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TIN(IV) MEDIATED SYNTHESIS OF *N*-HALO COMPOUNDS

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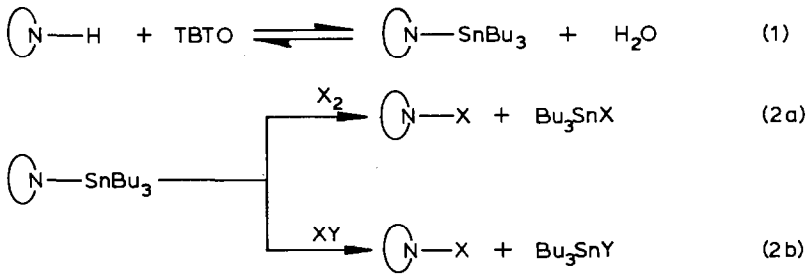
Summary

Some representative *N*-halo compounds like *N*-bromosuccinimide, *N*-iodosuccinimide, *N*-bromophthalimide, *N*-iodophthalimide, *N*-iodobenzimidazole and *N*-iodobenzotriazole have been synthesised in good yields under neutral and mild conditions via an intermediate formed from the parent NH species and bis(tri-n-butyltin) oxide. The tin oxide is recovered as recyclable tri-n-butyltin halide.

Introduction

In a search for new applications of bis(tri-n-butyltin) oxide (TBTO) it has been found that it can be used in the synthesis of *N*-halo compounds, which are generally prepared either by reaction of halogens with *N*-silver salt or reaction of halogens directly with the N–H compounds under alkaline conditions with or without added hypohalites [1]. Since the silver method involves the use of expensive silver oxide, a more economical and efficient method was envisaged. The process used is illustrated in eq. 1–3.



(X, Y = halogens)

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Results and discussion

Succinimide, phthalimide, benzimidazole and benzotriazole were used as model compounds. In each of these cases, the stannyl derivatives were prepared by refluxing them with TBTO using a Dean–Stork apparatus for azeotropic removal of water [2]. The *N*-bromo compounds were then prepared by treating the respective stannyl derivatives with dry bromine in dry carbon tetrachloride. However, 1-bromobenzimidazole and 1-bromobenzotriazole could not be prepared by this method even in polar solvents like acetonitrile, dimethylformamide, etc. The analogous method for the preparation of the iodo derivatives using iodine was also unsuccessful, but ICl in acetonitrile gave the iodo derivatives readily in all these model compounds. The results are summarised in Table 1.

The method followed here has the advantages of (a) mild and neutral conditions; (b) the use of less expensive metal oxide; (c) the possibility of recycling the metal oxide; and (d) reasonably good yields.

Experimental

Representative procedures for the preparation of *N*-bromo and *N*-iodophthalimides are as follows.

N-Bromophthalimide

Phthalimide (5 mmol) was refluxed in benzene with TBTO (2.5 mmol) for 3–4 h with continuous azeotropic removal of water. Benzene was then evaporated off in a rotary evaporator. The *N*-stannylphthalimide which separated as a thick liquid was then dissolved in 20 cm^3 of dry carbon tetrachloride. A solution of bromine (5 mmol) in 20 cm^3 of dry carbon tetrachloride was then added slowly with stirring under nitrogen at 0°C. The *N*-bromophthalimide which separated was filtered off, washed several times with dry carbon tetrachloride, dried, and recrystallized from chloroform/hexane (m.p. 200–203°C; lit. 206°C) [3.58 g (80%)].

TABLE 1

SYNTHESIS OF *N*-HALO COMPOUNDS

substrate	Reagent	solvent	product	yield [a] (%)	assay [b] (%)
Succinimide	Br_2	CCl_4	*N*-bromo-succinimide	93	98
Phthalimide	Br_2	CCl_4	*N*-bromo-phthalimide	80	93
Succinimide	ICl	CCl_4	*N*-iodo-succinimide	68	85
Phthalimide	ICl	CH_3CN	*N*-iodo-phthalimide	89	83
Benzimidazole	ICl	CH_3CN	*N*-iodo-benzimidazole	79	87
Benzotriazole	ICl	CH_3CN	*N*-iodo-benzotriazole	63	82

[a] Isolated yields: based on the substrate. [b] Determined by iodometric method.

N-Iodophthalimide

The same procedure was followed except that dry CH_3CN was used instead of CCl_4 and freshly prepared ICl in place of bromine (m.p. 225–228°C; yield 89%).

References

1 N.K. Mathur and C.K. Narang, Determination of organic compounds with *N*-bromosuccinimide and allied reagents, Academic Press, London, 1975.

2 K. Jones and M.F. Lappert, in A.K. Sawyer (Ed.), Organotin compounds, vol. II, Marcel Dekker, Inc., Amsterdam, 1971, p. 520.