

alcohol, if necessary. Table I indicates the results obtained.

Preparation of the hydantoins. In general, the hydantoic ester was mixed with 3 to 5 times its weight of 6*N* hydrochloric acid and heated for 15–20 min. to a temperature just below the boiling point of the mixture. On cooling, the hydantoin usually crystallized out, although, in some cases, the solution had to be evaporated down further before cooling afforded the crystalline product. The yields varied considerably, depending upon the amount of hydrochloric acid used in the reaction mixture.

In Table II are listed the various hydantoins obtained from the hydantoic esters shown in Table I.

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sym-Triazinetriphosphonic Acid Esters¹

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Cyanogen iodide and triethyl phosphite have been shown to interact forming diethyl cyanophosphate.² In the present work, the reaction of the

These esters are stable substances but show some tendency to hydrolyze in moist air, the hexamethyl ester being most reactive in this respect. The methyl, ethyl and β -chloroethyl esters were prepared, in addition to a crude *n*-propyl ester. Hydrolysis of the esters by long boiling with water gave a high-melting phosphonic acid which probably still contained ester groups as analysis gave high carbon values.³

The compounds, particularly the hexachloroethyl ester, were of interest in cancer chemotherapy due to the large number of alkylating groups present.

EXPERIMENTAL

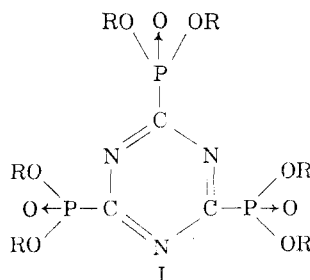
Melting points are uncorrected.

sym-Triazinetriphosphonic acid esters (I). The reaction was carried out by adding powdered cyanuric chloride, in portions, to the warmed (about 60°) phosphite ester (3.1–3.5 molar equivalents). With the two lower esters, the product formed a paste on cooling. The preparation could also be done using benzene as solvent for the phosphite. Cyanuric acid, if present in the mixture, was removed by extraction of the product with chloroform, filtration and evaporation. The description of the synthesis of the ethyl ester only is given as the others were prepared similarly. Constants and analyses are listed in Table I.

TABLE I
sym-TRIAZINETRIPHOSPHONIC ESTERS

Ester	Yield, %	M.P., °C	C		H	
			Calcd.	Found	Calcd.	Found
Methyl	89.4	123–124.5	26.67	26.89	4.44	4.70
Ethyl	98.9	94–95	36.81	36.81	6.14	6.12
β -Chloroethyl	76.1	51.5–54	25.86	25.59	3.45	3.38

trimeric cyanuric chloride with trialkyl phosphites was studied in the hope that the halogen would be active enough to permit the Arbusov rearrangement to occur. This was found to be the case, and 3 moles of the phosphite ester were observed to react easily with 1 mole of the cyanuric halide. The triazine ring system is apparently maintained in the products, which can be formulated as *sym*-triazine triphosphonic acid esters (I).



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(2) Saunders, Stacey, Wild, and Wilding, *J. Chem. Soc.*, 699 (1948).

Triethyl phosphite (15 ml., 0.0877 mole) was treated gradually with 4.6 g. of cyanuric chloride (0.025 mole) at 50–60°. Considerable heating occurred and some evolution of ethyl chloride was noticed. The addition was completed in 15 min., whereupon the mixture was kept at 100° for 15 min. After standing for 1 hr. at room temperature, the paste was ground and extracted thoroughly with petroleum ether. The dried product weighed 12.1 g. or 98.9% yield. It gave well formed crystals from ether. The ester was recrystallized three times from this solvent and vacuum-dried for analysis. The ethyl ester is readily soluble in water to yield a neutral solution, from which it separates on warming as an oil which redissolves again on cooling.

The methyl ester was recrystallized from acetone-petroleum ether.

The β -chloroethyl ester was obtained first as an oil, which slowly crystallized during 2 to 5 days. When crystallization was complete, the mass was ground with 15 to 20 portions of ether (with some loss) and dried *in vacuo*. The product was pure but could be recrystallized from acetone-ether.

A crude *n*-propyl ester was prepared as an oil, part of which crystallized slowly on keeping at 0°.

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(3) This acid showed weak chelating power for cupric ion in alkaline solution.