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Radical Additions to Olefins in the Presence of Iodobenzenediacetate: an Easy Route to Alkyl Dithiocyanates

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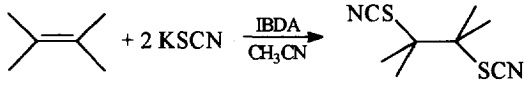
***Abstract**: We describe a new application of iodobenzenediacetate (IBDA), which is able to oxidize thiocyanate anion to the corresponding radical. Subsequent addition to nucleophilic olefins leads to dithiocyanate derivatives. The radical addition to olefins is more effective when performing the thiocyanation reaction in presence of $Mg(ClO_4)_2$ or TEMPO.*

Radical generation in the presence of a redox system is a well known procedure in organic chemistry. The availability of a great number of redox systems makes the radical process of high synthetic value.[1] The oxidation of inorganic anions, such as azide, to the corresponding radicals has been described to be performed by several oxidants (H_2O_2, $S_2O_8^{2-}$, MnO_4^-,$Ce^{(IV)}$, R_2NCl).[2] Recently, hypervalent iodine reagents have also proven to be useful for the generation of azido radical $N_3^{\cdot}$, which can be easily trapped by olefins.[3]

In connection with a program directed to broaden the applications in organic synthesis of hypervalent iodine reagents,[4] we have found that iodobenzenediacetate (IBDA) is able to oxidize thiocyanate anion to the corresponding radical, which then adds to olefins giving dithiocyanate derivatives (Scheme 1).



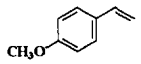
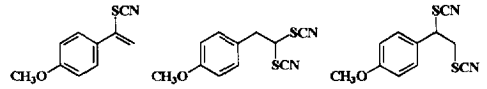
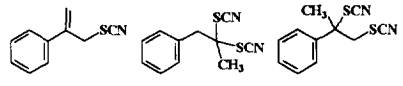
Scheme 1

To our knowledge, our report highlights an original and mild source of an electrophilic sulfur-centered radical, never described before. It is worth noting that thiols react exothermically with IBDA to afford disulfides in high yields.[5]

In a typical procedure 1 mmol of olefin, dissolved in 5 ml of CH_3CN, was treated with 2 mmol of KSCN and 2 mmol of IBDA at room temperature for 12 h; the reaction mixture was then diluted with Et_2O and treated with an aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$ and extracted 3 times with Et_2O. The two layers

were separated and the organic phase was washed with brine and dried over anhydrous Na_2SO_4. Evaporation under reduced pressure gave compounds as crude oils; column chromatography on SiO_2 (petroleum ether/Et_2O) furnished pure dithiocyanate derivatives (Table 1).The isomeric isothiocyanate products were never detected in the reaction mixture.

Table 1: Thiocyanation of olefins with IBDA/KSCN

Entry	Compound	Product	Yield[a]
1	 **1**	 **1a**	60% (cis:trans) 1:1
2	 **2**	 **2a**	60% (cis:trans) 1:1
3	 **3**	 **3a** **3b** **3c**	**3a**:15% **3b**:30% **3c**: 15%
4	 **4**	 **4a** **4b** **4c**	**4a**:10% **4b**:25% **4c**:20%

a: The reported yields refer to isolated, chromatographically pure compounds. All the structures have been confirmed by IR, ^{1}H-NMR,^{13}C-NMR and GC-MS analysis

The reaction has proven to be successful with dihydrofuran **1**, dihydropyran **2** and other electron rich substrates (Table1). 1-Octene, cyclohexene, styrene and electron poor olefins, such as *p*-nitrostyrene, *p*-bromostyrene, and *p*-vinylmethylbenzoate, did not furnish the corresponding dithiocyano-derivatives.

These results clearly show that the involved radical species has an electrophilic character. The above observed substituent effects in the reaction of styrene derivatives points out that the electron density on the double bond strictly influences the reactivity of the olefins. These effects can be explained in terms of orbital interactions between the SOMO of the radical and the HOMO of the olefins.[6,7]

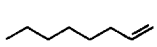
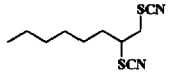
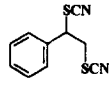
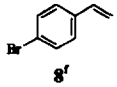
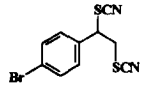
Electron rich aromatic olefins, such as **3** and **4**, besides the radical thiocyanation, can undergo a competing electrophilic addition-elimination process of the hypervalent iodine[8] with the nucleophilic participation of the thiocyanate anion, leading to the formation of side-products, such as **3a** and **4a**. In addition, the transposition products **3b** and **4b** were recovered from the reaction medium. These compounds could be derived from both ionic and radical mechanisms (Entries 3 and 4, Table1).

