α-Thiocyanation of Carbonyl and β-Dicarbonyl Compounds Using (Dichloroiodo)benzene−Lead(II) Thiocyanate

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Received October 23, 2000

The combination reagent (dichloroiodo)benzene and lead(II) thiocyanate in dichloromethane effects oxidation of various enol silyl ethers, ketene silyl acetals, and β-dicarbonyl compounds, thereby providing an efficient and convenient method for α-thiocyanation of carbonyl and β-dicarbonyl compounds.

Introduction

Thiocyanates have gained considerable importance in various areas of organosulfur chemistry.[1] For example, (i) the thiocyanato group occurs as an important functionality in certain anticancer natural products formed by deglycosylation of glucosinolates derived from cruciferous vegetables,[2,3] and (ii) α-thiocyanato carbonyl compounds constitute a preferred synthetic route for several types of thiazoles,[4] some of which are associated with herbicidal and other biological activity.[5]

Thiocyanation is usually carried out via a nucleophilic reaction using the thiocyanate anion. Thus, α-thiocyanato carbonyl compounds are prepared from α-halocarbonyl compounds[6] or α-tosyloxycarbonyls[7] or via nucleophilic epoxide ring opening using the thiocyanate anion.[8] However, this displacement frequently requires rather severe reaction conditions. Moreover, yields are typically very low as a result of the poor nucleophilicity of the SCN anion. Other methods for thiocyanation involve the use of electrophilic or radical reactions using thiocyanogen and thiocyanogen chloride.[9] α-Thiocyanation of enolizable carbonyl compounds can also be effected using thiocyanatotrimethylsilane and SO_2Cl_2,[10] which may be considered to be an electrophilic method.

Although some stable 2-thiocyanatoindan-1,3-diones[11] have been prepared and characterized, the α-thiocyanation of β-dicarbonyl compounds is not well established. Guy et al.[12] have reported that attempts to prepare 3-thiocyanatopentan-2,4-diones lead to a complex mixture of products. These products have been identified as thiazoles, formed as a result of cyclodimerization of enolizable α-thiocyanato-β-dicarbonyl compounds.

In connection with our ongoing program directed toward the development of the use of organoiodine(III) reagents in organic synthesis,[13,14] we briefly reported that reaction of enol silyl ethers and ketene silyl acetals using a combination of (dichloroiodo)benzene and lead(II) thiocyanate in dichloromethane (system i)[15] provides a new and efficient method for α-thiocyanation of ketones and esters. We have now examined the extension of this reaction to thiocyanation of β-dicarbonyl compounds.

Results and Discussion

The use of organohypervalent iodine reagents for the α-functionalization of carbonyl and β-dicarbonyl compounds has been extensively investigated and reviewed.[16] A general feature of these reactions is an electrophilic attack of the hypervalent iodine reagent PhI(X)Y at the α-carbon atom of a carbonyl group of the substrate **1** (or **1a)** to yield a tricoordinated iodine intermediate **2**. This

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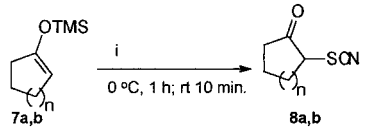
10.1021/jo001504i CCC: $20.00
Published on Web 02/24/2001

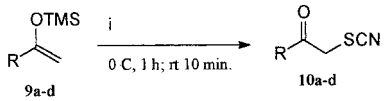
Scheme 1



a, n = 1; b, n = 2

i = $PhICl_2$, $Pb(SCN)_2/CH_2Cl_2$

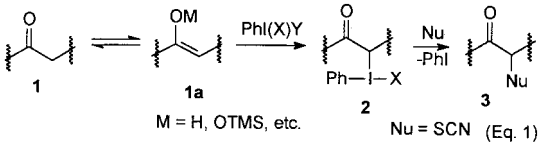
Scheme 2



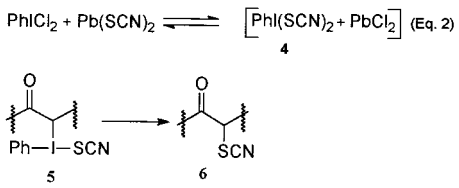
a, R = Ph; b, R = 2-furyl
c, R = 2-thienyl; d, R = 2-pyridyl

i = $PhICl_2$, $Pb(SCN)_2/CH_2Cl_2$

intermediate reacts further with an external or internal nucleophile to produce the α-functionalized derivatives **3** and iodobenzene (eq 1).

