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LETTER TO THE EDITORS

A NEW PROCEDURE FOR THE PREPARATION OF ALKYL METHANESULFONATES

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1. Introduction

Many reactions of long-chain alkyl methanesulfonates (mesylates) proceed in excellent yields and, therefore, these versatile intermediates are finding wide application in lipid synthesis [1]. A procedure [2] for their preparation from methanesulfonyl chloride and an alcohol, in pyridine solution, is well worked out, but it is rather time-consuming and it leads to the formation of small amounts of alkyl chlorides [3].

This communication describes a more convenient procedure for the preparation of saturated alkyl methanesulfonates which avoids the formation of alkyl chlorides. Methanesulfonic anhydride is reacted with an alcohol, in the molten state, in the presence of a small amount of pyridine. After 20 min, the reaction is complete and the alkyl methanesulfonate can be isolated in 80 to over 90% yield.

The reaction of methanesulfonic anhydride with unsaturated alcohols, under the previously described conditions, leads to the formation of yellow by-products. These can be removed by repeated crystallization, but yields are low. Therefore, unsaturated alkyl methanesulfonates are best prepared by reacting methanesulfonyl chloride with an alcohol in pyridine, as described previously [2, 3].

The preparation of octadecyl methanesulfonate is described as an example of the new method.

2. Procedure

Methanesulfonic anhydride. This reagent is not always available in satisfactory purity; it is best prepared from methanesulfonic acid and phosphorus pentoxide following a procedure published recently [4]. After crystallization of the crude product from dry diethyl ether, which must be free of alcohol [5], methanesulfonic anhydride is obtained as white prisms which melt at 71–72°C; it is stored under anhydrous conditions at −10°C.

Octadecyl methanesulfonate. A mixture of 5.4 g (0.02 mole) octadecanol, 4.5 g (0.026 mole) methanesulfonic anhydride and 600 mg of pyridide are placed in a 50 ml round-bottomed flask and heated to 120°C under magnetic stirring. After 20 min, the reaction mixture is cooled to 50–60°C and dissolved in 60 ml of warm abs. ethanol; the warm solution is filtered. Upon cooling to room temperature, white crystals are formed which are collected on a funnel. They are recrystallized from abs. ethanol to yield 5.7 g (80%) of pure octadecyl methanesulfonate, m.p. 60–60.5°C (lit. 2, m.p. 60.5°C).

Anal.: $C_{19}H_{40}O_3S$ (348.6) Calc.: S 9.24
Found: S 9.16

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