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(Dichloroiodo)benzene and lead(II) thiocyanate as an efficient reagent combination for stereoselective 1,2-dithiocyanation of alkynes

Om Prakash,† Vijay Sharma, Hitesh Batra and Robert M. Moriarty*

Department of Chemistry, University of Illinois at Chicago, IL 60607, USA

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Abstract—An efficient stereoselective 1,2-dithiocyanation of various alkynes has been accomplished by using a reagent combination of (dichloroiodo)benzene and lead(II) thiocyanate in dichloromethane at 0–5°C. © 2001 Elsevier Science Ltd. All rights reserved.

Recently, considerable attention has been directed towards the use of the reagent combination of organoiodine(III) compounds with metal salts[1] and silyl compounds[2] in organic synthesis. In connection with our ongoing studies on the synthetic utility of organoiodine(III) reagents,[3] we have reported that a combination of (dichloroiodo)benzene and lead(II) thiocyanate (system *i*) constitutes a very effective reagent for α-thiocyanation of carbonyl-[1a] and β-dicarbonyl-[4] compounds. Such reactions are thought to proceed via in situ generation of an I(III) species, namely, $PhI(SCN)_2$ (**1**) (Eq. (1)).[1,4] To broaden the synthetic utility of system *i* of Eq. (1) and to gain more insight into such combination reagents, we investigated the reaction of various alkynes with reagent system *i*.

$$PhICl_2 + Pb(SCN)_2 \longrightarrow \underset{\mathbf{1}}{\left[\, PhI(SCN)_2 \,\right]} \qquad (1)$$

As expressed in Scheme 1 and Table 1, the reagent combination of system *i* efficiently converted various alkynes **2a–j** into the corresponding 1,2-dithiocyanted alkenes **3a–j** in a stereoselective manner. The reaction occurred at 0–5°C to give the *E* isomers **3** in moderate to high yields with less than 5% of the corresponding *Z* isomer.

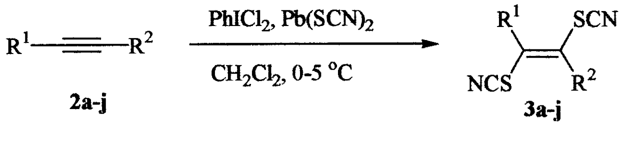
Some noteworthy points on the results accomplished in the present study (Table 1) are:

1. The reaction of 1-phenyl-2-trimethylsilylethyne (**2b**) with the reagent system *i*, which a priori, would be expected to yield phenylethynyl(phenyl)iodonium thiocyanate (**4**),[5,6] in fact undergoes the addition reaction (**2b**→**3b**).

$$\mathbf{2b} \overset{PhICl_2,\ Pb(SCN)_2}{\not\longrightarrow} \underset{\mathbf{4}}{Ph{-}{\equiv}{-}I^{+}Ph\ SCN^{-}}$$

2. The conversion **2i**→**3i** indicates that the hydroxyl group does not interfere in this thiocyanation process.[7]
3. The conversion **2j**→**3j** illustrates a case of 1,2-dithiocyanation of the C≡C bond leaving the conjugated C=C bond intact.
4. The effect of electron withdrawing groups is exemplified by the failure of the addition reaction of dimethyl acetylenedicarboxylate (**2k**).

Although the detailed mechanism of this thiocyanation process is not determined, a plausible pathway involving $PhI(SCN)_2$ (**1**) as reactive species and intermediates of type **5** and **6** is outlined in Scheme 2. Since there is no evidence for the existence of **1**,[1,4] it does not imply



Scheme 1.

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* Corresponding author. Fax: +312 9965242; e-mail: moriarty@uic.com

† On leave of absence from Kurukshetra University, Kurukshetra 136 119, India.

