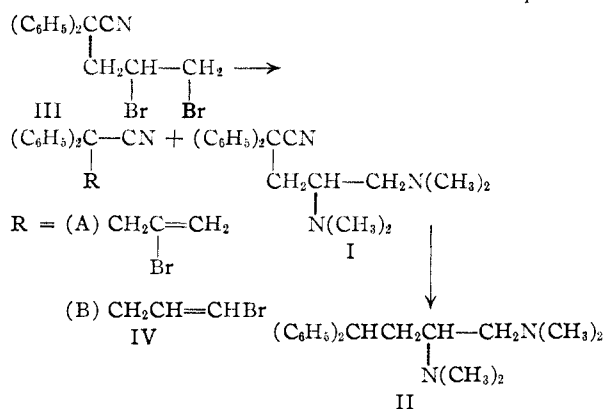


major portion of the dibromide suffered partial dehydrobromination to yield a liquid unsaturated monobromonitrile, IVA or IVB, but probably B since Attenburrow, *et al.*,<sup>5</sup> have reported that the compound to which they assign the structure A is a solid, m.p. 54–55°. No water-insoluble base and no bromide ion was formed when an alcoholic solution of the monobromide and piperidine was boiled for over two days. Upon catalytic hydrogenation, two moles of hydrogen was absorbed and one mole of hydrogen bromide was formed. This behavior indicates the saturation of a double bond by hydrogen and the hydrogenolysis of a carbon-bromine linkage. The hydrogenation product exhibited no basic properties, hence no hydrogen was absorbed by the cyano group to convert it to an amino group. Observation of a similar behavior by III and IVa was reported by Attenburrow, *et al.*,<sup>5</sup> after the work described here had been completed.



#### Experimental

**3,4-Dibromo-2,2-diphenylpentanenitrile.**—This compound was prepared by the method of Attenburrow, *et al.*<sup>5</sup> The compound exists in two forms, one melting at 63–64° and the other at 71–72°, as reported by Attenburrow, *et al.*<sup>5</sup>

**4,5-Bis-(dimethylamino)-2,2-diphenylpentanenitrile (I).**—A mixture of III (39.3 g., 0.1 mole), 33% alcoholic dimethylamine (60 g., 0.44 mole) and absolute alcohol (100 ml.) was heated in an autoclave at 70–80° for 20 hours. After evaporation of the alcohol, the semi-solid residue was stirred with 150 ml. of benzene and the dimethylamine hydrobromide (12.65 g., 0.087 mole) was removed by filtration. After evaporation of the benzene, the residue was shaken in a mixture of dilute hydrochloric acid and ether. The ether layer was removed, dried over anhydrous sodium sulfate and evaporated leaving 18.4 g. of neutral oil, IV.

The acidic water layer was made basic by the addition of 20% sodium hydroxide. The oil that separated soon solidified and was dried in a vacuum desiccator over phosphorus pentoxide. Upon crystallization from low-boiling petroleum ether, there was obtained 8 g. (25%) of white fluffy needles, m.p. 73–74°. For analysis, 0.5 g. was crystallized again from benzene to obtain a sample whose m.p. of 74.5–75.5° was unchanged by further crystallization.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{27}\text{N}_3$ : C, 78.40; H, 8.46; N, 13.07. Found: C, 78.41; H, 8.22; N, 13.02.

**Neutral Oil, IV.**—The neutral oil obtained by the evaporation of the ether solution in an experiment as described above was distilled; b.p. 156–159° (1 mm.),  $n_D^{20}$  1.5988.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{14}\text{BrN}$ : C, 65.39; H, 4.52; N, 4.48. Found: C, 65.15; H, 4.31; N, 4.46.

Qualitative tests showed that halogen and nitrogen were present. The compound did not decolorize bromine in carbon tetrachloride but did slowly decolorize permanganate in acetone. Upon refluxing 15.8 g. of the monobromonitrile and 12 g. of piperidine in 100 ml. of alcohol for 64 hours, no water-insoluble amine nor bromide ion was formed and the starting material (12.5 g.) was recovered.

The analyses and chemical properties coupled with the

fact that IVa is reported to be a solid<sup>5</sup> indicate that the neutral oil is IVb.

**4,5-Bis-(dimethylamino)-2,2-diphenylpentane (II).** **A. By Grignard Reaction.**—To a Grignard reagent prepared from magnesium (2.34 g., 0.096 atom) and ethyl bromide (10.46 g., 0.096 mole) in ether (50 ml.) was added a solution of I (12.8 g., 0.04 mole) in xylene (75 ml.); a gray precipitate formed at once. The water was removed from the reflux condenser and the ether was evaporated from the reaction mixture which then was heated for five hours on a steam-bath. The gray precipitate darkened and formed a thin brown insoluble sirup. After the mixture had stood overnight at 25–30°, it was poured slowly into 100 ml. of water containing 40 ml. of concentrated hydrochloric acid. The brown sirup reacted vigorously, its color was discharged and a colorless solid separated in the aqueous layer. The solid was collected by filtration and dissolved in water. The solution was extracted with ether and made basic with 20% sodium hydroxide. The oil that separated was extracted with ether and the ether solution was dried over sodium sulfate. Then 12 N alcoholic hydrogen chloride was added until no more precipitate formed. The white solid was collected by filtration and dried in air at 60°; m.p. 223–224° (dec.). The melting point was unchanged by crystallization from isopropyl alcohol and ethanol.

