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Organotin Chemistry. III.[1] Dibutyltin Diphenoxide

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Dialkyltin diphenoxides have been mentioned in the literature[2] but there are no details of the synthesis or characterization of a member of this class of materials. We prepared dibutyltin diphenoxide (I) by the action of sodium phenoxide on dibutyltin dichloride in heptane (1). The product is extremely sensitive to adventitious moisture and in order to prepare it, extreme care to exclude the atmosphere had to be exercised.

$$(n\text{-}C_4H_9)_2SnCl_2 + 2C_6H_5O^{\ominus}, Na^{\oplus} \longrightarrow (n\text{-}C_4H_9)_2Sn(OC_6H_5)_2 + 2NaCl \quad (1)$$

The diphenoxide I was hydrolyzed by water (2) to give tetrabutyl-1,3-diphenoxydistannoxane II in 95%

$$4Bu_2Sn(OC_6H_5)_2 \xrightarrow{H_2O} \underset{\text{II}}{\{[(n\text{-}C_4H_9)_2SnOC_6H_5]_2O\}_2} \quad (2)$$

$$2Bu_2Sn(OC_6H_5)_2 + 2Bu_2SnO \longrightarrow \text{II} \quad (3)$$

yield. II was also prepared by the reaction of dibutyltin oxide and I (3). The distannoxane II exist as a dimer.[1]

Experimental[3]

Dibutyltin Diphenoxide (I).—Sodium metal (46.0 g., 2 g.-atoms) was dissolved, during stirring, in 1 l. of absolute methanol contained in a three-necked flask provided with a nitrogen atmosphere, a drying tube, and a reflux condenser, with a Dean–Stark apparatus and mechanical stirring. To the freshly prepared solution of sodium methoxide, phenol (188.2 g., 2 moles) was added and the reaction mixture was refluxed for 2 hr. One liter of anhydrous heptane was then added and the methanol was removed by azeotropic distillation, and separation, in the Dean–Stark apparatus. Complete removal of methanol took some 18 hr. of reflux. Replenishment of the heptane lost by its solubility in methanol was made by periodic additions. As the stripping proceeded, a white solid, (sodium phenoxide) precipitated.

During stirring, a solution of dibutyltin dichloride (303.8 g., 1 mole) was added and the reaction mixture refluxed for 4 hr. The mass was then allowed to cool and the solids (NaCl) separated by vacuum filtration on a Büchner funnel, under a blanket of nitrogen; they were washed with 250 ml. of anhydrous heptane and air dried. These solids weighed 121.7 g. (104%, 2.08 moles).

The filtrate and heptane wash were combined and the heptane removed by vacuum distillation to give an orange oil which crystallized on cooling; yield 379.8 g. (90%; 0.90 mole). The crude yield was divided into two portions and characterized separately by both recrystallization and distillation.

Repeated recrystallizations from anhydrous pentane gave white crystals with a constant m.p. of 45–48° (sealed capillary).

Anal. Calcd. for $C_{20}H_{28}SnO_2$:Sn, 28.32; mol. wt., 419.12. Found: Sn, 28.47; mol. wt. (Thermistor Osmometer), 415.

Repeated vacuum distillations of a portion of the crude gave white crystalline material; b.p. 161°/0.35 mm.

Anal. Calcd. for $C_{20}H_{28}SnO_2$: Sn, 28.32. Found: Sn, 28.42. The infrared spectra of the two materials were identical.

Carbon and hydrogen analyses gave erratic results which were ascribed to hydrolysis by adventitious moisture during shipping and handling. Attempts to titrate the material with alkali gave very poor end points. Therefore, a quantitative saponification was done in order to provide a second reliable analytical determination. The sample was saponified with alcoholic potassium hydroxide and the dibutyltin oxide isolated, washed with acetone, dried, and weighed. The results are expressed as % dibutyltin oxide (% Bu_2SnO). For the material purified by recrystallization:

Anal. Calcd. for $C_{20}H_{28}SnO_2$: % Bu_2SnO, 59.39. Found: % Bu_2SnO, 58.72.

For the material purified by distillation:

Anal. Calcd. for $C_{20}H_{28}SnO_2$: % Bu_2SnO, 59.39. Found: % Bu_2SnO, 58.28.

Hydrolysis of Dibutyltin Diphenoxide.—Dibutyltin diphenoxide (4.19 g., 10 mmoles) was stirred for 2 hr. with 100 ml. of water. The white solid was isolated by filtration, washed with water, pressed dry, and dried over phosphorus pentoxide *in vacuo;* yield 3.17 g. (2.4 mmoles, 95%). Recrystallization from hexane gave tetrabutyl-1,3-diphenoxydistannoxane; m.p. 137–139° (lit.[1] 137–139.5°), undepressed when mixed with authentic material. The infrared spectra and X-ray powder patterns were identical with those of an authentic sample.

Reaction of Dibutyltin Diphenoxide with Dibutyltin Oxide.—Dibutyltin oxide (6.23 g., 25 mmoles) was added to a solution of dibutyltin diphenoxide (10.48 g., 25 mmoles) in 125 ml. of anhydrous benzene. During stirring, the mixture was heated to boiling to achieve complete solution. The only slightly hazy solution was filtered while hot and the benzene removed by vacuum distillation.

A white crystalline solid was obtained in 99% yield (16.5 g., 12 mmoles). After one recrystallization from hexane, the melting point was 137–139.5° (lit.,[1] 137–139.5); it was undepressed when mixed with authentic material. The infrared spectra and X-ray powder patterns were identical with those of an authentic sample of tetrabutyl-1,3-diphenoxydistannoxane.

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[1] Paper II, Wm. J. Considine, J. J. Ventura, A. J. Gibbons, Jr., and A. Ross, *Can. J. Chem.*, in press.

[2] See R. Ingham, S. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[3] All melting points are uncorrected.

Photodimerization of a Pseudoxazolone[1,2]

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Pseudoxazolones [(5-[2H]oxazolones)] have been postulated by Bergmann[3] as intermediates in the formation of 5-[4H]oxazolones from N-(α-haloacyl)amino acids. A few pseudoxazolones have been isolated, of which only 2-benzylidene-4-methylpseudoxazolone (I) has received much attention. Ring closure of N-(α-chlorophenylacetyl)alanine (II) gives compound I, for which a

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[2] Abstracted, in part, from the Ph.D. thesis of E. J. Piasek, Illinois Institute of Technology, June, 1962.

[3] M. Bergmann and F. Stern, *Ann.*, **448**, 20 (1926).