Anal. Calcd. for $C_9H_{11}N_3$: N, 26.0; equiv. wt., 161. Found: N, 26.2; equiv. wt., 163.

Treatment of the 2-anilinoimidazoline in alcohol with picric acid gave a picrate, recrystallized from alcohol, m.p. 201–202°. A mixed melting point with the authentic synthetic material was unchanged.

Anal. Calcd. for $C_{15}H_{16}N_6O_7$: N, 21.6. Found: N, 21.6.

The copper sulfide was recovered and weighed 14 g., equivalent to 4.6 g. hydrogen sulfide.

2-Anilinoimidazoline. This material was made by a modification of the process of Aspinall and Bianco.[9] A mixture of 12 g. of aniline, 16 g. of the methyl thioether of ethylenethiourea,[10] and 28 ml. of ethanol was refluxed for 2 days. The volatile material was removed by heating on a steam bath followed by evacuation for a few minutes. There remained a yellow, viscous oil which dissolved in dilute acid. Addition of base to the cold, filtered solution liberated an oil which solidified. The product, 1.8 g., is 2-anilinoimidazoline, m.p. 138–139° when recrystallized from water. The reported[6] value is 122°. Treatment of an alcohol solution with picric acid gave the picrate, recrystallized from alcohol, m.p. 201–203°.

Treatment of 2-anilinoimidazoline with benzoyl chloride in aqueous alkali gave *N,N'*-dibenzoylethylenediamine, m.p. 250° from alcohol.

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[9] S. Aspinall and E. Bianco, *J. Am. Chem. Soc.*, **73**, 602 (1951).

[10] A. McKay, M. Buchanan, and G. Grant, *J. Am. Chem. Soc.*, **71**, 766 (1949).

Formation of a Cyclic Ester from the Reaction of Di-*n*-butyltin Dichloride with Ethylene Glycol

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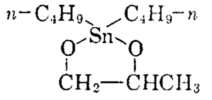
Recently, Ramsden and Banks[2] reported that the product formed from the reaction of di-*n*-butyltin dichloride with ethylene glycol in the presence of sodium hydroxide has the linear structure I.

$$HOCH_2CH_2OSn(C_4H_9\text{-}n)_2OCH_2CH_2OSn(C_4H_9\text{-}n)_2OCH_2CH_2OH$$

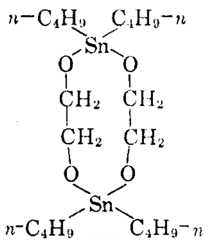
I

We have repeated this reaction and the resulting product has been found by means of its elemental analysis, melting point, and infrared spectrum to be identical to the compound obtained in this laboratory from the treatment of di-*n*-butyltin oxide with ethylene glycol. Our results of the investigation of the structure of this product do not support structure I, however. The following evidence shows that the product is a cyclic tin ester which should be formulated as III.

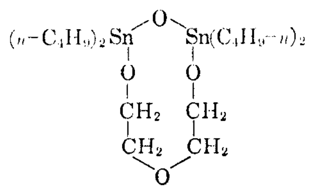
When equimolar amounts of ethylene glycol and di-*n*-butyltin oxide were heated under reflux in benzene, an equimolar amount of water was evolved and a crystalline product separated from the resulting solution. This solid was found consistently to have the molecular formula $C_{20}H_{44}O_4Sn_2$ from numerous elemental analyses[3] and from the determination of its molecular weight by three different methods. The infrared spectrum of the compound in the O—H stretching region was particularly interesting. The spectrum in chloroform solution displayed a broad, medium intense band at 3250 cm.$^{-1}$ which could be indicative of the presence of bonded O—H.[4] However, in carbon disulfide solution this band was completely absent. The identical behavior was observed with di-*n*-butyltin methyldioxolane (II).[5] In contrast, this band was not observed with di-*n*-butyltin dichloride in chloroform. These observations indicate that the band is not due to the presence of a hydroxyl group but, rather, may be due to hydrogen bonding involving the hydrogen of the chloroform and the oxygen of the glycol derivative. Tests for the presence of active hydrogen with methylmagnesium iodide and with lithium aluminum hydride were negative and, hence, provided additional proof of the absence of the hydroxyl function. These facts demonstrate that the product is a cyclic tin ester whose structure must be either III or IV. Structure IV is precluded, however, since the compound is very rapidly hydrolyzed in boiling aqueous ethanol



II



III



IV

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[1] Department of Chemistry, Boston College, Chestnut Hill, Mass.

[2] H. E. Ramsden and C. K. Banks, U. S. Patent 2,789,994 (Apr. 23, 1957).

[3] Ramsden and Banks (ref. 2) reported 36.95% Sn for their compound. Our Sn values were always significantly higher. *Cfr.* experimental section of this paper.

[4] Dr. Ramsden has kindly pointed out (private communication to J. B.) that although a hydroxyl group attached to tin is not always detectable by infrared, a hydroxyl bonded to carbon as in structure I should be observable.

[5] First prepared and characterized by Ramsden and Banks (ref. 2). Investigation of the structure of II in this laboratory supports their findings.

to di-*n*-butyltin oxide and ethylene glycol, which was characterized as its dibenzoate ester. No diethylene glycol was found in the products of hydrolysis.

EXPERIMENTAL[6]

The reaction of di-n-butyltin oxide with ethylene glycol. A mixture of di-*n*-butyltin oxide (25.0 g., 0.10 mole, dried at 110° for 2 hr.), freshly distilled ethylene glycol (6.0 g., 0.097 mole), and 250 ml. of dry benzene was heated under reflux for 1.5 hr. in an apparatus fitted with a Dean-Stark water separator. At the end of this time a clear solution was obtained and 0.1 mole of water was collected. The crystals which deposited from the solution on standing at room temperature overnight were removed by filtration and washed with petroleum ether. Recrystallization from benzene gave III as matted, white needles, 24.0 g. (85%), m.p. 223–229° with decomposition.

