

Synthesis of long-chain alkyl and alkenyl bromides

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SUMMARY Long-chain alkyl and alkenyl bromides are obtained in quantitative yields by the reaction of methanesulfonates with anhydrous magnesium bromide in absolute ether; *cis-trans* isomerization of double bonds does not occur.

KEY WORDS synthesis · alkyl · alkenyl · bromides · methanesulfonates · mesylates · *cis,trans* double bonds

PRESENT METHODS for the preparation of unsaturated long-chain alkyl bromides (3) are unsatisfactory because of reactions and isomerizations of double bonds and the formation of substantial amounts of by-products (3-5). Alterations of the double bonds cannot be circumvented by bromination-debromination techniques (6, 7). Unsaturated alkyl tosylates are difficult to obtain (1, 4) and their use for the preparation of bromides is therefore limited.

We have shown previously that unsaturated long-chain alkyl esters of methanesulfonic acid (mesylates) are easily accessible in pure form (1). However, their reaction with potassium bromide in boiling anhydrous acetone or ethanol, experimental conditions commonly employed for the conversion of tosylates to bromides (3), leads to large amounts of by-products. The formation of by-products will be reduced by the use of a bromide even more reactive than potassium bromide. Anhydrous magnesium bromide, a strong Lewis acid which forms a highly soluble and reactive solvent complex in ether, proved to be suitable.

The present communication describes the preparation of four representative aliphatic bromides having different numbers of double bonds in *cis* or *trans* configuration, by reaction of the corresponding mesylates with magnesium bromide in absolute ether. The products were obtained in quantitative yield and characterized by elemental analysis, melting point, critical solution temperature, thin-layer chromatography, and infrared spectroscopy. All compounds proved to be homogeneous in regard to compound class, as well as number and configuration of double bonds.

Abbreviation: CST, critical solution temperature.

This paper is Part III of the series "Reactions of aliphatic methanesulfonates." Parts I and II are references 1 and 2.

Critical solution temperatures (CST) (8) with nitromethane (Fisher Scientific Co., Fair Lawn, N.J., No. N 98) and melting points were determined under the microscope and are corrected. Infrared spectra were recorded with the Perkin-Elmer spectrophotometer Model 21 in carbon disulfide solution. Thin-layer chromatography (9) on Silica Gel G (Merck), and on the same adsorbent impregnated with silver nitrate (10), was employed to check the uniformity of the final products. The plates were developed with hexane or hexane-diethyl ether 90:10 (v/v) in tanks lined with filter paper. After chromatography the substances were made visible by spraying with chromic sulfuric acid solution and charring (1).

The alkyl methanesulfonates used were prepared in pure form as described previously (1). Anhydrous magnesium bromide was purchased from A. D. Mackay, Inc., New York, N.Y.

The procedure for the preparation of linoleyl bromide is as follows:

cis,cis-9,12-Octadecadienyl Bromide. *cis,cis-9,12-Octadecadienyl methanesulfonate* (2.7 g, 7.8 mmoles), 4.3 g (23.8 mmoles) of anhydrous magnesium bromide, and 100 ml of dry ether were placed in a 250 ml three-necked flask equipped with reflux condenser, inlet and outlet tubes for dry nitrogen, and mechanical stirrer. The mixture was stirred vigorously at room temperature for 24 hr. More ether, and cold, air-free water were added, and the water layer was extracted twice with ether. The combined ether phases were washed consecutively with water, 1% potassium carbonate solution, and water, and were dried over anhydrous sodium sulfate. Evaporation of the solvent yielded a colorless liquid, which was uniform as judged by thin-layer chromatography. Resolution in low-boiling hydrocarbon (Skellysolve F), filtration, and final evaporation in vacuo yielded 2.5 g (97%) of *cis,cis-9,12-octadecadienyl bromide*; mp -35°C , CST 87.5°C .

Analysis: $\text{C}_{18}\text{H}_{33}\text{Br}$; calculated: Br, 24.26
found: Br, 25.17; 23.41

The following alkyl bromides were prepared in essentially the same manner:

cis-9-Octadecenyl Bromide. *cis-9-Octadecenyl methanesulfonate* (3.4 g, 10 mmoles) and 5.4 g (30 mmoles) of magnesium bromide were allowed to react in 100 ml of dry ether, yielding 3.05 g (94%); mp -18°C , CST 105.5°C .

Analysis: $\text{C}_{18}\text{H}_{35}\text{Br}$; calculated: Br, 24.11
found: Br, 24.51

trans-9-Octadecenyl Bromide. *trans-9-Octadecenyl methanesulfonate* (1.75 g, 5 mmoles), and 2.75 g (15 mmoles)

of magnesium bromide in 50 ml of dry ether yielded 1.60 g (96%); mp 3.5–4.0°C, CST 110°C.

Analysis: C₁₈H₃₅Br; calculated: Br, 24.11
found: Br, 23.75

Octadecyl Bromide. Octadecyl methanesulfonate (1.05 g, 3 mmoles), and 1.65 g (9 mmoles) of magnesium bromide in 40 ml of dry ether yielded 0.98 g (97%); mp 27.5–28°C (reference 11, 27.4–27.6°C), CST 123.5°C.

Analysis: C₁₈H₃₇Br; calculated: Br, 23.97
found: Br, 24.08

The infrared spectra of all alkyl bromides showed strong bands near 2940 and 2860 cm⁻¹ associated with the C—H stretching vibrations of the CH₃ and CH₂ groups, respectively. In addition, *cis*-9-octadecenyl and *cis,cis*-9,12-octadecadienyl bromide exhibited the *cis* C—H stretching frequency at 3005 cm⁻¹, the *cis* C—H out-of-plane deformation (shoulder) near 690 cm⁻¹, and the C=C stretching near 1655 cm⁻¹. These frequencies did not occur in the spectrum of *trans*-9-octadecenyl bromide. The *trans* C—H out-of-plane deformation at 966 cm⁻¹ was detectable only in the spectrum of the latter compound. These spectra indicate that no *cis-trans* isomerization of the double bonds occurred in the course of this synthesis.

This investigation was supported by PHS Research Grant GM 05817 from the National Institutes of Health, U.S. Public Health Service.

Manuscript received 28 December 1965; accepted 1 March 1966.

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