Synthetic Applications of Di-2-pyridyl Thionocarbonate As a Dehydration, a Dehydrosulfuriation, and a Thiocarbonyl Transfer Reagent

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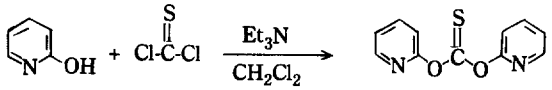
Di-2-pyridyl thionocarbonate, prepared from thiophosgene and 2-hydroxypyridine in the presence of triethylamine in dichloromethane, was found to be very effective for dehydration, dehydrosulfurization, and thiocarbonyl transfer reactions. Di-2-pyridyl thionocarbonate was successfully utilized for the esterification of carboxylic acids, dehydration of aldoximes into nitriles, preparation of isothiocyanates from amines, and preparation of cyclic thionocarbonates from 1,2- and 1,3-diols.

Introduction

Since the pioneering work by Staab during 1960's on the chemistry of N,N'-carbonyldiimidazole and N,N'-thiocarbonyl-diimidazole,[1] these reagents have found many useful applications in organic synthesis.[2] Although a variety of useful reagents derived from phosgene have been recently developed and successfully utilized in the synthesis of amides, peptides, and esters,[3] similar reagents derived from thiophosgene have not been actively investigated. The use of 1,1'-thiocarbonyl-1,2,4-triazole and related reagents as thiocarbonyl transfer reagents has been reported by Harpp.[4] Recently, we have reported the convenient method for the preparation of isothiocyanates and carbodiimides using di-2-pyridyl carbonate (DPT).[5] The lack of systematic investigation on the synthetic utility of thiophosgene related reagents prompted a detailed study of the reaction of a series of selected functional groups with DPT as a dehydration, a dehydrosulfurization, and a thiocarbonyl transfer reagent. This paper describes the results of these investigations.

Results and Discussion

DPT was conveniently prepared by treatment of thiophosgene with 2 equiv of 2-hydroxypyridine in the presence of 2-equiv of triethylamine in dichloromethane at 0 °C for 1 h and could be obtained in 80-90% yield as a white crystal, although it was often obtained as a pale yellow crystal due to the contamination of 1,1'-thiocarbonyldi-2,2'-pyridone having orange color.[6] Furthermore, DPT could be stored at room temperature for several months with little decomposition.



DPT

Esterification of Carboxylic Acids. Esterification of acids with equimolar amounts of alcohols and DPT in the presence of 0.1 equiv of 4-dimethylaminopyridine (DMAP)[7] in dichloromethane at room temperature proceeded smoothly, yielding esters in high yields in most cases. As we previously reported, the reaction did not occur to an observable extent in the absence of a base or in the presence of pyridine and triethylamine.[8] In order to demonstrate the effectiveness of DPT, as compared with N,N'-thiocarbonyldiimidazole, we performed the reaction of caprylic acid with equimolar amounts of benzyl alcohol and N,N'-thiocarbonyldiimidazole in the presence of 0.1 equiv of DMAP in dichloromethane at room temperature. Caprylic acid was completely converted into N-caprylyl imidazole within 1 h. However, alcoholysis of N-caprylyl imidazole was turned out to be relatively slow and benzyl caprylate was isolated in 33% yield after 24 h, indicative of the superiority of DPT over N,N'-thiocarbonyldiimidazole.

Table 1. Direct Esterification of Carboxylic Acids with DPT[a]

RCOOH + R'OH + DPT $\xrightarrow{0.1\text{ equiv DMAP}}$ RCOOR'

