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A NEW SYNTHESIS OF ARYLTHALLIUM(III) BISTRIFLUOROACETATES

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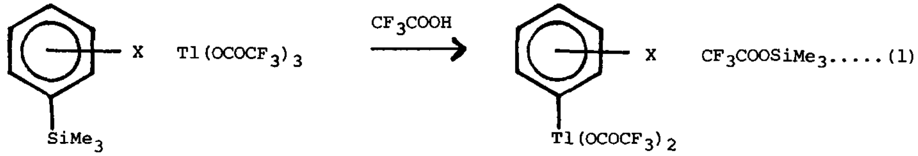
The utility of arylthallium(III) bistrifluoroacetates as synthetic intermediates is now well established[1,2] but their most convenient preparation involves direct thallation[3-5], which is dependent on the nature of existing substituents. For example, alkylbenzenes thallate predominately in the *para* position[4,5] and while isomerisation of the initially formed derivative may give a substantial proportion of the *meta* isomer, this reaction is not always synthetically useful. Thus we have found that refluxing of *p*-tolylthallium bistrifluoroacetate in trifluoroacetic acid results in an increasing proportion of the *meta* isomer (up to *ca* 30% after 13 h), but during this time the *total* yield of tolylthallium compounds decreases to only 20%.

Our successful preparation of aryllead(IV) tristrifluoroacetates[6] by treatment of aryltrimethylsilanes with lead tetrakistrifluoroacetate (LTTFA) lead us to believe that an analogous replacement (eq.1) of the trimethylsilyl group by the bistrifluoroacetoxythallium group could also be effected. Such a route would increase the variety of available arylthallium(III) bistrifluoroacetates as aryltrimethylsilanes are readily prepared[7].



The aryltrimethylsilane (5 mmoles) was dissolved in trifluoroacetic acid (5 ml) and the mixture was added slowly with stirring to a solution of thallium trifluoroacetate (7.3 mmoles) in trifluoroacetic acid (10 ml). After 30 minutes at room temperature the mixture[8] was poured into nitromethane (30 ml), washed with water (2 x 50 ml) and nitromethane was removed under reduced pressure at 30-40°. The residue, which appeared to be pure arylthallium bistrifluoroacetate (by NMR) could be conveniently purified by crystallization from dichloroethane keeping the temperatures of the solution below 40°.

Aryltrimethylsilanes which reacted rapidly with trifluoroacetic acid at room temperature (proto-desilylation[7]) were added to the solution of thallium trifluoroacetate in trifluoroacetic acid in the form of a solution in nitromethane. Reverse addition of reagents, heating or allowing the solutions of arylthallium bistrifluoroacetates to stand for prolonged periods gave diarylthallium trifluoroacetates[3-5].

The results obtained with a representative range of substrates (Table 1) show that this route indeed offers a method of preparing a wide range of arylthallium bistrifluoroacetates in good yields. It should be noted that the yields quoted in Table 1 are the amounts actually isolated. Investigation of reaction mixtures in trifluoroacetic acid by NMR suggests that conversions of aryltrimethylsilanes to arylthallium bistrifluoroacetates under our conditions are nearly quantitative in many cases, the only observable by-products being minor amounts of compounds resulting from proto-desilylation[7].

Mechanistically, reaction (1) appears to be a straightforward example of an electrophilic substitution closely analogous to electrophilic desilylations described by Eaborn[7]. A practical consideration arises from our observation that reaction (1) appears to proceed quite readily even with moderately electron-withdrawing substituents present in the ring, although [c.f. footnote _f_, Table 1] we may have observed a limiting case. By contrast, direct thallation proceeds extremely slowly with deactivated substrates[4,5].

While following the progress of the reaction summarized in equation 1 by NMR spectroscopy, we observed that tetramethylsilane used as internal standard was also attacked by thallium trifluoroacetate in trifluoroacetic acid to give trimethylsilyl trifluoroacetate

