

SYNTHESIS OF 1-[¹⁴C]-PHENYL-1-(3,4-DIMETHYL)PHENYLETHANE,
A COMPONENT OF SOME PCB REPLACEMENT MATERIALS

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SUMMARY

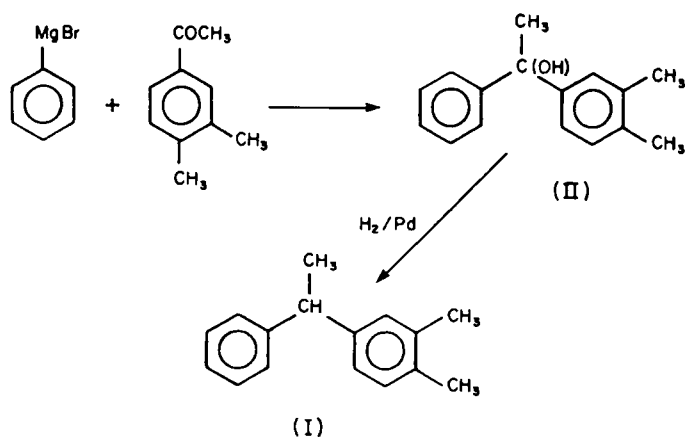
1-[¹⁴C]-phenyl-1-(3,4-dimethyl)phenylethane, a labelled analogue of a PCB replacement used as an ink solvent in pressure sensitive copying paper and as a capacitor dielectric, has been prepared. The Grignard reagent derived from ¹⁴C-bromobenzene was condensed with methyl(3,4-dimethyl)phenylketone and the resulting tertiary alcohol was hydrogenolysed. The final yield was 53.1% based on ¹⁴C-bromobenzene; final specific activity of the product was 1.29 mCi·mmole⁻¹, which is adequate for metabolic studies.

Key Words: 1-[¹⁴C]-phenyl-1-(3,4-dimethyl)phenylethane; phenylxylylethane; PCB replacement.

INTRODUCTION

Restrictions on the manufacture and use of polychlorinated biphenyls (PCB) have stimulated the chemical industry to develop replacement materials. Some of these are familiar chemicals used in new applications; others are new chemicals developed specifically as PCB substitutes. Among the latter group are the 1-phenyl-1-xylylethanes, mixtures of which have been developed for use as solvents for microencapsulated inks

used in pressure-sensitive copying paper^(1,2) and which are now being used in North America as capacitor dielectrics⁽³⁾. We wished to prepare representative isomers of these compounds labelled with ^{14}C for metabolic studies, and in this paper we describe a convenient synthesis based on the coupling of a Grignard reagent derived from ^{14}C -bromobenzene with the appropriate acetophenone (in this case, methyl(3,4-dimethyl)phenylketone); the resulting alcohol is hydrogenolysed over Pd to yield the desired product (I).



Scheme 1. Synthesis of 1-phenyl-1-(3,4-dimethyl)phenylethane

EXPERIMENTAL

^{14}C -bromobenzene (uniformly labelled, specific activity $1.14 \text{ mCi}\cdot\text{mmole}^{-1}$) was obtained from California Bionuclear, and methyl(3,4-dimethyl)phenylketone from Aldrich. 5% palladium on charcoal was obtained from Matheson Coleman and Bell. Other reagents and solvents were of reagent grade or were redistilled before use.

^{14}C -bromobenzene (4.4×10^{-4} moles; 68.6 mg) was dissolved in approx. 1 ml diethyl ether in a 5 ml roundbottomed flask containing an excess of dry Mg powder.

Formation of the Grignard reagent was stimulated with a small amount of iodine and the mixture was refluxed gently under a drying tube until most of the Mg had disintegrated. Methyl(3,4-dimethyl)phenylketone (6.7×10^{-4} moles, 99 mg) was added through the condenser and washed in with a little ether, and the mixture was refluxed for another hour. The reaction mixture was cooled, poured into 10% sulphuric acid, and the product was extracted several times with diethyl ether. The extract was dried over sodium sulphate and the ether removed under a stream of nitrogen. The residue (alcohol II) was dissolved in 1-2 ml absolute ethanol.

