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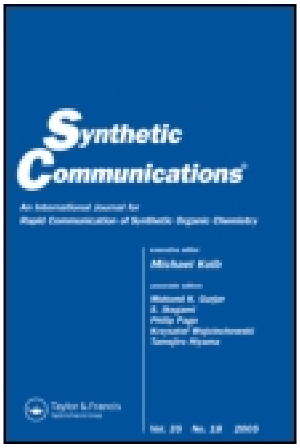

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A SIMPLE AND EFFICIENT METHOD FOR REDUCTIVE ACYLATION OF AZIDES USING ALUMINIUM IODIDE AND ACETIC ANHYDRIDE

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Published online: 16 Aug 2006.

To cite this article: Ghanashyam Bez (2002) A SIMPLE AND EFFICIENT METHOD FOR REDUCTIVE ACYLATION OF AZIDES USING ALUMINIUM IODIDE AND ACETIC ANHYDRIDE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:23, 3625-3628, DOI: 10.1081/SCC-120014976

To link to this article: http://dx.doi.org/10.1081/SCC-120014976

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SYNTHETIC COMMUNICATIONS
Vol. 32, No. 23, pp. 3625–3628, 2002

A SIMPLE AND EFFICIENT METHOD FOR REDUCTIVE ACYLATION OF AZIDES USING ALUMINIUM IODIDE AND ACETIC ANHYDRIDE

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ABSTRACT

A combination of aluminium iodide and acetic anhydride effectively converts a variety of azides to their corresponding acetamides in good to excellent yields without perturbing many active functionalities such as ether, ester, nitro etc.

Key Words: Reductive acylation; Azide; Acetamide; Aluminum iodide; Acetic anhydride

Introduction of an amino group into a carbon backbone, especially in the field of the synthesis of natural products, is usually performed through the substitution of azide anion for halogen like substitutents, followed by reduction of azide functionality. Although numerous reports[1] on the conversion of azides to amines are available in literature, an extensive literature survey could provide only a few methods[2] for direct conversion of azides to acyl amines.

Keeping in view of developing a mild and chemoselective reagent system, an attempt has been made to exploit the utility of relatively less

DOI: 10.1081/SCC-120014976
0039-7911 (Print); 1532-2432 (Online)
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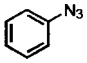
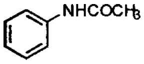
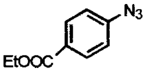
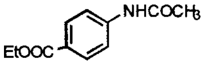
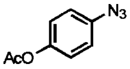
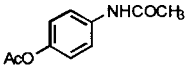
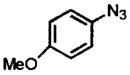
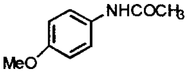
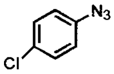
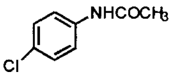
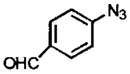
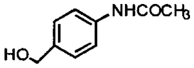
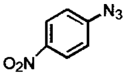
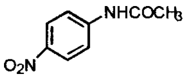
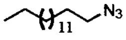
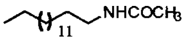
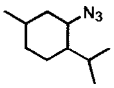
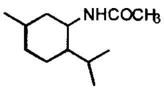
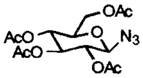
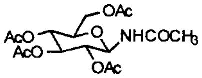
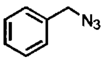
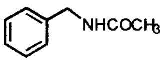
Table 1. Conversion of Azides to Acetamides

Entry	Substrate[a]	Reaction Time (in min)	Product[b]	% Yield[c]
1		20		85
2		30		80
3		30		80
4		20		90
5		30		90
6		30		75
7		25		80
8		75		70
9		75		72
10		60		75
11		90		80
12		30		90

[a] All azides were prepared by following standard literature procedures and characterised by IR, MS and ^{1}H NMR before performing the reactions; [b] All products were characterised by IR, MS and ^{1}H NMR; [c] Yields refer to pure isolated products.

