New Method for Preparing Alkyl (Amino-*s*-triazinyl)phosphonates

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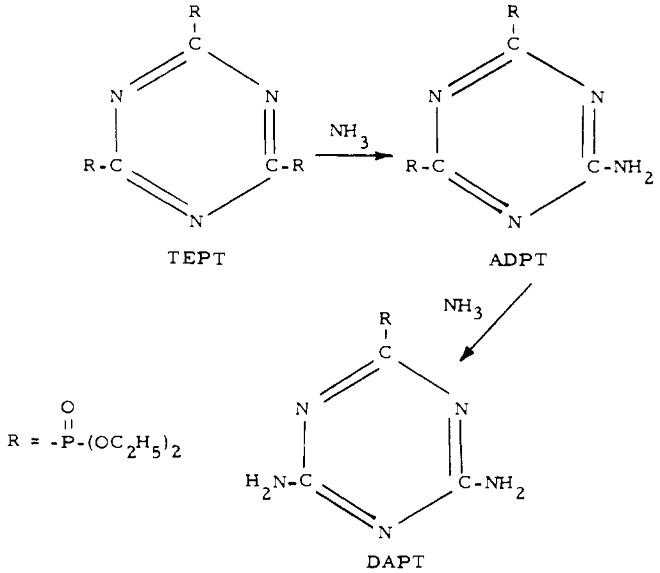
Diethyl (4,6-diamino-*s*-triazine-2-yl)phosphonate (DAPR) is prepared in 83% yield by the reaction of hexaethyl *s*-triazine-2,4,6-triyltriphosphonate (TEPT) with ammonia in ethanol solution. When this reaction is carried out in benzene, tetraethyl (6-amino-*s*-triazine-2,4-diyl)diphosphonate (ADPT) is obtained as the major product in 74% yield. The major by-product from this reaction is diethyl hydrogen phosphite. Mono- and diammonium salts of ADPT are also obtained in small yields. Some infrared and proton magnetic resonance data are also described.

Alkyl *s*-triazinylphosphonates are commonly prepared by the Arbuzov reaction of triethyl phosphite with the desired chloro-*s*-triazine (*4, 5, 7*).

It is also reported that amino-substituted *s*-triazinylphosphonates have been prepared by this method (*2*). However, the reaction of 4,6-diamino-2-chloro-*s*-triazine (DACT) with triethyl phosphite to produce diethyl (4,6-diamino-*s*-triazine-2-yl)phosphonate (DAPT) could not be duplicated in our laboratory. This reaction was tried in refluxing benzene, refluxing xylene, and refluxing dimethyl formamide without isolation of DAPT. DACT was also reacted with triethyl phosphite (neat) at refluxing temperature for four hours, but 92% of the starting material was recovered.

DAPT was therefore prepared by a new method in which hexaethyl *s*-triazine-2,4,6-triyltriphosphonate (TEPT) is reacted with NH_3 at room temperature or below to replace two phosphonate groups with NH_2 as shown in the reaction scheme.



The major by-product, diethyl hydrogen phosphite, is easily recovered by distillation.

The preferred procedure is to dissolve TEPT in absolute ethanol, saturate with NH_3 at approximately 5° C., and allow the solution to stand for at least three days. DAPT is obtained in approximately 83% yield. While it is insoluble in most common solvents, it is soluble in dimethyl sulfoxide at room temperature.

ADPT is obtained as a by-product in small yields in ethanol solution but when the reaction is carried out in benzene, ADPT is obtained as a 74% yield and DAPT as a 17% yield.

When DAPT is prepared without isolation and purification of TEPT, a 70.5% yield based on cyanuric chloride is obtained. The yield is reduced to only 67% when cyanuric chloride and triethyl phosphite are used without purification.

Low yields of DAPT (24%) are obtained when the reaction of TEPT with ammonia is carried out in ammonium hydroxide instead of alcoholic ammonia.

Small amounts of by-products, believed to be the mono- and diammonium salts of ADPT, are obtained from the reaction of TEPT with ammonia. In the monoammonium salt, only one phosphonate group is half ester and half salt, whereas in the diammonium salt both phosphonate groups are half ester and half salt.

The infrared (IR) and proton magnetic resonance (pmr) spectra of the triazinylphosphonates were studied and are consistent with proposed structures. In the IR spectra, the triazine ring stretching absorptions (6.4–6.7 microns) and the $P=O$ absorptions (7.9–8.3 microns) are of particular interest. The ring-stretching absorption is influenced by the nature of the substituent on the triazine ring—i.e., as the electron density on the ring decreases, the ring-stretching absorption increases in wavelength. Differentiation between mono-, di-, and trichlorotriazine has been reported by identification of the ring-stretching absorption, which increases in wavelength with the number of chlorine substituents (*3*).

