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Carbon-Nitrogen Bond Fission in Ureas and Thioureas. Preparation of Alkyl and Aryl Isothiocyanates Using Carbon Disulfide and Butyllithinm or a Grignard Reagent

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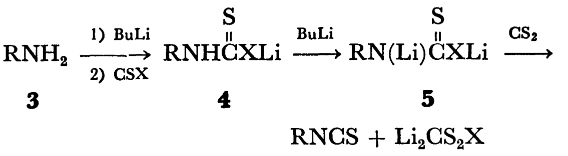
The carbon-nitrogen bond in *N,N'*-diaryl- and dialkyl-thioureas or -ureas was easily cleaved by the metallation of thioureas or ureas using butyllithium, followed by the addition of an excess of carbon disulfide or 1,3-dithiolan-2-thione in tetrahydrofuran under reflux, to afford about two mol of the corresponding isothiocyanates per mol of the thioureas or ureas used. Instead of butyllithium, ethylmagnesium bromide was also effective in such a type of carbon-nitrogen bond fission of the (thio)ureas in refluxing tetrahydrofuran, and in this case the addition of carbon disulfide was not required. To explain these results, a six-centered decomposition of the dilithium salt of *N*-dithiocarboxy(thio)urea in the reaction using butyllithium was tentatively proposed, while a four-centered mechanism seems applicable to the reaction using ethylmagnesium bromide.

The carbon-nitrogen bond in ureas or thioureas is difficult to cleave. In many instances, extreme conditions such as thermal decomposition with or without very concentrated acid have been applied. In such cases, the yield of isothiocyanate (**2**) is, in principle, less than one mol from one mol of **1**, and the reported yield of **2** is rather low (based on Eq. 1).[1]

$$\mathrm{RNHCSNHR} \xrightarrow{\Delta} \mathrm{RNCS} + \mathrm{RNH_2} \qquad (1)$$

1 **2** **3**

We have previously established a novel method for the preparation of aryl and alkyl isothiocyanates under moderate reaction conditions using amine, carbon disulfide, and butyllithium or a Grignard reagent.[2,3] The scheme for the reaction was proposed (Eq. 2; X=S)[2]:



$$\mathrm{RNH_2} \xrightarrow[\text{2) CSX}]{\text{1) BuLi}} \mathrm{RNH\overset{S}{\overset{\|}{C}}XLi} \xrightarrow{\text{BuLi}} \mathrm{RN(Li)\overset{S}{\overset{\|}{C}}XLi} \xrightarrow{\mathrm{CS_2}} \mathrm{RNCS} + \mathrm{Li_2CS_2X} \qquad (2)$$

3 **4** **5**

An anologous type of reaction for *N,N'*-substituted thiourea (X=NR in **5**) appear to be an interesting process for carbon-nitrogen bond fission, affording two mol of isothiocyanate from 1 mol of thiourea. In this report, we will describe a new method for the preparation of isothiocyanates by breaking the carbon-nitrogen bond in *N,N'*-disubstituted thioureas or ureas using butyllithium or a Grignard reagent, and carbon disulfide or 1,3-dithiolan-2-thione in anhydrous tetrahydrofuran (THF). Moreover, the reaction using butylithium will be compared with that using ethylmagnesium bromide from several mechanistic points of view.

Results and Discussion

Preparation of Isothiocyanates Using Butyllithium. *N,N'*-Dilithio-*N,N'*-diphenylthiourea (**7**; R=Ph), directly prepared from one mol of thiourea and two mol of butyllithium, was reacted with an excess of carbon disulfide for 3 h under a refluxing temperature of THF to give 1.45 mol of phenyl isothiocyanate (72% yield, based on Eq. 3; Direct Method). The yield of isothiocyanates obtained from various thioureas are summarized in Table 1.

$$\mathrm{RN(Li)C(S)N(Li)R} + 2\mathrm{CS_2} \longrightarrow 2\mathrm{RNCS} + \mathrm{Li_2CS_3} \qquad (3)$$

7 **8** **2** **9**

The results in Table 1 indicate that aromatic isothiocyanates were easily obtained by the distillation of the reaction mixture of the aryl-substituted ureas (**7**; R=arom.) with **8**. On the contrary, the yields of aliphatic isothiocyanates were low in the corresponding reactions of alkyl-substituted thioureas (**7**; R=aliph.) with **8**, and some amounts of the corresponding carbodiimides were found to be formed under the reaction conditions used.

