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Preliminary Note

Symmetrization of bispolyfluorophenylthallium(III) compounds

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Only one rearrangement (symmetrization) of a diorganothallium(III) compound into a triorganothallium(III) compound is known [1], *viz.*, conversion of diphenylthallium bromide into triphenylthallium by sodium in liquid ammonia [2]. We now report that two bispolyfluorophenylthallium(III) compounds can be symmetrized by copper powder in dioxan, whereas diphenylthallium bromide fails to react.

The bromobispolyfluorophenylthallium(III) compounds, R_2TlBr ($R = C_6F_5$ [3] or p-HC_6F_4*) were heated with copper powder (*ca.* 10 g atom Cu per 1 mol R_2TlBr) in refluxing 1,4-dioxan (diox) for 2 h. After filtration, evaporation to crystallization gave trispentafluorophenyl-1,4-dioxanthallium(III), m.p. (dec.) 260 - 265 °C, and tris(2,3,5,6-tetrafluorophenyl)-1,4-dioxanthallium(III), dec. temp. *ca.* 250 °C (yields, > 50%).

$$3R_2TlBr + 2Cu \xrightarrow{\text{1,4-dioxan}} 2R_3Tl\cdot diox + TlBr + 2CuBr$$

The complexes were identified by microanalyses, by peaks attributable to R_3Tl^+ in the mass spectra, and by features in the infrared spectra consistent with the presence of coordinated dioxan [4] and of the appropriate polyfluoroaryl groups. By contrast with free trispentafluorophenylthallium and $(C_6F_5)_3Tl\cdot OEt_2$ [5], the dioxan complexes are stable to atmospheric moisture for prolonged periods. Hydroxobispentafluorophenylthallium(III) [6] was also symmetrized by copper, but a lower yield of $(C_6F_5)_3Tl\cdot diox$ was obtained (27%). Diphenylthallium bromide was recovered in high yield after attempted rearrangement, even with use of a larger excess of copper and a longer reaction time than for the fluorocarbon derivatives.

Although trispentafluorophenylthallium can be obtained from thallic chloride and pentafluorophenylmagnesium bromide in a single preparative step [5], the procedure is complex and involves separation of $(C_6F_5)_3Tl$

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* Obtained analytically pure (yield, 46%, m.p. (dec.) 237 - 239 °C, from a preparation and purification similar to that [3] for $(C_6F_5)_2TlBr$.

and $(C_6F_5)_2TlBr$. Accordingly, preparation and rearrangement of bromobispolyfluoroarylthallium(III) compounds appears a promising alternative route to trispolyfluoroarylthallium compounds. The scope of the symmetrization is currently being investigated, with emphasis on determining what degree of fluorine substitution is necessary for rearrangement to occur.

Acknowledgements

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1 A. N. Nesmeyanov and R. A. Sokolik, The Organic Compounds of Boron, Aluminium, Gallium, Indium and Thallium, North-Holland Publ. Co., Amsterdam, 1967, p. 582.
2 H. Gilman and R. G. Jones, J. Amer. Chem. Soc., 62 (1940) 2357.
3 G. B. Deacon, J. H. S. Green and R. S. Nyholm, J. Chem. Soc., (1965) 3411.
4 See, for example, G. W. A. Fowles, D. A. Rice and R. A. Walton, Spectrochim. Acta, 26A (1970) 143; J. Chem. Soc. (A), (1968) 1842.
5 J. L. W. Pohlmann and F. E. Brinckman, Z. Naturforsch., 20b (1965) 5.
6 H. Luth and M. R. Truter, J. Chem. Soc. (A), (1970) 1287; P. Royo, Rev. Acad. Cienc. Exactas, Fis-Quim. Natur. Zaragoza, 26 (1971) 633.