Ring-stretching absorption can appear as two bands when the ring contains different substituents (*6*). The triazinyltriphosphonate, TEPT, gives a strong single band at 6.66 microns, whereas DAPT, ADPT, and the mono- and diammonium salts of ADPT give double bands in this region. The lower wavelength band is virtually stationary and occurs at 6.46, 6.45, 6.49, and 6.52 microns, respectively. This absorption band is characteristic of melamines, as is the NH_2 deformation absorption near 6.0 microns, and is attributed to the NH_2 substituent (*1*). The higher wavelength band is attributed to the phosphonate substituents and occurs at 6.56, 6.65, 6.72, and 6.72 microns, respectively.

The $P=O$ absorption bands of TEPT, ADPT, and DAPT occur at 7.93, 8.11, and 8.18 microns, respectively.

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Therefore, this band increases in wavelength as the number of phosphonate groups on the ring decreases and the number of amino groups increases. The P=O absorption bands of the mono- and diammonium salts of ADPT are influenced more by the salt structure than by the ring substituents and therefore appear at 8.20 and 8.29 microns, respectively.

In the pmr spectra of TEPT, ADPT, and DAPT, the ester and amino protons are readily assigned and the integration curves give accurate proton counts. Of particular interest are the methylene protons of the ester group, which appear as a quintet. It was expected that these protons would appear as a double quartet caused by the phosphorus coupling. This is, in fact, the case, but these protons appear as a perfect quintet because the coupling constants, J_{HH} and J_{PH} are both equal to 7 cps. This was shown to be true when the methylene protons in diethyl hydrogen phosphite did appear as a double quartet. This is because J_{HH} is equal to 7 cps and J_{PH} is equal to 9 cps. Also worthy of note, in the spectrum of diethyl hydrogen phosphite, is the single proton attached to the phosphorus atom. This proton appears as a doublet with a coupling constant of 688 cps.

EXPERIMENTAL

Proton magnetic resonance (pmr) spectra were determined in solvents indicated on a Varian Model A-60A equipped with V-6040 variable temperature probe. Chemical shifts were measured with respect to tetramethylsilane as an internal reference. Infrared (IR) spectra were obtained in KBr disk from a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Elemental analyses were performed in duplicate by Galbraith Laboratories, Knoxville, Tenn. Melting points were corrected.

2-Amino-4,6-dichloro-*s*-triazine (ADCT) and 2,4-diamino-6-chloro-*s*-triazine (DACT) were prepared according to Thurston *et al.* (*8*).

Hexaethyl *s*-triazine-2,4,6-triyltriphosphonate (TEPT) was prepared according to Hewertson *et al.* (*4*). The IR spectrum of TEPT had absorption bands of 6.66 microns (s) (ring stretching); 7.93 microns (s) (P=O); 8.60 microns (m) (P—O—Et); 9.65, 13.35 microns (s) (P—O—C) and 11.83, 12.35 microns (m) (ring bending). The pmr spectrum (DMSO) showed a triplet at δ 1.36 ppm and a quintet at δ 4.33 ppm ($J_{HH} = J_{PH} = 7$ cps). The spectrum integrated 3:2.

Tetraethyl (6-amino-*s*-triazine-2,4-diyl)diphosphonate (ADPT) was prepared from ADCT according to D'Alelio (*2*). ADPT was also prepared from TEPT using benzene as the solvent. A sample of ADPT, recrystallized from diethyl ether, had a mp of 104–105° C. The IR spectrum showed absorption bands at 2.99, 3.15 microns (s) (NH stretching); 5.98 microns (s) (NH deformation); 6.45, 6.65 microns (s) (ring stretching); 8.11 microns (s) (P=O); 8.58 microns (m) (P—O—Et); 9.77, 13.39 microns (s) (w) (P—O—C); and 11.70, 12.58 microns (m) (ring bending). The pmr spectrum ($CDCl_3$) showed a triplet at δ 1.41 ppm, a quintet at δ 4.37 ppm ($J_{HH} = J_{PH} = 7$ cps) and a singlet at δ 7.15 ppm. The spectrum integrated 6:4:1, respectively.

Elemental analyses were close to the theoretical values for ADPT.

Diethyl (4,6-Diamino-s-triazine-2-yl)phosphonate (DAPT). DAPT was prepared by the reaction of TEPT with ammonia in ethanol, benzene, and water.