Furthermore, the yields of isothiocyanates were increased when butyllithium and **8** were added step-by-step to the solution of the thiourea (Step-by-step Method): the *mono*-lithiothiourea formed by the reaction of **1** with one mol of butyllithium reacted with one mol of **8** with a slight exotherm, and the reaction mixture was treated with the second mole of butyllithium, followed by a reaction with **8** under reflux (see Note c in Table 1). The better results were obtained probably because of the higher degree of metallation of **1** needed to form **10a** or **10b**. The

TABLE 1. YIELDS OF ISOTHIOCYANATES (RNCS) FROM THE REACTION OF THIOUREAS ($(\mathrm{RNH})_2\mathrm{CS}$), BUTYLLITHIUM, AND CARBON DISLFIDE[a)]

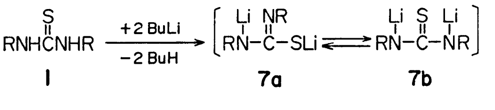
Thiourea R in thiourea	Yield of RNCS %	Bp °C/Torr	$\nu_{\mathrm{N=C=S}}$ cm^{-1}
C_6H_5	73(93)[c)]	95—100/ 5	2070
o-$CH_3C_6H_4$	82	104—105/10	2070
p-$CH_3C_6H_4$	73	105—108/10	2070
2,6-$(CH_3)_2C_6H_3$	91	114—116/10	2080
α-Naphthyl	82[c)]	108—112/0.1	2090
C_2H_5	40	72— 74/100	2090
$(CH_3)_3C$	43[d)]	73— 76/50	2090
Cyclohexyl	41[d)]	73— 74/20	2090

a) The *N,N'*-dilithiothiourea, prepared *in situ* using two mol of butyllithium, was reacted with mol of carbon disulfide for 3 h in refluxing THF (Direct Method). b) Based on Eq. 3. c) The yield obtained by the Step-by-step Method (see Experimental). d) Accompanied by the formation of carbodiimide.

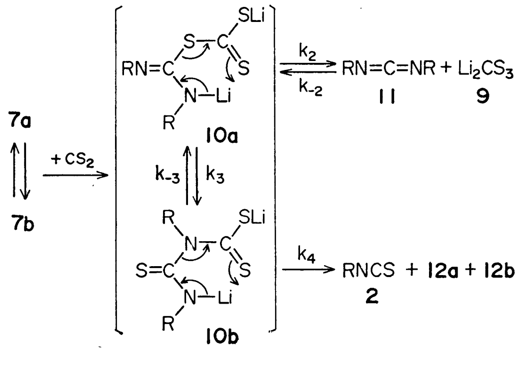
results from other thioureas by the Step-by-step Method are shown in Table 1.

To discuss the reaction course, the reaction of *N,N'*-di(*o*-tolyl)thiourea was precisely examined. The thiourea was treated with an equivalent of butyllithium to evolve one mol of butane, suggesting the formation of *N*-lithio-*N,N'*-di(*o*-tolyl)thiourea. The reaction mixture was allowed to react with one mol of carbon disulfide at room temperature with a slight exotherm, followed by a reaction with the second mole of butyllithium to evolve about one mol of butane. The total amount of butane evolved during the metallation reactions was almost twice the amount of **1** used. The reaction mixture was then stirred below room temperature to afford a heterogeneous solution containing the carbodiimide **11** (R=*o*-tolyl) and dilithium trithiocarbonate **9**.[4] The formation of carbodiimide was also observed in the initial stage of the reaction by the Direct Method below room temperature. The carbodiimide (**11**; R=*o*-tolyl) was separated from dilithium trithiocarbonate[4] by filtration. However, without filtration, a heterogeneous reaction mixture containing **11** and **9** was heated under reflux for 3 h to give a homogeneous solution. It showed the characteristic $\nu_{N=C=S}$ band of the isothiocyanate (**2**; R=*o*-tolyl) at 2070 cm^{-1}. The reaction mixture was subsequently distilled to afford **2** (R=*o*-tolyl) and a residue, which reacted with 1,2-dibromoethane in THF to form 2-(*o*-tolylimino)-1,3-dithiolane. The detection of the latter suggests the reaction of **12a** with 1,2-dibromoethane. Compound **12a** (or **12b**) has been reported to react rapidly with **8** below room temperature to afford **2** and **9**.[4]