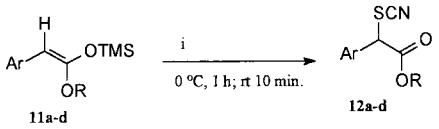


On the basis of these observations, coupled with the presumption that the reagent combination of (dichloroiodo)benzene and lead(II) thiocyanate generates in situ the hypervalent iodine compound [bis(thiocyanato)iodo]benzene (**4**) (eq 2),[17] it was anticipated that **4** might react with carbonyl compounds to give α-thiocyanated derivatives **6** via I(III) intermediate **5**.



α-Thiocyanation of Carbonyl Compounds. To determine the feasibility of the above synthetic strategy, we first attempted reaction of acetophenones with system i. The reaction, however, did not take place with several acetophenones, including *p*-nitroacetophenone. Aliphatic ketones, such as cyclopentanone and cyclohexanone, were also proved to be inert to this system. These observations led us to use more nucleophilic carbonyl derivatives such as silyl enol ethers, which have already been employed effectively in the hypervalent iodine-mediated functionalization of ketones.[18−21] This strategy, indeed, gave expected α-thiocyanation in the cases of enol silyl ethers derived from aliphatic (**7a,b → 8a,b**; Scheme 1), aromatic (**9a → 10a**), and heteroaromatic- (**9b−d → 10b−d**) ketones (Scheme 2) using $PhICl_2-Pb(SCN)_2/CH_2Cl_2$ at 0 °C (system i).

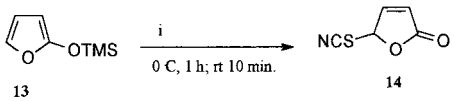
Scheme 3



a, Ar = C_6H_5, R = Me; b, Ar = *p*-ClC_6H_4, R = Me;
c, Ar = *p*-MeC_6H_4, R = Et; d, Ar = *p*-$OMeC_6H_4$, R = Me

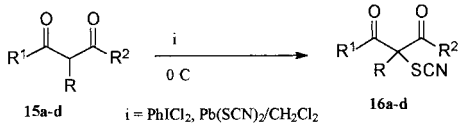
i = $PhICl_2$, $Pb(SCN)_2/CH_2Cl_2$

Scheme 4



i = $PhICl_2$, $Pb(SCN)_2/CH_2Cl_2$

Scheme 5



i = $PhICl_2$, $Pb(SCN)_2/CH_2Cl_2$

Compound (15, 16)	R^1	R^2	R
a	Me	Me	H
b	Me	Me	Me
c	Ph	Me	H
d	Ph	Ph	H

To extend the scope of this reaction, ketene silyl acetals derived from several 2-arylethanoates (**11a−d**) were reacted using system i under similar conditions. The reaction afforded the corresponding α-thiocyanated esters (**12a−d**) in good yields (Scheme 3). This method, however, was not successful for the α-thiocyanation of ketene silyl acetals derived from lactones such as 2-oxotetrahydropyran.

Interestingly, when applied to 2-trimethylsilyloxyfuran (**13**), this reaction led to γ-thiocyanation as shown in Scheme 4 (**13 → 14**).

