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Tellurolate-Induced Deprotection of 2,2,2-Trichloro-*tert*-butyloxycarbonyl (TCBOC) Derivatives

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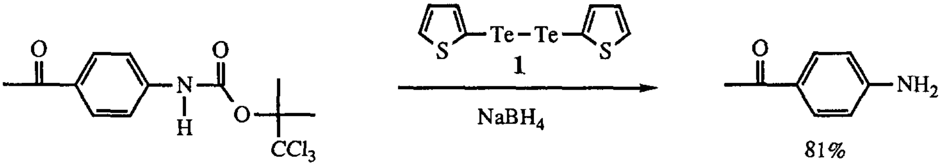
Summary: Sodium-2-thiophenetellurolate efficiently regenerates amines from their 2,2,2-trichloro-*tert*-butyloxycarbonyl (TCBOC) and 2,2,2-trichloroethoxycarbonyl derivatives.

In connection with another project, we required a protecting group for amino nitrogens which would be both acid and base stable. We found the 2,2,2-trichloro-*tert*-butyloxycarbonyl (TCBOC) moiety, which had been introduced by Ugi *et al.* to be appropriate.[1] This group is commonly removed with the powerful nucleophile lithium cobalt phthalocyanine or with zinc.[1] We now wish to report another method for deprotection of TCBOC-derivatives under mildly alkaline conditions using sodium-2-thiophenetellurolate. This nucleophile is readily obtained in a catalytic cycle by sodium borohydride reduction of bis(2-thienyl)ditelluride (**1**)[2], which is commercially available.

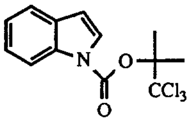
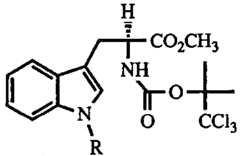
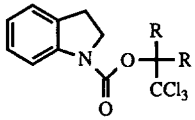
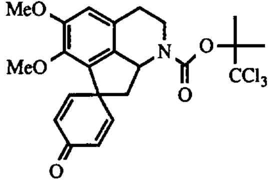
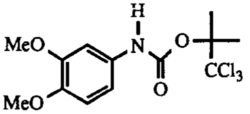
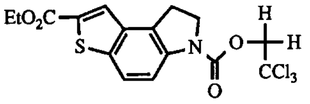
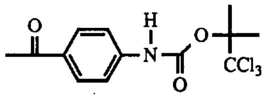
In 1980, Engman reported using sodium borohydride with a catalytic amount of bis(2-thienyl)ditelluride for the debromination of vicinal dibromides[3] and subsequently for the debromination of 1,4-dibromo-2-enes to 1,3-dienes.[4] This concept was readily extended to the deprotection of TCBOC-derivatives, with typical results shown in the table.



The reaction appears to be a general method for the deprotection of TCBOC-derivatives of amines as well as the corresponding 2,2,2-trichloroethoxycarbonyl derivatives. It is significant that the carbonyl group of substrate 5 and the dienone moiety of substrate 8 remain intact under the reaction conditions. Another interesting example is illustrated in entry 7 where under the non-acidic conditions the TCBOC group is removed selectively while the *tert*-butyloxycarbonyl (BOC)-protected indole remains intact to afford an indole-protected tryptophan which would otherwise be difficult to obtain.

In a typical procedure, a 1% solution of the TCBOC-derivative with 24 mole percent of bis(2-thienyl)ditelluride in THF was heated to 60°C under nitrogen. A 1% aqueous solution of $NaBH_4$ (stabilized with three drops of a 10% sodium hydroxide solution) was added dropwise until the red color of the catalyst disappeared. This usually required 4 or 5 equivalents of $NaBH_4$ and was done over a period of 30 minutes. The volatiles were removed *in vacuo* ; the mixture was poured into water and extracted with ether. The amines were then isolated either by flash chromatography or by acid extraction.[5]

TABLE: Tellurolate-Induced Removal of TCBOC-Derivatives

Entry	Substrate	Yield (%RR'NH)	Entry	Substrate	Yield (%RR'NH)
1		85	6 7		R=H:78 R=BOC:70
2 3		R = Me: 84 R = H: 79	8		71
4		84	9		93
5		81			

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References and Notes

1. H. Eckert, M. Listl and I. Ugi. *Angew. Chem. Int. Ed. Engl.*, **1978**, *17*, 361.
2. L. Engman and M. P. Cava. *Organometallics*, **1982**, *1*, 470.
3. L. Engman. *Tetrahedron Lett.*, **1982**, *23*, 3601.
4. L. Engman and S. E. Bystrom. *J. Org. Chem.*, **1985**, *50*, 3170.
5. Deprotected compounds were characterized by t.l.c., i.r. and n.m.r. comparison with authentic samples.

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