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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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]

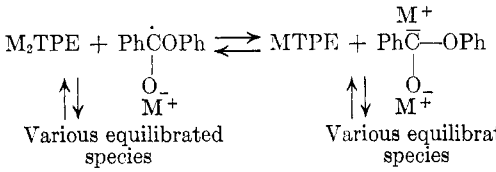
(1) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(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).

One novel feature did appear in our experiments. In performing the reactions, we titrated a solution of the ester with a solution of $Na_2TPE$ in ether (solution I) or with a solution of the tetraphenylethylene adduct from sodium–potassium alloy (referred to hereafter as $K_2TPE$, since qualitative flame tests on the resulting solution indicated more potassium than sodium) in 1,2-dimethoxyethane (solution II). We found that there was a distinct difference between the titration behavior of these two kinds of solutions. With solution I a stable deep red end point was reached which corresponded to the consumption of approximately one mole of $Na_2TPE$ per mole of ester, while with solution II the red end point tended to fade, and the molar ratio of $K_2TPE$ to ester was less than about 0.5 at the end point. These results suggest the occurrence of a reaction consuming $M_2TPE$ (but not ester) which is much slower in solution II than in solution I, or the occurrence of a reaction consuming phenyl benzoate (but not $M_2TPE$) which is much faster in solution II than in solution I. Alternatively, the phenomenon depends not on rates but on equilibria, the positions of which are solvent and/or metal ion dependent. Employing the intermediates proposed by Kharsch, Sternfeld, and Mayo,[2] reaction 1 is a reasonable speculation for the reaction with the rate or equilibrium constant which is sensitive to the nature of the solvent and/or the metal ion.[5]



$$M_2TPE + Ph\dot{C}(O^-M^+)OPh \rightleftarrows MTPE + Ph\overset{M^+}{\bar{C}}(O^-M^+){-}OPh \qquad (1)$$

### Experimental

Dialkali tetraphenylethylene was prepared in diethyl ether or 1,2-dimethoxyethane, by the reaction of sodium metal or sodium-potassium alloy with tetraphenylethylene, in approximately 2-l. quantities, and stored until used. The apparatus was so constructed that the solution could be transferred from the storage vessel through a sintered glass filter to a graduated buret, which could in turn be drained into a reaction flask, the whole being kept in an inert atmosphere (prepurified nitrogen) throughout these operations. The solutions of $Na_2TPE$ thus prepared were about $10^{-3}$ $M$ in diethyl ether and solutions of $K_2TPE$ in 1,2-dimethoxyethane were about $10^{-2}$ $M$.

The reaction vessel arrangement was such that three vessels were available for use at any one time. The usual procedure was to place weighed quantities of iodine or a weak acid in two of the vessels and ester in the third. The iodine and weak acid were titrated with the dialkali tetraphenylethylene solution until the red color no longer disappeared upon admixture with the solution in the flask. The ester was treated the same way. The titrations with iodine and acid led to the same (within 10%) estimates of the concentration of dialkali tetraphenylethylene in each case in which they were run, on the assumptions that the reactions were, respectively,

$$M_2TPE + I_2 \longrightarrow 2MI + TPE \qquad (2)$$

and

$$M_2TPE + 2HA \longrightarrow 2MA + H_2TPE \qquad (3)$$

These data enabled the calculation of the concentration of $M_2TPE$ and the stoichiometry of the reaction with the ester.

In diethyl ether, the stoichiometry of the reaction with the ester appeared to be 1.19, 1.02, 0.94, 1.22, 1.06 mole $Na_2TPE$ per mole of phenyl benzoate.

After the reaction, the solution was concentrated to about 2 ml. without exposing the reaction mixture to the atmosphere and the residue extracted with pentane several times. Vapor phase chromatography indicated the absence of phenol, biphenyl, phenyl benzoate, and benzil in this fraction. When the products were worked up after hydrolysis, vapor phase chromatography showed the presence of a small amount of benzaldehyde, some diphenylmethane, and some unidentified peaks, but no biphenyl.

In control experiments biphenyl was dissolved in ether, the ether concentrated, and the resulting solution subjected to vapor phase chromatography. When a concentration of biphenyl corresponding to a 100% yield in the above experiment was employed, a biphenyl peak sufficiently large that a peak $^1/_{50}$ of its size could be easily detected was observed. When the amount of biphenyl employed corresponded to a 7% yield, the recorded peak was over 12 cm. high. We conclude that a yield of biphenyl of 1% or less would have been detected by our methods.

From a basic aqueous extract of the reaction mixture there was obtained benzoic acid and phenol. Comparison of the infrared spectrum of the mixture with that of synthetic mixtures led to the estimates of a 60% yield of benzoic acid and a 50% yield of phenol. The amount of phenyl benzoate allowed to react was 0.21 g. ($1.1 \times 10^{-3}$ mole). Other products were not identified.

Similar experiments were run with $K_2TPE$ in 1,2-dimethoxyethane. In this solvent the ratios of the molar quantities of $K_2TPE$ and ester used in titrations of the ester were 0.46 and 0.36, with end points which tended to fade much more readily than in diethyl ether. Phenol and benzoic acid were isolated, the latter in 85% yield, from 0.80 g. of phenyl benzoate. The search for biphenyl *via* vapor phase chromatography was fruitless.

In another similar experiment employing $K_2TPE$ in 1,2-dimethoxyethane and *p*-methoxyphenyl benzoate, the molar ratio of reactants in the titration was 0.48 with a well defined end point. Vapor phase chromatography showed that all the ester had reacted.

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(5) Unpublished results from our laboratories indicate that for the related equilibrium, $2NaTPE \rightleftarrows Na_2TPE + TPE$, the equilibrium constant varies by a factor of at least $10^5$ between solvents diethyl ether and 1,2-dimethoxyethane, with the diethyl ether favoring the products as the equation is written.