RCOOH	R'	method[b]	time, h	isolated yield, % RCOOR'	RCOO-2-py
$CH_3(CH_2)_6$	$C_6H_5CH_2$	A	1.5	92	0
	Cl_3CCH_2	A	0.5	90	0
	$(CH_3)_2CH$	A	24	80	13
		B	6	95	0
	$(CH_3)_3C$	A	2	0	93
		B	24	64	25
$C_6H_5CH_2$	CH_3	A	0.5	87	0
	$C_6H_5CH_2$	A	1	98	0
c-C_6H_{11}	CH_3CH_2	A	3	86	0
	$(CH_3)_2CH$	A	24	77	18
		B	6	91	0
t-$C_6H_5CH=CH$	CH_3CH_2	A	0.5	71	15
		A	24	92	0
C_6H_5	CH_3CH_2	A	24	66	28
		B	30	85	0
	Cl_3CCH_2	A	5	85	0
	$C_6H_5CH_2$	B	20	95	0
	$(CH_3)_3C$	A	2	0	96
$(CH_3)_3C$	$C_6H_5CH_2$	A	24	40	50(5)[c]
		B	24	78	0(8)[c]

[a] The reaction was carried out with equimolar amounts of an acid, an alcohol, and DPT in the presence of 0.1 equiv of DMAP. [b] Method A: in dichloromethane at room temperature. Method B: in carbon tetrachloride at 70 °C. [c] The isolated yield of pivalic anhydride.

Table 1 shows some experimental results and illustrates the applicability, efficiency, and scope of this method. Under the present conditions, primary and secondary aliphatic acids worked well with primary alcohols to afford the corresponding esters in high yields. However, in the case of using tertiary aliphatic acids and aromatic acids as an acid component and secondary and tertiary alcohols as an alcohol component, a mixture of the desired esters and 2-pyridyl esters in vari-

Table 2. Preparation of Nitriles from Aldoximes[a]

R-CH = NOH + DPT → R-C ≡ N

oxime	method[b]	time, h	yield, %
C_6H_5CH = NOH	A	0.2	94
	B	6	96
p-CH_3-C_6H_4CH = NOH	A	0.3	97
	B	10	96
p-CH_3O-C_6H_4CH = NOH	A	0.2	94
p-Cl-C_6H_4CH = NOH	A	0.3	93
	B	5	84
p-NO_2-C_6H_4CH = NOH	A	0.3	95
	B	4	93
$CH_3(CH_2)_7CH$ = NOH	A	24	50
	B	1.5	88
$C_6H_5CH_2CH_2CH$ = NOH	B	1.5	92
C_6H_5-CH = CH-CH = NOH	A	24	64
	B	18	94

[a]The reaction was carried out with equimolar amounts of an aldoxime and DPT. [b]Method A: in the presence of 0.1 equiv of DMAP in dichloromethane at room temperature. Method B: in acetonitrile at 80 °C.

able ratios or exclusively 2-pyridyl esters were obtained. With the exception of using tertiary alcohols and tertiary aliphatic acids, the desired esters could be obtained by performing the reaction in carbon tetrachloride at 70°C. Since 2-pyridyl esters can be transesterified to the desired esters with the help of cupric bromide in acetonitrile,[9] we feel that the formation of 2-pyridyl esters as a byproduct does not cause any serious problems.

Dehydration of Aldoximes. Dehydration of p-methoxybenzaldoxime into p-methoxybenzonitrile using an equimolar amount of DPT and triethylamine in dichloromethane at room temperature occurred slowly, yielding 85% of p-methoxybenzonitrile along with 12% of the recovered starting material. We found that the reaction proceeded cleanly and rapidly in the presence of 0.1 equiv of DMAP (Method A). Several aromatic aldoximes were cleanly dehydrated to the corresponding nitriles within 20 min. However, dehydration of aliphatic aldoximes proceeded slowly under the same conditions and required 24 h for completion of the reaction. Furthermore, we found that conversion of aldoximes into the corresponding nitriles could be accomplished without adding a base in refluxing acetonitrile (Method B). The experimental results are summarized in Table 2.

We have investigated the reaction of ketoximes, primary amides, and formamides with DPT/DMAP. Reaction of cyclohexane-ketoxime with 1 equiv of DPT in the presence of 0.1 equiv of DMAP in dichloromethane at room temperature was very messy, showing several spots on thin layer chromatography. Attempts on the structure determination of several products were failed. Similar results were realized with other ketoximes. Primary amides and formamides were inert to DPT/DMAP and starting materials were recovered in essentially quantitative yields.

