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Tetrahedron Letters

Tetrahedron Letters 46 (2005) 5021–5023

An unexpected base-induced rearrangement of tritylamine

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Received 17 March 2005; revised 10 May 2005; accepted 19 May 2005
Available online 9 June 2005

Abstract—An unexpected rearrangement was observed during the treatment of tritylamine with *n*-butyllithium, leading to the formation of an imine.

We have recently reported[1] that primary alkyl halides and tosyl esters of primary alcohols are converted to the corresponding primary amines by the use of triphenylmethylamine as aminating agent (Eqs. 1 and 2).

We have also reported[1] that lithium tritylamide, prepared from tritylamine and *n*-butyllithium in dry tetrahydrofuran at low temperatures, reacts easily with primary alkyl halides to afford the *N*-alkyl tritylamines (Eq. 3), while it does not react with tosyl esters.

$$\mathrm{Ph_3CNH_2 \xrightarrow{RX} Ph_3CNHR + Ph_3CNH_2 \cdot HX} \tag{1}$$

$$\mathrm{Ph_3CNHR \xrightarrow[2.\ HCl/CH_3OH]{1.\ CF_3COOH} RNH_2 \cdot HCl + Ph_3COCH_3} \tag{2}$$

$$\mathrm{Ph_3CNH_2} + n\text{-}\mathrm{BuLi \xrightarrow{THF} Ph_3CNHLi \xrightarrow{RX} Ph_3CNHR + LiX} \tag{3}$$

Reaction (3) was faster than reaction (1), but gave a lower yield, about 60–65%, instead of 80–95% for reaction (1).

During the purification of $\mathrm{Ph_3CNHR}$ (or TrNHR) formed from reaction (3) by column chromatography, we isolated a yellow crystalline substance, mp 113–114 °C, giving a positive ninhydrin test, in a low yield, about 15–35%, depending on the reaction temperature. The absence of alkyl protons as well as the presence of only phenyl protons in its ^{1}H NMR spectrum (at δ 6.75–7.78 ppm) and its IR spectrum (3084, 3066, 3032, 1622 $\mathrm{cm^{-1}}$) indicated it to be an aromatic compound different from tritylamine, possibly a rearranged product of tritylamine. Based on the above observations, we realized that this aromatic compound was the imine of benzophenone with aniline: $\mathrm{Ph_2C{=}NPh}$.[2] We noticed that, when reaction (3) was performed at very low temperatures (−80 to −30 °C), where the nucleophilic substitution of the alkyl halide could not easily take place, the rearranged product was the sole product (Eq. 4), while at higher temperatures (−15 °C to rt) the yield of the desired product, TrNHR, was suitably increased (60–65%) at the expense of the by-product. No other products were detected under these reaction conditions.

$$\mathrm{Ph_3CNH_2 \xrightarrow{\mathit{n}\text{-}BuLi} Ph_3CNHLi \longrightarrow Ph_2C{=}N\text{–}Ph + LiH} \tag{4}$$

In view of these results, we tried to understand this transformation. We realized that the formation of the imine was taking place regardless of the addition, or not, of the alkyl halide to the solution of the tritylamide.

It is well known that the Stieglitz rearrangement[3] of *N*-substituted amines involves the migration of an aryl group from carbon to nitrogen with the subsequent formation of an imine. It is also known that the Stieglitz rearrangement of tritylamine is induced by its reaction with lead tetra-acetate[4] or with nitrobenzene sulfonyl peroxide,[5] resulting in the formation of the corresponding imine (Eq. 5).

$$\mathrm{Ar_3C\text{–}NHY \longrightarrow Ar_2C{=}N\text{–}Ar} \tag{5}$$

$$\mathrm{Y = –N_2,\ –OPCl_4,\ –OCOR,\ –Pb(OAc)_3,\ –OSO_2Ar,\ etc.}$$

A mechanism involving a concerted cationic migration of a phenyl (or aryl) group from carbon to nitrogen was postulated.

Keywords: Tritylamine; Tritylamide; Phenyl rearrangement; Imine formation.

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0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.05.085

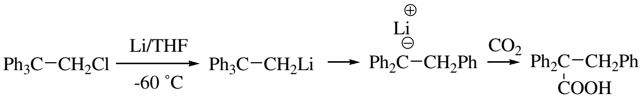
Earlier, Stieglitz had proposed that sodium methoxide promoted aryl rearrangement of *N*-chlorotritylamines[6] with initial loss of a proton from the amine, followed by loss of a chloride anion. The mechanism seems to be a concerted aryl migration from carbon to nitrogen, involving the loss of a chloride anion (Eq. 6).

$$Ar_3C\text{–}NHCl \xrightarrow{CH_3ONa} Ar_2C{=}N\text{–}Ar + Cl^{\ominus} \qquad (6)$$

An anionic rearrangement of tertiary benzylic amines, on treatment with *n*-BuLi was demonstrated by Eisch et al.,[7] where the base-promoted[1,2] intramolecular shift of a phenyl (or aryl) group from nitrogen to a benzylic carbon occurred by way of a bridging anionic aryl intermediate, leading to the formation of benzhydrylamine (Eq. 7).

$$PhCH_2\text{–}NPh_2 \xrightarrow[2.\ H_2O]{1.\ n\text{-BuLi}} Ph_2CH\text{–}NHPh \qquad (7)$$

On the other hand, Grovenstein and Williams[8] discovered that attempted preparation of triphenylethyllithium from the corresponding chloride leads, through a carbanion, to an analogous rearrangement and to the formation of 1,1,2-triphenylethyllithium. Confirmation of these results was provided by a direct carbonation of the lithium compound, with the production of the corresponding propanoic acid (Eq. 8).