α-Thiocyanation of β-Dicarbonyl Compounds. The central carbon of β-dicarbonyl compounds is generally more nucleophilic than in the α-carbon of monocarbonyl compounds, and therefore we investigated the reaction of various β-dicarbonyl compounds with system i. First, we carried out the thiocyanation of β-diketones, which lack a substituent in the α position. Thus, acetylacetone (**15a**), upon treatment with system i, afforded 3-thiocyanatopentan-2,4-dione (**16a**) as long light yellow crystalline needles, mp 79−80 °C (lit.[22] mp 78−81 °C) in 85% yield (Scheme 5). The ^1H NMR and IR spectral data were in agreement with the reported values.[12] Product (**16a**) decomposed readily at room temperature to a greenish-black semisolid and the β-dicarbonyl thiocyanate, in general, is relatively unstable (see below).

Under the same conditions, α-thiocyanation of benzoylacetone (**15c**), dibenzoylmethane (**15d**), and indan-1,3-dione (**18a**) proceeded to completion (as indicated by TLC, IR, and ^1H NMR of the crude products containing quantitative amount of iodobenzene as byproduct). However, it was not possible to isolate pure products in the cases of **16c** and **19a** (Scheme 7), because of their ready

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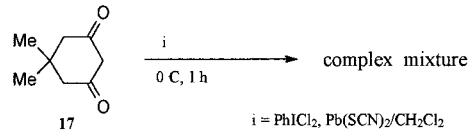
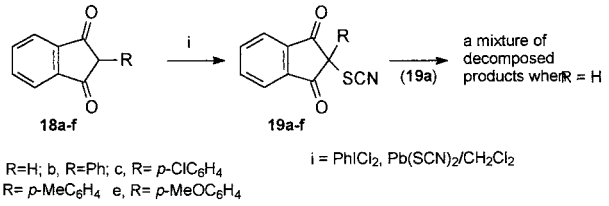
Scheme 6

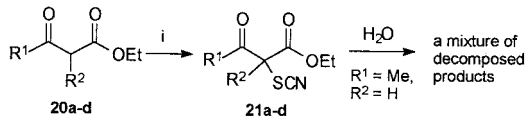


Scheme 7



a, R=H; b, R=Ph; c, R= *p*-ClC$_6$H$_4$
d, R= *p*-MeC$_6$H$_4$ e, R= *p*-MeOC$_6$H$_4$

Scheme 8



a, R^1 = Me, R^2 = H; b, R^1 = R^2 = Me;
c, R^1 = OEt, R^2 = H; d, R^1, R^2 = -(CH$_2$)$_3$-

i = PhICl$_2$, Pb(SCN)$_2$/CH$_2$Cl$_2$

decomposition into mixture of several products. Interestingly, the product **16d**, isolated as a pale yellow solid, mp 66−67 °C, was found to be fairly stable (Scheme 5). On the other hand the reaction of dimedone (**17**) with system i was more problematic as the reaction quickly turned to a yellow-orange suspension giving the indication of formation of a complex mixture (Scheme 6).

These observations clearly indicated that isolation and purification of the α-thiocyanato-*β*-diketones bearing no substituents at their α-position is difficult because of the occurrence of further reactions of these enolizable α-thiocyanato-*β*-diketones. The literature reports the use of other methods for obtaining α-thiocyanato compounds, and similar problems have been encountered.[12,23−25]

This led us to investigate α-thiocyanation of α-substituted-*β*-dicarbonyl compounds. Accordingly, we carried out thiocyanation of α-methyl acetylacetone **15b** and 2-arylindan-1,3-diones (**18b**−**f**), which underwent smooth conversion to the corresponding α-thiocyanato derivatives **16b** (Scheme 5) and **19b**−**f** (Scheme 7). These, being nonenolizable, were quite stable, crystalline solids.

Next, we examined the α-thiocyanation of *β*-ketoesters. The first example of this class that we attempted was the thiocyanation of ethyl acetoacetate (**20a**). Monitoring the reaction of **20a** with $PhICl_2-Pb(SCN)_2$ in $CDCl_3$ under argon atmosphere and anhydrous conditions at 0 °C gave indication of exclusive formation of ethyl α-thiocyanatoacetoacetate (**21a**). Attempts to isolate the product **21a** after evaporation of the solvent under vacuum resulted in a viscous orange oily mixture of several compounds (Scheme 8). Keeping in view that such a behavior of **21a** and the structures of its decomposition products are known in the literature,[12] we made no further efforts to purify this mixture by crystallization or column chromatography.