Dehydrosulfurization of Thioureas. Carbodiimides are particularly important condensing agents in the peptide synthesis and various methods for the preparation of carbodiimides from dehydrosulfurization of thioureas utilizing metal oxides and condensing agents have been developed.[10]

Table 3. Preparation of Carbodiimides from Thioureas

$$RNH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NHR' + DPT \xrightarrow[CH_3CN,\ r.t.]{0.1\ equiv\ DMAP} R\text{-}N=C=N\text{-}R'$$

R	R′	time, h	yield, %
C_6H_5	C_6H_5	0.5	84
C_6H_5	o-CH_3-C_6H_4	0.5	89
C_6H_5	$CH_3(CH_2)_3$	1	91
C_6H_5	$(CH_3)_3C$	1	90
C_6H_5	c-C_6H_{11}	2	87
$(CH_3)_3C$	c-C_6H_{11}	12	90
		2[a]	
c-C_6H_{11}	c-C_6H_{11}	15	84
$(CH_3)_3C$	$(CH_3)_3C$	6	92
		1[a]	86
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	12[a]	0[b]

[a]The reaction was done at 80 °C. [b]The starting material was recovered unchanged.

The reaction of N-cyclohexyl-N′-phenylthiourea with equimolar amounts of DPT as a dehydrosulfurization agent and pyridine in acetonitrile occurred only to an observable extent, yielding 5% of N-cyclohexyl-N′-phenylcarbodiimide with the recovery of the starting material at room temperature for 24 h and similar results were obtained with the use of triethylamine. We found that the use of DMAP was very effective in the conversion of thioureas into carbodiimides in high yields. For example, reaction of N-cyclohexyl-N′-phenylthiourea with 1 equiv of DPT in the presence of 0.01, 0.1, and 1 equiv of DMAP in acetonitrile at room temperature gave N-cyclohexyl-N′-phenylcarbodiimide in essentially quantitative yields in 10 h, 2 h, and 0.1 h, respectively. Thus, remaining reactions were carried out with 1 equiv of DPT in the presence of 0.1 equiv of DMAP in acetonitrile.

As shown in Table 3, N,N′-diaryl or N-aryl-N′-alkyl substituted thioureas were cleanly and rapidly converted into the corresponding carbodiimides in high yields at room temperature. However, the conversion of N,N′-diakyl substituted thioureas into the corresponding carbodiimides was normally slow and was dependant critically on the nature of alkyl groups. Thus, the reaction of N,N′-di-t-butylthiourea with DPT in the presence of 0.1 equiv of DMAP at room temperature in 6 h gave N,N′-di-t-butylcarbodiimide in 92% yield, whereas the reaction of N,N′-dicyclohexylthiourea required 15 h at 80°C for completion of the reaction. Furthermore, this procedure reaches a limit with N,N′-primary alkyl disubstituted thioureas. N,N′-di-n-butylthiourea and N-methyl-N′-n-butyl-thiourea were completely inert to DPT/DMAP at 80°C for 12 h and starting materials were recovered unchanged.

It is of interest to note that dehydrosulfurization of thioureas with N,N′-thiocarbonyldiimidazole proceeded less efficiently, as compared with the reaction using DPT. For instance, reaction of N-phenyl-N′-t-butylthiourea with 1 equiv of N,N′-thiocarbonyldiimidazole in the presence of 0.1 equiv of DMAP in acetonitrile at room temperature for 24 h gave 25% of N-phenyl-N′-t-butylcarbodiimide along with 62% of the original thiourea, whereas the reaction with DPT gave the desired carbodiimide in 90% yield after 1 h under the similar condition.

