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]

Acknowledgment.—Thanks are due to the Atomic Energy Commission and the Purdue Research Foundation for support of the work from which this note developed.

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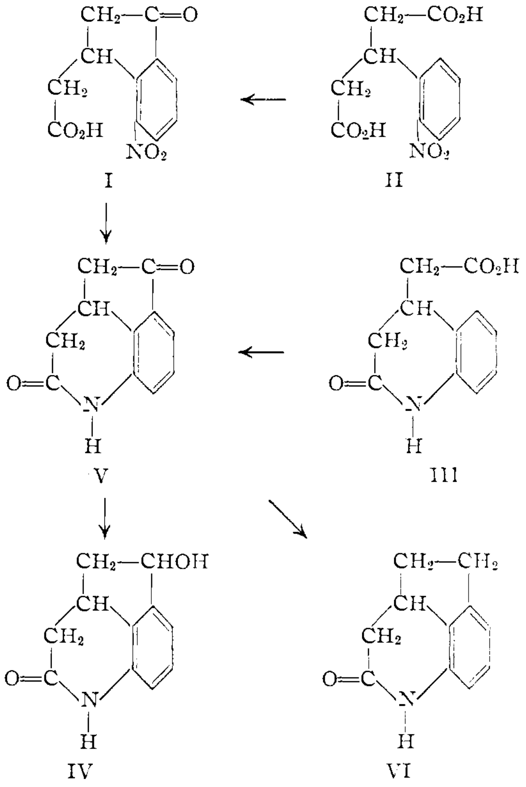
[1] R. H. Manske, THIS JOURNAL, **53**, 1104 (1931).

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

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



The carbonyl group of the carbocycle was shown to react normally. Catalytic hydrogenation converted the keto group to a hydroxyl group, yielding the amido-alcohol IV. The oxygen atom was removed by the Wolff–Kishner method to produce the derivative VI with the saturated bridge. Treatment of the ketone with hydroxylamine in mildly alkaline solution provided the oxime.

Experimental[4]

β-(*o*-Nitrophenyl)-glutaric Acid (II).—Direct nitration of β-phenylglutaric acid affords the *o*-nitro derivative in low yield. The compound is obtained in higher yields from 2,4-dinitroglutaric acid by removal of the *p*-nitro group according to the procedure of Schroeter and Meerwein.[5] In the present work this method was modified by using hypophosphorous acid instead of ethanol for the reduction of the diazonium salt.

To a solution of 23.6 g. of 4-amino-2-nitrophenylglutaric acid in 80 ml. of 5 *N* hydrochloric acid, which was maintained at −5°, was added a solution of 6.1 g. of sodium nitrite in 15 ml. of water followed immediately by a 60-ml. portion of hypophosphorous acid. After being allowed to stand for one hour at −5°, the mixture was heated on a steam-bath until evolution of nitrogen was complete, cooled to 0° and filtered. The nitro acid was washed with water and dried, yield 13.5 g. (61%), m.p. 196–198°. Evaporation of the mother liquor gave a further quantity of 6.5 g., for a total yield of 20 g. (90%).

4-Nitroindan-1-one-3-acetic Acid (I).—β-(*o*-Nitrophenyl)-glutaric acid (86 g.) was converted to the acid chloride by gentle warming with 141 g. of phosphorus pentachloride. After the phosphorus oxychloride had been removed by distillation under reduced pressure, the crude acid chloride was suspended in 250 ml. of carbon disulfide and 90 g. of aluminum chloride was added over a period of 10 minutes. After the reaction mixture had been allowed to stand for 48 hours, the carbon disulfide, in which the reaction product is not soluble, was decanted and the flask containing the tarry residue was nearly filled with crushed ice. The ice was allowed to melt, the mixture was heated to boiling, treated with 20 g. of Darco and filtered. From the cooled filtrate the keto acid was isolated as a crystalline solid; m.p. 177–178°, yield 48 g. (60%).

