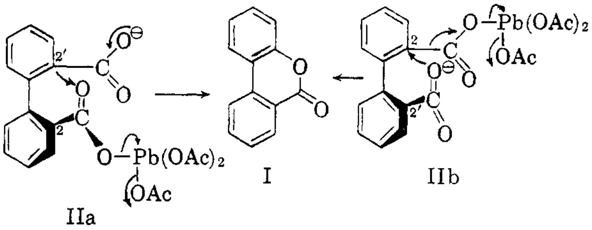

without participation by the C-2′ carboxyl, followed by collapse of the resultant zwitterion to I. Neither sequence appears to be as likely as path IIa which represents an electrophilic substitution at C-2′ by the —COOPb(OAc)$_3$ grouping.[7] This mode of reaction would be similar to that observed by Kenner, Murray, and Tylor,[8] who found that biphenyl-2-carboxylic acid can be oxidized to I with organic peracids or with chromic acid in aqueous acetic acid; these reactions were believed to involve electrophilic substitution by positive oxygen-type species, *i.e.*, the —COOX groupings of the mixed anhydrides formed from the biphenyl-2-carboxylic acid and the oxidizing agents. A slight tendency for diphenic acid to undergo conversion to I (3% in five hours at 90° with hydrogen peroxide in acetic acid) was also found.

In the present case, it is not likely that I was formed by cyclization of II at the 6′-position (*meta* to the 2′-carboxyl group) to give 3,4-benzocoumarin-5-carboxylic acid[9] since this acid would not be expected to decarboxylate (but might cyclize) in view of the failure of the acids noted above to decarboxylate. If the substitution occurs as indicated in IIa, the loss of carbon dioxide from C-2′ could be concerted with the cyclization (IIa then would represent the transition state), an event which should favor the process by minimizing the transitory disruption of the aromatic system.

## Experimental

**Materials.**—Lead tetraacetate, prepared by the procedure of Bailar,[10] was recrystallized from glacial acetic acid and was stored under this solvent. It was freed of acetic acid before use by placing it overnight under reduced pressure in a desiccator containing potassium hydroxide pellets. Diphenic acid was prepared by the procedure of Atkinson and Lawler.[11]

**3,4-Benzocoumarin.**—A mixture of 3.00 g. (0.0124 mole) of diphenic acid, 8.50 g. (0.0188 mole) of lead tetraacetate, 3.0 g. (0.038 mole) of pyridine, and 20 ml. of acetonitrile was heated to reflux in a round-bottomed flask fitted with a reflux condenser which led to a large gas buret. A steady evolution of gas resulted which virtually ceased after 35 min. At this time the flask was cooled to room temperature and the volume of the gas evolved was found to correspond to 0.018 mole. Subsequently, the gas was swept with nitrogen into aqueous barium hydroxide. The barium carbonate which formed was weighed and found to be equivalent to 0.016 mole of carbon dioxide. A large volume of benzene was added to the clear, amber reaction mixture. The benzene solution was decanted from the dark brown material which separated and the latter was washed several times with benzene. The combined benzene extracts were washed with dilute hydrochloric acid. Distillation of the benzene left a light tan solid which was dissolved in dilute aqueous sodium hydroxide. The solution was clarified with Norit and then was acidified with concentrated hydrochloric acid precipitating 1.21 g. (50%) of 3,4-benzocoumarin (I) as light cream crystals, m.p. 92–93° (lit.,[12] m.p. 92.5°); no depression upon admixture with an authentic sample[13] of I. The melting point was not changed upon recrystallization from methanol or pentane. The infrared spectrum of I, which shows a broad maximum in carbon tetrachloride at 1740 (1755 sh) cm.$^{-1}$, was identical with that of an authentic sample.[13]

The benzene-insoluble reaction residue was treated with concentrated hydrochloric acid and the mixture was extracted with benzene. Evaporation of the benzene gave a solid residue which upon recrystallization from benzene–hexane afforded 0.06 g. of a white solid, m.p. 167–170°. The infrared spectrum (potassium bromide) showed a very broad band at 3000–2500 cm.$^{-1}$ (CO$_2$H), broad maxima at 1730 and 1690 cm.$^{-1}$, and a fingerprint region similar to that of I, suggesting that this material might be 3,4-benzocoumarin-5-carboxylic acid. It was not further characterized.

