and petroleum ether (b.p. 60–70°) gave 5.0 g. (51.4%) of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142–143°. The infrared spectrum of this substance in carbon tetrachloride showed a strong absorption band at 3350 cm.$^{-1}$, characteristic of an NH group. Other prominent absorption bands were observed at 3080(s), 1590(s), 1485(s), 1430(s), 1270(s), 1095(s) and 1028(s) cm.$^{-1}$. The band at 1095 cm.$^{-1}$ appears to be due to Ge–phenyl group.

Anal. Calcd. for $C_{30}H_{26}N_2Ge$: C, 73.96; H, 5.38; N, 5.75; Ge, 14.9. Found: C, 73.39, 73.54; H, 5.44, 5.54; N, 5.80, 5.78; Ge, 15.18, 15.04.

The methanol solution on evaporation gave 5.8 g. of a solid melting at 177–179°. Crystallization from a toluene–petroleum ether (b.p. 60–70°) mixture gave 5.2 g. (83.1%) of hexaphenyldigermoxane, m.p. and mixed m.p. 187–189°.

The mother liquor after the removal of the digermoxane was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.9 g. (24.7%) of azobenzene, m.p. and mixed m.p. 65–67°.

Triphenylgermyllithium and Azobenzene.—An ethylene glycol dimethyl ether solution of triphenylgermyllithium prepared by the cleavage of 7.6 g. (0.02 mole) of tetraphenylgermane with 2.0 g. (0.288 g. atom) of lithium[14] was added to 3.64 g. (0.02 mole) of azobenzene dissolved in 50 ml. of ethylene glycol dimethyl ether. The solution became deep brown and it was stirred at room temperature for 20 hr. It was then hydrolyzed by addition to a saturated ammonium chloride solution. The hydrolyzed mixture was extracted with ether, and removal of the solvent from the ether solution gave a residue which when treated with petroleum ether (b.p. 60–70°) gave 7.5 g. of a product melting at 139–141°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 5.6 g. (58.0%) of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142–143°. The melting point was not depressed when admixed with an authentic sample of N,N′-diphenyl-N-triphenylgermylhydrazine, obtained from the previous reaction of azoxybenzene and triphenylgermyllithium. The infrared spectra of the two samples were also identical.

In a second run, using triphenylgermyllithium prepared by the lithium cleavage of hexaphenyldigermane in tetrahydrofuran, a 78.8% yield of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142–143°, was obtained.

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[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

Synthesis of Monoesters of Phosphonic Acids

BY ROBERT RABINOWITZ

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Dialkyl esters of aryl- and alkylphosphonic acids, $RP(O)(OR')_2$, can be hydrolyzed smoothly, rapidly, and in high yield by refluxing in aqueous or ethanolic alkali. Furthermore O,O-diethyl phenylphosphonothioate, $C_6H_5P(S)(OC_2H_5)_2$, was found to hydrolyze to the monoester using *excess* ethanolic or aqueous base. Attempts to prepare the monoester of $CCl_3P(O)(OC_2H_5)_2$, using excess aqueous alkali failed. Finally hydrolysis of $C_6H_5P(O)(OC_6H_5)_2$ with excess alkali presumably resulted in phenylphosphonic acid. Mechanistic interpretations for these findings are presented.

No systematic study of the preparation of monoesters of phosphonic acids exists.[1] Some specific syntheses are known. For example, the reaction of $C_6H_5PCl_4$ with ethanol was reported to yield ethyl hydrogen phenylphosphonate, $C_6H_5P(O)(OC_2H_5)OH$[2]; $(C_6H_5)_3COH$ and PCl_3 react to form $(C_6H_5)_3COPCl_2$ which, when heated with 2.5 *N* alcoholic $NaOC_2H_5$, gave various proportions of phosphonic acid and its monoethyl ester, depending on the heating time.[3] Sarin, isopropyl methylphosphonofluoridate, $CH_3P(O)(F)(OC_3H_7\text{-}i)$, was hydrolyzed by a rat serum enzyme[4] to the monoester. Phenyl hydrogen phenylphosphonate was prepared by the reaction of $C_6H_5P(O)Cl_2$ with one mole of phenol to give $C_6H_5P(O)(OC_6H_5)Cl$ which was then hydrolyzed in H_2O to the desired product.[5] $HO_2C\text{–}CH_2CH_2P(O)(OC_2H_5)OH$ was reported as the product of acid or basic hydrolysis of the corresponding triethyl ester[6]; however, most acid hydrolyses of phosphonates yield the phosphonic acid.[7] $(C_2H_5O)_2P(O)CH_2OCH_2P(O)(OC_2H_5)_2$ and $C_6H_5CH_2OCH_2P(O)(OC_2H_5)_2$ were converted to the sodium salts of their monoesters when refluxed in ethanolic NaCl or NaBr. The free monoesters were not isolated[8a]; other Russian workers have used this alkali halide method to prepare salts of monoesters of phosphonic acids[8b,8c,8d,8e]; Chadwick[8f] used alkaline earth halides to prepare salts of monoesters of vinylphosphonic acid:

$$CaCl_2 + 2CH_2{=}CHP(O)(OC_2H_5)_2 \longrightarrow 2C_2H_5Cl + [CH_2{=}CHP(O)(OC_2H_5)O^-]_2Ca^{++}$$

Monoesters of trichloromethylphosphonic acid have received some attention. $CCl_3P(O)(OC_2H_5)OH$ was prepared by allowing the diester to stand in

(1) When this work was essentially completed, a copy of a paper entitled, "The Preparation, Physical Properties, and Infrared Spectra of Several New Organophosphonates," by D. F. Peppard, J. R. Ferraro and G. W. Mason, which was presented at the March, 1959, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, was secured. Monoesters of phosphonic acids were prepared in a manner analogous to that described in this paper; however, no duplication occurred.

(2) A. Michaelis, *Ann.*, **181**, 265 (1876).

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(8) (a) V. S. Abramov, Ye. V. Sergeyeva and I. V. Chelpanova, *Zhur. Obshchei Khim.*, **14**, 1030 (1944); (b) V. S. Abramov and M. M. Azanovskaya, *ibid.*, **12**, 270 (1942); *C. A.*, **37**, 3048 (1943); (c) V. S. Abramov and E. A. Militskova, *ibid.*, **22**, 252 (1952); *C. A.*, **46**, 11100i (1952); (d) V. S. Abramov and M. N. Morozova, *ibid.*, **22**, 257 (1952); *C. A.*, **46**, 11099c (1952); (e) V. S. Abramov and O. D. Samoilova, *ibid.*, **22**, 914 (1952); *C. A.*, **47**, 4838d (1953); (f) P. H. Chadwick, U. S. Patent 2,784,206 (1957).

15% HCl solution for 2–3 months.[9,9a] The patent literature reveals that heating an equimolar mixture of $CCl_3P(O)(OH)_2$ + $CCl_3P(O)(OC_4H_9)_2$ for 32.5 hours at 100° resulted in an equilibrium mixture containing starting materials and mainly $CCl_3P(O)(OC_4H_9)OH$, which was separated by two extractions.[10] Although no indication was given, the synthesis may be made general; however, it suffers from the necessity of long reaction time and incomplete conversion. When an equimolar mixture of $CCl_3P(O)(OC_4H_9)_2$ and an amine hydrochloride were heated at about 200°, butyl chloride was evolved and the monoester amine salt, $CCl_3P(O)(OC_4H_9)OH\cdot NHR_2$, was formed.[11] Reasonable yields were claimed. Yakubovich and Ginsburg[9] have reported a similar reaction with aniline and diesters of trichloromethylphosphonic acid. The salt can probably be converted to the free monoester by titrating with an equimolar amount of HCl. This also may be a general reaction but no further experimental work was published.

The preparation of several α-hydroxy monoesters has been described[12] but these must be considered as a separate class.

$$C_6H_5CHO + ROPCl_2 + 2CH_3CO_2H \longrightarrow 2CH_3COCl + C_6H_5CH(OH)P(O)(OH)(OR)$$

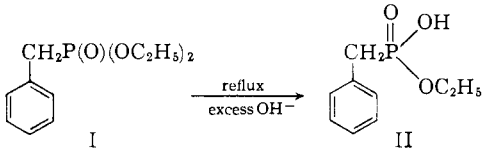
R = CH_3, C_2H_5, C_6H_5

Some thio analogs, $RP(S)(OR')_2$, have been converted to the monoesters, $RP(S)(OR')OH \rightleftarrows RP(O)(OR')SH$, by limited OH^- hydrolysis.[13,14] Hoffman and co-workers[14] experienced much difficulty when equivalent quantities of alkali were consumed and were only successful when the hydrolysis was halted before the stoichiometric amount of base had reacted.