The reagent system i readily reacted with diethyl malonate (**20c**) to give the stable thiocyanato derivative **21c**. As expected, thiocyanation of α-substituted-*β*-ketoesters such as ethyl α-methylacetoacetate (**20b**) and methyl 2-oxocyclopentanecarboxylate (**20d**) with system i gave stable α-thiocyanato products **21b** and **21d** (Scheme 8), respectively. It is to be noted that initial experiments on the reaction of **21d**[26] with system i gave a significant amount of an orange-colored solid mass, characterized as polymeric thiocyanogen[27,28] on the basis of elemental analysis and insolubility in most of the organic solvents. So, it became essential to take extra precautions such as maintaining the temperature at 0−5 °C in dark conditions till the reaction was complete (4−5 h)

The mechanistic pathway for this thiocyanation process is probably analogous to that of previously reported α-tosyloxylation of carbonyl compounds using Koser's reagent (PhI(OH)OTs, HTIB).[20,29] A ligand exchange reaction between $PhICl_2$ and $Pb(SCN)_2$ probably generates in situ the hypervalent compound [(dithiocyanato)-iodo]benzene (**4**), which reacts analogously to HTIB with silyl enol ethers of mono carbonyl compounds or the enolic form of dicarbonyl compound of general formula **1a** to give I(III) intermediate **5**. Intermediate **5** finally leads to the α-thiocyanato derivative **6** by intramolecular legand transfer of a thiocyanato anion (SCN^-) and reductive elimination of iodobenzene.

Since there is no evidence for the existence of I(III) species **4**, it does not imply that **4** is actually involved in this process.[30] It is possible that the in situ generated I(III) species (**4** or PhI(Cl)SCN) is converted to thiocyanogen[26−28] or thiocyanogen chloride,[31−33] which then participates in the thiocyanation process as a reactive species. There also exists the possibility of involvement of thiocyanato radical generated by homolytic fission of weak S−I bond of **4** as suggested by Bruno et al.[34] in the thiocyanation of alkenes with a combination of iodobenzene diacetate and trimethylsilyl isothiocyanate. More work is required to determine the actual reactive species of this thiocyanation process.

Conclusion

It may be concluded that the reagent combination $PhICl_2-Pb(SCN)_2$ in dry CH_2Cl_2 (system i) is very effective for α-thiocyanation of silyl enol ethers, silyl ketene acetals, and *β*-dicarbonyl compounds. Experimentation involved in the procedure is simple, giving products in good yield in most cases. The primary products of α-thiocyanation of *β*-diketones containing no substituent

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(25) Kaufmann, H. P.; Liepe, J. *Arch. Pharm. (Weinheim, Ger.)* **1923**, *33*, 139.
(26) This polymeric compound was formed in many cases in variable amounts, especially when the substrate was less reactive.
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(30) We were unable to isolate and characterize the in situ generated reactive species, presumably $PhI(SCN)_2$. The ^1H NMR, ^{13}C NMR, and IR of the filtrate obtained from the reaction of $PhICl_2$ and $Pb(SCN)_2$ in $CDCl_3$ under argon in dark at 0 °C gave indication of iodobenzene and thiocyanogen, probably resulted by the decomposition of I(III) compound.
(31) Bacon and Guy,[32] and Back et al.[33] used a combination of $PhICl_2$ and $Pb(SCN)_2$ as a source of thiocyanogen chloride for thiocyanation.
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(34) Bruno, M.; Margarita, R.; Parlanti, L.; Piancatelli, G.; Trifoni, M. *Tetrahedron Lett.* **1998**, *39*, 3848.

at the α-position are mostly unstable owing to their further cyclization reactions.

