

SHORT COMMUNICATIONS

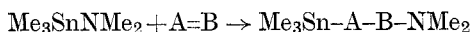
SOME REACTIONS OF ORGANOTIN AZIDES

By P. DUNN* and D. OLDFIELD*

[Manuscript received October 12, 1970]

We are prompted by recent interest in the chemistry of organometallic azides of Group IV elements^{1,2} to report the results of some addition reactions of organotin azides.

Aminostannylation of unsaturated substrates occurs readily³



so that it was of interest to see if tributyltin azide would undergo similar reactions.

Reaction with $-\text{N}=\text{C}=\text{S}$

Tri-*n*-butyltin azide, a stable, distillable liquid, reacted readily at room temperature with phenyl isothiocyanate to give a crystalline product analysing correctly for a 1 : 1 adduct to which we have assigned structure (1). Treatment of this compound with cold dilute hydrochloric acid produced 1-phenyltetrazole-5-thiol (2)⁴ and tributyltin chloride, whilst treatment with cold aqueous sodium hydroxide produced (2) and bis(tributyltin) oxide.

Phenyl isothiocyanate is reported⁴ to react with hydrazoic acid to give initially 5-phenylamino-1,2,3,4-thiatriazole (3) which is converted into (2) by base. A small amount of (3) was obtained in the reaction of crude tributyltin azide with phenyl isothiocyanate, but none was found when using the distilled azide. It was found that (3) was not converted into (2) by the acidic conditions employed in our hydrolysis. This means that the present hydrolysis conditions do not alter the structure of the ring system so that the adduct (1) must contain the tetrazole ring as postulated. Cleavage of the tin-nitrogen bond then leads to the observed products in both cases. The ultraviolet spectra of authentic specimens of (2) and (3) were found particularly useful in confirming that it was in fact (2) which has been isolated in both hydrolyses. The ultraviolet absorption of (1) (λ_{max} 265 nm) is closer to that of (2) (λ_{max} 276 nm) than to that of (3) (λ_{max} 302 nm).

Triphenyltin azide reacted smoothly at 140° with phenyl isothiocyanate to give the analogous adduct (4) which was cleaved by dilute hydrochloric acid to (2).

* Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, P.O. Box 50, Ascot Vale, Vic. 3032.

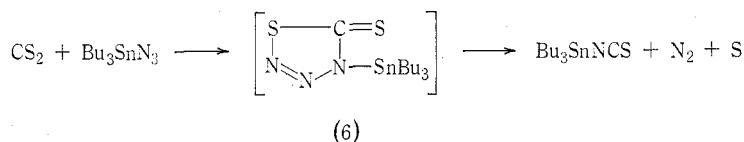
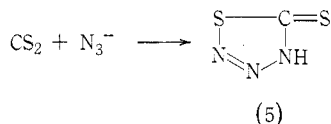
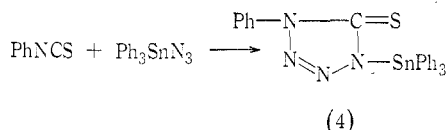
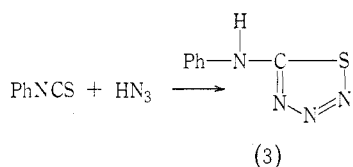
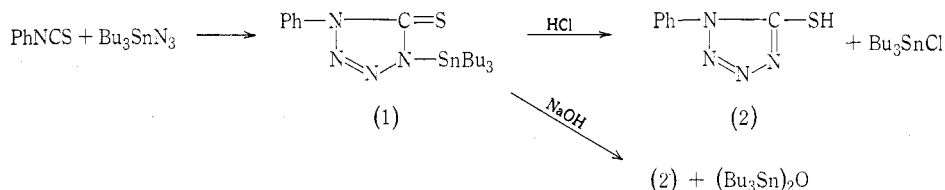
¹ Tsai, T.-T., Lehn, W. L., and Marshall, C. J., *J. organomet. Chem.*, 1970, **22**, 387.

² Wiberg, N., and Joo, W. C., *J. organomet. Chem.*, 1970, **22**, 333.

³ George, T. A., Jones, K., and Lappert, M. F., *J. chem. Soc.*, 1965, 2157.

⁴ Lieber, E., and Ramachandran, J., *Can. J. Chem.*, 1959, **37**, 101.

Diphenylurea was the only product isolated from the reaction of tributyltin azide with phenyl isocyanate even when precautions were taken to exclude moisture.



Reaction with S=C=S

Reaction of carbon disulphide with azide ion gives⁵ the cyclic thiazotriazoline-thione (5) which absorbs in the ultraviolet at 313 nm and decomposes above 10°.

Tributyltin azide has been found by other workers⁶ to react with carbon disulphide in boiling diethyl ether to give tributyltin isothiocyanate and sulphur.

