Pergamon

Tetrahedron Letters 39 (1998) 3847–3848

TETRAHEDRON
LETTERS

Hypervalent Iodine Chemistry: Novel and Direct Thiocyanation of Alkenes Using [Bis(acetoxy)iodo]benzene/Trimethylsilyl Isothiocyanate Reagent Combination. Synthesis of 1,2-Dithiocyanates.

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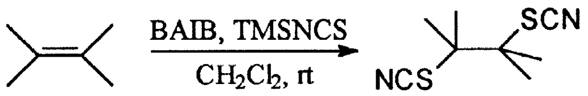
Received 5 February 1998; revised 16 March 1998; accepted 20 March 1998

Abstract: Novel and direct thiocyanation of alkenes using [bis(acetoxy)iodo]benzene/trimethylsilyl isothiocyanate reagent combination has been developed.

In the recent past years, the combination of the hypervalent I(III) reagents with trimethylsilyl derivatives of inorganic anions was exploited to develop new synthetic methods in organic chemistry.[1] The insight into the mechanism pointed to the formation of new hypervalent reagents, such as [bis(cyano)iodo]benzene by reaction of $(PhIO)_n$ with trimethylsilyl cyanide, which is a crystalline solid, stable at room temperature under nitrogen for several weeks.[1a] Other derivatives, usually prepared *in situ,* have been demonstrated to perform interesting reactions by a simple and efficient methodology.[2]

Continuing our studies on the chemistry of iodine (III) reagents,[3] we describe here the reactivity of [bis(acetoxy)iodo]benzene (BAIB) with trimethylsilyl isothiocyanate (TMSNCS), as reagent combination for a facile synthesis of 1,2-dithiocyanates from alkenes.(Scheme 1, Table 1).



Scheme 1

Since the manipulation of the thiocyanate group gives an easy access to various sulfur functional groups[4] and sulfur containing heterocycles,[5] the direct thiocyanation of alkenes is a valuable transformation.[6]

Treatment of primary alkenes with BAIB and TMSNCS in CH_2Cl_2 leads to the formation of 1,2-dithiocyanates as a single product in high yields (Table 1, Entries 1,3). In cyclic alkenes (Table 1, Entries 4, 5) the addition has been found to proceed in stereospecific manner, providing only the *trans* diastereoisomer, in agreement with previous reports of thiocyanogen addition to olefinic double bonds.[7]

Electron rich olefins, such as dihydropyran, provided a nearly 1:1 *cis/trans* mixture and this reactivity may be ascribed to the high stability of the cationic intermediate formed by the initial electrophilic attack.

Styrene derivatives, due a competing polymerisation process, gave lower yields of the corresponding 1,2-dithiocyanates. Electron poor alkenes were recovered unreacted from the reaction mixture.

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PII: S0040-4039(98)00629-7

Table 1. Thiocyanation of alkenes with BAIB/TMSNCS.[a]

Entry	Substrate	Yield (%)
1	1-octene	80
2	(*E*)-4-octene	80[b]
3	1-vinylcyclohexene	70
4	cyclohexene	65[c]
5	1-methylcyclohexene	55[c]
6	dihydropyran	70 (*cis*:*trans* 1:1)
7	styrene	25[d]
8	*p*-methoxystyrene	20[e]

a. Typical experimental procedure: the alkene (1 mmol) was added to a solution of BAIB (1.5 mmol) and TMSNCS (3 mmol) in CH_2Cl_2 (2 ml); the resulting reaction mixture was stirred at room temperature for 12-24 hours, after which the reaction was diluted with Et_2O and then treated with $Na_2S_2O_3$ and $NaHCO_3$. The usual workup afforded pure products.
b. 3 :1 diastereomeric mixture.
c. Only the *trans* adduct was obtained.
d. Additional 10% of $PhCH(OAc)CH_2SCN$ and 15% of $PhCH_2CH(SCN)_2$ were isolated.
e. 40% of p-$MeOC_6H_5CH_2CH(SCN)_2$ was isolated.

Treatment of BAIB with trimethylsilyl isothiocyanate is supposed to lead to a ligand exchange around the hypervalent iodine (III) atom (Eq 1). The formation of [bis(thiocyano)iodo]benzene **A** by reaction between [bis(chloro)iodo]benzene and lead thiocyanate has been described.[8] However, the compound was reported to be unstable. Our experiments were designed to use the thermodynamically favoured silicon-oxygen bond as driving force toward the formation of the hypervalent reagent, such as **A** (Eq. 1).

$$PhI(OAc)_2 + 2TMSNCS \xrightarrow[rt]{CH_2Cl_2} \left[\underset{\mathbf{A}}{PhI(SCN)_2}\right] \longrightarrow (SCN)_2 + PhI + 2TMSOAC \quad (Eq\ 1)$$

A series of NMR spectra were carried out to determine the nature of the thiocyanating species. NMR experiments show that BAIB and TMSNCS undergo a fast reaction, giving a pale yellow solution, stable at room temperature. ^{13}C-NMR spectra of the solution pointed out a clean and rapid (*ca.* 5 min) formation of iodobenzene, trimethilsilyl acetate and thiocyanogen (107.6 δ, SCN). Presumably, thiocyanogen arises from the dimerization of thiocyano radicals ($SCN^{\bullet}$), formed by a very fast homolytic dissociation of the weak I-S bond of A.[3c] In conclusion, we have developed a general method for the synthesis of 1,2-dithiocyanates from alkenes. Our studies broaden the utility of the hypervalent iodine (III) reagents, opening new routes to synthetic applications in organic chemistry. We are currently investigating other aspects of this reaction and its mechanism.

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