Experimental Section

General. Melting points were taken in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a Brucker 300 MHz instrument using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 1800 IR spectrophotometer. Mass spectra were recorded on Kratos MS-50 mass spectrometer. Most of the chemicals were obtained from commercial suppliers. Enol silyl ethers **9a**−**d**[35] and ketene silyl acetals **11a**−**d**,[36] α-substituted 1,3-indandiones (**22a**−**e**),[37,38] and (dichloroiodo)benzene[39] were prepared according to the literature methods. The structures of all new thiocyanato derivatives were confirmed by their spectral data and elemental analyses, whereas the products known in the literature were characterized by the comparison of melting points and spectral (IR and ^{1}H NMR) data. The IR spectra of all of the products showed a characteristic sharp SCN absorption band at ~2160 cm^{-1}. A downfield shift of the α-proton with respect to the substrate was observed in the ^{1}H NMR spectra of the products. This property was used for monitoring the progress of the reaction and determining the yields of the products in the cases of enolizable thiocayanato *β*-dicarbonyl compounds, which were unstable. In most such cases, the reactions were performed in dry $CDCl_3$, and the yields were determined on the basis of ^{1}H NMR data of the filtrate obtained after the filtration of reaction mixture. Unless and until mentioned, the thiocyanation reactions were carried out by using following general procedure.

General Procedure for Thiocyanation. (Dichloroiodo)-benzene (660 mg, 2.4 mmol) was added to a suspension of lead-(II) thiocyanate (970 mg, 3 mmol) in dry dichloromethane (20 mL) at 0 °C under argon. The mixture was stirred at the same temperature for 15−20 min, and then the enol silyl ether/ketene silyl acetal/dicarbonyl compound (2 mmol) in dry dicholoromethane (10 mL) was added. The reaction mixture was allowed to stir at 0 °C till the completion of reaction (1 h at 0 °C, then 10 min at room temperature for silyl enol ethers and silyl ketene acetal; 2−4 h at 0 °C, then 10 min at room temperature for the remaining cases). During the progress of the reaction, the color of the suspended mixture turned to light yellow. The solid was filtered, and the filtrate was evaporated in vacuo to give a crude mixture of thiocyanato derivative and iodobenzene.

Purification was carried out by column chromatography on silica gel using ethyl acetate−hexanes as eluant (for all liquids **8a**−**b**, **10d**, **12a**−**d**, **14**, **21b**−**d** and some solids **10b**−**c**) or triturating with hexane, followed by recrystallization with hexanes (for most of the solid products **16a**−**b**, **16d**, **19b**−**f**). The physical, spectral, and analytical data of the products are given herein.

2-Thiocyanatocyclopentanone (8a). Pale yellow oil (180 mg, 66%).[40] ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 1.86−2.44 (m, 5H), 2.60−2.66 (m, 1H), 3.75 (t 1H J = 8.7 Hz, COC*H*SCN). IR (ν_{max}): 2156 (SCN str.), 1750 (C═O str.) cm^{-1}.

2-Thiocyanatocyclohexanone (8b). Pale yellow oil (210 mg, 68%).[40] ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 1.68−1.79 (m, 2H), 1.90−2.04 (m, 2H), 2.11−2.21 (m, 1H), 2.38−2.49 (m, 1H), 2.60−2.66 (m, 1H), 2.71−2.82 (m, 1H) 4.26 (dd, 1H J = 6.3, 5.4 Hz, COC*H*SCN). IR (ν_{max}): 2155 (SCN str.), 1712 (C═O str.) cm^{-1}.

2-Thiocyanatoacetophenone (10a). Oil (210 mg, 60%).[7] ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 4.75 (s, 2H, COCH_2SCN), 7.51−7.56 (m, 2H), 7.65−7.70 (m, 1H), 7.93−7.97 (m, 2H). IR (ν_{max}): 2155 (SCN str.), 1712 (C═O str.) cm^{-1}.

