THE SYNTHESIS OF [β-^{14}C]STYRENE

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SUMMARY

[β-^{14}C]Styrene was prepared by the action of [^{14}C]paraformaldehyde on phenylmethylene triphenyl phosphorane; the latter was prepared from benzyl chloride and triphenyl phosphine via phenyl methyl triphenyl phosphonium chloride. No radiochemical impurities were detected in the product. The radiochemical yield was 30.8%.

Key Word: [β-^{14}C]styrene

INTRODUCTION

[β-^{14}C]Styrene has been prepared from sodium [2-^{14}C]malonate, via [2-^{14}C]cinnamic acid(1). Since the styrene was obtained from the labelled cinnamic acid by dry distillation, hydroquinone was added to inhibit the polymerization of styrene as it was formed. Such a preparation produced radiochemical impurities in the styrene, which were identified as ethylbenzene and toluene; corrections to allow for the presence of these had to be made in the studies of the polymerization of [β-^{14}C]styrene(2). The presence of ethylbenzene amongst the products of reaction of styrene and hydroquinone at 150 °C has already been reported(3) and it is likely that ethylbenzene, as radiochemical impurity in the above work, was formed by a similar reaction.

Toluene (b.p. 111 °C), if it occurs as radiochemical impurity, can readily be removed from styrene (b.p. 145 °C) by dilution, followed by a good

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fractional distillation. This technique is however not very efficient for separating ethylbenzene (b.p. 136 °C) from styrene; about 1% radiochemical impurity remained after a typical distillation. Since most inhibitors function by similar mechanisms, a change in the inhibitor is unlikely to have a significant effect in reducing the radiochemical impurity; even in the absence of inhibitor, ethylbenzene was still formed in appreciable, if smaller, quantities.

To avoid the formation of labelled ethylbenzene during the preparation, [β-^{14}C]styrene has now been synthesised by a method similar to that used by Drefahl et al.(4) for the preparation of 4,4'-divinyl diphenyl; the method of using an ylid (phosphorane) preparation was adapted for styrene; [^{14}C]paraformaldehyde was the labelled starting material. Good yields were obtained and radiochemical impurities were undetectable in the product.

EXPERIMENTAL

[^{14}C]paraformaldehyde was obtained from the Radiochemical Centre, Amersham. Radioactivity measurements were performed by liquid scintillation counting, using an Intertechnique SL40 Liquid Scintillation Counting Spectrometer.

Benzyl chloride (9.0 g, 71 mmol) and triphenyl phosphine (28.4 g, 108 mmol) were stirred under reflux for three hours in 100 ml of dimethyl formamide. A precipitate of benzyl triphenyl phosphonium chloride formed on slow cooling.

$$C_6H_5CH_2Cl + P(C_6H_5)_3 \longrightarrow C_6H_5CH_2P(C_6H_5)_3Cl$$

This was filtered, washed with benzene and dried (17.0 g, 43.8 mmol, 62% yield).

Sufficient n-butyl lithium solution in n-hexane was added to benzyl triphenyl phosphonium chloride (15 g, 38.6 mmol) in a dry box to change the colour of the white powder to orange. The resulting slurry was then carefully exposed to the atmosphere for several hours so that excess n-butyl lithium was destroyed. The mixture was then filtered and washed with n-hexane, phenylmethylene triphenyl phosphorane remaining as an orange solid (13.5 g, 38.3 mmol, 99% yield).

$$C_6H_5CH_2P(C_6H_5)_3Cl \xrightarrow[\text{lithium}]{\text{n-butyl}} C_6H_5CH{=}P(C_6H_5)_3 + HCl$$

Phenylmethylene triphenyl phosphorane (15.0 g, 42.6 mmol), paraformaldehyde (1.0 g, 33.3 mmol formaldehyde) and [^{14}C]paraformaldehyde (100 μCi, 339 μCi mg^{-1}) were stirred under reflux for two hours in 50 ml of n-hexane, the product being [β-^{14}C]styrene.

$$C_6H_5CH{=}P(C_6H_5)_3 + H^{14}CHO \longrightarrow C_6H_5CH{=}^{14}CH_2 + (C_6H_5)_3P{=}O$$

Styrene (50 ml, 433 mmol) was added and the resulting mixture was filtered; n-hexane was removed under reduced pressure at room temperature. Distillation under nitrogen (44 °C at 28 mmHg) yielded [β-^{14}C]styrene (40 ml, 346 mmol, specific activity 89 μCi mol^{-1}), which could be stored at -25 °C under vacuum; the overall radiochemical yield was 30.8%. No detectable radiochemical impurity (less than 0.1%) was found by gas-liquid chromatography.

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