Journal of Fluorine Chemistry, 10 (1977) 177 - 180
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands
Received: May 12, 1977

PRELIMINARY NOTE

The Thallation of Polyfluoroaromatic Compounds

G.B. DEACON and D. TUNALEY

Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia).

Thallic trifluoroacetate in trifluoroacetic acid, the most effective thallating agent currently available [1], requires fairly vigorous conditions (refluxing trifluoroacetic acid; reaction times 24 - 98 h) for thallation of substrates with only one deactivating substituent, e.g. benzoic acid and trifluoromethylbenzene [2]. Accordingly, thallation of polyfluoroarenes presents difficulties, since the compounds are severely deactivated to electrophilic aromatic substitution [3,4]. These difficulties are illustrated by the failure to thallate 2,3,5,6-tetrafluoroanisole with thallic trifluoroacetate during 72 h in refluxing trifluoroacetic acid (this work), despite the presence of the activating methoxy substituent. Use of forcing conditions similar to those needed for mercuration of polyfluorobenzenes (reaction temperature 150 - 200° / sealed tubes [4,5]) is precluded by the low thermal stability of thallic trifluoroacetate (dec. > 100° [2]). However, we have now developed a new procedure, which permits thallation of polyfluoroaromatic compounds.

The thallating agent was generated *in situ* by the addition of trifluoromethanesulphonic acid to a solution of thallic trifluoroacetate in trifluoroacetic acid. Since trifluoromethanesulphonic acid is a much stronger acid than trifluoroacetic acid [6], at least partial anion exchange must occur [reaction (1)], and the resulting species is probably more ionized and hence a more reactive thallating agent than thallic trifluoroacetate.

$$\begin{aligned}&Tl(O_2CCF_3)_3 + nCF_3SO_3H\\ &\qquad\longrightarrow Tl(O_3SCF_3)_n(O_2CCF_3)_{3-n} + nCF_3CO_2H \qquad (1)\end{aligned}$$

Reaction of 2,3,5,6-tetrafluoroanisole, 2,3,5,6-tetrafluorotoluene, 1,2,3,5-tetrafluorobenzene and pentafluorobenzene with the new reagent resulted in thallation.

$$\begin{aligned}&RH + Tl(O_3SCF_3)_n(O_2CCF_3)_{3-n}\\ &\qquad\longrightarrow RTl(O_3SCF_3)_n(O_2CCF_3)_{2-n} + CF_3CO_2H \qquad (2)\end{aligned}$$

$$(R = \underline{p}\text{-}CH_3OC_6F_4,\ \underline{p}\text{-}CH_3C_6F_4,\ \underline{m}\text{-}HC_6F_4,\ \text{or}\ C_6F_5)$$

Details of the reactions and the conditions are given in Table 1.

TABLE 1.

Thallation of Polyfluorobenzenes

Polyfluorobenzene (10 mmol)	Reagents	Reaction Temp(Time)(h)	Polyfluoroiodoarene	Yield (%)
P - $HC_6F_4OCH_3$	A	73°(72)	*p* - $IC_6F_4OCH_3$	0
p - $HC_6F_4OCH_3$	B	25°(20)	*p* - $IC_6F_4OCH_3$	39
p - $HC_6F_4CH_3$	B	25°(24)	*p* - $IC_6F_4CH_3$	24
p - $HC_6F_4CH_3$	B	73°(24)	*p* - $IC_6F_4CH_3$	77
p - $HC_6F_4CH_3$	C	73°(48)	*p* - $IC_6F_4CH_3$	10
m - $H_2C_6F_4$	B	25°(288)	*m* - HC_6F_4I	58
m - $H_2C_6F_4$	B	73°(72)	*m* - HC_6F_4I	77
C_6F_5H	B	73°(125)	C_6F_5I	67

[A] $Tl(O_2CCF_3)_3$ (10 mmol)/CF_3CO_2H (10 ml) [B] $Tl(O_2CCF_3)_3$ (10 mmol)/CF_3SO_3H (60 mmol)/CF_3CO_2H (10 ml) [C] $Tl(O_2CCF_3)_3$ (10 mmol)/CF_3SO_3H(1 drop)/CF_3CO_2H (10 ml).

The occurrence of thallation was established in each case by conversion of the product into the corresponding iodoarene by reaction with aqueous sodium iodide, a characteristic reaction of monoarylthallium(III) compounds.

$$RTl(O_3SCF_3)_n(O_2CCF_3)_{2-n} + 2NaI$$

$$\longrightarrow RI + TlI + nNaO_3SCF_3 + (2-n)\,NaO_2CCF_3$$

The polyfluoroiodobenzenes (Table 1) were unambiguously identified by ^{19}F NMR and PMR spectroscopy, and their yields were also obtained using NMR methods. Use of a catalytic amount of trifluoromethanesulphonic acid did not promote substantial thallation of 2,3,5,6-tetrafluorotoluene (Table 1).

The foregoing procedure [reactions (1) and (2)] was more convenient than use of isolated thallic trifluoromethanesulphonate, prepared by neutralization of thallic oxide with trifluoromethanesulphonic acid and obtained as the analytically pure trihydrate after crystallization from nitromethane. The compound had low solubility in trifluoromethanesulphonic acid, and attempts to use the dilute solution for thallation of 2,3,5,6-tetrafluoroanisole led to demethylation not thallation. Thallic trifluoromethanesulphonate in nitromethane and in sulpholane effectively thallated 2,3,5,6-tetrafluoroanisole (20 h at 25°), giving, after work up, 70 and 38% yields respectively of 2,3,5,6-tetrafluoro-4-iodoanisole, but attempts to thallate 2,3,5,6-tetrafluorotoluene (e.g. 72 h at 25° in nitromethane; 24 h at 60° in sulpholane) were unsuccessful. Reduction of the reagent to the thallous state occurred in these solvents, especially on heating, limiting its use for deactivated systems. Accordingly, simply adding trifluoromethanesulphonic acid to solutions of thallic trifluoroacetate in trifluoroacetic acid was not only more convenient but also more applicable than use of isolated thallic trifluoromethanesulphonate. Other possible applications of this new powerful thallation system are being studied.

We are grateful to Mr. R.N.M. Smith for experimental assistance.

1 A. McKillop and E.C. Taylor, Adv. Organometal. Chem., 11 (1973) 147.

2 A. McKillop, J.D. Hunt, M.J. Zelesko, J.S. Fowler, E.C. Taylor, G. McGillivray and F. Kienzle, J. Amer. Chem. Soc., 93 (1971) 4841.

3 V.M. Vlasov and G.G. Yakobson, Russ. Chem. Rev., 43 (1974) 781.

4 G.B. Deacon and F.B. Taylor, Aust. J. Chem., 21 (1968) 2675.

5 H.B. Albrecht and G.B. Deacon, Aust. J. Chem., 25 (1972) 57; J. Organometal. Chem., 57 (1973) 77.

6 T. Gramstad, Tidsskr. Kjemi. Bergvessen Met., 19 (1959) 62. [Chem. Abstr., 54 (1960) 12739].