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Synthesis of Aromatic Amines Using Allyl Azide

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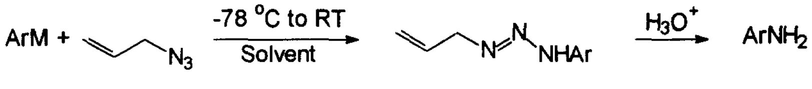
Abstract: Aromatic amines are conveniently prepared in good yields by reaction of aromatic Grignard and lithium reagents with allyl azide, followed by hydrolysis.

Aromatic amines play an important role in chemical industry and numerous preparative methods have been developed. The most common synthetic routes involve the reduction of nitrogen-containing aromatic compounds, such as nitroarenes[1] and aryl azides,[2] or rearrangements of the corresponding carboxylic derivatives.[3] Direct aminations of aryl halides also constitute an important synthetic method.[4] Indirect aminations of aryl halides *via* the reactions of aromatic organometallic reagents and NH_2^+ synthons such as chloroamine,[5] alkoxyamine,[6] and azides are also important.[7] Several azides RN_3 (R = $PhSCH_2$,[7a-7b] Me_3SiCH_2,[7c-7d] and vinyl[7e]) have been successfully employed for this purpose. We wish to report that allyl azide is useful for the preparation of aromatic amines from aromatic organometallic reagents.

Allyl azide is easily prepared *via* the reaction of sodium azide with ally bromide in water in the presence of a catalytic amount of tetrabutylammonium bromide.[8] On treatment with aromatic lithium or Grignard reagents, the allyl azide is transformed into an allylaryltriazene, which generates an aromatic amine in good yield after acidic hydrolysis. The results are summarized in the Table. It was reported that the reaction of $Me_3SiCH_2N_3$ with aryllithiums in Et_2O, followed by hydrolysis, generated the corresponding aromatic amines in poor yields (35-41%).[7c] In the present study, when the reaction of phenyllithium with allyl azide was carried out in hexane, aniline was obtained in higher yield (61%). It was further demonstrated that it is not necessary to isolate the allyl azide (Method A) since it can be prepared and used without purification (Method B). **Since organic azides are potentially explosive,[7a,9] Method B is the method of choice.**



In summary, we have shown that allyl azide (prepared *in situ*) is a useful reagent for the conversion of both aromatic lithium and Grignard reagents into the corresponding amines in good yields.

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Table: Synthesis of $ArNH_2$ from ArM (M = Li, MgBr) and allyl azide

Entry	Ar	M	Method[a]	Solvent	Yield (%)[b]
1	C_6H_5	MgBr	A	Et_2O	76
2	C_6H_5	MgBr	B	Et_2O	83
3	C_6H_5	Li	A	*n*-Hexane	61
4	C_6H_5	Li	B	*n*-Hexane	65
5	$3\text{-}ClC_6H_4$	MgBr	A	Et_2O	68
6	$3\text{-}ClC_6H_4$	MgBr	B	Et_2O	63
7	$4\text{-}ClC_6H_4$	MgBr	A	Et_2O	52
8	$4\text{-}ClC_6H_4$	MgBr	B	Et_2O	53
9	$2\text{-}MeOC_6H_4$	MgBr	A	Et_2O	71
10	$3\text{-}MeOC_6H_4$	MgBr	A	Et_2O	55
11	$4\text{-}MeOC_6H_4$	MgBr	A	Et_2O	75
12	$5\text{-}F\text{-}2\text{-}MeC_6H_3$	MgBr	A	Et_2O	66
13	1-Naphthyl	MgBr	A	Et_2O	77

[a] Method A: distilled allyl azide was used, ArM:Allyl azide = 1:1; Method B: the crude allyl azide[10] was used, ArM:Allyl bromide = 1:1.5. [b] Isolated yields of the free amines.

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10. The crude allyl azide was obtained by reacting sodium azide with allyl bromide. The allyl azide was then extracted into ether (or hexane), washed with brine solution, and dried over $MgSO_4$. The filtrate was stored over molecular sieves for 24 h prior to use.

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