Results and Discussion

It has been found that dialkyl esters of aryl- and alkylphosphonic acids, $RP(O)(OR')_2$, can be hydrolyzed to the corresponding monoesters smoothly, rapidly, and in high yield by refluxing in aqueous or ethanolic alkali. Furthermore O,O-diethyl phenylphosphonothioate, $C_6H_5P(S)(OC_2H_5)_2$, was found to hydrolyze to the monoester using *excess* ethanolic or aqueous base. Attempts to prepare the monoester of diethyl trichloromethylphosphonate, $CCl_3P(O)(OC_2H_5)_2$, by excess aqueous alkali hydrolysis failed. Finally, hydrolysis of diphenyl phenylphosphonate with excess alkali presumably resulted in phenylphosphonic acid.

Refluxing 15.6 g. of diethyl benzylphosphonate (I) in 150 ml. of 10% aqueous NaOH for 2 hours led to a 97.5% yield of monoester, ethyl hydrogen benzylphosphonate (II). Similarly, refluxing 12.4 g. of I in 100 ml. of 8% ethanolic KOH for 17.5 hours gave a 90% yield of II. Under excess aqueous



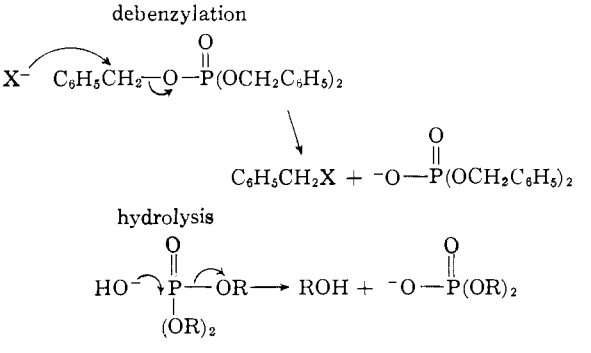
I II

NaOH conditions, dimethyl benzylphosphonate gave a high yield of monoester (86%).

When diethyl phenylphosphonate was refluxed for 80 minutes, or even for 16 hours, in excess aqueous NaOH, very high yields of monoester were obtained, 96 and 90%, respectively.

Di-*n*-butyl cyclohexylphosphonate was recovered unchanged after refluxing for 20 hours in excess aqueous NaOH. However, refluxing in excess ethanolic NaOH for 24 hours resulted in an 85% yield of monoester. It is believed that the stability of the ester under aqueous conditions is a solubility effect, *i.e.*, it is very insoluble in the boiling aqueous solution whereas the benzyl phosphonic acid esters already described probably have slight solubility.

In each of the above examples the hydrolysis halted at the monoester stage. Hudson and Keay[15] studied the kinetics of phosphonate hydrolysis and state that only the first group is removed under alkaline conditions. Organic phosphates behave similarly; basic hydrolysis of trimethyl phosphate is said to remove only one methyl group.[16] Clark and Todd[17] found that several neutral benzyl esters of phosphorus, for example, dibenzyl phosphite and tribenzyl phosphate, could be selectively monodebenzylated using salts. These results are similar to those mentioned earlier.[8a–8f] Some of the salts found effective were LiCl, KOAc, $LiNO_3$, LiOAc and 4-benzyl-4-methylmorpholinium chloride.[18] The mechanism proposed for this debenzylation differs from hydroxide ion hydrolysis in that the debenzylation involves C–O cleavage, whereas hydroxide ion hydrolysis involves P–O cleavage.



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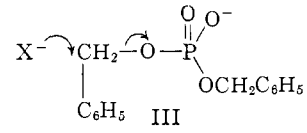
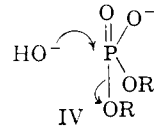
The latter fact has been clearly demonstrated by O^{18} studies[19,20] and is supported by strong kinetic arguments by Hudson and Keay.[15] The strict *mono*debenzylation is analogous to the basic hydrolysis stopping at the monoester stage. Both systems require for further reaction that the already negatively charged portion of the molecule accept an additional negative charge (III, IV). This is not a favorable situation and readily ac-



III



IV

counts for the removal of only one group during debenzylation as well as during the basic hydrolysis of phosphates and phosphonates.

The extreme stability of the second group to hydrolysis was clearly demonstrated in the aqueous NaOH hydrolysis of diethyl phenylphosphonate. Although the hydrolysis to monoester was complete in less than 2 hours, a mixture refluxed for 16 hours still gave an 88% yield of monoester. In contrast to the high order of base stability, refluxing a 10% solution of II in distilled water for 12 days gave a 97% yield of benzylphosphonic acid. Here, the monoester acted as its own acid catalyst.

