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Article

Facile Conversion of Aryl Amines Having No α-Methylene to Aryl Nitriles

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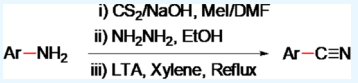
ABSTRACT: Dimethyl carbonimidodithioates, **2** derived from various primary aryl amines (**1**) by reacting with carbon disulfide and methyl iodide in dimethyl formamide in the presence of concentrated sodium hydroxide, are converted to the diaziridine derivatives, **3** by reacting with hydrazine in ethanol. The diaziridines, **3** on oxidation with lead tetraacetate in refluxing xylene, extrudes nitrogen, and intramolecular stabilization, particularly 1,2-carbon migration, takes place to give the product, **5**. The reaction may take place through the intermediates, diazirines, **4**, which have not been isolated. This work provides a new approach for the conversion of aryl amines having no α-methylene to aryl nitriles.



INTRODUCTION

Nitriles are useful organic molecules found in natural products and in synthetic organic chemistry. They are used for the synthesis of a wide variety of biologically active compounds.[1] Conventionally, they are prepared from alcohols,[2] aldehydes,[2a,3] and amines[4] by the nucleophilic displacement of substrates. Other traditional methods include dehydration of amides[5] and aldoximes,[6] conversion of methyl arenes,[7] carboxylic acids,[8] and amines,[4f−j] and the classic Sandmeyer reaction using $NaNO_2$/HCl/CuCN to nitriles. These methods were of low atom economy, produced stoichiometric wastes, required toxic reagents, had limited selectivity, and often required drastic reaction conditions.[9]

For the transformation of primary amines to nitriles, a number of oxidations using stoichiometric metal oxidants such as KI/I_2,[2e] Cu/nitroxyl,[4a] Ir,[4c] nanocatalysts,[10] OsO_4,[11] TiO_2,[12] nickel peroxide,[13] Nb_2O_5,[14] Au−Pd/ZrO_2,[15] RuO_2·xH_2O/TiO_2,[16] and copper reagents in combination with oxygen,[17] silver reagents,[18] cobalt peroxide,[19] lead tetraacetates (LTAs),[20] $NiSO_4$/$K_2S_2O_8$,[21] $RuCl_3$/O_2,[22] $RuCl_3$/$K_2S_2O_8$[23] ruthenium complex/O_2,[24] Ru supported on alumina/O_2,[25] molecular oxygen in the presence of transition-metal catalysts,[26,27] and so forth have been reported. Recently, use of various catalysts for oxidation of primary amines to nitriles is also reported.[28−31]

Aryl nitriles are useful organic compounds used in synthetic organic chemistry and natural product chemistry. Traditional methods for the preparation of aryl nitriles include Rosenmund−von Braun reactions, Sandmayer reactions, as well as dehydration of amides[5] and aldoximes.[6,32] Recently, it was reported that aryl nitriles could be obtained by various catalysts.[10,33,34] However, these methods involved toxic cyanating reagents, such as metal cyanides, harsh conditions, metal catalysts, and so forth. For the first time, we herein report a new approach for the conversion of primary aryl amines having no α-methylene to the corresponding aryl nitriles. Dimethyl carbonimidothioates **2**[35] derived from various primary amines (1) could be converted to the diaziridine derivatives **3** by reacting with hydrazine (Scheme 1). The diaziridine **3** on oxidation with LTA in refluxing xylene extrudes nitrogen, and intramolecular stabilization took place to give product **5**.

RESULTS AND DISCUSSION

The reaction of primary amines (**1**) having no α-methylene with carbon disulfide and methyl iodide in the presence of concentrated sodium hydroxide solution gave the corresponding dimethyl carbonimidothioates (**2a−o**).[36] The intermediate diaziridines, **3a−o**, were obtained by the reaction with hydrazine hydrate in ethanol. The reactivity of the carbonimidothioates (**2**) is due to the facility to displace two molecules of HSMe as leaving groups,[36] when they react with hydrazine to give the corresponding diaziridines (**3a−o**) (Table 1). On refluxing the diaziridines (**3**) with LTA in xylene yielded the corresponding nitriles **5a−o** in 68−93% overall yields (Table 1). The reaction may take place through the intermediate, diazirine **4** which has not been isolated (Scheme 1).[37,38] The position of the substituent on the aromatic ring (ortho- or para-) did not show any significant effect on the product formation (Scheme 2).