2-(2-Thiocyanatoacetyl)furan (10b). Colorless crystalline solid (155 mg, 46%), mp 101−103 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 4.44 (s, 2H, COCH_2SCN), 6.64 (dd, 1H, J = 3.6, 1.2 Hz, 4-furyl proton), 7.37 (d, 1H, J = 3.6 Hz, 3-furyl proton), 7.67 (d, 1H, J = 1.2 Hz, 5-furyl proton). IR (ν_{max}): 2158 (SCN str.), 1651 (C═O str.) cm^{-1}. MS (*m*/*z*, CI): 168 (M^+ + 1, 100), 140 (12.5), 122 (7.7), 111(31), 109 (22.3). Found: C, 50.27; H, 2.94; N, 8.32; S, 19.23. $C_7H_5NO_2S$ requires C, 50.30; H, 2.99; N, 8.38; S, 19.16.

2-(2-Thiocyanatoacetyl)thiophene (10c). Light brown crystalline solid (235 mg, 64%), mp 89−91 °C (lit.[41] mp 88 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 4.56 (s, 2H, COCH_2SCN), 7.21 (dd, 1H, J = 4.8, 3.9 Hz, 4-furyl proton), 7.77−7.80 (m, 2 H, 3- and 5-thienyl protons). IR (ν_{max}): 2160 (SCN str.), 1645 (C═O str.) cm^{-1}.

2-(2-Thiocyanatoacetyl)pyridine (10d). Light brown oil (230 mg, 65%) decomposed to dark colored mixture on standing. Unstability prevented obtaining an analytical sample of this product. Spectral data were obtained on almost pure sample after removing iodobenzene through column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 5.12 (s, 2H, COCH_2-SCN), 7.26−7.53 (m, 1H,pyridyl), 7.77−7.89 (m 1H, pyridyl), 8.09−8.20 (m, 1H, pyridyl), 8.67 (dd, 1H, J = 4.2, 1.8 Hz, pyridyl). IR (ν_{max}): 2165 (weak) (SCN str.), 1719 (C═O str.) cm^{-1}.

Methyl 2-Phenyl-2-thiocyanatoethanoate (12a).[42] Oil (290 mg, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 3.81 (s, 3H, CO_2CH_3), 5.18 (s, 1H, C*H*SCNHz), 7.42 (s, 5H, aromatic protons). IR (ν_{max}): 2158 (SCN str.), 1734 (C═O str.) cm^{-1}.

Methyl 2(4-Chlorophenyl)-2-thiocyanatoethanoate (12b). Oil (275 mg, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 3.80 (s, 3H, CO_2CH_3), 5.15 (s, 1H, C*H*SCN) 7.35−7.42 (m, 4H, aromatic protons). IR (ν_{max}): 2158 (SCN str.), 1739 (C═O str.) cm^{-1}. MS (*m*/*z*, CI): 241/243 (M^+ + 1, 100/33), 214/216 (75), 198/200 (63). Found: C, 50.01; H, 3.34; N, 5.82; S, 12.33; Cl, 14.73. $C_{10}H_8NO_2SCl$ requires C, 49.69; H, 3.31; N, 5.80; S, 13.25; Cl, 14.70. *p*-Chlorophenylacetic acid (10%), mp 106−108 °C (lit.[43] mp 105−108 °C), was also isolated as a side product of the reaction.

Ethyl 2(4-Tolyl)-2-thiocyanatoethanoate (12c). Oil (360 mg, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 1.27 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 2.37 (s, 3H, 4-$CH_3C_6H_4$), 4.27 (q, 2H, J = 7.2 Hz, OCH_2CH_3), 5.14 (s, 1H, C*H*SCN) 7.21 (d, 2H, J = 8.1 Hz, aromatic protons), 7.31 (d, 2H, J = 8.1 Hz, aromatic protons). IR (ν_{max}): 2157 (SCN str.), 1733 (C═O str.) cm^{-1}. Found: C, 61.23; H, 5.49; N, 5.89; S, 13.58. $C_{12}H_{13}NO_2S$ requires C, 61.28; H, 5.53; N, 5.96; S, 13.62.

