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CONVENIENT CONVERSION OF *CIS*-HOMOALLYLIC ALCOHOLS INTO CORRESPONDING BROMIDES WITH Ph_3PBr_2.

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Abstract : An mild and easy worked up procedure using the cheap reagent Ph_3PBr_2 allowed us to improve the conversion of sensitive alcohols (homoallylic and acetalized) into their corresponding bromides in high yields.

In the course of our studies in the field of the total synthesis of High Polyunsaturated Fatty Acids[1] we found it necessary to convert *cis*-homoallylic alcohols into corresponding bromides. Although, numerous efficient methods are reported in the literature to perform the conversion of alcohols into bromides,[2] in the last ten years most of natural or biological products syntheses involving preparation of, either, propargylic-, homopropargylic-, allylic- or homoallylic bromides used the system Phosphine/CBr_4 as reactant.[3,4] However, the bromoform, byproduct of the reaction, is, sometimes, very difficult to take off thoroughly. Moreover, if the following step is the preparation of the Wittig salt, unsaturated bromides must be free of bromoform to prevent further decomposition or modification of the substrat during the reaction.

In the aim of avoiding such problems with our compounds, we describe herein a very easy and improved procedure to convert *cis*-homoallylic alcohols into corresponding bromides by using the known reagent Ph_3PBr_2.[5] Reaction proceeds under very mild conditions by addition at 0°C of solid Ph_3PBr_2 to a mixture of

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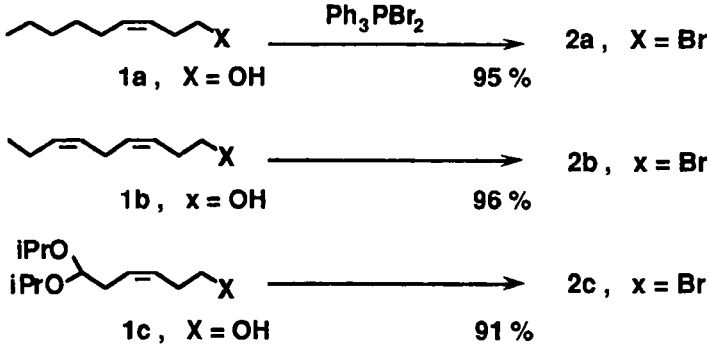
alcohol and pyridine in acetonitrile and is completed in 1 hour. Filtration of the reaction mixture on a short pad of silica gel gives the bromides **2** in very good yields.[6]

Bromides **2a** and **2b**, (which would not be separable from the bromoform using Ph_3P/CBr_4, either by chromatography or low pressure distillation) are obtained in excellent yield, pure and ready to be convert into their phosphonium salt without decomposition or modification of the double bond system. In the case of alcohol **1c**, the very sensitive diisopropyl acetal moiety is not affected.



Ph_3PBr_2 is a very cheap reagent compare to the corresponding $DIPHOSBr_4$;[7] indeed, it is either commercially available or can readily be prepared. This conversion of alcohols is easy to run on multigrams scale, does not affect sensitive functionnalities such as *cis* double bonds and ketals. We anticipate that the mildness and efficiency of this new procedure will find interesting use in organic synthesis.

Experimental :

To a solution of alcohol **1a** (0.81 g, 5.76 mmol, 1 equiv) and pyridine (0.72 g, 9.21 mmol, 1.6 equiv) in acetonitrile (12 mL) is added, at 0°C, in 10 min solid Ph_3PBr_2 (3.16 g, 7.48 mmol, 1.3 equiv). after stirring at room temperature for 1 h (disapearance of alcohol is checked byTLC), the reaction mixture is filtered though a short pad of silicagel and rinced with ether - pentane (1/10, 200 mL) to give pure bromide **2a** (1.12 g, 5.46 mmol, 95%).

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6 - All compounds show correct mass spectra or elemental anlyses. ^1H and ^{13}C NMR are, respectively, recorded at 200 and 50.32 MHz in $CDCl_3$. **2a** ^1H NMR δ 5.58-5.27 (2H, m), 3.34 (2H, t, J = 7.1 Hz), 2.58 (2H, td, J = 7.1, 6.5 Hz), 2.01 (2H, m), 1.26 (6H, br s), 0.84 (3H, t, J = 6.6 Hz) ; ^{13}C NMR δ 133.23, 125.77, 32.60, 31.52, 30.89, 29.25, 27.43, 22.60, 14.09 ; IR (film) 3000, 2950, 2920, 2850, 1650 cm^{-1}. **2b** : ^1H NMR δ 5.53-5.26 (4H, m), 3.35 (2H, t, J = 7.1 Hz), 2.77 (2H, m), 2.62 (2H, td, J = 7.1, 6.5 Hz), 2.05 (2H, qd, J = 7.5, 6.2 Hz), 0.95 (3H, t, J = 7.5 Hz) ; ^{13}C NMR δ 132.39, 131.34, 126.60, 126.14, 32.46, 30.67, 25.76, 20.65, 14.32 ; IR (film) 3010, 2970, 2940, 2880, 1660 cm^{-1}. **2c** : ^1H NMR δ 5.60-5.37 (2H, m), 4.51 (1H, t, J = 5.5 Hz), 3.84 (2H, sept., J = 6.1 Hz), 3.33 (2H, t, J = 7.1 Hz), 2.58 (2H, td, J = 7.1, 6.1 Hz), 2.30 (2H, dd, J = 6.3, 5.5 Hz), 1.14 (6H, d, J = 6.1 Hz), 1.09 (6H, d, J = 6.1 Hz) ; ^{13}C NMR δ 128.12, 127.51, 99.56, 66.03 (2c), 34.02,

32.45, 31.02, 23.35 (2c), 22.54 (2c) ; IR (film) 3000, 2950, 2800, 1640, 1345, 1100, 1020 cm^{-1}.

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