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.[3]

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,[4] 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.	$n^{25}{}_{D}$	$d^{25}{}_{4}$	Refraction of Sn–C (tert.) bond
Dimethyldi-*t*-butyltin	84.5–85	40	1.4662	1.1043	4.87
Dimethyldi-*t*-amyltin	119.5–120	29	1.4870	1.1229	4.52
Di-*n*-butyldi-*t*-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.[2] 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[5] 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 $CaCl_2$ and Na_2CO_3 and distilling through a fractionating column. Eastman Kodak Co. *t*-butyl chloride was dried over Na_2SO_4 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_2CO_3 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 $C_{12}H_{28}Sn$: 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 $C_{10}H_{24}Sn$: 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 $C_{16}H_{36}Sn$: 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.

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A New Synthesis of Eugenitin

BY W. B. WHALLEY[1]

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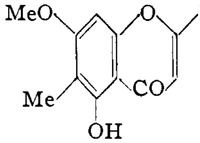
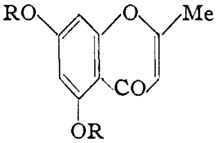
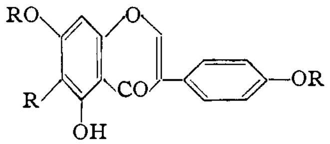
The formulation[2] of eugenitin (I) as 5-hydroxy-7-methoxy-2,6-dimethylchromone has been followed by the synthesis[3] in very low yield of this chromone using the Kostanecki sodium acetate–acetic anhydride cyclization of C-methylphloracetophenone. The present memoir describes a facile synthesis of eugenitin, in high yield. Demethylation of 5,7-dimethoxy-2-methylchromone (II)[4] readily gave rise to 5,7-dihydroxy-2-methylchromone[5] (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,



I



II, R = Me
III, R = H



IV, R = H
V, R = Me

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[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).

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[5] T. H. Simpson, Alexander Robertson and W. B. Whalley, unpublished.

and of their respective acetates. The production of 5-hydroxy-7-methoxy-2,6-dimethylchromone from 5,7-dihydroxy-2-methylchromone in this manner is in accordance with the well established behavior of phloroglucinol and its derivatives[6] and indicates the accuracy of the formulation (V) for the methylation product of genistein (IV) obtained under similar conditions.[7] Confirmation of the structure (V) will be provided in a forthcoming publication.

Experimental

5-Hydroxy-7-methoxy-2,6-dimethylchromone.—A solution of 5,7-dihydroxy-2-methylchromone (0.5 g.) in methanol (10 ml.) and methyl iodide (10 ml.) containing sodium (0.2 g.) was refluxed during 12 hours, when most of the solvent was removed under reduced pressure. Addition of water (50 ml.) and excess 2 *N* hydrochloric acid to the residue furnished a crystalline precipitate which after purification from methanol gave rise to eugenitin (0.4 g.) in colorless needles, m.p. 162–163°, undepressed on admixture with an authentic specimen and exhibiting an intense blue ferric reaction in alcohol.

Anal. Calcd. for $C_{11}H_9O_3(OMe)$: C, 65.44; H, 5.49; OMe, 14.09. Found: C, 65.35; H, 5.74; OMe, 13.24.

The acetate, prepared by the sodium acetate–acetic anhydride method had m.p. 171° alone or in admixture with an authentic specimen.

Acknowledgment.—The author thanks Smith, Kline & French Laboratories for the hospitality of their laboratories, where most of this work was performed, Mrs. Rita Preis for the analysis, Mr. Samuel Rump for the ultraviolet absorption curves which were determined in methanol solution using a Cary recording quartz spectrophotometer, Model 11 M, and Professor H. Schmid for specimens of natural eugenitin and the acetate.

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The Preparation of Nicotinaldehyde

BY H. N. WINGFIELD, W. R. HARLAN AND H. R. HANMER

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Although the preparation of nicotinaldehyde has been carried out by several methods,[1–5] the yields and the isolation procedures leave much to be desired. We have found that the conversion of acyl hydrazides to aldehydes by means of potassium ferricyanide[6] in ammoniacal solution can be applied to nicotinyl hydrazide. Nicotinaldehyde can be obtained in yields of 60–65% in form of its phenylhydrazone, but regeneration of the aldehyde is difficult. An improvement upon this procedure has been discovered in the reaction of nicotinyl hydrazide with sodium metaperiodate in ammoniacal solution whereby yields of 60–70% of crude nicotinaldehyde can be realized. Methylamine can replace ammonia in this synthesis.

Experimental

To a stirred and chilled solution of 11 g. of sodium metaperiodate in 150 cc. of water, 100 cc. of ammonium hydroxide was added slowly until the precipitate first formed went into solution. Usually a crystal mass separated on continued cooling.

A solution of 6.5 g. of crude nicotinyl hydrazide in 75 cc. of about 8% ammonium hydroxide was added to the stirred ice-cold periodate solution as rapidly as the gas evolution permitted. Stirring and cooling were continued for five minutes, the mixture was allowed to stand for 15 more minutes, and then precipitated with a solution of 12 g. of barium acetate in 50 cc. of water. The precipitate was filtered, the filtrate was nearly neutralized with acetic acid and saturated with sodium chloride. The aldehyde was extracted into chloroform, and was fractionated. It boiled at 97–99° (26 mm.).[4] Its phenylhydrazone melted at 157° (uncor.).[4] The aldehyde could also be purified through the bisulfite addition product.

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Physical Adsorption from Mixtures of Gases.[1] III. Ethane and Carbon Dioxide on Chromic Oxide Gel at −78°

BY LOCKE WHITE, JR., CHARLES H. SCHNEIDER AND WALTER WADE ROBINSON, JR.

RECEIVED JUNE 5, 1952

Hill[2] has suggested that perhaps the most important postulate of the Brunauer–Emmett–Teller[3] theory of multimolecular adsorption is that adsorbed molecules after the first layer have the evaporation–condensation properties of the liquid state. He further suggested that studies of adsorption from mixtures of gases would provide a test of this postulate, and he made the necessary extension of BET theory. At that time, there were no suitable data for comparison with the theory.

Since then Arnold[4] has reported studies of adsorption from mixtures of oxygen and nitrogen on anatase, and we[5] have reported similar studies from mixtures of oxygen–nitrogen and oxygen–argon on chromic oxide gel. Arnold's system showed considerable discrepancies between theory and experiment, even at low pressures, whereas our systems agreed at least semi-quantitatively with theory up to relative pressures of about 0.4, the maximum we used.

The mixtures used by both Arnold and us obeyed Raoult's law reasonably well. To test the theory under somewhat more drastic conditions, we have made similar studies with mixtures of carbon dioxide and ethane, which deviate so far from ideality that in most proportions they are not miscible in the condensed phase.

For the theoretical calculations, vapor pressure data for the mixtures were required. Because such data were not available for carbon dioxide and ethane, we determined them approximately.

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