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SYNTHESIS OF THE p-TOLUENESULFONATE OF OLEYL ACOHOL
UNDER CONDITIONS OF PHASE-TRANSFER CATALYSIS

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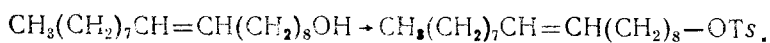
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The tosylation of oleyl alcohol under the conditions of phase-transfer catalysis has been studied. In this process oleyl p-toluenesulfonate of formed with a yield of up to 80%.

The p-toluenesulfonate of oleyl alcohol (octadec-cis-9-en-1-ol) is the main synthon in the synthesis of tricos-cis-9-ene — the pheromone of the house fly *Musca domestica* L. [1]. The use for these purposes of the p-toluenesulfonate of octadec-cis-14-en-1-ol is also known [2]. The tosylation of the alcohols has been performed with the use as condensing agent of triethylamine or pyridine at a temperature of -10 to 0°C for 15 h [1, 2].

The production of a number of sulfonic esters with the use of benzyltrimethylammonium chloride as phase-transfer catalyst has been described [3].

In order to simplify the method of synthesis and to shorten the reaction time we have studied the conditions for the tosylation of oleyl alcohol with the use of phase-transfer catalysis:



The two-phase system benzene -30% aqueous NaOH was used. Tetrabutylammonium iodide (TBAI), tetraethylammonium iodide (TEAI), tetramethylammonium bromide (TMAB), and dibenzo-18-crown-6 (DB18C6) were selected as phase-transfer catalysts. In all cases the reaction was performed at 20-25°C with a molar ratio of oleyl alcohol to p-toluenesulfonyl chloride of 1:1.1. The ratio of oleyl alcohol to catalyst was varied from 1:0.04 to 1:0.4. The course of the reaction was monitored by TLC. It follows from the experimental results, which are given in Table 1, that the tosylation reaction takes place most effectively at a molar ratio of oleyl alcohol to phase-transfer catalyst of 1:0.2, the best of the catalysts proving to be TBAI, with the use of which the reaction was complete in 6 h with an 80% yield of tosylate.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument in carbon tetrachloride, and PMR spectra on a Varian XL-200 spectrometer in deuteriochloroform with TMS as internal standard.

Thin-layer chromatography was performed on Silufol UV 254 plates (Czechoslovakia) in the ether-hexane (1:1) system. The revealing agent was iodine vapor.

Column chromatography was conducted on silica gel L 100/250 μm at a ratio of substance to sorbent of 1:30, with ether-hexane (1:1) as the eluent.

The p-toluenesulfonyl chloride was purified by Pelletier's method [4].

Oleyl p-Toluenesulfonate. A solution of 2.1 g (0.011 mole) of p-toluenesulfonyl chloride in 5 ml of benzene was added dropwise with vigorous stirring to a heterogeneous mixture of 10 ml of benzene, 2.68 g (0.01 mole) of oleyl alcohol, 0.74 g (0.002 mole) of tetrabutyl ammonium iodide, and 5 ml of 30% aqueous NaOH solution, the temperature of the reaction mixture being kept at 20-25°C. After predetermined intervals of time, samples were taken from

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TABLE 1. Tosylation of Oleyl Alcohol in the Benzene-30% Aqueous NaOH System (temperature 20-25°C; molar ratio of oleyl alcohol to p-toluenesulfonyl chloride 1:1.1)

Catalyst	Molar ratio of oleyl alcohol to catalyst	Reaction time h	Yield of oleyl p-toluene sulfonate, %*
TBAI	1:0.04	8	52
TBAI	1:0.12	7	60,8
TBAI	1:0.2	6	80
TBAI	1:0.4	7	76
TEAI	1:0.04	10	36,5
TEAI	1:0.12	10	46
TEAI	1:0.2	8	70,4
TEAI	1:0.4	8	65,8
TMAB	1:0.04	10	28,6
TMAB	1:0.12	10	32,5
TMAB	1:0.2	10	48
TMAB	1:0.4	10	45
DB18C6	1:0.04	10	47
DB18C6	1:0.12	10	55,2
DB18C6	1:0.2	9	70,4
DB18C6	1:0.4	8	69,8

*For the yield of product purified by column Chromatography on SiO₂.

the organic phase, and these were analyzed by TLC. Pure samples of oleyl alcohol (R_f 0.47) and of its p-toluenesulfonate (R_f 0.81) were used as controls.

According to the TLC results, the reaction was complete after 6 h. The organic layer was separated off, washed with water to neutrality, dried with anhydrous MgSO₄, and evaporated in vacuum at room temperature. The residue was purified by column chromatography. This gave 3.38 g (80%) of oleyl p-toluenesulfonate.

IR spectrum (ν , cm⁻¹): 665 m; 690 w; 1180 s; 1368 s; 1450 s; 1640 m. PMR spectrum (δ , ppm): 0.8 t (3 H, CH₃), 1.0-1.6 m (26H, CH₂), 1.8-1.9 s (4H, CH₂C=C), 2.35 s (3H, CH₃Ar), 3.85 t (2H, CH₂O), 5.17 t (2H, CH=CH), 7.18 d (2H, H-Ar), 7.63 d (2H, H-Ar)

SUMMARY

The tosylation of oleyl alcohol under the conditions of phase-transfer catalysis has been studied. In this process oleyl p-toluenesulfonate is formed with a yield of up to 80%.

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