Methyl 2(4-Anisyl)-2-thiocyanatoethanoate (12d). Oil (400 mg, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 3.81 (s, CO_2CH_3), 3.82 (s, 3H, 4-$CH_3OC_6H_4$), 5.16 (s, 1H, C*H*SCN) 6.92 (d, 2H, J = 9.0 Hz, aromatic protons), 7.35 (d, 2H, J = 9.0 Hz, aromatic protons). IR (ν_{max}): 2157 (SCN str.), 1734 (C═O str) cm^{-1}. Found: C, 55.69; H, 4.56; N, 5.93; S, 13.71. $C_{11}H_{11}NO_3S$ requires C, 55.70; H, 4.64; N, 5.91; S, 13.50.

5-Thiocyanato-2-(5*H*)-furanone (14). Oil (155 mg, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 6.32 [dd, 1H, J = 1.8, 1.5 Hz, C(5)-*H*], 6.56 [dd, 1H, J = 5.4, 1.8 Hz, C(3)-*H*], 7.53 [dd, 1H, J = 5.4, 1.8 Hz, C(4)-*H*]. IR (ν_{max}): 2162 (SCN str.), 1796 (C═O str.) cm^{-1}. Found: C, 42.78; H, 2.21; N, 9.87; S, 22.58. $C_5H_3NO_2S$ requires C, 42.55; H, 2.13; N, 9.91; S, 22.69.

3-Thiocyanatopentane-2,4-dione (16a). Pale yellow crystalline needles (280 mg, 90%), mp 79−80 °C (lit.[22] mp 78−81 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 2.51 (s 6H, 2 x CH_3), 17.08

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(s, 1H, enol O*H*). IR (ν_{max}): 2159 (SCN str.), 1602 (enol form of β-diketone) cm^{-1}.

3-Methyl-3-thiocyanatopentane-2,4-dione (16b). Pale yellow crystalline needles (290 mg, 85%), mp 88−89 °C. ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.51 (s 6H, 2 x C*H*$_3$), 3.15 (s, 3H, CH_3). IR (ν_{max}): 2161 (SCN str.), 1710 (C═O) cm^{-1}. MS (*m*/*z*): 171(M^+); 156 ($M^+ - CH_3$); 113 ($M^+ - SCN$); 43 (CH_3CO^+), Found: C, 49.11; H, 5.25; N, 8.26; S, 18.79. $C_7H_9NO_2S$ requires C, 49.12; H, 5.26; N, 8.18; S, 18.71.

1-Phenyl-2-thiocyanatobutane-1,3-dione (16c). The reaction was carried out in $CDCl_3$ at room temperature for 1 h, and the yield of the crude product in $CDCl_3$ was 95% (on the basis of ^1H NMR Cα-H at δ 5.74). IR (ν_{max}): 2159 (SCN str.) cm^{-1}. During the process of isolation and purification crude product decomposed readily to a complex mixture.

1,3-Diphenyl-2-thiocyanatopropane-1,3-dione (16d). Yellow crystalline needles (440 mg, 78%) (unstable in solution), mp 66−67 °C. ^1H NMR ($CDCl_3$, 300 MHz, δ): 6.42 (s,1 H, C*H*SCN), 7.49 (t 4H, $J \approx 8$ Hz, aromatic protons), 7.65 (t, 2 H, $J \approx 8$ Hz, aromatic protons), 7.98 (dd, 4 H, $J = 1.8$ Hz, 7.5 Hz, aromatic protons). IR (ν_{max}): 2159 (SCN, str.), 1677 (CO, str.) cm^{-1}. Found: C, 68.25; H, 3.89; N, 4.88; S, 11.34. $C_{16}H_{11}NO_2S$ requires C, 68.32; H, 3.91; N, 4.98; S, 11.38.

2-Thiocyanatoindan-1,3-dione (19a). Crude product in $CDCl_3$ (95% on the basis of ^1H NMR Cα-H at δ 5.74). IR (ν_{max}): 2159 (SCN str.) cm^{-1}. The product decomposed readily to a solid mixture having no signal for Cα-*H*SCN in its ^1H NMR.