The probable mechanism for the oxidation of diaziridines **3** by LTA in refluxing xylene to afford the nitriles **5** is shown in Scheme 3. As it is difficult to intercept the carbenes, it is

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Scheme 1. Conversion of Primary Aryl Amines to the Corresponding Aryl Nitriles via Carbonimidodithioates

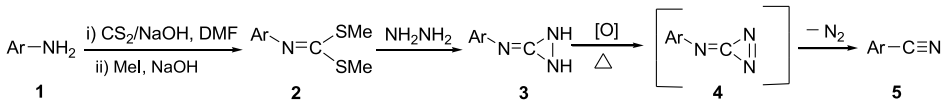
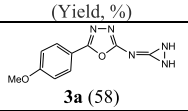
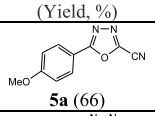
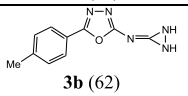
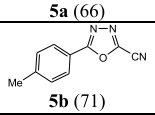
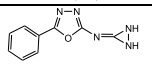
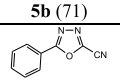
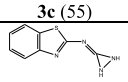
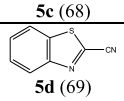
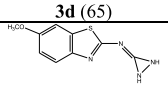
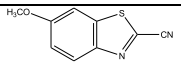
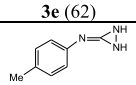
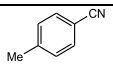
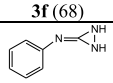
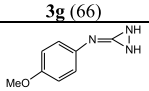
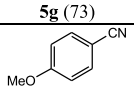
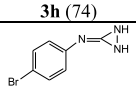
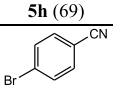
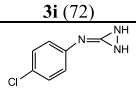
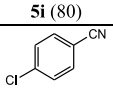
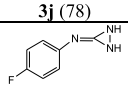
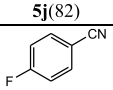
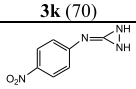
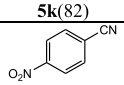
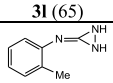
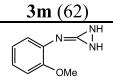
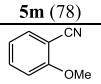
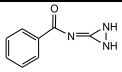
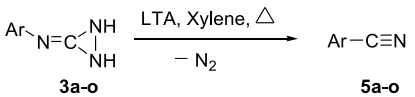


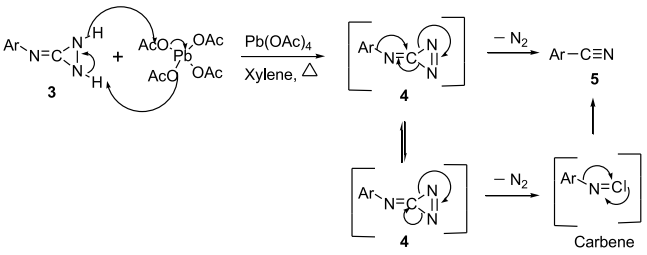
Table 1. Transformation of Diaziridines (3a−o) to Nitriles (5a−o)

Entry	Diaziridines, **3** (Yield, %)	Nitriles, **5** (Yield, %)
1	 **3a** (58)	 **5a** (66)
2	 **3b** (62)	 **5b** (71)
3	 **3c** (55)	 **5c** (68)
4	 **3d** (65)	 **5d** (69)
5	 **3e** (62)	 **5e** (65)
6	 **3f** (68)	 **5f** (78)
7	 **3g** (66)	 **5g** (73)
8	 **3h** (74)	 **5h** (69)
9	 **3i** (72)	 **5i** (80)
10	 **3j** (78)	 **5j**(82)
11	 **3k** (70)	 **5k**(82)
12	 **3l** (65)	 **5l** (77)
13	 **3m** (62)	 **5m** (78)
14	 **3n** (56)	 **5n** (68)
15	 **3o** (75)	 **5o** (93)

Scheme 2. Transformation of Diaziridines (3a−o) to Aryl Nitriles (5a−o)



Scheme 3. Plausible Mechanism for the Conversion of Diaziridines to Nitriles



presumed that intramolecular rearrangement, particularly 1,2-carbon migration, takes place. It was reported that the low yields of bimolecular products obtained upon photolysis of diazirine were due to the inefficiency of carbine production from the precursor.[32,33] It was proposed that an excited state of diazirine suffers rearrangement, without intervention of carbine.

CONCLUSIONS

In conclusion, we herein report an oxidative conversion of a wide range of primary aryl amines (**1**), which have no α-methylene to the corresponding nitriles (**5**). This work provides a new approach to aryl nitriles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03622.

Experimental procedures and spectral data of the compounds (PDF)

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Notes

The authors declare no competing financial interest.

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