

SYNTHESIS OF ^{14}C -LABELED SURFACTANTS:
SODIUM *p*-*n*-DODECYLBENZENESULFONATE-[PHENYL- $\text{U-}^{14}\text{C}$]

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SUMMARY

The synthesis of sodium *p*-*n*-dodecylbenzenesulfonate-[phenyl- $\text{U-}^{14}\text{C}$], III, from benzene- $\text{U-}^{14}\text{C}$ is described. The preparative method consists of simple Friedel-Crafts acylation, reduction of the resulting ketone, I, and sulfonation of II with chlorosulfonic acid. The specific activity of III was 6.8 mCi/mmole and the overall radiochemical yield was 25% (based on benzene- $\text{U-}^{14}\text{C}$).

Key Words: ^{14}C -Labeled surfactant, Acylation, Sulfonation of arenes, LAS

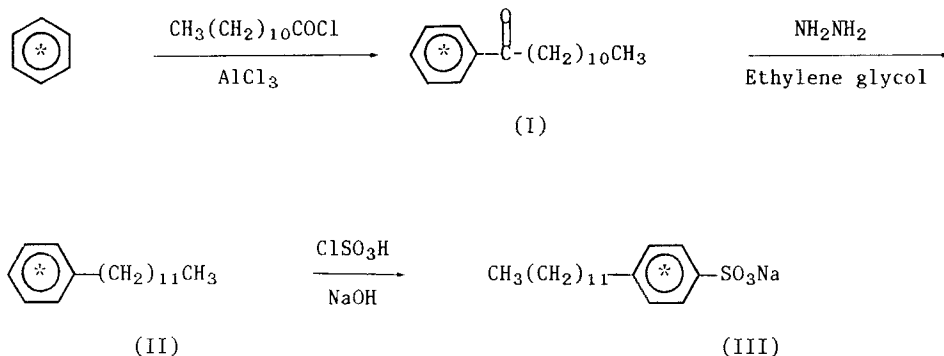
INTRODUCTION

Alkylbenzenesulfonates are a large-volume class of anionic surfactants [1]. In 1965 the sodium salt of linear dodecylbenzenesulfonic acid (LAS) was introduced as a replacement for branched alkylbenzenesulfonates due to the more readily biodegradable side chain. For continued investigations regarding metabolism and biodegradability of LAS the preparation of sodium *p*-*n*-dodecylbenzenesulfonate-[phenyl- $\text{U-}^{14}\text{C}$] was required.

SYNTHESIS

The synthesis of LAS labeled uniformly in the benzene ring was accomplished starting with benzene- $\text{U-}^{14}\text{C}$, as shown in the Scheme. Thus, benzene- $\text{U-}^{14}\text{C}$ was converted to undecylphenylketone-[phenyl- $\text{U-}^{14}\text{C}$], I, by the Friedel-Crafts acylation of benzene [2], and I was subsequently reduced with hydrazine hydrate by the Huang-Minlon variation of the Wolff Kishner method [3] to give dodecylbenzene-[phenyl- $\text{U-}^{14}\text{C}$], II. This arene was then sulfonated with an approximately equimolar amount of chlorosulfonic acid [4] and then neutralized with aqueous NaOH at 20-25°C to pH \sim 8 to give the required III in an overall radiochemical yield of 25%.

Scheme

EXPERIMENTAL

IR spectra were recorded with a Beckman Acculab I, either neat or as a Nujol mull. Radioactivity was determined in a Packard Model 3003 liquid scintillation counter using Econofluor scintillant (New England Nuclear). Thin layer chromatography was carried out on 5 x 20 cm plates coated with silica gel 60 F₂₅₄ (EM reagents). The bands were detected using UV light and with a Packard Model 7201 radiochromatogram scanner and by autoradiographic methods.

Undecylphenylketone-[phenyl-U-¹⁴C], (I)

To a 50-ml pear-shaped flask equipped with a reflux condenser and N₂ inlet tube were added aluminum chloride (1.23 g, 9.21 mmoles) and benzene-U-¹⁴C (0.229 g, 2.93 mmoles, 20 mCi, 6.8 mCi/mmole). While the mixture was stirring at 55°C, lauroyl chloride (0.8 ml, 3.45 mmole) was added dropwise. After the addition was complete, the mixture was stirred at 55°C for 2 hr. Dilute hydrochloric acid (10%) was added dropwise to the flask, which was cooled in an ice bath. The resulting solution was then extracted with 3 x 50 ml of diethyl ether. The organic extracts were washed with 50% sodium carbonate solution and water. The resulting ether solution was then dried (anhydrous sodium sulfate) and evaporated to dryness (*in vacuo*), leaving 0.75 g (97% yield) of a brown oil. TLC: silica gel, methylene chloride, R_f = 0.85. This ketone was estimated to be ca. 95% pure by TLC and was used without further purification in the next step.

Dodecylbenzene-[phenyl- ^{14}C], (II)

The previously prepared ketone, I, (0.75 g, 2.84 mmoles) was dissolved in 5 ml of ethanol, and 85% hydrazine hydrate (2 ml, 52.0 mmoles) was added. The resulting solution was then heated at 95°C for 17 hr. Excess hydrazine hydrate and ethanol were removed by distillation after 5 ml of ethylene glycol was added to the solution. The distillation was stopped when the temperature reached 200°C. To the resulting residue, 400 mg of solid potassium hydroxide was added. The mixture was then stirred at 195°C for 15 hr and, after cooling, was poured into water and the resulting slurry extracted with 3 x 50 ml of benzene. After removal of the benzene (*in vacuo*) 0.73 g of a light brown oil was obtained and subsequently passed through a silica gel column (EM silica gel 60, 2.5 x 37 cm). Elution with methylene chloride resulted in collection of 0.45 g (63% yield) of dodecylbenzene-[phenyl- ^{14}C] as a light yellow oil at $\geq 98\%$ purity by TLC (silica gel, methylene chloride, $R_f = 0.70$).

p-Dodecylbenzene sodium sulfonate-[phenyl- ^{14}C], (III)

To a 25-ml pear-shaped flask equipped with a reflux condenser and N_2 inlet tube were added dodecylbenzene-[phenyl- ^{14}C] (0.45 g, 1.81 mmoles) and 1 ml of 1,2-dichloroethane. The flask was cooled in an ice bath, and chlorosulfonic acid (126 μl , 1.90 mmoles) was added dropwise. After the addition was complete, the mixture was stirred at 45°C for 0.5 hr. The solvent was then evaporated and the resulting thick brown oil was diluted with 5 ml of water and brought to a pH of ~ 8 with 1 N sodium hydroxide. The resulting mixture was filtered, and the filtrate passed through a silica gel column (EM silica gel 60, 2.5 x 37 cm). Eluting with ethyl acetate:methanol (65:35) and evaporation of the solvent (*in vacuo*) resulted in collection of III, 262 mg (41% yield) as an off-white solid. The specific activity (6.8 mCi/mmole) was in good agreement with the starting material. The purity of III was determined by TLC (ethyl acetate:methanol 65:35, R_f 0.60, and ethyl acetate:methanol:water 65:35:11, $R_f = 0.70$) radiochromatogram scanning and found to be $\geq 98\%$. The R_f in both systems was identical to that of the cold standard.

ACKNOWLEDGMENTS

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