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A CONVENIENT PREPARATION OF α-METHOXYALKYLTRIPHENYLPHOSPHONIUM TETRAFLUOROBORATES

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Abstract: The reaction of acetals with triphenylphosphine in the presence of $BF_3\cdot OEt_2$ provides a convenient method for the synthesis of α-alkoxyalkyltriphenylphosphonium tetrafluoroborates.

Phosphonium salts bearing oxygen substituents in α position[1] are important reagents for the homologation of carbonyl compounds. Their most general preparation is accomplished by reacting PPh_3 with toxic α-chloroethers. In the course of work directed to another goal, we found a one-step alternative and briefly investigated some examples. The reaction is closely related to a recently published synthesis of α-alkoxyphosphonates.[2]

$$RCH(OMe)_2 \xrightarrow[\text{toluene}]{PPh_3,\ BF_3\cdot OEt_2} RCH(OMe)PPh_3{}^+BF_4{}^-$$

Procedure. To 10 mmol each of the acetal and PPh_3 in 10 ml of toluene is added via syringe 15 mmol of $BF_3\cdot OEt_2$. The mixture is stirred at the temperature and for the period specified in the table.[3] The workup depends on the crystallization properties of the product. Variant A: The product is sucked off, washed with toluene and hexane, and dried. B: Volatiles are removed at 1 atm (a) or in vacuo (b), or the upper phase is decanted (c), the oily residue is dissolved in warm THF, and crystallization allowed to occur at r.t., then at -10°C. C: The amorphous solid is isolated as under A, and recrystallized as specified in the table. - Some of the salts prepared exhibit a pronounced tendency to separate from their solutions as an oil. In most cases, analytical samples are conveniently obtained by dissolving the crude material in methylene chloride, adding toluene without mixing the layers, and allowing crystallization to proceed slowly at r.t. Warming in vacuo for extended periods may be necessary to remove residual traces of solvent from the crystals.

Slightly excess of $BF_3\cdot OEt_2$ was necessary for the complete formation of phosphonium salts.[4] The dimethyl acetals of cyclohexanone and acetophenone react readily at r.t., but the products are too unstable to be isolated in a pure state. Benzyl methyl ether yields benzyltriphenylphosphonium tetrafluoroborate.[5]

Table 1. Synthesis of α-methoxyalkyltriphenylphosphonium salts

Entry	Product (anion: BF_4^-)	Reaction Temp(°C)	Time(h)	Workup variant	Yield (%)	mp (°C) solvent
1[a]	$MeOCH_2PPh_3^+$	23	1.5	B(b)[b,c]	64	161-162[d,e]
2[f]		23	0.3	B(a)[b,c]	57	
3	$ClCH_2CH(OMe)PPh_3^+$	80	5	B(a)[g]	87	136.5-139 (CH_2Cl_2/Et_2O)
4	$PhCH(OMe)PPh_3^+$	23	3	A	92	173-174.5
5[h]		23	1	A	92	(CH_2Cl_2/toluene)
6	p-$MeOC_6H_4CH(OMe)PPh_3^+$	23	0.5	B(c)[b]	87	137-138 (CH_2Cl_2/toluene)
7	p-$O_2NC_6H_4CH(OMe)PPh_3^+$	80	4.5	C[i]	80	176-176.5 (acetone/toluene)
8[j]	$[PhCH(PPh_3^+)OCH_2-]_2$	80	5	C[k]	66	179-180 (CH_2Cl_2/toluene)

a) 3 eq. of $BF_3 \cdot OEt_2$. b) 10 ml of THF for crystallization. c) Workup of the mother liquid is necessary to obtain the quoted yield. d) Known compound (ref. 6). e) See ref. 7. f) Solvent: benzene. g) 1 ml of THF for crystallization. h) Solvent: CH_2Cl_2 (10 ml); product crystallized on addition of toluene (20 ml). i) Dissolved in 20 ml of hot $ClCH_2CH_2Cl$, diluted with 20 ml of toluene, crystallized at r.t., then at -10°C. j) Starting material: 2-phenyl-1,3-dioxolane. k) Recrystallized from CH_2Cl_2/toluene as described in the text. Analytical and spectral data support the structure depicted, although the reaction mechanism is not clear.

References and Notes

1. (a) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961). (b) G. Wittig, W. Böll, and K.-H. Krück, *ibid.*, **95**, 2514 (1962). (c) D. R. Coulson, *Tetrahedron Lett.*, **1964**, 3325. (d) U. Schubert and E. O. Fischer, *Chem. Ber.*, **106**, 1062 (1973). (e) H. Schlude, *Tetrahedron*, **31**, 89 (1975). (f) K. Schönauer and E. Zbiral, *Tetrahedron Lett.*, **24**, 573 (1983). (g) E. Anders, T. Gaßner, and A. Stankowiak, *Chem. Ber.*, **118**, 124 (1985).
2. D. Burkhouse and H. Zimmer, *Synthesis*, **1984**, 330.
3. No attempt was made to define the minimum required reaction time. Extended periods seem not to decrease the yield significantly.
4. We are tempted to assume following stoichiometry for the reaction.

$$RCH(OMe)_2 + PPh_3 + \frac{4}{3}BF_3 \longrightarrow RCH(OMe)PPh_3^+BF_4^- + \frac{1}{3}B(OMe)_3$$

5. 80°C, 4 h. Workup C (80 ml of boiling ethanol/water 1:1). Yield 51%.
6. G. P. Schiemenz and K. Röhlk, *Chem. Ber.*, 104, 1219 (1971).
7. Preparation of $Ph_3P^+CH_2OMeI^-$ from $MeOCH_2OMe$ via ICH_2OMe has been reported. M. E. Jung, M. A. Mazurek, and R. M. Lim, *Synthesis*, **1978**, 588.

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