Ethanol Procedure. TEPT (97.9 grams, mp 93–95° C) was dissolved in 400 ml of absolute ethanol. The solution was cooled in an ice-salt bath to approximately 0° C., and then saturated with ammonia gas. The addition was regulated so that the reaction temperature did not rise above 15° C. The solution was allowed to stand at least three days. After cooling, the precipitated white solid was removed by filtration, washed thoroughly with water then acetone, and dried to give 41.2 grams (83% yield) of DAPT. From another run, a small amount of a water-soluble white powder was obtained after removal of ethanol. Elemental analyses were within the range of the theoretical values of a monoammonium salt of ADPT (see by-products). Diethyl hydrogen phosphite was recovered by vacuum distillation as the major by-product in 75% yield (see below).

A sample of DAPT, recrystallized from boiling water, had a mp of 273° C. with decomposition. The IR spectrum showed absorption bands at 2.99, 3.12 microns (s) (NH stretching); 6.00, 6.14 microns (s) (NH deformation); 6.46, 6.56 microns (s) (ring stretching); 8.18 microns (s) (P=O); 9.77, 13.47 microns (s) (w) (P—O—C); and 12.24, 12.59 microns (w) (ring bending). The pmr spectrum (DMSO) gave a triplet at δ 4.17 ppm ($J_{HH} = J_{PH} = 7$ cps) and a singlet at δ 7.00 ppm. The spectrum integrated 3:2:2, respectively.

Anal. Calcd. for $C_7H_{14}N_5O_3P$: C, 34.01, H, 5.71; N, 28.33; P, 12.53. Found: C, 34.00; H, 5.66; N, 28.38; P, 12.60.

Benzene Procedure. TEPT (0.023 mole, 11.4 grams) was dissolved in 35 ml of benzene, the solution cooled, and then was saturated with ammonia. After cooling overnight, the white precipitate was removed by filtration to give 0.93 gram (0.004 mole, 17.4% yield) of DAPT. The filtrate was concentrated and diethyl hydrogen phosphite (0.022 mole, 3.1 grams) removed by vacuum distillation. The residue, which solidified overnight, was triturated in petroleum ether, filtered, and dried to give 6.21 grams of a white crystalline compound. A sample of this compound, after recrystallization from diethyl ether, had elemental analyses and melting point consistent with an authentic sample of ADPT prepared by the method of D'Alelio (*2*).

Water Procedure. TEPT (0.05 mole, 24.5 grams) was added in increments to 75.5 grams of NH_4OH (28% NH_3). The reaction temperature rose spontaneously to 34° C. After standing at room temperature for five days, the white precipitate was removed by filtration, washed thoroughly with water then acetone, and dried to give 2.11 grams (0.009 mole, 18% yield) of DAPT. The filtrate was cooled to 10° C., saturated with ammonia gas, and allowed to stand three days. A water-soluble white precipitate (2.42 grams) was recovered by filtration. Analyses (see by-products) indicate that it is a diammonium salt of ADPT.

By-products. Diethyl hydrogen phosphite—The IR spectrum showed major absorption bands at 2.90 microns (w) (OH stretching); 4.12 microns (m) (PH stretching); 7.93 microns (s) (P=O) and 8.60 microns (m) (P—O—Et). The pmr spectrum (CCl_4) showed a triplet at δ 1.35 ppm, a doublet quartet at δ 4.10 ppm ($J_{HH} = 7$ cps, $J_{PH} = 9$ cps), and a doublet centered at 6.68 ppm ($J_{PH} = 688$ cps). The spectrum integrated 6:4:1, respectively. *Anal.* Calcd. for $C_4H_{11}O_3P$: C, 34.79; H, 8.03; P, 22.43. Found. C, 34.87; H, 8.03; P, 22.44.

Monoammonium salt of ADPT—This compound had a mp of 295° C. with decomposition and liberated ammonia when added to 25% NaOH. The IR spectrum showed strong absorption bands at 3.15 microns (NH stretching); 6.07 microns (NH deformation); 6.49, 6.72 microns (ring stretching); 8.20 microns (P=O) and 9.52 microns (P—O—C). *Anal.* Calcd. for $C_9H_{21}N_5O_6P_2$: C, 30.26, H, 5.93; N, 19.60; P, 17.34. Found: C, 28.89; H, 6.30; N, 20.17; P, 17.61.

