIA.¹⁶ The dried diazonium salt was suspended in ethyl acetate and treated with phosphorus trichloride and cuprous bromide in the usual manner.¹⁵ When the reaction mixture was steam distilled, an oil, consisting largely of phosphinic acid, separated in the distilling flask. The hot aqueous layer was decanted through a filter, and the oil remaining in the beaker was washed several times with boiling water. The crude phosphinic acid was then purified by reprecipitation from alkaline solution and subsequent recrystallization from 95% ethanol. The yield of pure bis(3-chloro-4-tolyl)phosphinic acid was 3%, m.p. 189–192°.

Anal. Calcd. for $C_{14}H_{13}Cl_2O_2P$: Cl, 22.50; P, 9.83; neut. equiv., 315.1. Found: Cl, 22.26; P, 9.86; neut. equiv., 310.5.

The phosphinic acid was isolated as its hemi-sodium salt¹⁵ from the aqueous layer mentioned above, and the salt was converted to the free acid by recrystallization from a mixture of 1 vol. of 95% ethanol to 5 vol. of 6 *N* hydrochloric acid. The yield was 50%, m.p. 160–162°.

Anal. Calcd. for $C_7H_5ClO_3P$: Cl, 17.16; P, 15.00; neut. equiv., 103.3. Found: Cl, 16.97; P, 14.50; neut. equiv., 104.4.

2-Nitro-5-chloro-4-tolylphosphonic Acid.¹⁷—3-Chloro-4-tolyl phosphonic acid (40.6 g.) was added in small portions to 185 ml. of stirred fuming nitric acid (*d* 1.5) maintained at 15–20°. Stirring was continued for 1 hr. after the addition was complete, and the reaction mixture was then poured onto 400 g. of cracked ice. The mixture was allowed to stand in the ice box overnight after which the solid was removed by filtration. The yield of crude mononitrated material was 36.5 g. (73%), m.p. 169–184°. After several recrystallizations from 3 *N* hydrochloric acid, the material melted with decomposition at 223–227°.

Anal. Calcd. for $C_7H_5ClNO_3P$: Cl, 14.09; N, 5.57; P, 12.31; neut. equiv., 125.8. Found: Cl, 14.12; N, 5.54; P, 12.06; neut. equiv., 126.0.

The structure of this substance was not established unequivocally, but it is probably 2-nitro-5-chloro-4-tolylphosphonic acid for the following reasons. (1) The compound does not form a water-insoluble magnesium salt either at room temperature or when heated. This behavior is characteristic of arylphosphonic acids containing bulky *ortho* substituents such as the nitro group.¹⁸ (2) The nitration of 3-chloro-4-toluenesulfonic acid yields almost exclusively 2-nitro-5-chloro-4-toluenesulfonic acid.¹⁹ Since the sulfo and the phosphono groups have similar electronic structures, it seems reasonable to assume that the nitration of 3-chloro-4-tolylphosphonic acid gives 2-nitro-5-chloro-4-tolylphosphonic acid.

4-Chloro-3-tolylphosphonic Acid and Bis(4-chloro-3-tolyl)phosphinic Acid.—4-Chloro-3-methylaniline,²⁰ m.p. 85.5–86.5°, was diazotized in fluoroboric acid in the usual manner.¹⁶ The cold reaction mixture was filtered by suction on a sintered-glass filter, and the solid diazonium fluoroborate was washed with a small amount of cold fluoroboric acid (40 ml./mole of amine) and then several times with copious quantities of ether. After being dried in a desiccator, the salt was converted to the corresponding phosphonic and phosphinic acids, which were separated by the procedure used for the 3-chloro-4-tolyl isomers. After several recrystallizations from aqueous alcohol, the yield of pure bis(4-chloro-3-tolyl)phosphinic acid was 3%, m.p. 178–181°.

Anal. Calcd. for $C_{14}H_{13}Cl_2O_2P$: C, 53.36; H, 4.16. Found: C, 53.48; H, 4.30.

The phosphonic acid was recrystallized from 6 *N* hydrochloric acid; the yield was 15%, m.p. 158–161°.

Anal. Calcd. for $C_7H_5ClO_3P$: C, 40.70; H, 3.90. Found: C, 40.78; H, 4.01.

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(15) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(16) A. Roe, *Org. Reactions*, **5**, 204 (1949).

(17) This compound is mentioned in ref. 4, but no information concerning its structure is presented.

(18) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 6221 (1955).

(19) E. G. Turner and W. P. Wyne, *J. Chem. Soc.*, 707 (1936).

(20) J. P. Lambooy and E. E. Haley, *J. Am. Chem. Soc.*, **74**, 1087 (1952).

Dialkyl Esters of Acylphosphonic Acids¹

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During the course of studies involving the reaction of compounds containing adjacent carbonyl-phosphoryl groups³ we have synthesized several new alkyl acylphosphonates by a very convenient method. Early work by Arbuzov⁴ and more recent data by Kabachnik⁵ demonstrate that acetyl chloride, ethyl chloroformate, phosgene, and benzoyl chloride react with phosphites to give phosphonates in a Michaelis-Arbuzov rearrangement.⁶ Acetic anhydride behaves similarly⁷ while α -haloacyl halides⁸ react in a pattern similar to the Perkow reaction of α -halo ketones with trisubstituted phosphorus esters.