Basic hydrolysis of diphenyl phenylphosphonate did not produce any monoester, although all the starting material disappeared and phenol was formed. It was assumed that, in this case, hydrolysis went completely to the phosphonic acid. A possible explanation of this result is that, in spite of the fact that the second step in the hydrolysis probably goes through an intermediate similar to IV, the transition state involves the partial formation of the more stable phenoxide ion as compared with the alkoxide ion. This effect undoubtedly lowers the energy of the transition state, possibly to a point such that the second step can occur under the hydrolysis conditions.

Diethyl trichloromethylphosphonate was hydrolyzed in excess aqueous base; however, little, if any monoester was produced. This result supports the work of Yakubovich and Ginsburg[9] who found that this ester was cleaved in the presence of aqueous $Ba(OH)_2$ to chloroform, phosphoric acid and ethanol. Furthermore it is in agreement with the detailed findings of Bengelsdorf[9a] who has established the following stoichiometry for the hydrolysis in 0.5 *M* ethanolic KOH solution.

$$2CCl_3P(O)(OC_2H_5)_2 + 9OH^- \longrightarrow CO + HCOO^- + 6Cl^- + 4H_2O + 2(C_2H_5O)_2P(O)O^-$$

It appears reasonable that this reaction also involves attack of hydroxide ion on phosphorus; however, in this case the relatively more stable trichloromethyl anion is released in preference to the ethoxide ion. This line of reasoning is justified in comparing this ester to dialkyl alkyl- and dialkyl arylphosphonates, since the trichloromethyl anion is much more stable than the phenyl or alkyl anion.

The basic hydrolysis of phosphonothioates, $RP(S)(OR')_2$, has been reported successful only when less than a stoichiometric amount of base was used.[13,14] In view of the fact that the desired product, $RP(S)(OR')O^-$, is expected to be inert in basic media (where R′ = alkyl), the necessity of limiting the amount of base consumed, as Hoffman and co-workers[14] claim, did not seem justified. Hydrolysis of O,O-diethyl phenylphosphonothioate using aqueous NaOH (48 hours) and excess ethanolic KOH (15 hours) resulted in the isolation of 65 and 94% of the monoester, respectively. The monoester was an oil but it was identified by its crystalline dicyclohexylamine salt. This confirmed the contention that limiting the amount of base to less than the stoichiometric amount was not necessary.

Experimental

A. Materials.—Dimethyl and diethyl benzylphosphonates were prepared in high yield by the reaction of benzyl chloride with the corresponding trialkyl phosphite. Analytically pure products were obtained. Diethyl phenylphosphonate and diphenyl phenylphosphonate were prepared by the reaction of benzenephosphonyl dichloride with ethanol and phenol, respectively, in the presence of pyridine. O,O-Diethyl phenylphosphonothioate was similarly prepared from benzenephosphonyl thiodichloride and ethanol. Diethyl trichloromethylphosphonate was obtained by refluxing triethyl phosphite in carbon tetrachloride for several hours.[9a] The di-*n*-butyl cyclohexylphosphonate was of unknown origin. It was probably prepared by the air oxidation of cyclohexane in the presence of PCl_3[21] followed by reaction with 1-butanol in the presence of a tertiary amine.

Hydrolysis of Diethyl Benzylphosphonate. (a) **Aqueous.**—Diethyl benzylphosphonate (15.6 g., 0.069 mole) was refluxed in 150 ml. of 10% aqueous NaOH (0.375 mole). After 1.5 hours, the solution was homogeneous. Refluxing was continued for an additional 20 minutes whereupon the mixture was cooled and acidified with concentrated HCl. An oil separated. It was extracted with chloroform, the extract dried over Na_2SO_4, and the chloroform removed by heating on a steam-bath at 8 mm. The residual material slowly crystallized on standing, 13.36 g. (97.5%), and was recrystallized from 175 ml. of heptane, m.p. 63–64°. It was identified as ethyl hydrogen benzylphosphonate.

Anal. Calcd. for $C_9H_{13}O_3P$: C, 54.00; H, 6.50; P, 15.50; neut. equiv., 200.0, Found: C, 53.99; H, 6.55; P, 15.85; neut. equiv., 200.6.

