1 W. Drenth, M. J. Janssen, G. J. M. van der Kerk and J. A. Vliegenthart, *J. Organometal. Chem.*, 2 (1964) 265.
2 E. Krause and A. von Grosse, *Die Chemie der metall-organischen Verbindungen*, Borntraeger, Berlin, 1937, p. 377.
3 W. T. Grubb and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 72 (1950) 419; J. C. D. Brand and J. R. Davidson, *J. Chem. Soc.*, (1956) 15; J. H. Day, *Chem. Rev.*, 63 (1963) 65.
4 E. Müller, F. Günter, K. Scheffler and H. Fettel, *Chem. Ber.*, 91 (1958) 2888; U. Belluco, G. Tagliavini and P. Favero, *Ric. Sci., Rend., Sez. A.*, [2] 2 (1962) 98; *Chem. Abstr.*, 57 (1962) 13786*g*; L. C. Willemsens, *Organolead Chemistry*, Institute for Organic Chemistry T.N.O., Utrecht, 1964, p. 43.

Received April 30th, 1964

J. Organometal. Chem., 2 (1964) 279–281

Effect of solvents on reactions of organometallic compounds

IV*. Preparation of triethylthallium by organomagnesium synthesis

In the course of our investigation on the influence of strong donor solvents on the nucleophilic reactivity of organometallic compounds[1,2] we have re-examined the action of ethylmagnesium bromide on diethylthallium chloride. It has been widely held that Grignard reagents are unable to convert dialkylthallium halides, R_2TlX, to trialkylthallium compounds, and hitherto only lithium alkyls have been used for this purpose[3]. Nevertheless we have found that it is possible to prepare triethylthallium by treating ethylmagnesium bromide with diethylthallium chloride in tetrahydrofuran. The reaction takes place at 0–5° and is accompanied by passage of the chloride into solution. Deposition of metallic thallium is insignificant. After the solvent has been removed *in vacuo*, triethylthallium may be distilled directly from the reaction mixture (b.p. 43°/1 mm, d_4^{20} 1.96); the yields are comparable to those obtained when ethyllithium is used. Triethylthallium may also be prepared from ethylmagnesium bromide, ethyl bromide and thallous chloride in tetrahydrofuran; Gilman and Jones have used this technique with lithium alkyls[4].

The fact that thallium trialkyls may be prepared by organomagnesium synthesis in more strongly solvating media than diethyl ether, is in accordance with the conclusion that the nucleophilic reactivity of organometallic compounds increases in such media[1]. We suggest that this phenomenon is due not only to greater solvent basicity but predominantly to solvating of the metal cation and increasing carbanion reactivity.

Institute of Organo-Element Compounds,
Moscow (U.S.S.R)

O. Yu. Okhlobystin
K. A. Bilevitch
L. I. Zakharkin

1 L. I. Zakharkin, K. A. Bilevitch and O. Yu. Okhlobystin, *Dokl. Akad. Nauk SSSR*, 152 (1963) 338.
2 L. I. Zakharkin, O. Yu. Okhlobystin and K. A. Bilevitch, *J. Organometal. Chem.*, 2 (1964) 309.
3 G. E. Coates, *Organometallic Compounds*, Methuen, London, 1960, p. 155.
4 H. Gilman and R. Jones, *J. Am. Chem. Soc.*, 72 (1950) 1760; 68 (1946) 517.

Received February 24th, 1964

---

* For Part II of this series see ref. 2