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Reaction of Azides with Dichloroindium Hydride: Very Mild Production of Amines and Pyrrolidin-2-imines through Possible Indium–Aminyl Radicals

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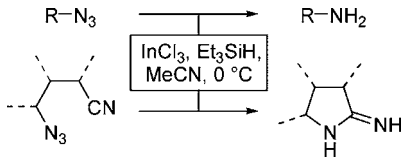
ABSTRACT



Organic azides are easily reduced to the corresponding amines by reaction with dichloroindium hydride under very mild conditions and in a highly chemoselective fashion. γ-Azidonitriles give rise to outstanding five-membered cyclizations affording pyrrolidin-2-imines. A rationalization of the overall experimental data cannot exclude the occurrence of competitive radical and nonradical pathways, but certain results are, however, soundly consistent with the intermediacy of indium-bound nitrogen-centered radicals.

Although radical reactions are by now recognized as very powerful tools for synthetic organic chemists,[1] their applications are sometimes limited by the use of toxic metal reagents or, especially, organotin compounds, which still play a dominating role in radical chemistry. This is the reason novel ways of carrying out radical reactions are under intensive investigation, particularly in the search for efficient purification procedures and sound tin substitutes.[2]

In recent years, organic synthesis has witnessed the use of indium metal, indium halides, and organoindium reagents as benign, *green* alternatives to other metal-based catalysts.[3] Dichloroindium hydride, in particular, besides being applied to alkene reduction[4a,b] and aldol reactions,[4c,d] has been successfully employed as a valid alternative to organostannanes in many radical processes.[5]

Following our interest in the synthetic utility of azides and their radical reactions,[6] we have been prompted to test the reactivity of organic azides with dichloroindium hydride. Indeed, one of the most common radical reactions involving azides is the addition of tin radicals to generate stannylaminyl radicals,[7] which are useful intermediates leading to either reduction of the azide functionality or products derived from cyclization onto suitable radicophilic groups.[6a,c,7d−g,m] Therefore, we aimed at investigating the chance that indium-centered radicals could add to the azido moiety to give rise to indium−aminyl radicals that might replace the tin

(1) For a comprehensive review on synthetic radical chemistry, see: *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001; Vols. 1 and 2.

(2) For recent papers on this subject, see: (a) Baguley, P. A.; Walton, J. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3072. (b) Gagosz, F.; Moutrille, C.; Zard, S. Z. *Org. Lett.* **2002**, *4*, 2707. (c) Kim, S.; Lim, C. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3265. (d) Gagosz, F.; Zard, S. Z. *Org. Lett.* **2002**, *4*, 4345. (e) Kim, S.; Song, H.-J. *Synlett* **2002**, *12*, 2110. (f) Studer, A.; Amrein, S. *Synthesis* **2002**, 835. (g) Ouvry, G.; Zard, S. Z. *Chem. Commun.* **2003**, *6*, 778. (h) Benati, L.; Calestani, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S. *Org. Lett.* **2003**, *5*, 1313. (i) Boivin, J.; Jrad, R.; Juge, S.; Nguyen, V. T. *Org. Lett.* **2003**, *5*, 1645. (j) Schaffner, A.-P.; Renaud, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2658. (k) Osornio, Y. M.; Cruz-Almanza, R.; Jimenez-Montano, V.; Miranda, L. D. *Chem. Commun.* **2003**, 2316. (l) Studer, A.; Amrein, S.; Schleth, F.; Schulte, T.; Walton, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 5726. (m) Studer, A. *Chem. Soc. Rev.* **2004**, *33*, 267. (n) Benati, L.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Strazzari, S.; Zanardi, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 3598. (o) Molawi, K.; Schulte, T.; Siegenthaler, K. O.; Wetter, C.; Studer, A. *Chem. Eur. J.* **2005**, *11*, 2335.

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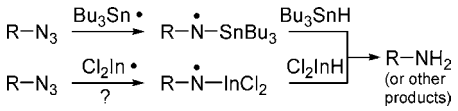
analogues in *green*, synthetically useful transformations (Scheme 1).[8,9] Of course, the first, simplest test of this project

Scheme 1

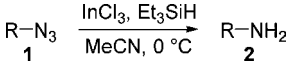


was to verify whether dichloroindium hydride could act as an effective, mild reducing agent capable of converting simple organic azides to the corresponding amines.

