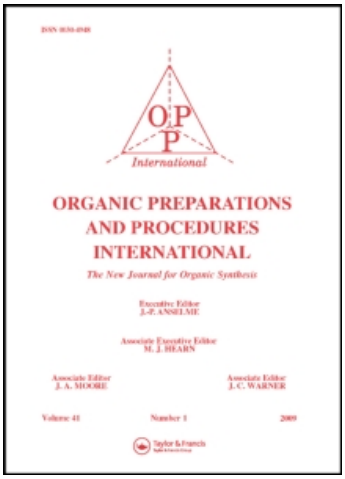

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AN ECONOMICAL PREPARATION OF 2-(2-BROMOETHYL)-1,3-DIOXANE

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AN ECONOMICAL PREPARATION OF 2-(2-BROMOETHYL)-1,3-DIOXANE

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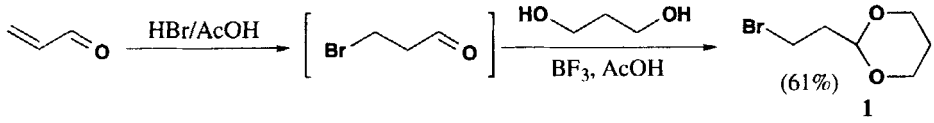
2(2-Bromoethyl)-1,3-dioxane (**1**) is a useful three-carbon synthon, that has been used in an elegant cyclopentane annelation sequence[1]. Other uses includes preparation of γ-keto aldehydes,[2] the synthesis of optically active butyrolactones,[3,5] three-carbon homologation of aldehydes,[5] cyclohexene annelations[6] and prostaglandin synthesis.[7] The conventional preparation of **1** involve the use of gaseous HBr,[8,9] which is expensive and highly corrosive. We describe a modification of the existing

procedure based on the use of aqueous HBr. A solution of HBr in acetic acid is formed by reacting aqueous HBr with the calculated amount of acetic anhydride followed by addition of acrolein, 1,3-propanediol and boron trifluoride as solutions in acetic acid.



1

EXPERIMENTAL SECTION

Caution: *The reaction between acetic anhydride and aqueous HBr is highly exothermic.*

2-(2-Bromethyl)-1,3-dioxane.- In a 250 mL 3-necked flask equipped with a thermometer, an addition funnel and a mechanical stirrer was placed acetic anhydride (70 mL); then aqueous 47% HBr (14 mL, 0.12 mole) was added dropwise with stirring. The temperature was kept below 60° by occasional cooling with water. The resulting solution of HBr in acetic acid was cooled in ice-water to 10° and a solution of acrolein (6.7 mL, 0.098 mole) and 1,3-propanediol (7.6 g, 0.10 mole) in acetic acid (35 mL) was added at such a rate that the temperature remained below 15°. Finally boron trifluoride in acetic acid (2 mL) was added, and the reaction mixture was stirred at room temperature for 3 hrs. The mixture was then poured onto crushed ice (~400 g) and extracted with pet. ether (two 250 mL portions). The organic phase was washed with 2M NaOH (two 100 mL portions) followed by saturated $NaHCO_3$ solution (two 100 mL portions), dried over $MgSO_4$ and concentrated *in vacuo*. Approximately 2g of anhydrous NaOAc was added to the residue which was distilled through a 15 cm Vigreux column to yield 11.6 g (61%) of a colorless liquid, bp. 96-99°/13 mmHg, lit.[4] bp.72-75°/2 mmHg;

^{1}H NMR ($CDCl_3$): δ 4.7 (t, J = 5 Hz, 1 H), 4.3-3.5 (m, 4 H), 3.4 (t, J = 4 Hz, 2 H), 2.3-1.9 (m, 3 H), 1.4 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ 100.0, 66.7, 38.2, 27.8, 25.8.

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SYNTHESIS OF *N*-PHOSPHORYLUREAS BY REACTION OF PHOSPHORYLAMIDES WITH *N*-SUBSTITUTED TRICHLOROACETAMIDES

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N-Phosphorylureas have been synthesized by reaction of phosphorylisocyanates with amines or by isocyanates with phosphorylamides.[1,2] However only a limited number of them have been checked for pesticide activity.[2] Recently we reported the application of *N*-substituted trichloroacetamides for the synthesis of substituted ureas as well as acyl- or sulfonylureas, by reaction with amines, carboxamides or sulfonamides in alkaline medium.[3,4] This paper describes a convenient procedure for the synthesis of phosphorylureas **3** by reaction of *N*-aryl- or *N*-benzyltrichloroacetamides **1** with phosphorylamides **2** in a molar ratio 1:2 in the presence of sodium hydroxide.

The reaction proceeds in dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) or acetonitrile. The best results were obtained in DMSO. Partial hydrolysis of the ester of **3** occurred under the reaction conditions which accounts for the relatively low yields. The low yields of **3c** probably is due to competiting formation of the symmetrical urea.[4]

$$\underset{\mathbf{1}}{RNHCOCCl_3} + \underset{\mathbf{2}}{H_2NPO(OR^1)_2} \xrightarrow[DMSO]{NaOH} \underset{\mathbf{3}}{RNHCONHPO(OR^1)_2}$$

a) R = 2,6-$(C_2H_5)_2C_6H_3$, R^1= Et; b) R = 2,6-$(CH_3)_2C_6H_3$, R^1= Et; c) R = 3-$CH_3OC_6H_4$, R^1= *i*-Pr;
d) R = $C_6H_5CH_2$, R^1= Et; e) R = $C_6H_5CH_2$, R^1= *i*-Pr; f) 4-$CH_3OC_6H_4CH_2$, R^1= Et;
g) R = 3,4-$(CH_2O_2)C_6H_3CH_2$, R^1= Et;