BRIEF NOTE

IMPROVED METHODS FOR THE SYNTHESIS OF ANTIMONY TRIACETATE, TRIPHENYLANTIMONY DIACETATE, AND PENTAPHENYLANTIMONY[1]

In the past several years, we have conducted studies on the effect of thermal neutron bombardment (Szilard-Chalmers reaction) on pentaphenylantimony. While analogous work has been reported on pentaphenylarsenic (Grossmann, 1969), no investigation has been described on the antimony compound. Part of the special interest in pentaphenylantimony lies in the fact that its solid-state structure has been shown to be square-pyramidal rather than the expected trigonal bipyramid (Beattie and Livingston, 1972). We will report the result of the Szilard-Chalmers investigation in a later paper, but we would like to describe the simplified and improved syntheses of certain organo-antimony compounds used in our research.

Antimony triacetate was prepared by a modification of the procedure of Nerdel and Kleinwachter (1957) using a combination of acetic anhydride and glacial acetic acid on antimony (III) oxide. The synthesis of triphenylantimony diacetate can be expediently done by the careful addition of 30% hydrogen peroxide to a glacial acetic acid-acetic anhydride solution of triphenylantimony. Earlier methods (Wittig and Hellwinkel, 1964) are much more involved. Our preparation of pentaphenylantimony employs an excess of phenylmagnesium bromide on the readily preparable triphenylantimony dibromide in tetrahydrofuran to give a crude yield of better than 90%. The nearest approach to this is the method of Zaharkin *et al*, (1965) who employed the action of phenylmagnesium bromide on triphenylantimony dichloride in glyme-ether solvent. Other methods have often used the more difficult to prepare phenyllithium (Wittig and Clauss, 1952).

ANTIMONY TRIACETATE

Ten grams of antimony(III) oxide, reagent grade, was gently refluxed with 35 ml of freshly distilled acetic anhydride until dissolution was effected (about 2 hr). While hot, the solution was diluted with 25 ml glacial acetic acid and cooled to give well-formed crystals of the triacetate in better than 75% yield. The triacetate is extremely sensitive to moisture and should be kept under glacial acetic acid until needed. Washing with a variety of dry solvents (cyclohexane, chloroform) by decantation followed by quick drying gives a product melting at 124–125° (Nerdel and Kleinwachter, 1957).

TRIPHENYLANTIMONY DIACETATE

Fifteen grams (0.042 mole) of triphenylantimony (M and T Chemicals) was dissolved in a mixture of 75 ml of glacial acetic acid and 35 ml of freshly distilled acetic anhydride by gentle warming. The solution was cooled to room temperature and 10 ml of 30% hydrogen peroxide (0.088 mole) was added dropwise with stirring. A white precipitate appeared in the course of the peroxide addition and this was filtered, washed with a little chilled methanol, and dried in a vacuum oven at 90° for two hours.

[1]Note received July 26, 1976 and in revised form November 1, 1976 (#76-63).

The yield was 85% and the product melted at 214–216°.

PENTAPHENYLANTIMONY

Triphenylantimony dibromide was first prepared (Hagihara *et al*, 1968) by dissolving 20 g of triphenylantimony (0.057 mole) in a minimum amount of glacial acetic acid (about 200 ml) with gentle warming as needed. Elemental bromine (*ca.* 5 ml, 0.098 mole) was then added dropwise (in a chemical hood) with stirring until a persistence of a yellow color (excess bromine) was observed. The precipitated product was filtered, washed with chilled glacial acetic acid followed by chilled methanol, and air-dried. The product is pure enough for most uses (m.p. 218–219°) and the yield better than 85%, but the material may be further purified by recrystallization from benzene or glacial acetic acid and vacuum-oven dried to give a product melting at 221–222° in 75% yield.

Phenylmagnesium bromide was then prepared in the usual manner from dry bromobenzene (36.3 g, 0.231 mole), magnesium turnings (5.62 g, 0.234 mole), in 150 ml of tetrahydrofuran (anhydrous reagent). The Grignard solution was cooled to 0° and triphenylantimony dibromide (30.8 g, 0.60 mole) dissolved in 75 ml of anhydrous tetrahydrofuran was added over a period of 15 minutes. The mixture was then slowly heated to reflux temperature and maintained at gentle reflux for 3 hours. It was then poured with stirring, after cooling to room temperature, into a mixture of 150 ml of water, several ice cubes, and 50 ml of concentrated hydrochloric acid. The resultant yellowish solid was filtered, washed with water, and air dried. Crude yields were as high as 94%. Purification can be effected by recrystallization from cyclohexane to give a product which melts at 162–165° and which retains some solvent tenaciously. Recrystallization from acetonitrile followed by vacuum drying at 80° gives a product melting at 164–165° and analyzing for antimony as follows:

% Sb, calculated for $C_{30}H_{25}Sb$: 24.0
Found: 23.8

THEODORE C. THEPE, S.J., RICHARD J. GARASCIA, MARY A. SELVOSKI, AND ASHOK N. PATEL, *Department of Chemistry, Xavier University, Cincinnati, Ohio 45207.*

LITERATURE CITED

Beattie, I. and K. Livingston. 1972. The shape of pentaphenylantimony and pentaphenylarsenic in solution. J. Chem. Soc. Dalton Trans. 1: 784–786.

Grossman, G. 1969. Szilard-Chalmers effect in phenylarsenic compounds. Isotopenpraxis 5: 370–375.

Hagihara, N., M. Kumada and R. Okawara. 1968. Handbook of organometallic compounds. W. A. Benjamin, N. Y., p. 739.

Nerdel, F. and J. Kleinwachter. 1957. The mixed anhydrides of carboxylic acids and oxy acids of group V of the periodic system. Chemische Berichte 90: 598–600.

Wittig, G. and K. Clauss. 1952. Pentaphenylarsenic and pentaphenylantimony. J. Liebigs Ann. Chem. 577: 26–29.

——— and D. Hellwinkel. 1964. Novel syntheses of aromatic derivatives of pentaphenylantimony and bimsuth. Chemische Berichte 97: 789–793.

Zaharkin, L. Y., O. Y. Okhlobystin and K. A. Bilevitch. 1965. The effect of solvents on reactions of organo-metallic compounds. Tetrahedron 21: 881–886.