explored and inexpensive reagent, AlI_3 and acetic anhydride for direct conversion of azides to acetamides. A number of observations (Entry 1–12 in Table 1) reveal that when an azide in acetonitrile is refluxed for about half an hour with this reagent system, it undergoes excellent conversion to acetamides. To the best of my knowledge, no such reagent system has so far been reported for the reductive acylation of azide.

$$R-N_3 \xrightarrow[CH_3CN,\ reflux]{AlI_3 - Ac_2O} RNHCOCH_3$$

R = alkyl or aryl

TYPICAL PROCEDURE

A freshly prepared solution of 1.3 g AlI_3 (prepared by refluxing 1.2 g aluminium foil and 17 g iodine in 40 mL dry acetonitrile till color of the solution became pale yellow) in acetonitrile was added to a refluxing solution of phenyl azide (1.3 g, 14.24 mmol) and acetic anhydride (2 mL) in acetonitrile (2 mL) and allowed to reflux until completion while monitoring the reaction by TLC. The temperature of the reaction mixture was allowed to cool down to RT, and diluted with $CHCl_3$ (10 mL), washed successively with aqueous $Na_2S_2O_3$ solution (20 mL) and brine. The organic layer was separated, dried (over Na_2SO_4) and evaporated to get the crude which was purified by column chromatography (EA/hexane = 1.5).

Although AlI_3 is an established ether cleaving agent,[3] the AlI_3–acetic anhydride combination is found to have little effect on ether (Entry 4) and ester (Entry 2) functionalities under this reaction condition. Therefore this method carries the preferences to the existing ones for being mild, selective and cheap. This method provides a straightforward procedure for conversion of azides to their corresponding acetamides in excellent yield avoiding amino reduction and carboxyl activation usually required for two steps conversion.

In conclusion, this reagent system describes one step conversion of azides to acetamides using a easily made, cheap but excellent reagent system.

ACKNOWLEDGMENT

Author is grateful to Vice Chancellor, Dibrugarh University for providing laboratory facilities for this work. Author is also grateful Dr. N. C. Barua, Scientist, RRL, Jorhat, (India) for helpful discussion.

REFERENCES

1. (a) Scrivens, E.F.V.; Turnbull, K. Chem. Rev. **1988**, *88*, 297 and references cited therein; (b) Samano, M.C.; Rabins, M. J. Tetrahedron Lett. **1991**, *32*, 6293; (c) Poopeiko, N.E.; Protica, T.I.; Mikhailopulo, I.A.; Synlett. **1991**, 342; (d) Ranu, B.C.; Sarkar, A. Chakrabarty, R. J. Org. Chem. **1994**, *69*, 4114; (e) Corey, E.J.; Nicolao, K.C.; Balanson, R.D.; Machida, Y. Synthesis **1975**, 590; (f) Kirk, D.N.; Wilson, M.A. J. Chem. Soc. Chem. Commun. **1970**, 64; (g) Konodo, T.; Nakai, H.; Goto, T.; Tetrahedron **1973**, *29*, 1801; (h) Rolla, E. J. Org. Chem. **1982**, *47*, 4327.
2. (a) Rosen, T.; Lico, I.M.; Chu, D.T.W. J. Org. Chem. **1988**, 1580; (b) Garcia, J.; Urpi, F.; Vilarrasa. Tetrahedron Lett. **1984**, *25*, 4841; (c) Kotsuki, H.; Ohishi, T.; Araki, T. Tetrahedron Lett. **1997**, *38*, 2129; (d) Baruah, R.N.; Ind. J. Chem. **2000**, *39B*, 300; (e) Baruah, A.; Bez, G.; Barua, N.C. Synlett **1999**, 553–554.
3. Bhatt, M.V.; Babu, J.M. Tetrahedron Letters **1984**, *25*, 3497.

Received in the Netherlands November 22, 2001