Addition of acyl halide to phosphite required cooling as expected.^{3,4} It was found that high yields of dialkyl acylphosphonates could be realized if the reaction mixtures were permitted to stand at room temperature overnight before distillation was attempted. In the case of the cyclohexyl derivatives, an additional 1–2 hr. at reflux was necessary to complete the process after the mixture had stood for a day. In all examples, the vacuum distillation proceeded very smoothly to give colorless oils when this procedure was followed. Physical properties are recorded in Table I for all esters, and the 2,4-dinitrophenylhydrazones derivatives were analyzed for nitrogen and phosphorus. Infrared (Table II) and n.m.r. data (Table III) support the structures. As in the examples with dialkyl aroylphosphonates,³ the dialkyl acylphosphonates are hygroscopic and presumably undergo carbon-phosphorus bond cleavage. The surprisingly low frequency of absorption for the carbonyl function in these novel esters is similar to the situation reported with the aroylphosphonates. It was suggested that one of the nonbonding orbitals on the oxygen atom of the phosphoryl group could orient properly for overlap with the *p*-orbital on the carbonyl carbon atom which could result in alteration of the force constant of the carbon-oxygen bond.³ Such a phenomenon could be operative in the compounds described herein.

(1) We gratefully acknowledge support of the National Institutes of Health, GM-10367-03.

(2) Postdoctorate, 1963–1965.

(3) K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964).

(4) A. E. Arbuzov and A. A. Dunin, *J. Russ. Phys. Chem. Soc.*, **46**, 295 (1914); *Chem. Abstr.*, **8**, 2551 (1914); see also *Ber.*, **60B**, 291 (1927); *Chem. Abstr.*, **21**, 1627 (1927).

(5) M. I. Kabachnik and P. A. Rossiiskaya, *Bull. acad. sci. URSS, Classe sci. chim.*, 597 (1945); *Chem. Abstr.*, **41**, 88 (1947); M. I. Kabachnik, P. A. Rossiiskaya, and E. S. Shepeleva, *Bull. acad. sci. URSS, Classe sci. chim.*, 163 (1947); *Chem. Abstr.*, **42**, 4132 (1948); M. I. Kabachnik and P. A. Rossiiskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **48** (1957); *Chem. Abstr.*, **51**, 10366 (1957); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1398 (1958); *Chem. Abstr.*, **53**, 6988 (1959).

(6) This reaction has been reviewed recently: R. G. Harvey and E. R. DeSombre, "Topics in Phosphorus Chemistry," M. Grayson and E. T. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964.

(7) H. W. Coover, Jr., and J. B. Dickey, U. S. Patent 2,784,209 (1957); *Chem. Abstr.*, **51**, 13903 (1957); G. Kamai and V. A. Kukhtin, *Zh. Obshch. Khim.*, **27**, 949 (1957); *Chem. Abstr.*, **52**, 3665g (1958); V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105 (1959).

(8) A. N. Pudovik and L. G. Biktimirova, *Zh. Obshch. Khim.*, **27**, 2104 (1957); *Chem. Abstr.*, **52**, 6156 (1958).

TABLE I
 ALKYL ACYLPHOSPHONATES AND DERIVATIVES

Compd.	R	R'	B.p., °C. (mm.)	Yield, %	M.p., °C.	2,4-DNP			
						Calcd., %		Found, %	
						N	P	N	P
1 ^a	CH ₃	C ₂ H ₅	181-186 (3-4)	73.6					
2	C ₂ H ₅	C ₂ H ₅	105 (7)	85.7	93-94	14.97	8.28	15.37	8.10
3 ^a	(CH ₃) ₂ CH	C ₂ H ₅	99-100 (4)	85.5	126-127				
4	(CH ₃) ₃ C	C ₂ H ₅	97-100 (5)	65	140-141	13.89	7.68	13.44	7.41
5	Cyclopropyl	C ₂ H ₅	119-120 (5)	69	114-115	14.50	8.02	14.30	7.95
6	Cyclobutyl	C ₂ H ₅	120-124 (5)	64.5	136-136.5	14.00	7.74	14.20	7.82
7	Cyclopentyl	C ₂ H ₅	121-126 (3)	81.5	123-125	13.52	7.48	13.32	7.26
8	Cyclohexyl	CH ₃	98-99 (0.5)	82	125-126	13.94	7.75	14.00	7.75
9	Cyclohexyl	C ₂ H ₅	89-90 (0.2)	88	113.5-115	13.07	7.22	13.08	7.24
10	Cyclohexyl	(CH ₃) ₂ CH	100-102 (0.4)	83	84-86	12.43	6.83	12.28	6.80

^a Both 1 and 3 have been reported but the yields were much lower and thus the esters are included here for completeness. See R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4450 (1956): 1, b.p. 62-65° (1.5 mm.), and 3, b.p. 92-97° (3.9 mm.).