The use of 1.10 moles of lead tetraacetate per mole of diphenic acid resulted in 42–44% yields of I. Lower yields resulted when the lead tetraacetate was not freed of acetic acid before use.

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[7] In this and related cases, for steric reasons attack at the carbonyl oxygen rather than the oxygen bonded to lead should be favored.

[8] G. W. Kenner, M. A. Murray, and C. M. B. Tylor, *Tetrahedron*, **1**, 259 (1957).

[9] Such cyclization might have occurred to some extent since a small amount of material was isolated which could have been this acid.

[10] J. C. Bailar, Jr., *Inorg. Syn.*, **1**, 47 (1939).

[11] E. R. Atkinson and H. J. Lawler, "Organic Syntheses," Coll. Vol. I, J. Wiley & Sons, Inc., New York, N. Y., 1941, p. 222.

[12] C. Graebe and P. Schestakow, *Ann.*, **284**, 306 (1895).

[13] Kindly provided by Professor F. D. Greene; *cf.* F. D. Greene, *et al.*, *J. Org. Chem.*, **25**, 1790 (1960).

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# Triphenyltin Nitrate

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*Received July 31, 1962*

When triphenyltin hydride was treated with nitric acid, a violent reaction took place in which copious, noxious brown fumes (NO$_2$?) were evolved. Nitrobenzene was identified when the reaction had subsided (equation 1). Neither hexaphenylditin nor tetraphenyltin reacted with concentrated nitric acid.

$$(C_6H_5)_3SnH + HNO_3 \longrightarrow C_6H_5NO_2 + (C_6H_5)_2SnO \quad (1)$$

It was assumed first that triphenyltin hydride reacted with the nitric acid to form an unstable intermediate, triphenyltin nitrate, which then rearranged to form nitrobenzene and diphenyltin oxide (equation 2). To test this hypothesis triphenyltin nitrate was synthesized by treating

$$(C_6H_5)_3SnH + HNO_3 \longrightarrow [(C_6H_5)_3SnONO_2] \longrightarrow C_6H_5NO_2 + (C_6H_5)_2SnO \quad (2)$$

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[1] From the B.S. thesis of P.J.S., June, 1962.

[2] To whom inquiries should be directed.

[3] Supported in part by U.S. Army Research Office (Durham) under Grant No. DA-ORD-31-124-61-G39.

silver nitrate with triphenyltin chloride in acetone solution (equation 3). The triphenyltin nitrate

$$AgNO_3 + (C_6H_5)_3SnCl \longrightarrow (C_6H_5)_3SnONO_2 + AgCl \quad (3)$$

was found to decompose to give benzene, nitrobenzene, diphenyltin oxide, and a brown gas believed to be nitrogen dioxide (equation 4).

$$(C_6H_5)_3SnONO_2 \longrightarrow C_6H_5NO_2\,(33\%) + C_6H_6(65\%) + (C_6H_5)_2SnO + [NO_2] \quad (4)$$

Analysis of the triphenyltin nitrate by titration with base showed the product to be impure. Since the reaction appeared to be a simple double decomposition, it was believed that decomposition of the product had occurred even at room temperature. When triphenyltin nitrate was prepared at −80° using the same technique for isolation, the product had the correct analysis. When allowed to come to room temperature and to remain at room temperature for five days, decomposition once again took place, but only nitrobenzene and diphenyltin oxide were formed. No benzene or nitrogen dioxide was observed in a vapor phase chromatogram under these mild conditions (equation 5).

$$(C_6H_5)_3SnONO_2 \longrightarrow C_6H_5NO_2\,(87\%) + (C_6H_5)_2SnO\,(100\%) \quad (5)$$

To review, at low temperatures reaction 5 occurs, while at high temperatures reaction 4 occurs. This suggests that two reactions are taking place: the reaction of equation 5 (just a rearrangement of triphenyltin nitrate) and another reaction in which there is hydrogen abstraction with the possible formation of more highly oxidized compounds, the second reaction being favored at higher temperatures.