Dichloroindium hydride was first generated by transmetalation between indium trichloride and tributyltin hydride,[5a,b] but it can be produced as well by reduction of the halide with $NaBH_4$ in acetonitrile[5c] or DIBAL-H in THF[5d−f] or transmetalation with triethylsilane in acetonitrile[5g] or diphenylsilane in THF.[5h] Although we observed that all methods are suitable to perform reduction of azides, the most convenient one was by far the transmetalation between $InCl_3$ and Et_3SiH, in terms of both product yields and ease of procedure and workup.

Therefore, all of the reactions reported in Table 1 were normally carried out by adding the azide (1 equiv) to an acetonitrile solution of dichloroindium hydride (1.1 equiv), generated in situ by stirring anhydrous indium trichloride (1.1 equiv) and triethylsilane (1.1 equiv) in acetonitrile (4 mL) for 5 min at 0 °C.[5g] The resulting mixture was stirred at 0 °C until disappearance of the starting material. The final crude product was quenched with an acid aqueous solution and extracted with diethyl ether to remove the silane residues. The aqueous phase was neutralized and extracted with diethyl ether to give the amine, which was in a few cases eventually purified by column chromatography.[10,11]

Table 1. Reduction of Azides **1** to Amines **2** with Dichloroindium Hydride (1.1 equiv) in Acetonitrile at 0 °C



entry	compd	R	time (min)	yield[a] (%)
1	**a**	4-MeO-C_6H_4	15	96
2	**b**	4-NC-C_6H_4	15	97
3	**c**	4-Cl-C_6H_4	15	95
4	**d**	4-I-C_6H_4	15	88
5	**e**	4-MeOCO-C_6H_4	30	83
6	**f**	4-O_2N-C_6H_4	15	63
7	**f**	4-O_2N-C_6H_4	15	99[b]
8	**g**	1-naphthyl	90	70
9	**h**	4-MeCO-C_6H_4	overnight	60[b]
10	**i**	$PhSO_2$	210	80
11	**j**	PhCO	180	71
12	**k**	$Ph(CH_2)_3$	15	55[c]
13	**l**	$Ph(CH_2)_2$	15	56[c]
14	**g**	1-naphthyl	60	70[d]
15	**i**	$PhSO_2$	90	82[d]
16	**j**	PhCO	60	75[d]

[a] Yields are for pure amines isolated after workup and/or chromatography. [b] Reaction carried out at −20 °C. [c] Reaction carried out with 2 equiv of hydride. [d] Reaction carried out in the presence of triethylborane (0.2 equiv).

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(10) Under the reaction conditions all azides were totally inert toward both triethylsilane and $InCl_3$ alone. All of the products reported in Table 1 are commercially available compounds, and their identification was based on spectral comparison with authentic samples.

(11) Interestingly, in many cases, foils of indium metal, unequivocally identified by SEM-EDAX analysis, separated from the mixtures during the first aqueous workup, thus allowing recovery of part of the precious reagent. This observation has never been reported in previous $HInCl_2$-mediated reactions. Since separation of In metal is strictly linked to the workup stage, we think it is not tied in with the radical mechanism but it might rather arise from hydrolysis of the intermediate indium amides.

The reactions with aromatic azides **1a**−**f** were usually very fast, and yields were often excellent (Table 1, entries 1−7). However, 1-azidonaphthalene **1g** required 1.5 h for complete consumption and gave amine **2g** in lower yield (70%) (Table 1, entry 8). Reducible groups such as cyano, iodo, and methoxycarbonyl remained totally unaffected (Table 1, entries 2, 4, and 5). The nitro group of **1f** was partially reduced at 0 °C, giving a mixture of **2f** (63%) and *p*-phenylenediamine (30%); the reaction became, however, completely chemoselective at −20 °C, yielding quantitative amounts of **2f** (Table 1, entries 6 and 7). Similar results were obtained with 4-azidoacetophenone **1h**: at 0 °C, this azide gave a quite complicated mixture of **2h**, 1-(4-aminophenyl)-ethanol, and other unidentified products, whereas at −20 °C it reacted overnight to afford, in addition to unreacted azide **1h** (12%), amine **2h** (68%, based on the converted azide) and minor amounts (10%) of the corresponding ethanol (Table 1, entry 9).