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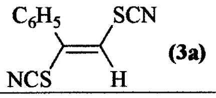
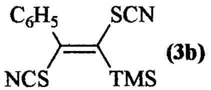
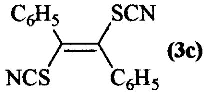
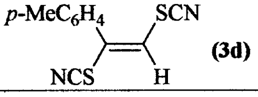
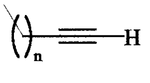
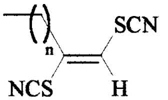
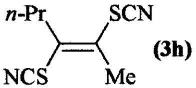
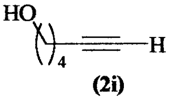
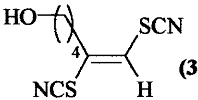
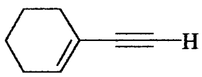
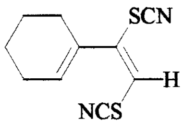
Table 1. Thiocyanation of alkynes using $PhICl_2$–$Pb(SCN)_2/CH_2Cl_2$

Alkyne	Product[a]	Physical state/mp °C (lit. mp °C) of the product	Yield (%)[b]	Mol. Formula
$C_6H_5-\equiv-H$ **(2a)**	 **(3a)**	Colorless needles, 65-66 (67-68)[10,11]	58	[c]
$C_6H_5-\equiv-TMS$ **(2b)**	 **(3b)**	Pale yellow crystalline solid, 49-50	91	$C_{13}H_{14}SiN_2S_2$[c,d]
$C_6H_5-\equiv-C_6H_5$ **(2c)**	 **(3c)**	Colorless plates, 196-198 (197-199)[10]	73	[c]
p-$MeC_6H_4-\equiv-H$ **(2d)**	 **(3d)**	Colorless needles, 94-95	91	$C_{11}H_8N_2S_2$[c,d]
 **(2e)**, n = 3 **(2f)**, n = 5 **(2g)**, n = 7	 **(3e)**, n = 3 **(3f)**, n = 5 **(3g)**, n = 7	Light yellow liquid[10,11] Light yellow liquid Light yellow liquid	84 92 93	[c] $C_{10}H_{14}N_2S_2$[c,d] $C_{12}H_{18}N_2S_2$[c,d]
n-Pr$-\equiv-$Me **(2h)**	 **(3h)**	Light yellow liquid	86	$C_8H_{10}N_2S_2$[c,d]
 **(2i)**	 **(3i)**	Brown liquid	68	$C_8H_{10}N_2OS_2$[c,d]
 **(2j)**	 **(3j)**	Pale yellow liquid	48	$C_{10}H_{10}N_2S_2$[c,d]
$MeO_2C-\equiv-CO_2Me$ **(2k)**	No reaction			

[a] The crude products did not show any significant amount of the Z-isomer (less than 5% as determined by ^1H NMR spectra) and were purified by column chromatography on silica gel and/or recrystallization from alcohol or hexanes.

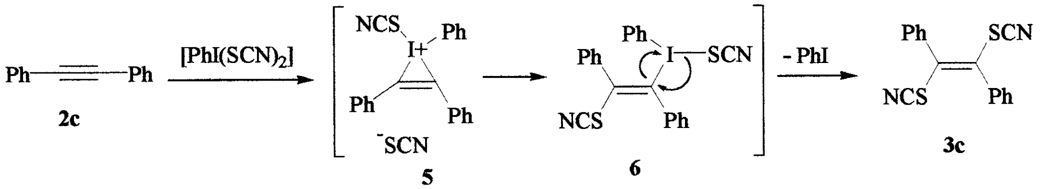
[b] Yields of the isolated pure products with respect to the quantity of alkyne and are not optimized.

[c] Spectral properties (IR and ^1H NMR) were in total agreement with those previously reported or required.

[d] Elemental analyses (C, H, N, S) were satisfactory.

that **1** actually participates as a reactive species in this reaction. The possibility of involvement of other reactive species such as thiocyanogen[1,2a,10,11] or thiocyanogen chloride[8,9] in ionic or free radical mechanism also exists. In a preliminary experiment, the thiocyanation of phenylacetylene (**2a**) in the presence of 2,6-di-t-butyl-4-cresol as a radical inhibitor in the dark under the standard conditions of Scheme 1 gave **3a** in the same yield. More detailed work in order to determine the pathways and reactive species involved in this process is in progress.