**Base.**—One gram of the hydrochloride was dissolved in 20 ml. of water and the solution was made basic by adding 20% sodium hydroxide. The solid base was collected by filtration and dried in vacuum over phosphorus pentoxide. After crystallization from low-boiling petroleum ether, from which it separated in large prisms, the compound melted at 59–60° and when mixed with I, the melting point was greatly depressed.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{28}\text{N}_2$ : C, 81.04; H, 9.52; N, 9.45. Found: C, 80.58; H, 9.29; N, 9.41.

**Picrate.**—The picrate was prepared from an aqueous solution of the dihydrochloride by addition of aqueous picric acid solution. After drying and crystallizing from absolute alcohol (1 l./g.), it melted at 191–192°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4$ : N, 14.84. Found: N, 14.82.

**B. By Degradation of 4,5-Di-(dimethylamino)-2,2-diphenylpentanenitrile (I).**—The procedure of May and Mosettig,<sup>3</sup> as applied by them to the decyanoation of 4-dimethylamino-2,2-diphenylpentanenitrile, was followed.

**Picrate.**—From one-fourth of the crude product the picrate was prepared in alcohol and crystallized from absolute alcohol. The derivative melted at 191–192° alone or when mixed with the picrate of the Grignard product.

**Base.**—The remainder of the crude product was dissolved in low-boiling petroleum ether (25 ml.) and filtered, the filtrate was treated with Norite and the solvent was evaporated. The solid (3.05 g.) that formed on cooling the residue was dissolved in low-boiling petroleum ether (20 ml.) and the solution was cooled to –20° whereupon the product separated in heavy prisms, yield 2 g., m.p. 59–60°, mixed m.p. with free base from Grignard reaction 59–60°.

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### Exaltation of Refraction in Branched-Chain Organometallic Compounds. Tertiary Alkyl Tin Compounds<sup>1</sup>

BY ROBERT WEST, MARION H. WEBSTER AND GEOFFREY WILKINSON

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In the course of surveying the literature in order to establish a system of bond refractions for tin compounds, it was found that isoalkyl tin compounds had consistently higher molecular refraction than their straight-chain analogs.<sup>2</sup> This increase

(1) This work was partly supported by a grant from the Office of Naval Research.

(2) R. West and E. G. Rochow, *THIS JOURNAL*, **74**, 2490 (1952).

averaged 0.15 ml. in the twenty-four cases observed; the bond refraction values tentatively proposed were 4.09 ml. for the Sn-C (primary) bond, and 4.24 ml. for the Sn-C (secondary) bond. A similar exaltation has been observed previously for mercury and lead compounds.<sup>3</sup>

This effect led to the speculation that *t*-alkyl tin compounds might show a still greater increase in refraction. Although a number of *t*-alkyl tin compounds have been prepared,<sup>4</sup> measurements of the refractive indices and densities of these compounds were not reported. Tin tetraalkyls were used in this present study, since they are stable and easily purified. The compounds reported are all new. They are colorless oils with an irritating pepper-like odor; their physical constants are given in Table I.

TABLE I  
TERTIARY ALKYL TIN COMPOUNDS

Compound	Boiling range, °C.	Pressure, mm.	$n_D^{25}$	$d_4^{25}$	Refraction of Sn-C (tert.) bond
Dimethyldi- <i>t</i> -butyltin	84.5-85	40	1.4662	1.1043	4.87
Dimethyldi- <i>t</i> -amyltin	119.5-120	29	1.4870	1.1229	4.52
Di- <i>n</i> -butyldi- <i>t</i> -butyltin	123-125	40	1.4809	1.0527	4.89

The refraction ascribed to the bond from the tertiary carbon atom to tin was calculated as explained in a previous paper.<sup>2</sup> The results show a much higher refractivity for *t*-alkyl tin compounds than for those containing only primary and secondary alkyl groups. While the few cases studied do not permit the assignment of a definite value for the tertiary carbon-tin bond, they indicate that the increase in refraction going from a secondary to a tertiary group will be greater than from a primary to a secondary group. A possible explanation for this effect is that replacement of an alpha hydrogen atom by a more negative element (carbon) may increase the polarity of the carbon-metal bond. It is interesting to note that among organosilicon compounds, where the polarity of the carbon-metal bond is much less, no analogous exaltation for secondary or tertiary<sup>5</sup> alkyl compounds has been observed.