Sulfonyl and acyl azides **1i**,**j** gave good yields as well of the corresponding amides, although over longer times (Table 1, entries 10 and 11). Azide **1j** was examined with a particular interest since, should a radical pathway be confirmed (see also below), its reaction would represent a novel, mild entry to amidyl radicals from acyl azides under conditions that totally avoid competitive Curtius rearrangements.[7h]

Aliphatic azides **1k**,**l** were a little less rewarding, but nonetheless synthetically useful: they in fact afforded the corresponding amines in 55−56% yield, although they required 2 equiv of hydride for complete consumption (Table 1, entries 12 and 13).[12]

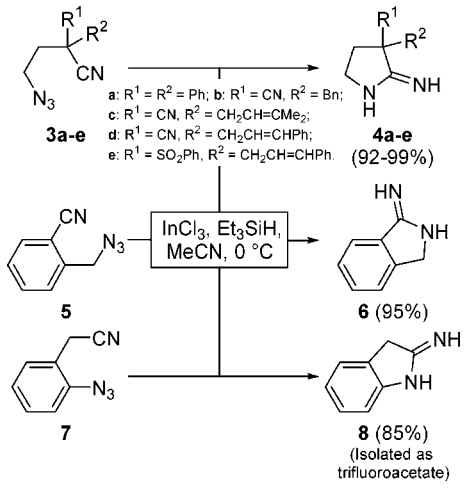
An amazing result was, however, obtained from aliphatic (and aromatic) azides bearing cyano groups in the side chain. Indeed, when azidonitriles **3a**−**e**, **5**, and **7** were allowed to react with dichloroindium hydride under the usual conditions over ca. 1 h, they gave the cyclized pyrrolidin-2-imines **4a**−**e**, isoindole **6**, and indole **8** in practically quantitative yields (Scheme 2).[13] Interestingly, the outcome of these cyclizations was virtually independent of the aliphatic or aromatic nature of the azido and/or cyano moieties (products **6** and **8**). These amidine products are not very common, but recent studies have disclosed that they can act as potent, selective, non-amino acid based inhibitors of human NOS (nitric oxide synthases), and they therefore represent the foundation for potential therapeutic agents.[14] The reported syntheses are rather complicated or involve cyclizations of aminonitriles at high temperatures. To date, no reported procedure makes use of such a very mild environment and entails such a high product yield. It is worth emphasizing that analogous amidines can also be obtained by radical (even nonradical) cyclization of azidonitriles with Bu_3SnH in boiling benzene,[6c,7i] but yields and ease of workup are by no means comparable with the present method.

The full potential of the reaction of azides with dichloroindium hydride and the study of its mechanistic features are currently underway, but as far as the latter are concerned, some points can be already highlighted.

Dichloroindium hydride, although it has been used in a few nonhomolytic reactions[4] and Baba has clearly shown that it seems to possess both radical and ionic characters, depending on substrates and reaction conditions,[5a] is an already well-established radical reagent[5] that is known to generate indium-centered radicals either in the presence of triethylborane[5d−h] or even spontaneously in the absence of any radical initiator.[5a−c] In our case, the use of triethylborane did not affect significantly the fast reactions of aromatic and aliphatic azides, where spontaneous production of the dichloroindium radical could be sufficient to sustain the radical chain reaction. The radical initiator had instead an unambiguous effect on the slower reactions of azides **1g**,**i**,**j**, providing a substantial reduction of the reaction time (Table 1, entries 8, 10, 11, and 14−16). This result clearly substantiates the occurrence of a radical pathway that can be accelerated by the presence of triethylborane.

Moreover, additional support for a radical mechanism came from the reaction of azide **1a** in the presence of TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl, 1 equiv). In this case, we observed a major reaction inhibition since more than 80% of unreacted azide was recovered after many hours at 0 °C.[15] On this basis, a mechanism of formation of the

Scheme 2



(12) In the reactions of aliphatic azides **1k**,**l** the amine product was accompanied by small amounts of another, still unidentified compound having a molecular mass 28 amu higher than that of the corresponding amine. It is worth pointing out that the DIBAL-H/THF method for generating $HInCl_2$, while being strictly comparable to Et_3SiH/MeCN for the aromatic azides, was not applicable to the aliphatic ones. Under these conditions, the azides were completely consumed but we could not isolate any trace of the correponding amines under any sort of workup.

