

## Preliminary communication

### NEW ASPECTS OF THALLATION

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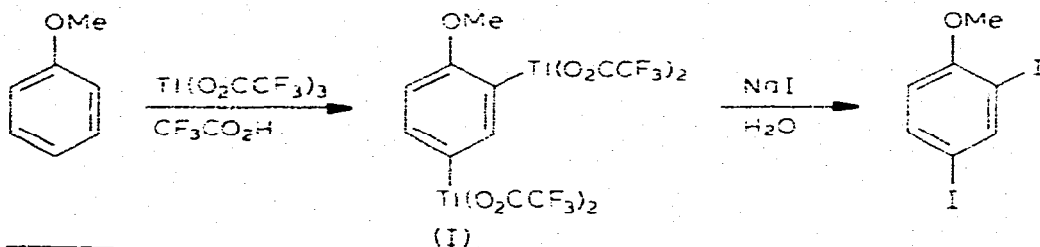
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#### Summary

Thallation of anisole with an excess of thallic trifluoroacetate in trifluoroacetic acid at room temperature yields 2,4-bis[bis(trifluoroacetato)thallio]anisole, and thallation with an equimolar amount of thallic trifluoroacetate using a long reaction time gives predominantly *o*-[bis(trifluoroacetato)thallio]anisole.

Polythallation of monocyclic arenes has not been observed [1–3]\*\*, whereas polymercurration [4] and even permercuration [5] are common. This has been attributed [3,6] to the powerful electron-withdrawing effect of the  $Tl(O_2CCF_3)_2$  group [3,6,7], by contrast with the small electronic effect of mercury substituents [8]. However, despite this deactivation to further thallation, we have now achieved dithallation of anisole. In addition, we have found that the monothallation of anisole using long reaction times gives an isomer distribution very different from that reported [1] for short reaction times.

After reaction of thallic trifluoroacetate and anisole (mol. ratio 3:1) in trifluoroacetic acid (containing ca. 15% water) for 65 h at room temperature, evaporation to crystallization under vacuum at room temperature gave 2,4-bis[bis(trifluoroacetato)thallio]anisole (I) in 70% yield. The compound was obtained analytically pure, dec. temp. 195°C, after recrystallization from

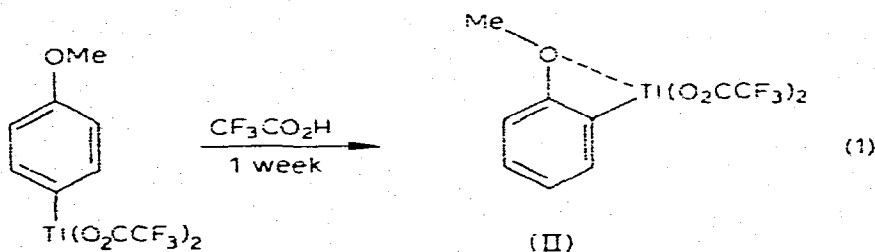


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\*\* The only known cases of polythallation are the dithallation of 2,2'-bithiophen [1] and biphenyl [3], where one thallium substitutes per ring.

aqueous trifluoroacetic acid. Treatment of both crude and recrystallized products with iodide ions gave 2,4-diiodoanisole as the sole organic product, thereby establishing unequivocally (see ref. 1) the positions of the thallium substituents. 2,4-Diiodoanisole was independently obtained as the sole organic product from thallation and iododethallation of both *o*- and *p*-iodoanisole. The aromatic proton resonances of I in  $(\text{CD}_3)_2\text{SO}$  show a triplet [ $\delta$  7.81 ppm;  $^3J(\text{Tl-H})$  999 Hz; H3], and poorly resolved features (partly owing to low solubility), which can be rationalised as arising from overlap of a doublet of doublets [ $\delta$  7.45 ppm;  $^3J(\text{Tl-H})$  980 Hz;  $^5J(\text{Tl-H})$  67 Hz; H5] and a triplet [ $\delta$  7.44 ppm;  $^4J(\text{Tl-H})$  430 Hz; H6]. The coupling constants are similar in magnitude to those [9] of monothallated arenes.

Reaction of equimolar amounts of thallic trifluoroacetate and anisole in trifluoroacetic acid for one week at room temperature followed by treatment with iodide ions gave a 59% yield of monoiodoanisoles (*o/m/p* 79:0:21) and a 13% yield (based on anisole) of 2,4-diiodoanisole, whereas the reported [1] thallation at  $-25^\circ\text{C}$  for 15 min gave a 75% yield of monoiodoanisoles (*o/m/p* 7:0:93). Thus, the rearrangement 1 occurs, and can be attributed to stabilization of the *ortho*-thallated isomer (expected to be destabilized by steric repulsion) by formation of a four-membered chelate ring (II). The conclusion



that the *ortho*-thallated isomer is thermodynamically the most stable is consistent with the outcome of the transthallation reaction between anisole and phenylthallium(III) bis(trifluoroacetate) [10], and the occurrence of reaction 1 explains the observation [1] that thallation of anisole using short reaction times gives more of the *ortho* isomer at room temperature than at  $-25^\circ\text{C}$ . Reaction 1 contrasts with known [11] rearrangements of *para*-thallated arenes, which give *meta*-thallated isomers, and with previous *ortho*-thallations [11], which proceed via five- and six-membered chelate rings under conditions of kinetic control.

The observation of dithallation and a *para*→*ortho* rearrangement suggests a wider role for thallation in organic synthesis than previously realised.

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