In order to have an effective method for the synthesis of alkyl dithiocyanates, we have studied the effect of adding inorganic salts [$Mg(ClO_4)_2$], or catalysts [TEMPO (2,2,6,6-tetramethyl-piperidine-*N*-oxyl, a stable radical)], to the reaction medium. Both magnesium perchlorate[4,9] and TEMPO[10] have recently been reported to promote reactions involving radical species generated by hypervalent iodine reagents. It was found that both the reagent combinations can be used to modify the outcome of the reaction. The competing ionic pathway was

completely suppressed, while the thiocyano-radical addition process takes place smoothly to give good yields of the dithiocyanate compounds (Entry 3, Table 1 and 2,). Moreover, the above unreactive olefins were able to furnish the corresponding derivatives in the presence of either magnesium perchlorate or TEMPO (Entries 1, 2 and 4, Table 2). Electron poor olefins, such as **8**, gave the dithiocyanate derivative **8a**, albeit in a moderate yield (Entry 5, Table 2). The use of TEMPO in this sense is very interesting and original. The only previous report concerns a trapping of the azido radical that occurs when cyclohexene is treated with the $PhIO/TMSN_3$/TEMPO reagent system to yield the corresponding bis-azide.[10]

In conclusion, we have collected evidences that both IBDA/KSCN/$Mg(ClO_4)_2$ and IBDA/KSCN/TEMPO react with alkenes in a radical addition process to give dithiocyanate derivatives.[11,12] However, the overall mechanism of the reaction is under investigation.

Table 2: Thiocyanation of olefins (1 mmol) with IBDA/KSCN (2 mmol) and $Mg(ClO_4)_2$ or TEMPO in CH_3CN.

Entry	Compound	Product	Yield[a]	Reaction time (h)
1	 **5**[b]	 **5a**	60%	10
2	 **6**[c]	 **6a**	50% (cis:trans) 2:1	5
3	**3**[d]	**3b** **3c**	**3b**:20% **3c**:60%	15
4	 **7**[e]	 **7a**	50%	12
5	 **8**[f]	 **8a**	40%	15

a: The reported yields refer to isolated, chromatographically pure compounds. All the structures have been confirmed by IR, ^{1}H-NMR, ^{13}C-NMR and GC-MS analysis
b: $Mg(ClO_4)_2$ (3mmol). **c**: TEMPO (0.1mmol). **d**: TEMPO (0.3mmol). **e**: $Mg(ClO_4)_2$ (2mmol). **f**: $Mg(ClO_4)_2$ (1mmol).

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10. Magnus, P.; Roe, M. B. and Hulme C. *J. Chem. Soc., Chem. Commun.* **1995**, 265.
11. Representative ^{13}C NMR spectra ($CDCl_3$), δ. **3b**: 41.1, 55.3, 60.6, 110.8 (SCN), 114.8, 127.6, 128.1, 160.7;**3c**: 38.3, 51.3, 55.3, 110.0 (SCN), 115.2, 125.8, 129.1, 161.3. **4b**: 28.5, 47.7, 66.8, 11.4 (SCN), 125.0, 129.1, 129.4, 140.0. **5a**: 13.9, 22.4, 26.8, 28.4, 31.4, 33.2, 39.0, 49.9, 109.1 (SCN), 110.7 (SCN). **6a**: *cis* 25.4, 34.7, 51.7, 109.3 (SCN); *trans* 23.5, 25.3, 32.5, 34.3, 52.3, 59.9, 109.5 (SCN), 116.3 (SCN). **8a**: 38.1, 51.1, 109.8 (SCN), 110.4 (SCN), 125.1, 129.6, 133.5, 133.8.
12. Representative IR spectra ($CDCl_3$), cm^{-1}. **2a**: *cis trans* 2000 (SCN, broad peak). **3b**: 2165, 2050 (SCN, broad peak). **3c**: 2170 (SCN, sharp peak). **4a**: 2155 (SCN, sharp peak). **4b**: 2035 (SCN, broad peak). **5a**: 2175 (SCN, broad peak). **6a**: *cis trans* 2170 (SCN, sharp peak). **7a**: 2165 (SCN, sharp peak).

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