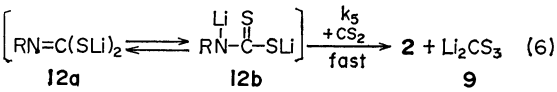
Judging from these results, it seems that the reaction by the Step-by-step or Direct Method probably proceed *via* **10a** to form **11** and **9** in the initial stage of the reaction below room temperature. However, in the final stage of the reaction at room temperature or under reflux in THF, **11** and **9** will be converted to **2** and **12a** (or **12b**), probably *via* **10a** or **10b**. The unstable intermediates, **10a** and **10b**, could not be characterized, but their identification is supported by the fact that **11** (R=*o*-tolyl) reacted with **9** for 4 h under reflux to give **2** in an almost quantitative yield. In the next step, **12a** (or **12b**) reacted with **8** to afford **2** and **9**. The reaction course are tentatively shown by Eqs. 4, 5, and 6.



$$\underset{\mathbf{1}}{\mathrm{RNH\overset{S}{\overset{\|}{C}}NHR}} \xrightarrow[-2\,\mathrm{BuH}]{+2\,\mathrm{BuLi}} \left[\underset{\mathbf{7a}}{\mathrm{R\overset{Li}{N}-\overset{NR}{\overset{\|}{C}}-SLi}} \rightleftarrows \underset{\mathbf{7b}}{\mathrm{R\overset{Li}{N}-\overset{S}{\overset{\|}{C}}-\overset{Li}{N}R}}\right] \quad (4)$$



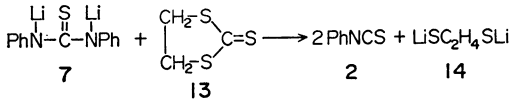
(5)



$$\left[\underset{\mathbf{12a}}{\mathrm{RN{=}C(SLi)_2}} \rightleftarrows \underset{\mathbf{12b}}{\mathrm{R\overset{Li}{N}-\overset{S}{\overset{\|}{C}}-SLi}}\right] \xrightarrow[\mathrm{fast}]{k_5,\ +\mathrm{CS_2}} \mathbf{2} + \underset{\mathbf{9}}{\mathrm{Li_2CS_3}} \quad (6)$$

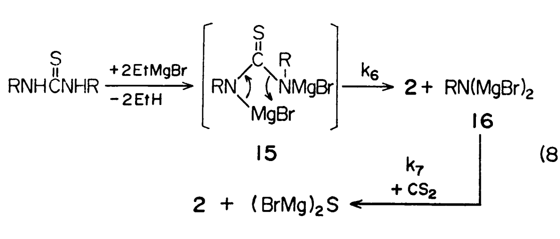
The fact that the characteristic $\nu_{N=C=N}$ band appeared in the initial stage of all the reactions using both the Direct and Step-by-step Methods below room temperature suggests that the rate constant, k_2, in Eq. 5 is much larger than k_4 or k_{-2}. From **7a** (or **7b**) with bulky groups, such as *o*-tolyl, 2,6-xylyl, or cyclohexyl, the corresponding carbodiimide, **11**, was isolated, probably because of a steric effect (smaller k_{-2}), while only **2** was isolated in the reaction of **7a** (or **7b**) with less bulky groups, such as phenyl or *p*-tolyl, probably because of the larger k_{-2} value.

In the reaction of Eq. 3, 1,3-dithiolan-2-thione was also used instead of carbon disulfide. It reacted with an equivalent amount of **7** (R=Ph) for 5 h in THF under reflux to afford phenyl isothiocyanate in a 67% yield (Eq. 7).



(7)

Preparation of Isothiocyanate Using Ethylmagnesium Bromide. The thermal decomposition of the dilithiothiourea **7**, (R=Ph), did not afford **2** but small amount of diphenylcarbodiimide and a resinous product were found to be formed. On the other hand, *N,N'*-bis(bromomagnesio)-*N,N'*-diphenylthiourea **15** (R=Ph) was thermally decomposed at about 140 °C to afford the isothiocyanate (**2**; R=Ph; 35% yield) and the *N,N'*-bis(bromomagnesio)amine **16**, which reacted exothermically with carbon disulfide to give an additional yield of **2** (38%). Table 2 shows the results of the reaction of **15** with an excess amount of carbon disulfide. The yields were moderate, but the purity of the isothiocyanates obtained was better than when butyllithium was used.



