Alternative preparation of IV–VI. Compounds IV–VI were prepared by dissolving the methyl iodide salt of hexamethylenetetramine, PAA, and PAAO, respectively (0.001 mol), in methanol (60 ml) and sodium picrate (0.001 mol) in methanol (10 ml). The precipitate produced was filtered and dried. Infrared and NMR spectra of each of the compounds were identical to those of samples prepared by the other method. The methyl chloride salt of PAAO with sodium picrate also produced VI.

Reaction of 2-thia-1,3,5-triaza-7-phosphaadamantane 2,2-dioxide ($PASO_2$) with formaldehyde and acid. Reaction conditions were the same as for the preparation of VII: $PASO_2$ (2.07 g, 0.01 mol), picric acid (2.52 g, 90%, 0.01 mol), and formalin (3.0 g, 37.5%, 0.033 mol) in ethanol (150 ml). Evaporation to half volume and filtration produced 4.0 g (92.8% yield) of 5-hydro-5-azonia-2-thia-1,3-diaza-7-phosphaadamantane-2,2-dioxide picrate (VIII).

The same procedure with hydrochloric acid in lieu of picric acid produced 2.0 g (82.3% yield) of 5-hydro-5-azonia-2-thia-1,3-diaza-7-phosphaadamantane-2,2-dioxide chloride (IX). The NMR spectrum of a deuterated dimethyl sulfoxide solution showed a singlet at δ 6.83 which appears to be a mixture of water protons and N—H since it did exchange with D_2O. A doublet caused by a P—H proton was not found.

	I	II	III	IV	V
Mp	179[6]	182–3	184–5	196[6]	197–8
Solvent		H_2O–EtOH	H_2O–EtOH	...	H_2O–EtOH

	VI	VII	VIII	IX
Mp	203–4	217.5–8.5	139–40	202–3
Solvent	H_2O–EtOH	EtOH–EtOAc	EtOH	EtOH–EtOAc

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Preparation of Diethyl Formamidomalonate

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A rapid and convenient synthesis of diethyl formamidomalonate is described.

Diethyl acetamidomalonate (*3*) is an important intermediate in the synthesis of a large number of amino acids. Diethyl formamidomalonate is even more suitable for this purpose owing to the much more facile hydrolysis of the formyl group. Several derivatives of tryptophan cannot be made via the acetamidomalonate, because the compounds are not stable enough to withstand the conditions required for the hydrolysis of the acetyl groups, but are smoothly synthesized using diethyl formamidomalonate. Unfortunately, the preparation of this material without high-pressure hydrogenation has been unsatisfactory.

In accordance with results obtained earlier (*1*), we found that the procedure described by Galat (*2*) gave erratic results. Although the reduction of the intermediate diethyl isonitrosomalonate took place, the formylation mostly failed. Therefore, it was decided to remove the water formed in the course of the reduction. The removal was carried out by azeotropic distillation with benzene. The use of benzene has the additional advantage of maintaining the reaction temperature at the desired level.

This method has also been carried out on much larger scales and secures 68–70% yields of the formylated ester.

Experimental

A solution of 621 g (9 mol) of commercial sodium nitrite in 750 ml of water is added through a separating funnel to a well-stirred mixture of 480.5 g (3 mol) of commercial diethyl malonate and 525 ml of glacial acetic acid below 5°. After the addition the cooling is terminated, and the mixture stirred for 6 h. The aqueous layer is then separated and extracted with three 300-ml portions of ether. The ethereal extracts are combined with the main fraction, and the water is separated again. The solution is dried over anhydrous magnesium sulfate, and, after filtration, concentrated on a water bath at 20 mm. The oily residue (about 530 g) is dissolved in 2200 ml of formic acid (90% or better) and placed in a 5-l. three-neck flask equipped with an efficient stirrer and a Dean-Stark water trap.

Benzene (600 ml) and 10 g of zinc powder are added, and the mixture is stirred and heated to reflux. After the reaction has started, the heating is terminated, and 405 g of zinc powder are added rapidly enough to maintain a steady reflux. The water formed is collected and removed through the trap. The hot solution is filtered 15 min after the last addition, and the solvents are removed on a water bath under reduced pressure. The residue is dissolved in 150 ml of methanol and placed in a refrigerator.

The diethyl formamidomalonate separates in the form of white crystals, mp 51–52°. The yield is 400–410 g (68–70%). The material may be distilled in vacuo (bp 130° at 2 mm), but there is danger of decomposition.

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