Details of the mechanism are now under investigation.

### Experimental

**Synthesis of Triphenyltin Nitrate.**—One-tenth mole of triphenyltin chloride was dissolved in 500 ml. of acetone and was treated with 0.1 mole of silver nitrate in 25 ml. of water. A white precipitate weighing 14.336 g. was formed. This precipitate dissolved in dilute ammonium hydroxide and reformed upon the addition of dilute nitric acid.

The acetone was removed under vacuum and a white crystalline material weighing 41.201 g. was isolated. Upon titration with base a neutralization equivalent of 700 was obtained (triphenyltin nitrate requires 412). Triphenyltin nitrate was once again synthesized as above at −80°. A neutralization equivalent of 411 was obtained.

*Anal.* Calcd. for $C_{18}H_{15}NO_3Sn$: Sn, 28.31. Found: Sn, 28.60, 28.58, 28.65.

**High Temperature Decomposition of Triphenyltin Nitrate.**—Triphenyltin nitrate (10.2 mmoles) was heated to 115° in 10 ml. of *o*-dichlorobenzene and maintained at this temperature for 30 min. The temperature was then raised to 150° and held there for 2 hr. The mixture was cooled and the sample was separated using a Vapor Fractometer. The nitrobenzene and benzene formed in this reaction were identified through their infrared spectra. The per cent nitrobenzene and benzene formed were determined by measuring the area under the vapor phase chromatogram and comparing it to a standard chromatogram. It was found that 33% nitrobenzene and 65% benzene had formed.

**Low Temperature Decomposition of Triphenyltin Nitrate.**—The reaction mixture from the low temperature synthesis of triphenyltin nitrate was allowed to come to room temperature slowly and then to stand at room temperature for 5 days. At the end of this time a portion of the mixture was analyzed using a Vapor Fractometer, an 87% yield of nitrobenzene was obtained. No peak was observed for benzene.

**Synthesis of Nitrobenzene from Triphenyltin Hydride and Nitric Acid.**—Ten mmoles of triphenyltin hydride was slowly added to 250 ml. of concentrated nitric acid with constant stirring. A violent reaction took place with the generation of a brown gas. The nitric acid was neutralized with sodium hydroxide and the reaction products were distilled with steam. Nitrobenzene (3.3. mmoles) was recovered and identified by its infrared spectrum.

**Acknowledgment.**—We gladly express our appreciation to Mr. D. H. Lorenz, who suggested a mechanism for the violent reaction of triphenyltin hydride with nitric acid.

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## The Reaction of Phenyl Benzoate with Alkali Metal Adducts of Tetraphenylethylene. A Brief Reinvestigation

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*Received August 2, 1962*

Schlenk and co-workers reported, in 1928, that the reaction of disodium tetraphenylethylene ($Na_2TPE$) with phenyl benzoate in diethyl ether led to biphenyl in an unspecified, but presumably significant, yield, since this was the only reaction product mentioned.[1] We were struck by the novelty of this reaction, for which we were unable to construct a reasonable course, and so began a reinvestigation. We regret to report that we were unable to detect biphenyl among the products, even though control experiments indicated that we should easily have been able to do so, but found instead indications of the same kinds of products which have heretofore been reported for the reaction of phenyl benzoate with sodium in liquid ammonia,[2] or sodium metal.[3] Our investigation was thereupon terminated. Others have reported the absence of biphenyl as a product from the reaction of $Na_2TPE$ with bromobenzene in tetrahydrofuran,[4] in spite of Schlenk's earlier report to the contrary.[1]

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(1) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(2) M. S. Kharasch, E. Sternfeld, and F. R. Mayo, *J. Org. Chem.*, **5**, 362 (1940).

(3) F. F. Blicke, *J. Am. Chem. Soc.*, **47**, 229 (1925).

(4) E. Müller and G. Röscheisen, *Ber.*, **91**, 1106 (1958).