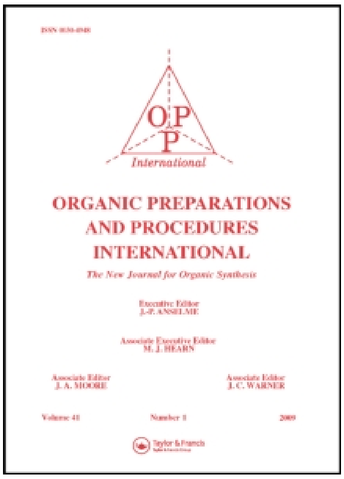

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A SIMPLIFIED SYNTHESIS OF LOWER ALKYL BROMIDES

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bonate (3 X 15 ml). The aqueous phase was acidified with 10% hydrochloric acid (15 ml) and extracted with ethyl acetate (3 X 15 ml). The extracts were washed with water (3 X 15 ml), dried over sodium sulfate and evaporated to afford 1.10 g of 3c. Sublimation at 50-55°C/0.1 torr gave 1.08 g (90%) of pure material, mp. 68°C; IR ($CHCl_3$): 3500-2500 (br) and 1713 cm^{-1} (br). For other spectroscopic data, see Table 3.

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A SIMPLIFIED SYNTHESIS OF LOWER ALKYL BROMIDES

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(03/09/87)

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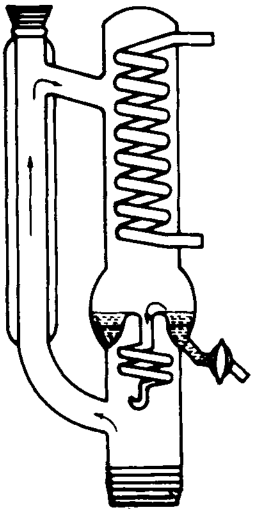
A commonly used laboratory-scale synthesis of alkyl bromides involves the action of hydrogen bromide on the corresponding alcohol, often conveniently modified by the use of sodium or potassium bromide and sulfuric acid. The amount of hydrogen bromide, added or generated from inorganic bromide, ranges from 1.25 to 4.00 mol/mol of alcohol. Details of the preparation depend on physicochemical properties of the substrates and on those of the product formed. For example. the resulting bromide is distilled from a reaction mixture as it is formed with the separated aqueous phase being returned periodically, or after several hours of heating for less reactive alcohols, respectively. The crude bromides are always contaminated with the starting alcohols and thus have to be purified by washing with sulfuric or hydrochloric acid and distilled.[1,2] Herein we described a simplified procedure for the synthesis of very volatile alkyl bromides from the alcohol, potassium bromide and sulfuric acid.

The reaction vessel is fitted with an efficient rectification column and a distillation head enabling phase separation of distillate (see Figure). After addition of the reactants, the apparatus is heated until equilibrium is reached (about 0.5 hr) and distillation begins, it is stopped after a clear distillate is obtained. Thus, the use of only equimolar amounts of inorganic bromide provides better or equal yields of bromides as those in the literature and within shorter periods of time than in earlier procedures and including isopropyl and isobutyl bromides for which the sulfuric acid procedure is <u>not</u> recommended.[1] The crude bromides have a purity higher than 98.5% by GC and thus do not have to be purified nor distilled for further use. The present modification is particularly useful for large scale syntheses in that it saves reagents, energy and



time. For instance, from 50 mol of an alcohol, the pure bromide can be obtained within 5.0-5.5 hrs. Table lists several synthesized bromides.

TABLE Yield and Physical Constants of Bromides

Bromide	Yield [%]	lit.[2]	n_D^{20}	lit.[3]	bp [°C]	lit.[3]
Ethyl	92[a]	91	1.4231	1.4235	38-39	37-40
n-Propyl	92	86	1.4332	1.4336	70-71	71
iso-Propyl	95	81	1.4248	1.4250	58-59	59
n-Butyl	92	95	1.4385	1.4390	100-103	100-104
iso-Butyl	91	91[b]	1.4347	1.4350	90-92	90-92

a) The distillate was collected in a receiver cooled in an ice-salt bath.

b) From the reaction with red phosphorus and bromine.

EXPERIMENTAL SECTION

The purity of products was checked by GC using a GIEDE GCHF 18.3.6 apparatus (GDR) and on column 15%SE-30CQ 100/120, ϕ 3 mm, L 2 m.

Alkyl Bromides.- A 50 L flask equipped with an addition funnel, a stirrer, 1.5 m fractionating column filled with Raschig rings (4.5 mm) and a distillation head (see Fig.) enabling phase separation of distillate, was charged with water (4.5 L), potassium bromide (6.0 kG, 50 mol) and alcohol (50 mol). Then concd sulfuric acid (6.5 L, 122 mol) was rapidly introduced and the reaction mixture heated. After temperature at the top of the column became constant, distillation of the product started and was discontinued when the distillate became clear (about 4.5 hrs).[4] The alkyl bromide obtained was washed with saturated sodium carbonate followed by water to pH 7 and dried over $MgSO_4$. Yields of crude bromides, their refractive indexes and bps of 20 ml distilled samples are given in the Table.

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4. Water was added to the residue in the reaction vessel immediately after the completion of distillation in order to avoid problems in cleaning.

A CONVENIENT SYNTHESIS OF t-BUTYL ESTERS OF AMINO ACIDS

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The t-butyl esters of amino acids are valuable precursors of peptide synthesis. The compounds can be prepared from the free amino acids with 2-methyl-1-propene[1] or with t-butyl acetate.[2] The main disadvantages of these methods are the rather low yields and large solvent requirement. Satisfactory yields were obtained, when N-protected amino acids were used as starting compounds, but the average reaction time was still 3-4