Preparation of Isothiocyanates. The widely used

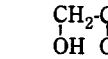
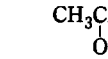
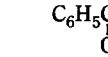
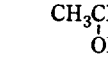
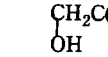
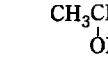
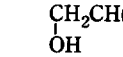
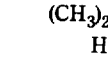
Table 4. Preparation of Isothiocyanates from Amines[a]

$RNH_2 + DPT \rightarrow R\text{-}N=C=S$

amine	yield, %[c]	bp, °C (mmHg) mp, [°C]	IR, cm^{-1}
$CH_3(CH_2)_3NH_2$	94	57-59 (15)	2110
c-$C_6H_{11}NH_2$	85	57-59 (1)	2110
$(CH_3)_3CNH_2$	87	47-50 (25)	2120
$CH_3CH_2CH(CH_3)NH_2$	85	60-63 (30)	2100
$CH_2=CHCH_2NH_2$	85	63-65 (40)	2090
$C_6H_5CH_2NH_2$	90	78-82 (2.2)	2100
$C_6H_5NH_2$	90	75-77 (6)	2090
p-CH_3-$C_6H_4NH_2$	95	73-74 (0.5)	2100
p-NO_2-$C_6H_4NH_2$[b]	90	[106-018]	2090
-naphthylamine	95	[119-120]	2100

[a]The reaction was carried out with equimolar amounts of an amine and DPT in dichloromethane at room temperature for 5 min. [b]The reaction was complete in 2h. [c]Isolated yields after Kugelrohr distillation.

Table 5. Preparation of Cyclic Thionocarbonates from Diols

diol	method[a]	time, h	yield, %
	A	1	90
	A	1	85
	B	12	82
	A	1	89
	B	4	96
	A	1	89
	B	6	81
	B	10	87
	A	2	88
	A	1	92
	B	16	86
	A	12	0

[a]Method A: in refluxing toluene. Method B: in the presence of 0.1 equiv of DMAP in dichloromethane at room temperature.

method for the preparation of isothiocyanates involves the reaction of amines with carbon disulfide in the presence of a base to form dithiocarbamate salts and their conversion into isothiocyanates can be often achieved by a variety of reagents. They include phosphoryl chloride,[11] DCC,[12] 2-chloropyridinium salts,[13] triphenylphosphine dibromide,[14] and Grignard reagent.[15]

Aliphatic and aromatic amines were directly converted to the corresponding isothiocyanates in high yields on treatment with DPT in dichloromethane at room temperature. The reaction most likely proceeded via 2-pyridyl thiocarbamates followed by rapid elimination of 2-hydroxypyridine at room temperature. The reaction was usually complete within 10 min at room temperature, though unreactive p-nitroaniline required 2 h. It is noteworthy that the reaction of N,N′-thiocarbonyldiimidazole with amines involves (1-alkyl- or arylthiocarbamoyl) imidazole as intermediates, which can be thermally decomposed into isothiocyanates and imidazole,[16] while N,N′-thiocarbonyl-1,2,4-triazole results in the formation of stable (1-akyl- or arylthiocarbamoyl)-1,2,4-triazole even with heating.[4] Thus, the present method seems to be very attractive in terms of its simplicity, rapidity, mildness, and high yields of products.

Preparation of Cyclic Thionocarbonates. Cyclic thionocarbonates are important intermediates for Corey-Winter olefin synthesis[17] and deoxygenation of one hydroxy group[18] from 1,3-diols and have been prepared most frequently using N,N′-thiocarbonyldiimidazole. Although cyclic thionocarbonates can be generally prepared with thiophosgene in relatively low yields, an improved procedure usng thiophosgene and DMAP has been recently reported.[19]