Table 1. Preparation and properties of arylthallium (III) bistrifluoroacetates

Substrate $Me_3Si-C_6H_4-X$	Product $(CF_3COO)_2$ $Tl-C_6H_4X$		NMR data[c]				
X	Yield[a] (%)	mp[b] (°)	H-2[d]	H-3[d]	H-4	H-5	H-6
3 - Me	90	110-113	7.33 (1102)	2.38 (57)	7.26 (117)	7.42 (474)	7.30 (1054)
3 - F	90	139-155	7.37 (1143)	-	7.16 (57)	7.57 (503)	7.37 (976)
3 - Cl	90	125-140	7.57 (1088)	-	7.51 (76)	7.47 (476)	7.43 (1004)
3 - Br	80	252-264[e]	7.75 (1070)	-	7.67 (82)	7.46 (468)	7.52 (1013)
3 - CF_3	70	255-265[e]	7.90 (1076)	-	7.75 (108)	7.67 (388)	7.80 (1016)
3 - OMe	60	246-252[e]	7.08 (1228)	3.83	7.01 (72)	7.43 (552)	7.05 (1018)
2 - F	90	103-109	-	7.18 (570)	7.50 (54)	7.22 (314)	7.48 (1114)
2 - Cl	95	149-163	-	7.53 (504)	7.43 (89)	7.46 (329)	7.55 (1082)
2 - Me	95	146-165	2.57 (114)	7.40 (537)	7.30 (124)	7.34 (372)	7.49 (1071)
4 - CF_3	40[f]	[g]	7.75 (1015)	7.81 (353)	-	7.81 (353)	7.75 (1015)
4 - Ph	95	155(dec.)	7.67 (1013)	7.79 (379)	*ca* 7.5	7.79 (379)	7.67 (1013)
4 - H	95	184-190[h]	7.50 (1057)	7.51 (428)	7.49 (142)	7.51 (428)	7.50 (1057)

[a] Isolated material (see text). Unless otherwise stated all new compounds gave correct elementary analyses.

[b] Melting points were obtained with rapid heating. Slow heating gives rise to widely varying melting points due to the formation of diarylthallium trifluoroacetates[3].

[c] The chemical shifts (δ in ppm ex TMS) and average $^{1}H-^{205}Tl/^{1}H-^{203}Tl$ coupling constants[3] (figures in brackets, in Hz) were obtained from 60 MHz NMR spectra of *ca* 10% w/v solutions in a solvent consisting of: $CDCl_3$ (95%), CD_3OD (5%) and CF_3COOD (trace).

[d] Or substituent.

[e] This melting point refers to the corresponding diarylthallium trifluoroacetate, which was formed [3-5] from the initially obtained arylthallium bistrifluoroacetate on recrystallization and was consequently used for characterisation (mp , elementary analysis). The NMR data refer, however, to the arylthallium bistrifluoroacetate.

[f] The NMR spectrum of the reaction mixture before work-up indicated that the reaction was complete after *ca* 24 hrs. and the yield of *p*-$CF_3-C_6H_4-Tl(OCOCF_3)_2$ was only *ca* 55%.

[g] This compound melted over a very wide range.

[h] c.f. lit.[4] m.p. 184-189°

and methyl trifluoroacetate in stoichiometric proportions. We rationalise this observation by proposing the reaction sequence 2 and 3:

$$Me_4Si + Tl(OCOCF_3)_3 \longrightarrow Me\text{-}Tl(OCOCF_3)_2 + CF_3COOSiMe_3 \ldots\ldots (2)$$

$$Me\text{-}Tl(OCOCF_3)_2 \longrightarrow CF_3COOMe + TlOCOCF_3 \ldots\ldots\ldots\ldots (3)$$

The occurence of reactions of the type summarized in equation (3) is well established[9] while reaction (2) represents an electrophilic attack on a saturated carbon atom.

The NMR spectra of arylthallium(III) compounds and in particular the large thallium-proton coupling constants, have been the subject of systematic studies[3,10]. The coupling constants listed in Table 1 follow the trends observed by Maher[10] for an extensive series of arylthallium dichlorides as far as the influence of substituents is concerned, although the actual magnitudes of thallium-proton coupling constants in the two series are not identical. Assuming the principle of simple additivity[11], the subtraction of the chemical shifts of the appropriate monosubstituted benzene[11] from the parameters listed in Table 1 gives the following ranges for the shielding parameters of the $-Tl(OCOCF_3)_2$ group: $S^{\underline{o}}$ 0.15-0.31 ppm; $S^{\underline{m}}$ 0.10-0.28 ppm; $S^{\underline{p}}$ 0.10-0.17 ppm, in qualitative agreement with the electron-withdrawing character of this substituent.

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