

REDUCTION OF ARYL THALLIUM DITRIFLUOROACETATES: A CONVENIENT METHOD

FOR SPECIFIC INTRODUCTION OF A SINGLE DEUTERIUM ATOM

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Thallation of aromatic substrates with thallic trifluoroacetate proceeds in good yield to give monothallated products, the position of substitution being markedly affected by the nature of the substituent.¹ It has been reported that aryl thallium compounds are reduced with lithium aluminium hydride and sodium or aluminium amalgam in deuterium oxide, but the details are unfortunately available only in thesis form.² Reduction of alkyl thallium derivatives with sodium borohydride in monodeuterio-ethanol yields among other products compounds in which thallium is replaced by deuterium.³ We have found that similar reduction in neutral solution⁴ of aryl thallium compounds gives the corresponding monodeuterio derivatives in good yield, thus providing a convenient method for the introduction of a single deuterium or tritium atom into an aromatic nucleus under mild reducing conditions. By appropriate choice of substituent either the ortho or para deuterio derivative may be prepared; subsequent modification allows the synthesis of a wide variety of specifically monodeuteriated aromatic compounds. The results appear in the Table.

Table

| Compound deuteriated | Deuterium % position [†] | Yield % |
|---------------------------------------------------|--------------------------------------|------------|
| PhCH ₂ CH ₂ CH ₃ | 84 <u>para</u> | 72 |
| PhOCH ₃ | 84 <u>para</u> | 84 |
| PhCO ₂ Me | 85 <u>ortho</u> | 71 |
| PhCO ₂ H | 73 <u>ortho</u> | 65 |
| PhCH ₂ CO ₂ H | 88* <u>ortho</u> | |
| | 73 <u>ortho</u> | 70 |

[†] As thallation gives small amounts of the other positional isomers,¹ the deuterio compounds are similarly contaminated.

* Reduction of thallated compound crystallized from 1,2-dichloroethane.

The position of the deuterium atom in each product is that expected from the position of thallation¹ and confirmed by examination of the n.m.r. spectra of the deuteriated anisole, benzoic acid and methyl benzoate. More complete mono-deuteriation could be achieved by reduction of the aryl thallium ditrifluoroacetates with sodium borodeuteride in monodeuterio-ethanol and it could be shown by use of this reagent in ethanol that 2-8% of hydrogen isotope in the product arose from the reducing agent. (This contrasts with the results of borohydride reduction of alkyl thallium derivatives in alkaline solution, where the hydrogen isotope in the product was shown to arise exclusively from the solvent.³) Further, a higher incorporation of deuterium was obtained by reduction of the isolated aryl thallium compound (see Table).

References

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2. M.J. Zelesko, Ph.D. thesis, Princeton University, 1969; E.C. Taylor and A. McKillop, Accounts Chem. Research, 3, 338 (1970); A. McKillop and E.C. Taylor, Chem. in Britain, 9, 4 (1973).
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4. The aryl thallium compounds were prepared as in ref. 1, except that a 20% excess of thallic trifluoroacetate was used. To the residue obtained after removal of the trifluoroacetic acid, EtOD was added and then recrystallized sodium borohydride (3 molar equivalents) with ice cooling. The product was isolated conveniently after stirring the reaction mixture overnight at room temperature.