spectra were taken with a Beckman spectrophotometer, model DU, on at least two different samples. All measurements were made at room temperature, approximately 30°.

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An Improved Synthesis of Tin Tetramethyl[1]

BY WALTER F. EDGELL AND C. H. WARD[2]

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During the course of studies employing various organotin compounds, it was necessary to prepare quantities of tin tetramethyl. Of the several preparative methods reported,[3–6] those employing the Grignard reagent[5–6] were considered more feasible. Although a yield of 80-85% has been reported,[5] the yields obtained in this Laboratory by this method have approximated 35%. These methods have the disadvantages of being time consuming, of requiring a very large excess of methyl Grignard reagent, and of yielding a product which can be isolated only after fractional[7] distillation of large quantities of ethyl ether.

The low-boiling reaction media employed by previous workers (ethyl ether or ethyl ether–hydrocarbon mixtures) appear to be responsible for these difficulties. Di-*n*-butyl ether has been used successfully with Grignard reagents where a higher boiling solvent was desired.[8] We have found that the Grignard method gives superior results when *n*-butyl ether is used as the reaction medium. The tin tetramethyl is readily isolated from the *n*-butyl ether in high yield. Smaller excesses of methyl Grignard reagent have been employed with equal success[9] and the over-all time requirements are much lower. Pertinent data for three preparations are given in Table I.

TABLE I

TIN TETRAMETHYL PREPARATION DATA

$SnCl_4$ used, mole	CH_3MgI in excess, mole	Yield of $Sn(CH_3)_4$ (based on $SnCl_4$), %
0.20	0.80	90
.23	.68	85
.29	.44	91

Experimental

Fifty grams (2.06 g. atoms) of magnesium turnings and about 600 ml. of *n*-butyl ether were placed in a 1-liter three-necked round-bottom flask fitted with a mercury-sealed stirrer of the Hershberg type, an Allihn reflux condenser with a thermometer and drying tube, and a dropping funnel. The *n*-butyl ether was prepared for use according to the procedure described by Vogel.[10] A solution of 225 g. (1.59 moles) of freshly distilled methyl iodide in an equal volume of *n*-butyl ether was placed in the dropping funnel and then, after the addition of a few crystals of iodine to the magnesium suspension, a 3–5 ml. portion of this methyl iodide solution was added with stirring to the reaction flask. Formation of the Grignard reagent usually occurs immediately, but gentle heating was sometimes required. The remaining methyl iodide solution was added dropwise at a rate sufficient to cause only gentle refluxing. About three hours was required for this step. After allowing the reaction mixture to cool to room temperature, 50–75 g. (0.19–0.29 mole) of anhydrous stannic chloride was added dropwise. Only gentle refluxing should occur during this step which requires 2–2.5 hr. to complete. The reaction mixture was heated under steady reflux (85–95°) for one hour and then allowed to stand for several hours. After replacing the Allihn condenser with a Claisen head and West condenser, the crude product was distilled from the reaction mixture. A mixture of tin tetramethyl and *n*-butyl ether, distilling at 85–95°, is obtained. The tin tetramethyl was isolated by fractional distillation using a Todd column (35–40 plates). The main fraction of tin tetramethyl distils at 76.6°, uncor. (748 mm.). The refractive index and the infrared spectrum were used in establishing the purity of the fractionated product.[11,12]

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[1] Abstracted from the Ph.D. thesis of C. H. Ward.

[2] Purdue Research Foundation Fellow, 1950–1952, and Allied Chemical and Dye Corporation Fellow, 1952–1953.

[3] J. Schmidt, "Organo-Metallverbindungen," II Teil, Edward Brothers, Inc., Ann Arbor, 1943, p. 242.

[4] (a) C. A. Krause and C. C. Callis, U. S. Patent 1,639,947 (1927); (b) R. H. Bullard and W. B. Robinson, THIS JOURNAL, **49**, 1368 (1927).

[5] S. N. Naumov and Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 281 (1935).

[6] (a) C. E. Waring and W. S. Horton, THIS JOURNAL, **67**, 540 (1945); (b) H. Korsching, *Z. Naturforsch.*, **1**, 219 (1946).

[7] The marked affinity of tin tetramethyl for ethyl ether precludes simple distillation.

[8] C. S. Marvel, A. T. Blomquist and L. E. Vaughn, THIS JOURNAL, **50**, 2810 (1928), and many others.

[9] No effort was made to determine the minimum amount of Grignard reagent which might be employed.

[10] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 2nd Ed., Longmans, Green and Co., London, 1951, p. 254.

[11] Infrared spectrum to be published soon.

[12] Tin tetramethyl is an excellent solvent for Silicone stopcock greases and the presence of extremely small amounts of these lubricants gives rise to strong spurious infrared bands in the 8–10 μ region.

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A Hydrocarbostyril Derivative with a Two-Carbon *Peri* Bridge

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The literature describes no derivative of hydrocarbostyril containing a two-carbon *peri* bridge. We have been able to prepare an example of this tricyclic system in two ways, β-(*o*-nitrophenyl)-glutaric acid (II) being the starting material in both syntheses. In the first of these, the chloride of the nitro acid was converted to 4-nitroindan-1-one-3-acetic acid (I) by the Friedel–Crafts reaction. The ring closure had been effected earlier by Manske[1] on the unnitrated acid, and a similar closure was realized by Hoyer[2] with *o*-nitrohydrocinnamic acid. The heterocycle was then closed by subjecting the keto acid I to hydrogenation over Raney nickel, the tricyclic compound being produced in 90% yield.

In the second method, the heterocycle was formed first by the reductive cyclization of β-(*o*-nitrophenyl)-glutaric acid by essentially the method used by Blout and Silvermann[3] on *o*-nitrocinnamic acid, and the product, hydrocarbostyril-4-acetic acid (III), was converted to the tricyclic compound V by the Friedel–Crafts method. The identity of the two tricyclic products serves to establish the structure.

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[1] R. H. Manske, THIS JOURNAL, **53**, 1104 (1931).

[2] H. Hoyer, *J. prakt. Chem.*, **139**, 94 (1934).

[3] E. R. Blout and D. C. Silvermann, THIS JOURNAL, **66**, 1442 (1944).