Hydrogen was generated⁽⁴⁾ from NaBH₄. 1.5 ml of 1 M NaBH₄ (0.95 g NaBH₄ in 25 ml ethanol plus 1.25 ml 2 M NaOH) was added to 0.25 g 5% Pd/C in a three-necked flask fitted with a stirrer; 2 ml 6N HCl was added and the mixture was stirred for 10 mins and cooled. The entire sample of alcohol II was added, followed over a period of one hour by the remaining NaBH₄ solution. The mixture was then poured into cold distilled water and extracted several times with ether. The product was purified by preparative TLC on silica gel GF 254 using *n*-hexane as the developing solvent.

Physical data were obtained on unlabelled analogues prepared as described above on a larger scale. Electron impact mass spectra were obtained using a Finnigan 4000 GC-MS system fitted with a 30 m fused silica column coated with SE-30 and programmed from 100-150°C. Flame ionisation GC was carried out on a Hewlett-Packard 5730 instrument fitted with a 12.5 m fused silica column coated with SP-2100, and operated at 150°C. ¹³C NMR (natural abundance) spectra were recorded in CDCl₃. UV spectra were recorded in *n*-hexane in a Unicam SP-1700 instrument in 1 cm quartz cells.

RESULTS AND DISCUSSION

The product I was a colourless oil. It ran as a single peak under the GLC conditions described above with a retention time identical to that of the major component of the commercial PCB replacement SAS-295 (Nisseki Co., Japan) which had previously been identified^(2,5) as 1-phenyl-1-(3,4-dimethyl)phenylethane. (These GLC conditions allowed resolution of the 2,4-, 3,4- and 2,5-isomers⁽⁵⁾.) Mass spectral

analysis showed a parent ion at m/e 210 (expected for $C_{16}H_{18}$) and fragments at 195, 180 and 165 (loss of one, two and three Me groups, respectively). ^{13}C NMR showed each ring methyl group to be coupled to one ortho H atom; the only asymmetric dimethyl substituted structure in the 1-phenyl-1-xylylethanes to allow this pattern is that of 3,4-substitution. UV absorbance spectra had showed a maximum at 222 nm (molar absorbance 1.5×10^4) and shoulders at 268, 271 and 277 nm, consistent with an aromatic system which is not extensively conjugated.

The specific activity of the product was 1.29 mCi-mmole, based on GLC determination of the product mass. Yield was 53.1% based on ^{14}C -bromobenzene.

Few comparable data are available in the literature since the phenylxylylethanes have been a relatively obscure group of compounds. Most of the earlier syntheses were based on Friedel-Crafts alkylations of the appropriate xylene with styrene and to judge by the composition of the commercial mixtures of PCB replacements, this procedure is used for their manufacture; depending on the xylene source, this reaction may yield a mixture of products. Some physical data for such mixtures - or occasionally discrete compounds - have been reported: boiling points are $150-160^\circ C/10\text{mm}^{(6)}$, $130^\circ C/3\text{mm}^{(7)}$, $136^\circ C/5\text{mm}^{(8)}$ or around $300^\circ C/760\text{ mm}^{(9)}$. Densities^(7,8) are around 0.98 and refractive indices⁽⁷⁻⁹⁾ around 1.56.

The only other report of the use of dimethylacetophenones of defined structure as starting materials for the unambiguous synthesis of phenylxylylethane isomers is that of Malan⁽⁹⁾. In that work, the intermediate tertiary alcohol was isolated, as was the alkene formed by its dehydration. Physical data for both these intermediates were recorded. We found it more convenient to proceed straight from the alcohol to the alkane by hydrogenolysis.

In conclusion, the method we describe is a simple and convenient approach to a series of compounds which may be of appreciable environmental significance.

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