Anal. Calcd. for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96; neut. equiv., 235.2. Found: C, 56.02; H, 4.11; N, 6.21; neut. equiv., 237.

Hydrocarbostyril-4-acetic Acid.—A solution of 3.5 g. of β-(*o*-nitrophenyl)-glutaric acid in 75 ml. of 95% ethanol was treated with hydrogen at 3 atm. pressure over Raney nickel for 16 hours at room temperature. After the removal of the catalyst, the solution was evaporated under reduced pressure at room temperature to a volume of 10 ml. and allowed to stand overnight to complete crystallization. The hydrocarbostyril-4-acetic acid was recrystallized from water; yield 1.7 g. (61%), m.p. 182–183°.

Formation of the Tricyclic Nucleus. A. From Hydrocarbostyril-4-acetic Acid.—The acid chloride was prepared by treating 2.05 g. of the acid with 2.4 g. of thionyl chloride. After the mixture had stood until no more hydrogen chloride was evolved, 50 ml. of carbon disulfide and 1.0 g. of aluminum chloride were added. The mixture was allowed to stand overnight, then the carbon disulfide was removed by distillation under reduced pressure. After the addition of 50 ml. of 1 *N* hydrochloric acid, the mixture was again allowed to stand overnight and the crystalline product was isolated and recrystallized from water; yield 0.8 g. (42.8%), m.p. 267–268°.

Anal. Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.95; H, 5.15; N, 7.45.

B. **From 4-Nitroindan-1-one-3-acetic Acid.**—A solution of 7 g. of this acid in 100 ml. of 95% ethanol was treated with hydrogen at 3 atm. pressure in the presence of 2 g. of Raney nickel at room temperature for a period of 16 hours. After removal of the catalyst by filtration, the solvent was distilled under reduced pressure and the residual solid recrystallized from 50% acetic acid. The yield was 5 g. (91%), and the melting point, 267–268°. The infrared spectrum of this compound, identical with that of the product obtained in A, offers strong corroboration of the structure. A mixed melting point of the two samples of the tricyclic compound showed no depression.

The *oxime* melts, with decomposition, at 274–275°.

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.99; N, 13.86. Found: C, 65.14; H, 5.04; N, 13.79.

Reduction of the Ketone Group. A. By Catalytic Hydrogenation.—A suspension of 10 g. of the keto amide V in 100 ml. of absolute ethanol was treated with hydrogen under 4 atmospheres pressure in the presence of 0.1 g. of a 5% palladium-on-charcoal catalyst for a period of 4 hours. The reaction mixture was filtered to remove the catalyst and diluted with 100 ml. of water. After recrystallization from acetic acid, the product weighed 9 g. (90% yield); m.p. 253–255°.

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.85; H, 5.84; N, 7.61.

B. **By the Wolff–Kishner Method.**—A mixture containing 5.9 g. of 85% hydrazine hydrate, 1.9 g. of the keto amide V and 10 g. of triethylene glycol was heated gently until solution was complete and then 2.6 g. of potassium hydroxide was added to the solution one pellet at a time. The alkaline solution was heated at reflux temperature for one hour, after which the temperature was gradually increased to 190° by distillation of part of the water and excess hydrazine. A vigorous evolution of nitrogen occurred at about 145°.

After two hours at 190°, the mixture was cooled to 100°, diluted with 100 ml. of hot water, neutralized with 3.3 ml. of concentrated hydrochloric acid and treated with Darco. From the cold filtrate was isolated 1.0 g. (58% yield) of the reduction product VI, which melted at 163–164° after recrystallization from 10% acetic acid.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.16; H, 6.24; N, 8.28.

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[4] The infrared spectra were recorded and interpreted by Miss Helen Miklas. The microanalyses were carried out by Mrs. Esther Fett, Mrs. Lucy Chang and Mr. Joseph Nemeth.

[5] G. Schroeter and H. Meerwein, *Ber.*, **35**, 2073 (1902); **36**, 2670 (1903); **40**, 1586 (1907).