The preparation of cyclic thionocarbonates were performed on a variety of structurally different 1,2- and 1,3-diols using a stoichiometric amount of DPT in refluxing toluene (Method A). Under the present conditions, the reaction was normally complete within 4 h. Furthermore, the reaction occurred smoothly in the presence of 0.1 equiv of DMAP in dichloromethane at room temperature (Method B), but the reaction rate was relatively slow. The present method could be successfully applied for the preparation of cyclic 1,2-thionocarbonates from various 1,2-diols as shown in Table 5. However, sterically hindered pinacol was recovered unchanged even upon prolonged stirring in refluxing toluene. In a similar manner, various 1,3-diols including sterically hindered 2-methyl-2,4-pentanediol were converted into the corresponding cyclic 1,3-thionocarbonates in high yields. Furthermore, it is noteworthy that ethylene glycol and 1,3-butanediol were not cleanly converted into the desired cyclic thionocarbonates using N,N′-thiocarbonyldiimidazole in refluxing toluene, yielding only several unknown byproducts, although 1-phenyl-1,2-ethanediol and 2-methyl-2,4-pentanediol were converted into 4-phenyl-1,3-dioxolane-2-thione and 4,4,6-trimethyl-1,3-dioxane-2-thione in 84% and 69% yield, respectively.

Conclusions

The results obtained in this study confirm the versatility and a general understanding of the chemical property of DPT. DPT shows unique and characteristic chemical properties not present in other similar reagents like N,N′-thiocarbonyldiimidazole and also has certain advantages over N,N′-thiocarbonyldiimidazole such as the wide applicability, the mildness, the stability of the reagent, and high yields of products. Thus, we strongly believe that DPT should find many useful applications in organic synthesis.

Experimental

Preparation of Di-2-pyridyl Thionocarbonate. To a stirred solution of 2-hydroxypyridine (1.90 g, 20 mmol) and triethylamine (2.93 m*l*, 21 mmol) in dichloromethane (50 m*l*) at 0 °C was added thiophosgene (0.76 m*l*, 10 mmol) drowise over 10 min. After being stirred at 0 °C for 1 h, the reaction mixture was washed with 5% aqueous NaHCO (30 m*l*) and saturated brine (30 m*l*). The organic layer was dried over anhydrous $MgSO_4$ and concentrated to dryness. The residue

was purified by silica gel column chromatography with ethyl acetate/hexane (1:1) as eluant or the crude product was recrystallized from dichloromethane/petroleum ether to afford di-2-pyridyl thionocarbonate (DPT) (1.97 g, 85%) as a white solid. mp 98-100 °C; NMR ($CDCl_3$) δ 7.10-7.47 (m, 2H), 7.72-8.07 (m, 1H), 8.37-8.57 (m, 1H); IR (KBr) 3030, 1600, 1470, 1440, 1310, 1280, 1225, 1150 cm^{-1}. Calcd for $C_{11}H_8O_2N_2S$: C, 56.89; H, 3.47; N, 12.06. Found: C, 56.71; H, 3.42; N, 12.20.

General Procedure for the Preparation of Esters. To a solution of carprylic acid (288 mg, 2.0 mmol) and benzyl alcohol (216 mg, 2.0 mmol) in dichloromethane (6 m*l*) was added DPT (464 mg, 2.0 mmol), followed by the addition of DMAP (24 mg, 0.2 mmol). After being stirred at room temperature for 1 h, the reaction mixture was diluted with dichloromethane (20 m*l*), washed with 0.5M HCl solution, saturated $NaHCO_3$ solution, and brine, dried and evaporated to dryness. The residue was distilled with Kugelrohr apparatus to give benzyl caprylate (431 mg, 92%).