2-Phenyl-2-thiocyanatoindan-1,3-dione (19b). Crystalline yellow solid (480 mg, 86%), mp 124−125 °C (lit.[11] mp 124−126 °C).

2-(4-Chlorophenyl)-2-thiocyanatoindan-1,3-dione (19c). Crystalline yellow solid (560 mg, 90%), mp 124−125 °C (lit.[11] mp 127 °C).

2-Thiocyanato-2-(4-toyl)indan-1,3-dione (19d). Crystalline yellow solid (530 mg, 90%), mp 108−110 °C. ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.32 (s, 3H, CH_3); 7.14−7.26 (dd, 2H, J = 9.1, 2.3 Hz, Aryl H); 7.50−7.53 (d, 2H, $J = 9$ Hz, Aryl H); 7.94−7.97 (m, 2H, Aryl H); 8.09−8.11 (m, 2H, Aryl H). IR (ν_{max}): 2150 (SCN str.); 1716 (C═O str.) cm^{-1}. HRMS (*m*/*z*): 293.4049 (M^+); 235.0854 ($M^+ - SCN$), calcd for $C_{17}H_{11}NO_2S$: 293.4052.

2-(4-Anisyl)-2-thiocyanatoindan-1,3-dione (19e). Crystalline yellow solid (500 mg, 84%), mp 139−40 °C (lit.[11] mp 138−140 °C).

2-(4-Nitrophenyl)-2-thiocyanatoindan-1,3-dione (19f). Crystalline yellow solid (500 mg, 87%), mp 125−127 °C (lit.[11] mp 126−128 °C).

Ethyl 2-Thiocyanato-3-oxobutanoate (21a). Crude product in $CDCl_3$ (97% on the basis of ^1H NMR Cα-H at δ 5.74). IR (ν_{max}): 2159 (SCN str.) cm^{-1}; readily decomposed on workup and purification.

Ethyl 2-Methyl-2-thiocyanato-3-oxobutanoate (21b).[12] Yellow oil (300 mg, 75%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.31 (t, 3 H, $J = 7.18$ Hz, CH_2CH_3); 3.19 (s, 3 H, CH_3); 3.77 (s, 3 H, CH_3); 4.28 (q, 2 H, $J = 7.18$ Hz, OCH_2CH_3). IR (ν_{max}): 2160 (SCN str.); 1720 (C═O str.). MS (*m*/*z*): 201(M^+); 186 ($M^+ - CH_3$); 142 ($M^+ - HSCN$); 43 (CH_3CO^+).

Diethyl Thiocyanatomalonate (21c).[12] Yellow oil (300 mg, 76%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.33 (t, 6 H, J = 7.18 Hz, 2 x OCH_2CH_3); 4.41 (q, 4 H, $J = 7.18$ Hz, 2xOCH_2-CH_3); 4.71 (s, 1 H, C*H*SCN). IR (ν_{max}): 2168 (SCN str.); 1728 (C═O str.). MS (*m*/*z*): 217 (M^+); 190 ($M^+ - HCN$); 159 ($M^+ - SCN$).

Methyl 2-Oxo-1-thiocyanatocyclopentanecarboxylate (21d).[10] The reaction was carried out at room temperature for 1 h. Workup followed by purification by column chromatography on silica gel using ethyl acetate−hexanes as eluant gave a semisolid (180 mg, 45%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.76−2.10 (m, 4 H, CH_2CH_2), 2.42 (t, 2 H, $J = 7.16$ Hz, $COCH_2$), 3.81 (s, 3 H, OCH_3). IR (ν_{max}): 2154 (SCN str.), 1724 (C═O str.), 1731 cm^{-1}.

Acknowledgment. We are thankful to Council of Scientific and Industrial Research (CSIR), New Delhi, India and NIH (U.S.) under program P01 CA48112 for financial assistance.

JO001504I