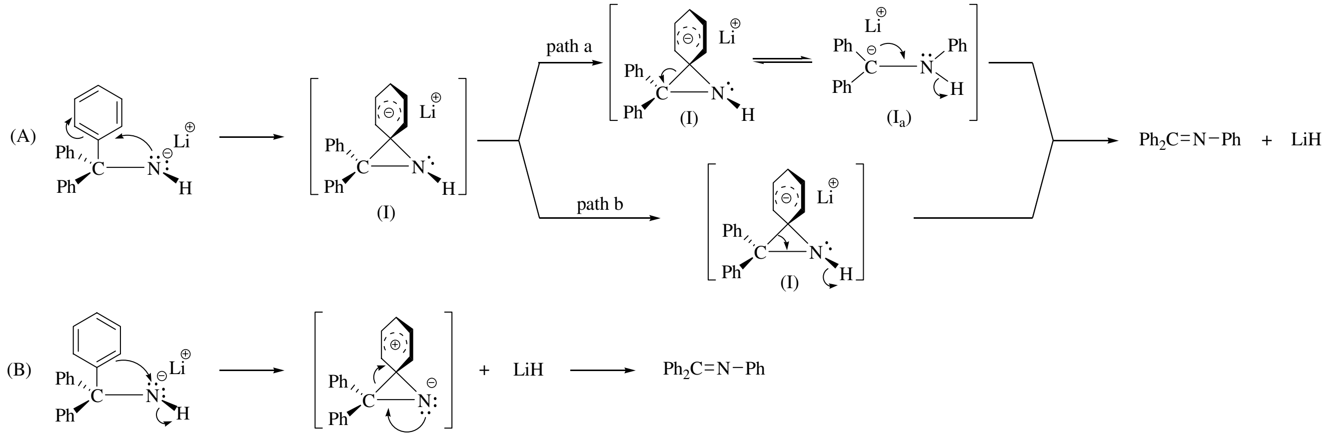
$$Ph_3C\text{−}CH_2Cl \xrightarrow[-60\ ^{\circ}C]{Li/THF} Ph_3C\text{−}CH_2Li \longrightarrow Ph_2\overset{\overset{\overset{\oplus}{Li}}{\ominus}}{C}\text{−}CH_2Ph \xrightarrow{CO_2} Ph_2\underset{COOH}{C}\text{−}CH_2Ph \qquad (8)$$

While the formation of imines in the Stieglitz reactions of triarylmethylamines through a cationic intermediate and the base-induced rearrangement of tertiary benzylic amines, as well as the rearrangement of triphenylethyllithium, through an anionic intermediate, as mentioned above, are well known, we are not aware of any reports on similar reactions of lithium tritylamide involving a phenyl migration from carbon to nitrogen and a hydride loss.

An intramolecular view of the reaction may lead to a mechanism where the migrating group moves either without its electron pair (electrophilic or cationotropic rearrangement) or with its electron pair (nucleophilic or aniotropic rearrangement). Such a view suggests a nucleophilic attack of the nitrogen on the adjacent C-bonded phenyl group and a bridging anionic intermediate (I), which may rearrange to a carbanion (Ia), (Scheme 1, A), or an attack of the phenyl on the nitrogen atom, with the loss of a hydride, and a bridging cationic intermediate (II), (Scheme 1, B). In order to attain the intermediate (I) or (II), in which the migrating phenyl group is partially bonded to both the N and C centers, it is clear that the migrating phenyl group must present its [π] face to the N atom, so that its antibonding [π] orbitals can accept or release, respectively, electron density.

Further, phenyl rearrangement followed by the expulsion of a hydride anion with the aid of the lithium cation (path a) or loss of a hydride and subsequent phenyl rearrangement (path b), would lead to the formation of the imine (Scheme 1). This abstraction may seem to be difficult, however, there is reason to think that tritylamine contains considerable strain relative to the imine. The release of this strain by phenyl rearrangement and hydride abstraction may act as the driving force.

In order to elucidate further the mechanism of this base promoted tritylamine rearrangement, we are exploring its sensitivity to the electronic nature of several aryl substituents and their relative migratory aptitudes, taking into account that the charge development on the migrating aryl group is influenced by the leaving group and the mechanism. We are also attempting readdition reactions.



Scheme 1. Proposed mechanisms for the imine formation: (A) electrophilic phenyl rearrangement; (B) nucleophilic phenyl rearrangement.

References and notes

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