Spectral and Physical Data. 2,2,2-Trichloroethyl Caprylate: bp 95-97 °C (1.3 mmHg); NMR ($CDCl_3$) δ 0.70-1.60 (t, 3H), 1.13-2.06 (m, 10H), 2.43 (t, 2H), 4.70 (s, 2H); IR(film) 1765 cm^{-1}. Isopropyl Caprylate: bp 48-50 °C (0.8 mmHg); NMR ($CDCl_3$) δ 0.93 (br t, 3H), 1.10-1.83 (m, 10H), 1.28 (d, J = 6 Hz, 6H), 2.26 (t, J = 6 Hz, 2H), 5.10 (m, 1H); IR(film) 1735 cm^{-1}. t-Butyl Caprylate: bp 54-57 °C (1.6 mmHg); NMR ($CDCl_3$) δ 0.92 (br t, 3H), 1.06-1.86 (m, 10H), 1.50 (s, 9H), 2.23 (t, J = 6 Hz, 3H); IR(film) 1735 cm^{-1}. Methyl Phenylacetate: bp 54-57 °C (0.7 mmHg); NMR ($CDCl_3$) δ 3.62 (s, 2H), 3.67 (s, 3H), 7.30 (s, 5H); IR(film) 1745 cm^{-1}. Benzyl Phenylacetate: bp 134-136 °C (1.3 mmHg); NMR ($CDCl_3$) δ 3.56 (s, 2H), 5.05 (s, 2H), 7.23 (s, 10H); IR(film) 1735 cm^{-1}. Ethyl Cyclohexanecarboxylate: bp 41-43 °C (1.4 mmHg); NMR ($CDCl_3$) δ 0.97-2.60 (m, 11H), 1.30 (t, J = 7 Hz, 3H), 4.30 (q, J = 6 Hz, 2H); IR(film) 1735 cm^{-1}. Isopropyl Cyclohexanecarboxylate: bp 49-51 °C (1.8 mmHg); NMR ($CDCl_3$) δ 1.33 (d, J = 6 Hz, 6H), 1.00-2.60 (m, 11H), 5.10 (m, 1H); IR(film) 1735 cm^{-1}. Ethyl t-Cinnamate: bp 90-92 °C (0.7 mmHg); NMR ($CDCl_3$) δ 1.38 (t, J = 7 Hz, 4.30 (q, J = 7 Hz, 2H), 6.46 (d, J = 14 Hz, 1H), 7.43 (m, 5H), 7.73 (d, J = 14 Hz, 1H); IR(film) 1715 cm^{-1}. Benzyl Benzoate: bp 127-129 °C (1.5 mmHg); NMR ($CDCl_3$) δ5.40 (s, 2H), 6.97-7.87 (m, 8H), 7.97-8.27 (m, 2H); IR(film) 1730 cm^{-1}. Benzyl Pivalate: bp 54-56 °C (1.5 mmHg); NMR ($CDCl_3$) δ 1.28 (s, 9H), 5.17 (s, 2H), 7.37 (s, 5H); IR(film) 1730 cm^{-1}. 2-Pyridyl Caprylate: NMR ($CDCl_3$) δ 0.72-2.03 (m, 13H), 2.58 (t, J = 7 Hz, 2H), 6.94-7.20 (m, 2H), 7.50-7.82 (m, 1H), 8.20-8.40 (m, 1H); IR(film) 1760 cm^{-1}. 2-Pyridyl Cyclohexanecarboxylate: NMR ($CDCl_3$) δ 0.80-2.93 (m, 11H), 6.80-7.33 (m, 2H), 7.46-7.96 (m, 1H), 8.16-8.53 (m, 1H); IR (film) 1760 cm^{-1}. 2-Pyridyl Benzoate: NMR ($CDCl_3$) δ 7.10-7.70 (m, 6H), 8.00-8.40 (m, 3H); IR(KBr) 1740 cm^{-1}.

General Procedure for the Preparation of p-Methoxybenzonitrile. (Method A) A solution of p-methoxybenzaldoxime (152 mg, 1.0 mmol), DPT (232 mg, 1.0 mmol), and DMAP (12 mg, 0.1 mmol) in dichloromethane was stirred at room temperature for 10 min and diluted with dichloromethane (30 m*l*). The dichloromethane solution was washed with 0.1 N HCl solution, saturated $NaHCO_3$, and brine, dried, and evaporated to dryness. The residue was distilled with Kugelrohr apparatus to give p-methoxybenzonitrile (125 mg, 94%). mp 59-60 °C; NMR ($CDCl_3$) δ 3.9 (s, 3H), 6.83-7.10 (m, 2H), 7.47-7.73 (m, 2H); IR(film) 2230 cm^{-1}. (Method B). To a solution of nonanaldoxime (315 mg, 2.0 mmol) in acetonitrile (8 m*l*) was added DPT (465 mg, 2.0 mmol) and the reaction mixture was refluxed for 1.5 h. After evaporation of solvent under reduced pressure, the residue was diluted with dichloromethane (30 m*l*), washed with water and brine, dried, and evaporated to dryness. The residue was distilled with Kugelrohr apparatus to give nonanitrile (245 mg, 88%). bp 62-63 °C (4.5 mmHg); NMR ($CDCl_3$) 0.93 (br t, 3H), 1.36 (m, 12H), 2.30 (t, 2H); IR(film) 2250 cm^{-1}.