(b) **Ethanolic.**—Diethyl benzylphosphonate (12.4 g., 0.055 mole) was refluxed in 100 ml. of 8% ethanolic KOH (0.14 mole). After 1.5 hours, dilution of 5.0 ml. of the reaction mixture with water gave no oil, indicating that all the starting material had reacted. Refluxing was continued for a total of 16 hours. Most of the ethanol was removed by distillation, the reaction mixture diluted with 150 ml. of H_2O and acidified. The oil that separated was extracted with $CHCl_3$ and work-up as in (a) resulted in 9.33 g. (90%) of oil which crystallized fairly quickly. Recrystallization from 125 ml. of heptane gave a crystalline solid, m.p. 63–65°.

Hydrolysis of Dimethyl Benzylphosphonate.—Dimethyl benzylphosphonate (13.7 g., 0.0685 mole) was refluxed for 2 hours in 150 ml. of 10% NaOH (0.375 mole). At this point the solution was completely homogeneous. Acidification of the chilled reaction mixture with concentrated HCl gave a crystalline white precipitate, 8.31 g. The mother liquor was extracted with $CHCl_3$ and removal of the dried solvent left an additional 2.69 g. (total 11.0 g., 86%). Recrystallization from 1200 ml. of heptane gave a crystalline solid, m.p. 96–97°. This material was methyl hydrogen benzylphosphonate.

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(20) E. Blumenthal and J. M. Herbert, *Trans. Faraday Soc.*, **51**, 611 (1955).

(21) J. O. Clayton and W. L. Jensen, THIS JOURNAL, **70**, 3880 (1948).

Anal. Calcd. for $C_8H_{11}O_3P$: C, 51.61; H, 5.91; P, 16.66; neut. equiv., 186.0. Found: C, 51.68; H, 6.04; P, 16.39; neut. equiv., 187.8.

Hydrolysis of Di-*n*-butyl Cyclohexylphosphonate. (a) **Aqueous.**—Di-*n*-butyl cyclohexylphosphonate (13.7 g., 0.0424 mole) was refluxed for 20 hours in 100 ml. of 10% NaOH (0.25 mole). No hydrolysis occurred during this period.

(b) **Ethanolic.**—Di-*n*-butyl cyclohexylphosphonate (8.2 g., 0.0297 mole) was refluxed in 100 ml. of 7% ethanolic NaOH (0.175 mole). Diluting 0.5 ml. of the red reaction mixture with water after 23.5 hours refluxing gave no oil. The entire reaction mixture was then diluted to 450 ml. with water and a slight cloudiness formed. The solution was extracted with ether, removing the cloudiness and most of the coloration. The water layer was heated to remove the dissolved ether and was then acidified with concentrated HCl. The oil that separated was extracted with $CHCl_3$ and the $CHCl_3$ removed after drying. The residue was a red-brown oil, 5.57 g. (85%). It was identified as the monobutyl ester of cyclohexylphosphonic acid by preparing the crystalline dicyclohexylamine salt (see below). An 81% yield of salt was obtained even after 1 recrystallization, m.p. 160–163°.

Anal. Calcd. for $C_{22}H_{44}NO_3P$: C, 65.85; H, 10.98; P, 7.73; N, 3.49. Found: C, 65.47; H, 10.83; P, 8.00; N, 3.53.

If ester interchange had occurred prior to or after the hydrolysis, the monoethyl ester would have been expected. This would have required C, 64.40; H, 10.75; P, 8.31; N, 3.85. The analysis, however, agreed much better with the monobutyl ester and therefore no interchange occurred.

Hydrolysis of Diethyl Phenylphosphonate.—Diethyl phenylphosphonate (13.2 g., 0.062 mole) was refluxed in 100 ml. of 10% aqueous NaOH (0.25 mole). After 105 minutes the solution was homogeneous. The mixture was cooled and acidified with concentrated HCl. The oil that separated was extracted with $CHCl_3$. Evaporation of the dried $CHCl_3$ extract gave 11.0 g. of a cloudy white oil (96%) which was identified as the monoester, ethyl hydrogen phenylphosphonate, by preparing the crystalline dicyclohexylamine salt, m.p. 140.7–141.8°.

Anal. Calcd. for $C_{20}H_{34}NO_3P$: C, 65.30; H, 9.28; N, 3.82; P, 8.44. Found: C, 65.00; H, 9.38; N, 3.79; P, 8.22.