Diammonium salt of ADPT—This compound had a mp of 308° C. with decomposition and liberated ammonia when added to 25% NaOH. The IR spectrum showed strong absorption bands at 3.20 microns (NH stretching); 6.03 microns (NH deformation); 6.52, 6.72 microns (ring stretching); 8.29 microns (P=O) and 9.48 microns (P—O—C). *Anal.* Calcd. for $C_7H_{20}N_6O_6P_2$: C, 24.88; H, 5.82; N, 24.27; P, 17.89. Found: C, 24.19; H, 5.76; N, 23.81; P. 17.19.

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LITERATURE CITED

(1) Colthup, N.B., Daly, L.H., Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy," pp. 234-5, 358, Academic Press, New York, 1964.
(2) D'Alelio, G., U.S. Patent **3,210,350** (Oct 5, 1965).
(3) Herman, T.S., *Appl. Spectros.*, **20** (3), 159-60 (1966).
(4) Hewertson, W., Shaw, R.A., Smith B.C., *J. Chem. Soc.* **1963**, p. 1670.
(5) Morrison, D.C., *J. Org. Chem.* **22**, 444 (1957); Coover, H.W., Jr., U.S. Patent **2,685,581** (Aug. 3, 1954).
(6) Reimschuessel, H.K., McDevitt, N.T., *J. Am. Chem. Soc.* **82**, 3756-62 (1960).
(7) Schroeder, Hasjuergen, *Ibid.*, **81**, 5658-63 (1959).
(8) Thurston, J.T., Dudley, J.R., Kaiser, D.W., Heckenbleikner, I., Schaefer, F.C., Holm-Hansen, D., *Ibid.*, **73**, 2981-3 (1951).

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Solubilities of Some Normal Saturated and Unsaturated Long-Chain Fatty Acid Methyl Esters in Acetone, *n*-Hexane, Toluene, and 1,2-Dichloroethane

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Solubility data have been obtained for a number of highly pure long-chain fatty acid methyl esters: methyl stearate, methyl palmitate, methyl heptadecanoate, methyl petroselaidate, methyl elaidate, methyl petroselinate, methyl oleate, methyl palmitoleate, and methyl linoleate in acetone, *n*-hexane, toluene, and 1,2-dichloroethane. All methyl esters were completely miscible in the solvents used. Two polymorphic forms of methyl linoleate were observed.

In recent publications from this laboratory the solubility behavior of a number of normal long-chain saturated and unsaturated fatty acids were reported in isopropyl ether, methanol, acetone, and toluene (*1*), in dimethylsulfoxide (*2*), and in *N,N*-dimethylformamide and *N,N*-dimethylacetamide (*3*). Earlier, Ralston, Harwood, Hoerr *et al.* reported on a careful extensive study of the solubilities of a number of long-chain saturated and unsaturated fatty acids and saturated fatty acid esters in a wide variety of solvents (*5-8, 10, 12*). Privett *et al.* (*9*) reported the solubilities of a number of saturated fatty acids, their methyl esters, alcohols, and triglycerides in acetone in an attempt to fill in the gap in solubility data which existed at that time. Thus, the solubility behavior of the saturated fatty acids, the unsaturated fatty acids, and the saturated fatty acid esters has been investigated extensively in a wide variety of solvents. However, not a great deal has been reported concerning the solubility characteristics of the methyl esters of the unsaturated fatty acids, partly because of lack of suitable highly pure materials and a practical apparatus for accurately determining solubilities at the necessary low temperatures required for unsaturated fatty acid esters. With the advent of modern gas-liquid and thin-layer chromatographic techniques, materials with a certified high purity became available. A recent publication from this laboratory (*4*) described an apparatus for determining solubilities by the thermostatic sealed tube method at temperatures approaching that of dry ice. Thus, the present investigation into the solubility behavior of a number of low melting saturated and unsaturated fatty acid methyl esters was possible.

EXPERIMENTAL

Methyl stearate, methyl palmitate, and methyl heptadecanoate were recrystallized products prepared from samples obtained by fractional distillation. The methyl elaidate and methyl petroselaidate were recrystallized materials prepared from the highly pure acids. The methyl oleate, methyl petroselinate, methyl palmitoleate, and methyl linoleate, purchased from the Hormel Institute with purity estimated to be greater than 99% by GLC and thin-layer chromatographic analyses, were used with no further purification. The final estimate of purity and the freezing points of the materials were determined using the method of heating curves and apparatus described by Skau (*13*). Liquid nitrogen was used as the coolant. Temperature measurements were made using a thermocouple calibrated at the freezing points of benzoic acid, naphthalene, and mercury using thermometric cells and at the equilibrium sublimation temperature of solid carbon dioxide (*11*). The freezing points obtained are: methyl stearate, 38.24; methyl palmitate,