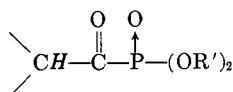
TABLE II

INFRARED SPECTRA OF DIALKYL ACYLPHOSPHONATES^a

Compd.	C=O	P→O	P-O-C
1	1695	1257	1021
2	1695	1265	1020
3	1691	1265	1022
4	1666	1250	1022
5	1670	1260	1022
6	1691	1257	1022
7	1690	1253	1019
8	1695	1266	1040
9	1695	1263	1026
10	1695	1260	990

^a All spectra were made of films of the esters on sodium chloride plates; values are in cm.⁻¹.

As part of a study to evaluate P-H coupling constants in a variety of organophosphorus compounds, the n.m.r. spectra of the acylphosphonates are particularly interesting. In the example of diethyl acylphosphonate (1) the P-H coupling constant for the methyl group adjacent to the carbonyl function is 5 c.p.s. This is a marked drop in value compared with that of methyl esters of phosphorus acids such as in trimethyl phosphate ($J = 11.2$ c.p.s.), dimethyl methylphosphonate (CH₃, $J = 17.5$ c.p.s.; OCH₃, $J = 11$ c.p.s.), trimethyl phosphite ($J = 10$ c.p.s.), and methyl diphenylphosphinate⁹ ($J = 11$ c.p.s.).^{10,11} The α -hydrogens, as shown below, in several of the esters were



complex from coupling with vicinal protons, but the multiplets displayed shoulders in all cases suggesting a P-H coupling.¹² A variety of solvents did not provide for better separation suggesting that the coupling may

(9) K. D. Berlin, T. H. Austin, and M. Nagabhushanam, to be published.

(10) All spectra were measured in carbon tetrachloride for this comparison.

(11) Recent results by Martin and co-workers demonstrate the variation in J when sharp differences exist in the electronegativity of atoms attached to phosphorus; see G. Martin and A. Besnard, *Compt. rend.*, **257**, 898 (1963). Two interesting examples reported which might be compared to our work are (CH₃)₂P→O ($J = 11$ c.p.s.) and (CH₃)₂P→O ($J = 9.25$ c.p.s.), both measured in cyclohexane, however.

(12) Double resonance experiments with triethyl phosphite have shown that $J_{\text{CH}_2-\text{P}}$ and $J_{\text{CH}_2-\text{CH}_3}$ must be nearly equal and the resulting quartets overlap to give a five-line system; see J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963), ref. 95.

TABLE III

N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF DIALKYL ACYLPHOSPHONATES

Compd.	Parameters of structure units ^a					
	R		R'			
	CH ₃	CH ₂	CH	CH ₃	CH ₂	CH
1	2.43 ^d (5) ^b			1.37 t (7.5)	4.22 qt (7)	
2	1.05 t (7.5)	2.80 q (7)		1.32 t (7.5)	4.16 qt (7)	
3	1.14 d (7)		3.10 m (7)	1.35 t (7.5)	4.16 qt (7)	
4				1.33 t (7.2)	4.14 qt (7)	
5 ^c			2.58 m (6)	1.22 t (7.5)	4.10 qt (7)	
6 ^d			3.70 m	1.33 t (7.2)	4.19 qt (7)	
7 ^e				1.30 t (7.3)	4.05 qt (7)	
8 ^f				3.81 d (11) ^b		
9				1.35 t (7.5)	4.18 qt (7)	
10				1.43 d (6.5)		4.85 m (7.5)

^a In CCl₄ solution; δ -values downfield from TMS (J , c.p.s.); multiplicity of signals: d, doublet; t, triplet; m, multiplet; q, quartet; qt, quintet; s, singlet. ^b $J_{\text{P-H}}$ coupling constants. ^c A multiplet for ring protons was centered near δ 1.15. ^d Complex multiplets for ring protons visible at δ 2.2 and 4.2. ^e Complex multiplets for ring protons visible at δ 1.65 and 4.05. ^f All cyclohexyl compounds had complex multiplets for ring protons centered at approximately δ 1.65.

be small. Paramagnetic shielding by carbonyl groups on α -protons is well known,¹³ but the resultant influence by an adjacent phosphoryl group is not easily defined. Proton decoupling (β -protons from α -protons) should be instructive in this matter and will be reported at a later date.¹⁴

(13) L. M. Jackman "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York N. Y., 1959, Chapter 4.

(14) A recent paper summarizes considerable data on P³¹-H spin-spin coupling constants in several organophosphorus compounds; see J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

Experimental¹⁵

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.¹⁵ 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°.

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(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

(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.

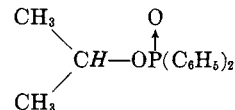
(5) K. Issleib and H. M. Möbius, *Ber.*, **94**, 102 (1961).

(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.

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–CH₃ coupling and the other from H–P³¹ coupling assuming the $J_{\text{CH}-\text{CH}_3}$ and $J_{\text{CH}-\text{P}^{31}}$ constants were close in value. It has been demonstrated that $J_{\text{CH}_2-\text{P}^{31}}$ and $J_{\text{CH}_2-\text{CH}_3}$ 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.

Experimental¹²

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 chloride¹³ 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

(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**.