When 13.3 g. of diethyl phenylphosphonate was refluxed in 100 ml. of 10% aqueous NaOH for *16 hours*, 10.46 g. of monoester (88%) was isolated.

Hydrolysis of Diphenyl Phenylphosphonate.—Diphenyl phenylphosphonate (9.6 g., 0.0310 mole) was refluxed in 100 ml. of 10% aqueous NaOH (0.25 mole). After 4 hours the solution was completely homogeneous. Refluxing was continued for an additional 0.5 hour, the solution cooled and acidified with concentrated HCl. An oil separated. The oil was extracted with $CHCl_3$ and the $CHCl_3$ solution washed with saturated $NaHCO_3$. Acidification of the $NaHCO_3$ extract gave no precipitate at all. The $CHCl_3$ layer was dried over Na_2SO_4 after washing with water and the $CHCl_3$ evaporated. The oily residue crystallized on standing. The infrared spectrum was identical with that of phenol.

Hydrolysis of Ethyl Hydrogen Benzylphosphonate.—The monoester (2.98 g., 0.0149 mole) was refluxed in 30 ml. of distilled water. The mixture was cooled at frequent intervals to check the course of the reaction. When no oil separated the hydrolysis was assumed complete (12 days). The water was evaporated and 2.56 g. of benzylphosphonic acid (97%) was found, m.p. 167–169° after recrystallization from a minimum of water.

Hydrolysis of Diethyl Trichloromethylphosphonate.—The ester (9.0 g., 0.035 mole) was refluxed in 100 ml. of 10% aqueous NaOH (0.25 mole). After 45 minutes, the solution was completely homogeneous. It was cooled and acidified with concentrated HCl. No sign of precipitation was noted. The mixture was extracted with three 75-ml. portions of $CHCl_3$, the extract dried and the $CHCl_3$ evaporated. The residue was 4.02 g. of an oil. Infrared analysis showed typical monoester absorption.[1] However, the crystalline dicyclohexylamine salt, m.p. 138–141° contained only 1.5–2.0% Cl, whereas the salt of the desired monoester requires 26.15%.

Hydrolysis of O,O-Diethyl Phenylphosphonothioate. (a) **Aqueous.**—The ester (9.45 g., 0.041 mole) was refluxed in 100 ml. of 10% aqueous NaOH (0.25 mole). After 24 hours, the mixture was almost homogeneous; however, a few oil droplets were observed. Refluxing was continued for an additional 24 hours, traces of oil droplets still being present. The solution was cooled and extracted with ether. The water layer was heated to drive off dissolved ether, cooled, and acidified with concentrated HCl. A precipitate formed and acidification continued until the precipitation halted. The solid was collected and dried, 2.16 g.; it was not identified. Continued acidification of the filtrate resulted in the separation of an oil. The oil was extracted with $CHCl_3$, the solution dried over Na_2SO_4, and the $CHCl_3$ evaporated. The residue, 5.35 g. (65%) of oil, was identified as the monoester by means of the dicyclohexylamine salt, m.p. 151.5–154.0°.

Anal. Calcd. for $C_{20}H_{34}NO_2PS$: C, 63.00; H, 8.90; S, 8.38; N, 3.66; P, 8.10. Found: C, 62.81; H, 9.17; S, 8.66; N, 3.87; P, 8.14.

(b) **Ethanolic.**—The ester (10.0 g., 0.036 mole) was dissolved in 100 ml. of 7% ethanolic KOH (0.125 mole). When a 1.0-ml. sample of this solution was diluted with water, milkiness developed. After 2, 10.5 and 13.5 hours of refluxing a similar test produced cloudiness; however, in the last test it was very faint. The reaction mixture was reduced in volume to 50 ml. and then diluted to 200 ml. with water. A cloudiness developed and the solution was extracted with ether. The water layer was heated to remove dissolved ether, cooled and acidified with concentrated HCl. Work-up of the monoester was analogous to (a); 7.91 g. of oil was recovered (94%). A dicyclohexylamine derivative was made, m.p. 150–153°.

Preparation of Dicyclohexylamine Salts.—To the monoester dissolved in 4–5 volumes of benzene was added dicyclohexylamine (0–20% excess) dissolved in 4–5 volumes of benzene. A temperature rise to approximately 50° occurred. On standing, the salt crystallized from the solution and was collected. If the salt did not crystallize, the benzene was evaporated and the solid residue recrystallized. Heptane was used as the recrystallization solvent. The yields in most cases were nearly quantitative.