

AN IMPROVED PREPARATION METHOD OF BENZYL AND THENYL TRIPHENYLPHOSPHONIUM SALTS

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Abstract

New benzyl and thenyl phosphonium salts have been prepared by an improved method in solution from the parent alcohols and triphenylphosphine hydrobromide. Benzyl-type alcohols containing a tertiary amine can also be converted within high yields to phosphonium salts by removing the formed water by azeotropic distillation. Solvent (methylene chloride, chloroform and acetonitrile) and temperature have been chosen in close relation to the alcohol reactivity. Purification is straightforward and yields are relatively high.

The Wittig reaction is a well known and very efficient method for the incorporation of a carbon-carbon double bond in an organic molecule¹. This opportunity is largely exploited in the field of organic conjugated materials²⁻⁴. The basic reagent in Wittig reaction, i.e. alkyl triphenylphosphonium salt, is usually prepared from the parent halide by reaction with triphenylphosphine. Although the quaternization reaction of triphenylphosphine usually works well, its application is limited to the halides that are stable enough to be properly worked up. For instance, 4-dimethylaminobenzyl triphenylphosphonium chloride cannot be prepared by using the traditional method.

This paper will report on the improvement of the Hamanaka's method⁵ in order to prepare phosphonium salts of various aromatic compounds by reacting benzyl or thenyl alcohols with triphenylphosphonium hydrobromide (Scheme 1). A special attention will be paid to aromatic derivatives substituted by a tertiary amine, for which the synthesis of the phosphonium salts has never been reported, at least at our best knowledge. 2-Thiophenemethanol **1a** has been reacted with **2** in refluxing methylene chloride for 4 hours. As shown in Table 1, 52% of 2-thenyl triphenylphosphonium bromide **3a** have been recovered by precipitation in diethyl ether.

In order to shift the reaction equilibrium toward formation of the expected product, the azeotropic distillation of the solvent has been carried out all along the reaction and very high yields, even quantitative in some cases, have been observed, as shown in Table 1. Various solvents, i.e. methylene chloride, chloroform and acetonitrile, have been selected for their ability to dissolve the final phosphonium salt and to be distilled off in the required reaction temperature range. It is worth pointing out that the removal of water either by azeotropic distillation or with drying agents has been proposed by Pommer et al. for the preparation of phosphonium salts from alcohols, e.g. -ionol, and triphenyl-phosphine hydrohalides⁶. However only reactions involving non functionalized allylic alcohols were reported.

Benzyl and thenyl phosphonium salts **3c-f** have also been successfully recovered within high yields and purity even though a clear difference in the reaction yields is observed when benzyl alcohols and thenyl alcohols in the series of dimethylamino compounds are compared (Entry c to fin Table 1), which might reflect the higher reactivity of benzyl alcohols compared to thenyl analogues.

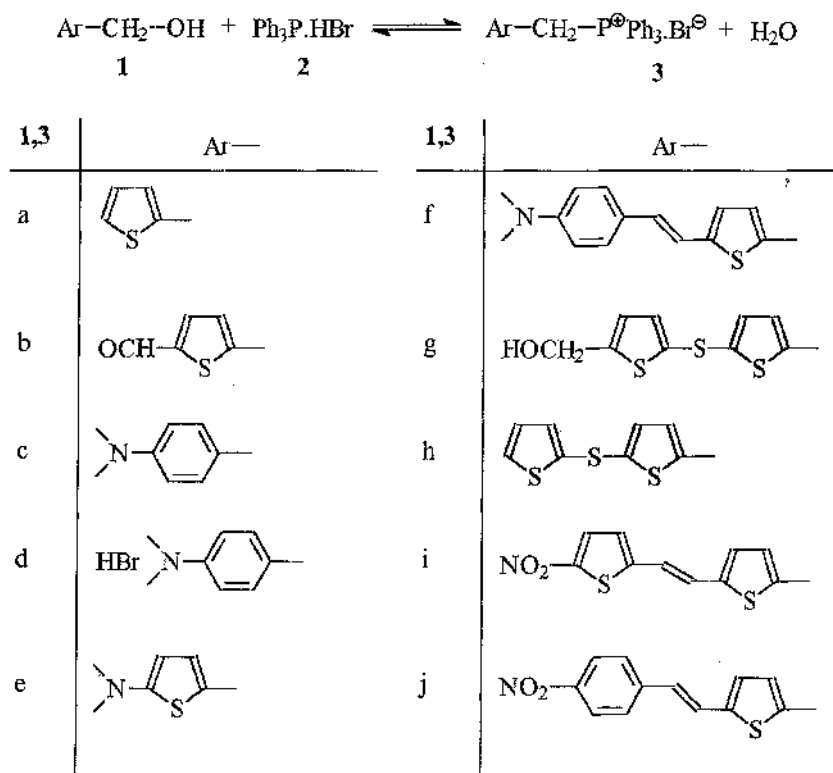
General Procedure to Prepare Benzyl and Thenyl Phosphonium Bromide **3**: Triphenylphosphine hydrobromide **2** was prepared according to the procedure reported by Hercouet⁷. In a flask equipped with a cooler, 0.1 mole of alcohol and 0.09mole of **2** were added to ca. 100 ml of a suitable solvent (see Table 1) under magnetic stirring. After refluxing for the desired period of time, the cooler was replaced by a distillation equipment. The solvent was distilled off slowly until dryness for ca. 1 hour. The crude product was then solubilized in chloroform, and the pure phosphonium bromide was recovered by precipitation in diethyl ether, washed two times with ether, and isolated by filtration.

Table 1. Synthesis of Phosphonium Bromides 3 from the Parent Alcohols 1 and Triphenylphosphine Hydrobromide 2 with Removing the Formed Water by Azeotropic Distillation.

Entry ⁽¹⁾	Phosphonium bromide	Solvent	Refluxing time (hr)	Yield ⁽²⁾ (%)
a	3a	CH ₂ Cl ₂	4	52 ⁽³⁾
		CH ₂ Cl ₂	1	99
		CHCl ₃	1	100
b	3b	CH ₂ Cl ₂	1	96
c	3c	CH ₂ Cl ₂	1	97 100
		CHCl ₃	1	
d	3d	CHCl ₃	2	100
e	3e	CH ₂ Cl ₂ - CH ₃ CN	1	82 81
		CH ₃ CN	2.5	
f	3f	CH ₂ Cl ₂	6	—(4) 82
		CH ₃ CN	2	
g	3g + ⁽⁵⁾	CH ₃ CN	1	97 ⁽⁶⁾
h	3h	CH ₃ CN	2	100
i	3i	CH ₃ CN	1	91
j	3j	CH ₃ CN	1	99

(1) see Scheme 1; (2) yield of the isolated product; (3) without solvent distillation; (4) no reaction; (5) bis-substituted phosphonium; (6) yield calculated for mono-substitution.

Scheme 1



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