Anal. Calcd. for $C_{20}H_{44}O_4Sn_2$: C, 40.99; H, 7.57; Sn, 40.52; mol. wt., 586. Found: C, 41.2; H, 7.5; Sn, 40.79, 40.81, 40.87; mol. wt., 606 (Rast, camphor), 611 (ebullioscopic, benzene), 638 (isothermal distillation, chloroform).

Refluxing of di-*n*-butyltin oxide with a three-fold excess of ethylene glycol in the absence of benzene afforded the same product. The material was identical with that prepared from di-*n*-butyltin dichloride and the glycol by the method of Ramsden and Banks,[2] m.p. 223–226°, mixed m.p. not depressed.

Hydrolysis of III was readily effected by adding as light excess of water to a stirred, boiling solution of the compound in ethanol. Di-*n*-butyltin oxide precipitated immediately. After stirring and refluxing for an additional 10 min., the mixture was cooled to room temperature and filtered to remove the oxide. The filtrate was concentrated by heating gently under reduced pressure in order to remove the ethanol. The residue was dissolved in a small quantity of water, made alkaline with aqueous 10% sodium hydroxide, and shaken with benzoyl chloride. Crystallization of the product from petroleum ether gave the dibenzoate of ethylene glycol as felted needles m.p. 72.5–73.0°, which was found to be identical to an authentic sample[7] by means of m.p., mixed m.p., and comparison of the infrared spectrum.

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(6) Melting points are corrected. Infrared measurements were made using a Baird double beam recording spectrophotometer equipped with a sodium chloride prism. Analyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass., and Dr. S. M. Nagy, Microanalytical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

(7) E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds, Order I*, John Wiley and Sons, Inc., New York, 1941, p. 469.

Use of Tetracyanoethylene as a Color-Forming Reagent in Paper Chromatography of Aromatic Compounds[1]

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In earlier publications,[2a] we have reported on a system for paper chromatography of polycyclic aromatic compounds, which has proved useful in separation and identification of benzyprene derivatives and other polycyclic compounds.[2b-4] In this scheme, the position of spots on the paper was determined by observation of the fluorescence of the spots under ultraviolet light. A spray reagent which would indicate the position of spots of aromatic compounds which were not fluorescent would be of obvious advantage in this procedure.[5]

The observation[6] that tetracyanoethylene[7] forms colored complexes with many aromatic compounds, including simple ones, suggested an examination of this reagent in paper chromatography of aromatic compounds. It is the purpose of the present note to indicate that it does have promise in this connection.

EXPERIMENTAL

The pyrene derivatives were prepared by published procedures,[8] with some modifications, or were commercial samples purified by chromatography on alumina with petroleum ether as the eluant. The hydrocarbons were used as benzene solutions having concentration of 1 mg. per ml. About 10 γ of the material was applied as a spot on the paper.

The dry developed paper chromatogram, prepared by the published procedure,[2] was laid on paper towels in the hood. The freshly prepared tetracyanoethylene (TCNE) solution in distilled acetone[9] (*ca.* 0.01*M*) was sprayed gently and evenly over the surface. The acetone was dried rapidly by playing a stream of air over the surface, or by waving the sheet in the air if it was not too wet. As the solvent evaporated, the temporary dark gray complex of TCNE-acetone-paper disappeared and a permanent yellow color was left on the paper. If a spot was not visible, even when the paper was scrutinized against the light, the spraying was repeated. Often three or four applications were necessary.

In the Table are given the R_f values in hexane saturated with dimethylformamide, the color with TCNE, and for comparison, the color of the spots developed by spraying with picric acid in ethanol and with trinitrofluorenone[10] in acetone solution. As can be seen, the TCNE colors cover a much wider range than those produced with picric acid or

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(1) Aided by Grant C-2654 from the National Institutes of Health.

(2) (a) D. S. Tarbell, E. G. Brooker, A. Vanterpool, W. Conway, C. J. Claus, and T. J. Hall, *J. Am. Chem. Soc.*, **77**, 767 (1955); (b) W. Conway and D. S. Tarbell, *J. Am. Chem. Soc.*, **78**, 2228 (1956).

(3) D. S. Tarbell, E. G. Brooker, P. Seifert, A. Vanderpool, C. J. Claus, and W. Conway, *Cancer Research*, **16**, 1 (1956).

(4) B. L. Van Duuren, *J. Nat. Cancer Inst.*, **21**, 1 (1958).

(5) Tetrachlorophthalic anhydride forms complexes with a variety of aromatic compounds: P. Pfeiffer, *Ber.*, **55**, 413 (1922); Ng. Ph. Buu-Hoï and P. Jacquignon, *Compt. rend.*, **234**, 1056 (1952).

(6) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(7) T. L. Cairns *et al.*, *J. Am. Chem. Soc.*, **79**, 2340 (1957); **80**, 2775 (1958).

(8) H. Vollman *et al.*, *Ann.*, **531**, 1 (1937); M. de Clercq and R. H. Martin, *Bull. soc. chim. Belg.*, **64**, 367 (1955).

(9) Chloroform proved to be an unsatisfactory solvent because TCNE is only slightly soluble (less than 2 mg./100 ml.), and also it does not evaporate fast enough; rapid evaporation is necessary to prevent the dissolving of the complex and consequent spreading of the spot.

(10) M. Orchin and W. O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).