Spectral and Physical Data of Nitriles. Benzonitrile: bp 55-56 °C (5.0 mmHg); NMR ($CDCl_3$) δ 7.17-7.73 (m, 5H); IR(film) 2225 cm^{-1}. p-Tolunitrile: bp 63-64 °C (1.5 mmHg); mp 28-29 °C; NMR ($CDCl_3$) δ 2.42 (s, 3H), 7.10-7.63 (m, 4H); IR(film) 2245 cm^{-1}. p-Chlorobenzonitrile: mp 92-93 °C; NMR ($CDCl_3$) δ 7.40-7.77 (m, 4H); IR(KBr) 2230 cm^{-1}. p-Nitrobenzonitrile: mp 144-146 °C; NMR ($CDCl_3$) δ 7.83-8.07 (m, 2H), 8.27-8.53 (m, 2H); IR(KBr) 2240 cm^{-1}. Hydrocinnamonitrile: bp 85-86 °C (1.2 mmHg); NMR ($CDCl_3$) δ 2.40-2.73 (m, 2H), 2.80-3.13 (m, 2H), 7.30 (s, 5H); IR(film) 2250 cm^{-1}. Cinnamonitrile: bp 91-92 °C (1.6 mmHg); NMR ($CDCl_3$) δ 5.87 (d, J = 15 Hz, 1H), 7.38 (d, J = 15 Hz, 1H), 7.45 (s, 5H); IR(film) 2250 cm^{-1}.

General Procedure for the Preparation of Carbodiimides. To a solution of N-t-butyl-N'-phenylthiourea (208 mg, 1.0 mmol) in acetonitrile (4 m*l*) was added DPT (232 mg, 1.0 mmol), followed by the addition of DMAP (12 mg, 0.1 mmol). The reaction mixture was stirred at room temperature for 1 h and the solvent was evaporated. After dichloromethane (30 m*l*) was added to the flask, the resulting solution was washed with water, dried, and evaporated to dryness. The residue was distilled with Kugelrohr apparatus to yield the desired product (157 mg, 90%). bp 85-88 °C (0.5 mmHg); NMR ($CDCl_3$) δ1.45 (s, 9H), 7.03-7.40 (m, 5H); IR(film) 2120 cm^{-1}.

Spectral and Physical Data of Carbodiimides. $C_6H_5N=C=N-C_6H_5$: bp 130-133 °C (1.0 mmHg); NMR ($CDCl_3$) 6.80-7.53 (m, 10H); IR(film) 2140 cm^{-1}. $C_6H_5N=C=N-OCH_3C_6H_4$: bp 137-139 (0.6 mmHg); NMR ($CDCl_3$) δ 2.35 (s, 3H), 6.70-7.57 (m, 9H); IR(film) 2130 cm^{-1}. $C_6H_5N=C=N-n-C_4H_9$: bp 90-92 °C (0.5 mmHg); NMR ($CDCl_3$) δ 1.07 (br t, 3H), 1.37-1.93 (m, 4H), 3.53 (t, 2H), 7.10-7.60 (m, 5H); IR (film) 2135 cm^{-1}. $C_6H_5N=C=N-c-C_6H_{11}$: bp 95-97 °C (0.7 mmHg); NMR ($CDCl_3$) δ1.03-2.27 (m, 10H), 3.27-3.83 (m, 1H), 6.93-7.50 (m, 5H); IR(film) 2125 cm^{-1}. $(CH_3)_3C-N=C=N-c-C_6H_{11}$: bp 65-67 °C (1.8 mmHg); NMR ($CDCl_3$) δ 1.07-2.07 (m, 10H), 2.97-3.43 (m, 1H); IR(film) 2120 cm^{-1}. $(CH_3)_3C-N=C=N-C(CH_3)_3$: bp 71-73 °C (50 mmHg); NMR ($CDCl_3$) δ1.30 (s, 18H); IR(film) 2100 cm^{-1}.