In the present work tributyltin azide was added to an excess of carbon disulphide at room temperature and the ultraviolet spectra of aliquots of the mixture dissolved in methanol were examined at regular intervals. A new strong absorption maximum near 285 nm appeared after 19 hr. The reaction mixture decomposed to tributyltin isothiocyanate, identified by its i.r. and u.v. spectra,⁷ when the carbon disulphide was allowed to evaporate at room temperature. Heating the reaction mixture on a steam-bath for only 5 min also produced the same decomposition reaction, with evolution of

⁵ Lieber, E., Oftedahl, E., and Rao, C. N. R., *J. org. Chem.*, 1963, **28**, 194.

⁶ Luijten, J. G. A., personal communication.

⁷ Cummins, R. A., and Dunn, P., *Aust. J. Chem.*, 1964, **17**, 411.

gas. We believe that the spectroscopic evidence supports the reaction mechanism outlined, which proceeds via the intermediate (6). No reaction was observed between tributyltin azide and carbon dioxide.

Experimental

Tri-*n*-butyltin azide and triphenyltin azide were prepared by the reported procedures.⁸ Microanalyses were performed by Australian Microanalytical Service, Melbourne.

1-Phenyl-4-(tributylstannyl)tetrazole-5-thione (I)

Tributyltin azide (2.0 g; 6 mmol) was added to phenyl isothiocyanate (0.7 ml; 6 mmol) and the mixture was allowed to stand at room temperature for 24 hr. The solid product was crystallized from hexane as colourless plates of *1-phenyl-4-(tributylstannyl)tetrazole-5-thione* (2.13 g; 4.5 mmol), m.p. 45–48° (Found: C, 49.5; H, 6.9; N, 12.1; S, 6.6. $C_{19}H_{32}N_4SSn$ requires C, 48.8; H, 6.8; N, 12.0; S, 6.9%).

Hydrolysis by Hydrochloric Acid

1-Phenyl-4-(tributylstannyl)tetrazole-5-thione (1.0 g; 2 mmol) in ether (50 ml) was stirred with 4*N* hydrochloric acid (30 ml) at room temperature for 8 hr. Ether (100 ml) was then added, the organic layer was separated, washed with water (2 × 150 ml), and dried ($MgSO_4$), and the ether was distilled to leave a mixture of a white solid and a yellow liquid. The mixture was filtered; the filtrate (0.38 g; 1 mmol) had the correct i.r. spectrum for tributyltin chloride. After rinsing with a little hexane, the white solid (0.2 g; 1 mmol), m.p. 145–150°, was shown to have the same u.v. spectrum as an authentic sample of *1-phenyltetrazole-5-thiol* (lit.⁴ m.p. 147–150°), and with mixed melting point undepressed.

Hydrolysis by Sodium Hydroxide

1-Phenyl-4-(tributylstannyl)tetrazole-5-thione (1.0 g; 2 mmol) was stirred with sodium hydroxide (1.5 g) in water (30 ml) at 18° for 6 hr. The resulting clear solution was extracted with ether (2 × 150 ml), the aqueous layer was acidified with 4*N* hydrochloric acid and the white precipitate formed was filtered and crystallized from ethanol as *1-phenyltetrazole-5-thiol* (0.25 g; 1.4 mmol), m.p. 145–150°, with the correct u.v. spectrum. The ether extracts were combined, dried ($MgSO_4$), and the ether distilled to leave a colourless liquid (0.99 g; 1.6 mmol) identified by its i.r. spectrum as bis(tributyltin) oxide.

1-Phenyl-4-(triphenylstannyl)tetrazole-5-thione

Triphenyltin azide (1.0 g; 2.5 mmol) and phenyl isothiocyanate (0.3 ml; 2.5 mmol) was stirred together at 140° for 3 hr. The brown residue was extracted with boiling hexane and on cooling the extract gave white crystals of *1-phenyl-4-(triphenylstannyl)tetrazole-5-thione* (0.3 g; 0.6 mmol), m.p. 129–137° (Found: C, 57.1; H, 3.8; N, 10.8; S, 6.1. $C_{25}H_{20}N_4SSn$ requires C, 56.9; H, 3.8; N, 10.6; S, 6.1%).

Hydrolysis by Hydrochloric Acid

1-Phenyl-4-(triphenylstannyl)tetrazole-5-thione (0.096 g) in ether (50 ml) was stirred with 4*N* hydrochloric acid (30 ml) at room temperature for 6 hr. The ether layer was separated, washed with water (200 ml), dried ($MgSO_4$), and the ether distilled to leave a light green solid (0.09 g) whose u.v. spectrum showed it to contain *1-phenyltetrazole-5-thiol*.

⁸ Luijten, J. G. A., Janssen, M. J., and van der Kerk, G. J. M., *Recl Trav. chim. Pays-Bas*, 1962, **81**, 202.