

Preparation of Aromatic Nitro-compounds through Nitrosodestannylation. 1,2-Dihydro-3-nitrobenzocyclobutene and Trimethyl-*p*-nitrophenylstannane

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Cleavage of aryltrimethylstannanes by nitrosyl chloride followed by oxidation of the resulting nitroso-compound has been shown to provide a useful route to some aromatic nitro-compounds. The method is illustrated by the preparation of 1,2-dihydro-3-nitrobenzocyclobutene ('3-nitrobenzocyclobutene') from 1,2-dihydro-3-trimethylstannylbenzocyclobutene and of trimethyl-*p*-nitrophenylstannane from *p*-bis(trimethylstannyl)benzene.

THE reaction between nitrosyl chloride and aryltrimethylstannanes has previously been shown to be of value in preparing aromatic nitroso-compounds.¹ We describe here two examples, involving the preparation of previously unknown compounds, which illustrate the use of such nitrosodestannylation, followed by oxidation, to give aromatic nitro-compounds not easily accessible by conventional nitration procedures.

1,2-Dihydro-3-nitrobenzocyclobutene ('3-nitrobenzocyclobutene')—for an explanation of the nomenclature see ref. 2) cannot be made satisfactorily by direct nitration of 1,2-dihydrobenzocyclobutene, which gives the 4-nitro- but little if any (<5%) of the 3-nitro-product.³ Treatment of 1,2-dihydro-3-trimethylstannylbenzocyclobutene² with nitrosyl chloride in methylene chloride followed by oxidation of the product with potassium permanganate in aqueous ethyl acetate gave 1,2-dihydro-3-nitrobenzocyclobutene in 65% yield.

Trimethyl-*p*-nitrophenylstannane cannot be made by nitration of trimethylphenylstannane because of the high reactivity of the aryl-SnMe₃ bond. The desired nitro-compound was obtained in 64% yield by treatment of *p*-bis(trimethylstannyl)benzene with nitrosyl chloride followed by oxidation of the product as before. We

have previously referred briefly to the preparation of this compound by treatment of *p*-bis(trimethylsilyl)benzene with copper nitrate in acetic anhydride;⁴ this procedure was once used with apparent success⁵ but we have not subsequently been able to reproduce the result. This is not surprising in view of the recent demonstration that analogous aromatic nitrosodesilylation reactions really involve nitrosodesilylation followed by oxidation, and that their occurrence can depend on the chance presence of catalytic species.⁶

EXPERIMENTAL

1,2-Dihydro-3-nitrobenzocyclobutene ('3-Nitrobenzocyclobutene').— 1,2-Dihydro-3-trimethylstannylbenzocyclobutene, prepared as previously described² by metallation of 1,2-dihydrobenzocyclobutene with *n*-butyl-lithium-tetra-*N*-methylethylenediamine in ether followed by treatment with bromotrimethylstannane and careful fractionation of the products, had b.p. 118.5–119° at 11 mmHg; δ (CCl₄) 6.8–7.3 (3H, m, aryl H), 3.19 (4H, s, CH₂), and 0.34 (9H, s, Me).

A solution of nitrosyl chloride (165 mg, 2.5 mmol) in methylene chloride (2.5 ml) was added through a serum

¹ J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, 1964, **20**, 2185; L. Horner, H. G. Schmelzer, and B. Thompson, *Chem. Ber.*, 1960, **93**, 1774; I. W. Klundt, *Chem. Rev.*, 1970, **70**, 471.

² C. Eaborn, *Pure Appl. Chem.*, 1969, **19**, 375.

³ K. Dey, D.Phil. Thesis, University of Sussex, 1968.

⁴ C. Eaborn, Z. S. Salih, and D. R. M. Walton, *J.C.S. Perkin II*, 1972, 172.

¹ E. H. Bartlett, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc. (C)*, 1970, 1717.

² C. Eaborn, A. A. Najam, and D. R. M. Walton, *J.C.S. Perkin I*, 1972, 2481.

cap to a well-stirred solution of 1,2-dihydro-3-trimethylstannylbenzocyclobutene (0.535 g, 2 mmol) in anhydrous methylene chloride (5 ml) at 0° under nitrogen. The mixture was allowed to warm to room temperature and stirred for 1 h. Solvent was removed on a rotary evaporator, and ethyl acetate (20 ml) was added, followed by potassium permanganate (0.3 g) in water (20 ml). The mixture was shaken for 40 min, then the organic layer was separated, washed well with water, dried (Na₂SO₄), and evaporated to leave a faintly yellow liquid (194 mg, 65%); $\nu(\text{NO}_2)$ 1520s and 1350s cm⁻¹; δ (CCl₄) 7.1—7.8 (3H, m, C₆H₃) and 3.3 (4H, A₂B₂m, CH₂). The sample gave only one spot on t.l.c. on silica gel (elution with benzene). Material recovered by elution with light petroleum followed by light petroleum-chloroform from a silica gel column was sublimed at 100° and 0.2 mmHg to give off-white crystals of 1,2-dihydro-3-nitrobenzocyclobutene, m.p. 35—37° (Found: C, 64.3; H, 4.7; N, 9.4. C₈H₇NO₂ requires C, 64.4; H, 4.7; N, 9.4%).

Trimethyl-p-nitrophenylstannane.—A solution of *p*-bis-(trimethylstannyl)benzene (4.04 g, 10 mmol) in anhydrous ether (60 ml), was treated under nitrogen at room tem-

perature with nitrosyl chloride (1.3 g, 2.0 mmol) in ether. The green solution was stirred for 30 min, then evaporated to dryness. Ethyl acetate (50 ml) was added, followed by a solution of potassium permanganate (2.0 g) and sulphuric acid (3 ml) in water (50 ml). The mixture was shaken for 45 min, then the organic layer was separated, washed well with water, dried (Na₂SO₄), and evaporated, to give pale yellow crystals of *trimethyl-p-nitrophenylstannane* (1.83 g, 64%), m.p. 52—53° (from aq. MeOH); $\nu(\text{NO}_2)$ 1520s and 1350 cm⁻¹; δ (CDCl₃) 8.16 (2H, d, $J_{1,2}$ 8.7 Hz, aryl H), 7.66 (2H, d, $J_{1,2}$ 8.7 Hz, aryl H), and 0.40 (9H, s, Me) (Found: C, 37.9; H, 4.9; N, 4.8. C₉H₁₃NO₂Sn requires C, 37.8; H, 4.6; N, 4.9%).

In some of the repetitions of this preparation the yields were, for no apparent reason, substantially smaller. Methylene chloride was satisfactorily used as solvent in place of ether in some experiments.

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