(13) In all of these reactions, no traces of uncyclized amines and/or hydrolysis products (lactams) were ever observed.

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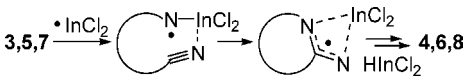
(15) Radical inhibitors (e.g., TEMPO) have been previously used to test the mechanism of some indium hydride-mediated reactions such as halogen abstractions/cyclizations and hydroindations of alkynes. They were shown to be very effective (in sizable amounts) in suppressing the radical reactions, whereas the ionic ones were completely unaffected (ref 5a,d,f).

amines based on the intermediacy of nitrogen-centered radicals (see Scheme 1) would be highly reasonable.

Strictly comparable results were also obtained with azidonitriles. Compound **3a** was totally converted to pyrrolidinimine **4a** in 1 h at 0 °C in the absence of any initiator, but the same reaction required only 10 min in the presence of triethylborane (0.2 equiv). In addition, **3a** was recovered virtually unchanged (98%) after 1 h at 0 °C in the presence of TEMPO (1 equiv).

Although we do not have any certain explanation for the impressive outcome of our azidonitrile reactions, on the basis of the above results we can tentatively suggest that indium aminyl radicals could form and the dichloroindium moiety, with its Lewis acid properties, might chelate the two nitrogen atoms, thus favoring the cyclization process (Scheme 3).[16]

Scheme 3



As additional support, azidonitriles **3c**−**e**, which afford tandem-cyclization bicyclic compounds by reaction with tin radicals,[6c] gave only the monocyclic products **4c**−**e**. This result could be well-interpreted in terms of complexation of the resonance-stabilized aminoiminyl radical arising from ring closure, since this chelated species would not be able to approach the alkene to attain the subsequent cyclization and would thence prefer to abstract hydrogen from the hydride to yield the monocyclic amidine.

We cannot exclude the possibility that the indium−aminyl radical could alternatively abstract a hydrogen atom from the hydride and the resulting indium−amine could give rise to a dichloroindium-catalyzed ring closure.[17] However, in our opinion, very efficient cyclization of amine to amidine is highly unlikely to occur under our very mild experimental conditions (0 °C).

In conclusion, we have shown that dichloroindium hydride can perform the smooth reduction of aromatic, aliphatic, acyl, and sulfonyl azides to the corresponding amines/amides. The reaction does not use any toxic reagent, takes place under very mild conditions, is chemoselective, and does not need any tedious purification procedure. The indium hydride also brings about outstanding five-membered ring closures of γ-azidonitriles to pyrrolidin-2-imines and thence provides a novel, highly appealing entry to these interesting heterocycles. At this stage, it seems possible that indium−aminyl radicals generated by addition of initial dichloroindium radicals to the azido function might intervene as key intermediates, but additional information is clearly required to exclude competing intervention of alternative nonradical pathways.[18] Regardless of interesting mechanistic implications, our azide reactions with dichloroindium hydride revealed a noteworthy synthetic potential that we will attempt to exploit in future studies.

Acknowledgment. We acknowledge financial support from MIUR (2004-2005 funds for "Free Radicals in Oxidation Reactions and in New Synthetic Processes"). We also gratefully thank Dr. Rita Mazzoni for valuable suggestions and Dr. Fabrizio Tarterini for EDAX analysis.

Supporting Information Available: Procedure for the reactions of azides with Cl_2InH; characterization data for the unknown azides, pyrrolidin-2-imines **4a**−**e**, isoindole **6**, and indole **8**; copies of NMR spectra of compounds **1e**,**k**,**l**, **3a**,**e**, **7**, **2a**−**l**, **4a**−**e**, **6**·TFA, and **8**·TFA. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Chelated, four-membered coordinated indium species containing formamidinate ligands have recently been observed: Baker, R. J.; Jones, C.; Junk, P. C.; Kloth, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3852.

(17) Dichloroindium hydride is not expected to be a significantly stronger hydrogen donor than Bu_3SnH (the rate constant for the reaction of aryl radicals with Cl_2InH was determined as 1.0×10^9 M^{-1} s^{-1}, see ref 5c).

(18) In principle, the amines could be also formed by a hydride-transfer process from dichloroindium hydride to the azido group.