#### Experimental

**Materials.**—Dimethyltin dichloride was donated by Dr. E. G. Rochow of this department. After recrystallization from benzene it melted at 105-106°. *t*-Amyl chloride was prepared from commercial *t*-amyl alcohol by shaking with excess concentrated HCl, separating the organic layer, drying with CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> and distilling through a fractionating column. Eastman Kodak Co. *t*-butyl chloride was dried over Na<sub>2</sub>SO<sub>4</sub> and distilled before use, while di-*n*-butyltin dichloride from Anderson Laboratories was used without further purification.

**Dimethyldi-*t*-amyltin.**—A Grignard reagent was made up in the usual way from 40 g. (0.38 mole) of *t*-amyl chloride in 200 ml. of anhydrous ether. A solution of 20 g. (0.09

mole) of dimethyltin dichloride in 100 ml. of anhydrous ether was added dropwise, and the mixture was heated to reflux for an hour. The excess Grignard reagent was decomposed with ice and HCl; the organic layer was separated, and washed well with aqueous Na<sub>2</sub>CO<sub>3</sub> solution and with water. After drying, the ether was distilled off, and the residue was distilled from a modified Claisen flask under vacuum. The center cut was redistilled from the same apparatus, and the center cut from the second distillation was used for physical measurements. The refractive index was changed only 0.0001 by the second distillation.

*Anal.* Calcd. for C<sub>12</sub>H<sub>28</sub>Sn: C, 49.52; H, 9.70. Found: C, 49.38; H, 9.63.

**Dimethyldi-*t*-butyltin.**—This compound was prepared and purified similarly, starting with *t*-butylmagnesium chloride.

*Anal.* Calcd. for C<sub>10</sub>H<sub>24</sub>Sn: C, 45.66; H, 9.20. Found: C, 45.34; H, 8.91.

**Di-*n*-butyldi-*t*-butyltin.**—This compound was prepared in the same way, but the final product was distilled only once.

*Anal.* Calcd. for C<sub>16</sub>H<sub>36</sub>Sn: C, 55.35; H, 10.45. Found: C, 55.15; H, 10.18.

**Di-*n*-butyldi-*t*-amyltin.**—Distillation yielded a considerable quantity of an oil identified as nearly pure di-*n*-butyl-*t*-amyltin chloride. A waxy white residue remained, presumably the desired product. Since only liquids were of use in the refraction study, purification was not attempted.

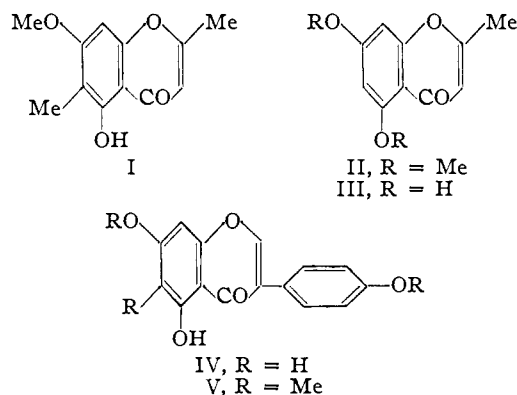
MALLINCKRODT LABORATORY  
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## A New Synthesis of Eugenitin

By W. B. WHALLEY<sup>1</sup>

RECEIVED MAY 29, 1952

The formulation<sup>2</sup> of eugenitin (I) as 5-hydroxy-7-methoxy-2,6-dimethylchromone has been followed by the synthesis<sup>3</sup> in very low yield of this chromone using the Kostanecki sodium acetate-acetic anhydride cyclization of *C*-methylphloracetophenone. The present memoir describes a facile synthesis of



eugenitin, in high yield. Demethylation of 5,7-dimethoxy-2-methylchromone (II)<sup>4</sup> readily gave rise to 5,7-dihydroxy-2-methylchromone<sup>5</sup> (III) which furnished eugenitin (I) upon methylation with methyl iodide and sodium methoxide in methanol. The identity of the natural and synthetic eugenitins was confirmed by a direct comparison (including the ultraviolet absorption curves) of the chromones,

(3) W. J. Jones, D. P. Evans, T. Gulwell and D. C. Griffiths, *J. Chem. Soc.*, 39 (1935).

(4) E. Krause and K. Weinberg, *Ber.*, **63**, 381 (1930).

(5) The only liquid *t*-alkylsilicon compound for which constants are known, di-*t*-butyldichlorosilane, has *MR* calculated 57.32, found 57.44; L. J. Tyler, L. H. Sommer and F. C. Whitmore, *THIS JOURNAL*, **70**, 2876 (1948).

(1) Smith, Kline & French Labs., Philadelphia, Pa.

(2) H. Schmid, *Helv. Chim. Acta*, **32**, 813 (1949).

(3) H. Schmid and A. Bolleter, *ibid.*, **33**, 917 (1950).

(4) J. B. D. MacKenzie, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 2965 (1950).

(5) T. H. Simpson, Alexander Robertson and W. B. Whalley, unpublished.