



A mild procedure for the clay catalyzed selective removal of the *tert*-butoxycarbonyl protecting group from aromatic amines

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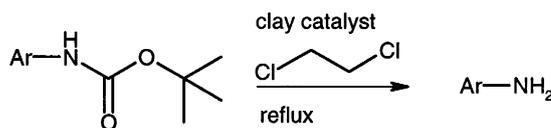
Abstract

The application of solid acidic catalysts for the selective removal of *N*-Boc protection is presented in this report. Montmorillonite K10 was found to be an effective catalyst in removing aromatic *N*-Boc groups while leaving aliphatic *N*-Boc amines untouched. © 2000 Elsevier Science Ltd. All rights reserved.

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The *tert*-butoxycarbonyl group (Boc) is frequently used as a protecting group for 1° and 2° amines¹ and amino acids in peptide chemistry² due to its stability to mildly acidic as well as basic conditions. A number of reagents have been known³ to effect clean removal of this protecting group, most under homogeneous conditions. The only example known of this cleavage using solid reagents is the use of silica gel under reduced pressure.⁴ Developing new applications for heterogeneous catalysts for organic transformations has been a subject of ongoing research in our laboratory.⁵ Recently there has been an upsurge in new applications of clays as catalysts for several organic reactions.⁶ We wish to report in this communication a preliminary account of the use of acidic clays as catalysts for the selective removal of the *N*-Boc group.

A mixture of the *N*-Boc aromatic amine and kaolinitic clay (KC)⁷ or commercial montmorillonite K10 (20% w/w) was refluxed in dichloroethane to afford the deprotected amine in excellent yield (Scheme 1).



Scheme 1.

A series of *N*-Boc amines were subjected to the deprotection conditions with different catalysts and the results are presented in Table 1. The recoverability and reusability of each catalyst was tested by the

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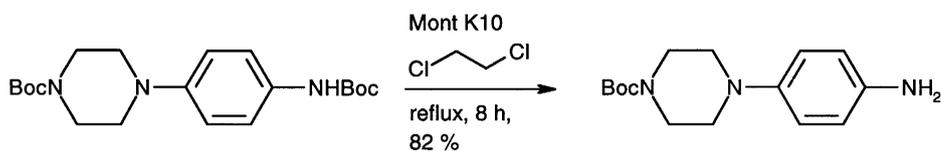
Table 1
Catalytic deprotection of *N*-Boc amines

Entry	Substrate	Catalyst (time in h)	% Yield ^a	Entry	Substrate	Catalyst (time in h)	% Yield ^a
1.		none (15) KC (2.0) Mont K10 (1.5) EPZGF [†] (1.5)	no reaction 98 98 99	6.		Mont K10 (2.25)	86
2.		Mont K10 (2.5)	94	7.		Mont K10 (4.0)	94
3.		Mont K10 (2.5)	77 72 ^b	8.		Mont K10 (4.0)	64
4.		Mont K10 (2.0)	97	9.		Mont K10 (15)	no reaction
5.		KC (1.5)	97	10.		Mont K10 (15)	no reaction

^aIsolated yields. Amines characterized by usual spectral analyses. ^bWith recovered catalyst from the 1st cycle.

experiment recorded in entry 3 of Table 1.

The *N*-Boc group of aromatic amines was removed with ease leaving other protecting groups unaffected (entries 5 and 8) while aliphatic amines failed to undergo cleavage (entries 9 and 10). The selective nature of the catalyst was confirmed by Scheme 2.



Scheme 2.

Thus we present our preliminary findings on the application of acidic clays as catalysts for the selective removal of the *tert*-butoxycarbonyl group from aromatic amines.

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