LETTER TO THE EDITORS

A NEW PROCEDURE FOR THE PREPARATION OF ALKYL BROMIDES FROM ALKYL METHANESULFONATES

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Saturated and unsaturated alkyl methanesulfonates (mesylates) are conveniently prepared from alcohols in good purity and high yields^{1, 2}). They can be converted quantitatively to the corresponding alkyl bromides by reaction with anhydrous magnesium bromide in diethyl ether³). As both reactions proceed without *cis, trans*-isomerization or other alterations of double bonds this synthetic route is finding wide application, especially in the preparation of unsaturated alkyl bromides for Grignard reactions⁴) and in spin label chemistry⁵).

The yields of the mesylate-bromide conversion are highly dependent upon the quality of the magnesium bromide. Difficulties may be encountered with commercial preparations of the anhydrous salt which occasionally are of unsatisfactory quality.

Therefore, we wish to describe a simple procedure which does not require anhydrous magnesium bromide in the crystalline state. Instead, a solution of magnesium bromide etherate is prepared from elemental magnesium and elemental bromine⁶). Its reaction with an alkyl methanesulfonate affords the corresponding alkyl bromide in quantitative yield.

As an example, the preparation of *cis*-9-octadecenyl bromide is described in detail.

Procedure

cis-9-Octadecenyl bromide. Dry magnesium turnings (Grignard grade), 3.65 g, 0.15 equ., and 650 ml of absolute diethyl ether are placed in a 2-l multiplenecked flask equipped with an inlet tube for dry nitrogen, reflux condenser with calcium chloride tube, thermometer, and a dropping funnel with a tube extending into the ether. Bromine (sulfuric acid-washed and distilled), 16.0g, 0.1 equ., is added dropwise over a period of 2 hr, while the mixture is stirred vigorously, and a reaction temperature of 15–18°C is maintained.* After the

* Careful control of the temperature is essential. A bluish colored product may be formed at higher temperature.

reaction mixture has turned colorless, 100 ml of anhydrous benzene is added immediately, and stirring is continued for a few minutes to ensure complete solution. The colorless solution is decanted at once into a 1-1 three-necked reaction flask through a U-shaped ground-jointed tube permitting transfer of the solution under nitrogen. The flask is then fitted with an inlet tube for dry nitrogen, reflux condenser with calcium chloride tube, dropping funnel, and stirrer. cis-9-Octadecenyl methanesulfonate, 17.3 g, 0.05 moles, in 50 ml of anhydrous ether is added, and the mixture is stirred vigorously at room temperature for approximately 20 hr. Ice-cold, air-free water (250 ml) is added, and the separated aqueous phase is re-extracted with two 100 ml portions of ether. The combined organic extracts are washed consecutively with 100 ml of water, 1% potassium carbonate solution (until basic), 100 ml of water, and are dried over anhydrous sodium sulfate. Evaporation of the solvent in a rotary evaporator yields a colorless liquid, which is pure as judged by the criterion of thin-layer chromatography (Silica Gel G, hexane). The residue is dissolved in hexane; the solution is filtered, and the solvent removed in a rotary evaporator. Drying in high vacuum yields 16.2 g (98%) of cis-9-octadecenyl bromide which melts between -18.5 and -18 °C; CST with nitromethane 105.5 °C.

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