General Procedure for the Preparation of Isothiocyanates. A solution of benzylamine (214 mg, 2.0 mmol) and DPT (465 mg, 2.0 mmol) in dichloromethane (6 m*l*) at room temperature was stirred for 5 min. After the solvent was removed in vacuo, petroleum ether (10 m*l*) was added and the resulting mixture was cooled in an ice bath. The precipitated 2-hydroxypyridine was recovered by filtration in 93% yield. The filtrate was evaporated to dryness and the residue was distilled with Kugelrohr apparatus to yield benzyl isothiocyanate (268 mg, 90%).

General Procedure for the Preparation of Cyclic Thionocarbonates. (Method A) A solution of 1-phenyl-1,2-ethanediol (276 mg, 2.0 mmol) and DPT (465 mg, 2.0 mmol) in

toluene (6 m*l*) was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane (30 m*l*), washed with water and brine, dried, and evaporated to give analytically pure 4-phenyl-1,3-dioxolane-2-thione (335 mg, 93%). (Method B) To a stirred solution of 1-phenyl-1,2-ethanediol (276 mg, 2.0 mmol) and DPT (466 mg, 0.2 mmol) in dichloromethane (6 m*l*) was added DMAP (22 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 4 h, diluted with dichloromethane (30 m*l*), washed with 2N HCl solution and brine, and dried over $MgSO_4$. Evaporation of the solvent afforded pure 4-phenyl-1,3-dioxolane-2-thione (346 mg, 96%). NMR ($CDCl_3$) δ 4.54 (dd, J = 9, 8 Hz, 1H), 5.00 (dd, J = 9, 9 Hz, 1H), 5.89 (dd, J = 9, 8 Hz, 1H), 7.42 (s, 5H).

Spectral Data of Cyclic Thionocarbonates. 1,3-Dioxolane-2-thione: NMR ($CDCl_3$) δ 4.80 (s, 4H); IR(KBr) 1485, 1380, 1300 cm^{-1}. 4-Methyl-1,3-dioxolane-2-thione: NMR ($CDCl_3$) δ 1.65 (d, J = 6 Hz, 3H), 4.32 (dd, J = 8, 8 Hz, 1H), 4.84 (dd, J = 8, 8 Hz, 1H), 4.93-5.40 (m, 1H); IR(film) 1485, 1460, 1170 cm^{-1}. 4-Methyl-1,3-dioxane-2-thione: NMR ($CDCl_3$) δ 1.58 (d, J = 6 Hz, 3H), 2.07-2.50 (m, 2H), 4.37-4.93 (m, 3H); IR(film) 1480, 1420, 1360 cm^{-1}. 5,5-Dimethyl-1,3-dioxane-2-thione: NMR ($CDCl_3$) δ 1.30 (s, 6H), 4.33 (s, 4H); IR(KBr) 1475, 1420, 1380, 1330 cm^{-1}. 4,4,6-Trimethyl-1,3-dioxane-2-thione: NMR ($CDCl_3$) δ 1.53 (d, J = 6 Hz, 3H), 1.60 (s, 6H), 1.87-2.47 (m, 2H), 4.47-5.10 (m, 1H); IR(film) 3000, 1230, 1050 cm^{-1}. 5-Ethyl-6-n-propyl-1,3-dioxane-2-thione: NMR ($CDCl_3$) δ 0.8-1.22 (m, 6H), 1.23-2.37 (m, 7H), 3.97-4.83 (m, 3H); IR(film) 1470, 1410, 1380 cm^{-1}.

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