Finally, the use of the combination of $PhICl_2$ and $Pb(SCN)_2$ in dichloromethane at 0–5°C provides a convenient and efficient way for the stereoselective 1,2-dithiocyanation of various alkynes. Other reactive functionalities such as double bonds and hydroxyl groups present in the alkynes are not affected.



Scheme 2.

Acknowledgements

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References

1. (a) Prakash, O.; Rani, N.; Sharma, V.; Moriarty, R. M. *Synlett* **1997**, 1255–1256. (b) De Mico, A.; Margarita, R.; Mariani, A.; Piancatelli, G. *J. Chem. Soc., Chem Commun.* **1997**, 1237–1238. (c) Ibid *Tetrahedron Lett.* **1996**, *37*, 1889–1890. (d) Kita, Y.; Okuno, T.; Egi, M.; Iio, K.; Takeda, Y.; Akai, S. *Synlett* **1994**, 1039–1040. (e) Kita, Y.; Takeda, Y.; Okuno, T.; Egi, M.; Iio, K.; Kawagauchi, K.; Akai, S. *Chem. Pharm. Bull.* **1997**, *45*, 1887–1890.
2. (a) Moira, B.; Margarita, R.; Parlanti, L.; Piancatelli, G.; Malia, T. *Tetrahedron Lett.* **1998**, *39*, 3847–3848. (b) Magnus, P.; Lacour, J.; Evans, P. A.; Roe, M. B.; Hulme, C. *J. Am. Chem. Soc.* **1996**, *118*, 3406. (c) Kita, Y.; Takeda, T.; Mihara, S.; Whelan, B. A.; Tohma, H. *J. Org. Chem.* **1995**, *60*, 7144. (d) Zhdankin, V. V.; Tykwinski, R.; Williamson, B. L.; Stang, P. J. *Tetrahedron Lett.* **1991**, *32*, 733–736.
3. (a) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic: New York, 1996. (b) Varvoglis, A. *The Organic Chemistry* of *Polycoordinated Iodine*; VCH: New York, 1992. (c) Moriarty, R. M.; Prakash, O. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic: New York, 1998; Vol. 69, Chapter 1, pp. 1–87. (d) Moriarty, R. M.; Prakash, O. *Org. React.* **1999**, *54*, 273–418. (e) Kitamura, T.; Fujiwara, Y. *Org. Prepn. Proced. Int.* **1997**, *29*, 409–458. (f) Stang, P.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123–1178. (g) Koser, G. F. In *The Chemistry of Halides, Pseudohalides and Azides, Suppl. D2*; Patai, S.; Rappoport, Z., Eds.; Wiley Inc: New York, 1995; Chapter 21, p. 1173. (h) Kita, Y.; Tohma, H.; Yakura, T. *Trends in Organic Chemistry* **1992**, *3*, 113. (i) Ochiai, M. *Rev. Heteroatom Chem.* **1989**, *2*, 92–111.
4. Prakash, O.; Kaur, H.; Batra, H.; Rani, N.; Singh, S. P.; Moriarty, R. M. *J. Org. Chem.*, accepted for publication.
5. Various organoiodine(III) reagents react with terminal alkynes and alkynylsilanes to give similar alkynyl(phenyl)iodonium salts, which subsequently undergo reaction with nucleophiles.[6]
6. For a review of chemistry of alkynyl- and alkenyl(phenyl)iodonium compounds see: Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274–285.
7. Alcohols are known to undergo oxidation with hypervalent iodine reagents under suitable conditions.[3a,3b]
8. Bacon and Guy[9] reported generation of thiocyanogen chloride by the reaction of $PhICl_2$ and $Pb(SCN)_2$.
9. Bacon, R. G. R.; Guy, R. G. *J. Chem. Soc.* **1960**, 318–324.
10. Guy, R. G.; Cousins, D. M.; Hendreson, A. D.; Wilson, C. L. *Tetrahedron* **1980**, *36*, 1839–1842.
11. Barluenga, J.; Martinez-Gallo, J. M.; Najera, C.; Yus, M. *J. Chem. Soc., Perkin Trans 1* **1987**, 1017–1019.