(8)

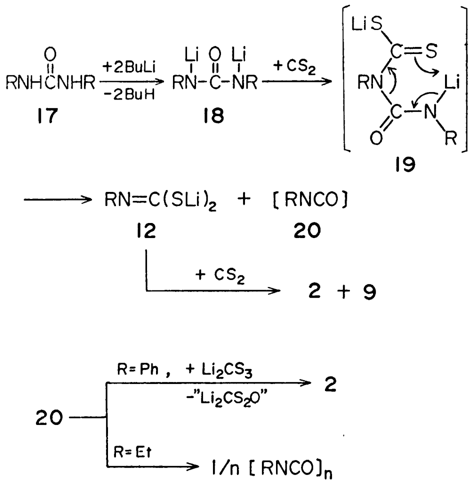
TABLE 2. YIELDS OF ISOTHIOCYANATES FROM THE REACTION OF THIOUREAS, ((RNH)$_2$CS), ETHYLMAGNESIUM BROMIDE, AND CARBON DISULFIDE

Thiourea	Reaction condition		Yield of RNCS
R in thiourea	Temp/°C	Time/h	%[b]
C_6H_5	a	40	65
p-$CH_3C_6H_4$	a	8	51
C_2H_5	a	34	48

a) The *N,N'*-bis(bromomagnesio)thiourea, prepared *in situ* using two mol of EtMgBr, was reacted with an excess of carbon disulfide in refluxing THF. b) Based on Eq. 8.

As has already been mentioned, dilithio-thiourea was easily decomposed by the addition of carbon disulfide, while the thermal decomposition of bis-(bromomagnesio)-compound (k_6 in Eq. 8) was not accelerated by the addition of carbon disulfide. However, the carbon disulfide used in the following step (k_7) is effective in improving the yield of **2**. These results suggest that **15** is thermally decomposed *via* a four-centered mechanism to give **2** and **16**, which is then converted to **2** by the action of the added carbon disulfide, as was shown in Eq. 8.

Carbon-Nitrogen Bond Fission of Urea. Carbon-nitrogen bonds are generally stable. However, we found that these bonds are easily cleaved by the reaction of carbon disulfide and butyllithium or a Grignard reagent in anhydrous THF. For example, *N,N'*-diphenylurea was allowed to react with two mol of butyllithium to form the *N,N'*-dilithio-derivative, **18** (R=Ph), and butane. Compound **18** was treated with an excess of carbon disulfide for 30 min in THF at room temperature. The reaction mixture showed the characteristic band of isothiocyanate at 2090 cm^{-1}. After the reaction mixture had been refluxed for 3 h, phenyl isothiocyanate, **2**, was obtained in an 80% yield (based on Eq. 9).



(9)

In the reaction of aryl ureas, the corresponding isothiocyanates were formed in good yields, because aryl isocyanates reacted with dilithium trithiocarbonate to form isothiocyanates. Thus, two mol of **2** (R=Ph) was obtained from one mol of *N,N'*-diphenylurea. On the other hand, the yield of ethyl isothiocyanate was low in the reaction of an alkyl-substituted urea, $(\mathrm{EtNH})_2\mathrm{CO}$, probably because of the base-catalyzed oligomerization of the ethyl isocyanate formed as an intermediate. At present, the mechanism of carbon-nitrogen bond fission in urea may tentatively depicted analogously to the case of thiourea.

A Grignard reagent, EtMgBr, was sometimes used in the carbon-nitrogen bond fission in alkyl- and aryl-substituted ureas instead of the butyllithium shown in Eq. 9, but the yields of isothiocyanates were low.

Experimental

All the melting and boiling points are uncorrected. The IR and NMR spectra were recorded with a JASCO IRA-1 spectrometer, and a Hitachi Perkin-Elmer R-24 spectrometer, respectively. The *N,N'*-disubstitued thioureas (**1**; $(\mathrm{RNH})_2\mathrm{CS}$) used were prepared mainly from amines and carbon disulfide by the reported methods[5-7]; mp (R): 154—155 (Ph), 160—163 (*o*-tolyl), 189—190 (*p*-tolyl), 230—232 (2, 6-xylyl), 206—207 (α-naphtyl), 131—132 (*t*-butyl), and 187—188 °C (cyclohexyl). The 1, 3-dithiolan-2-thione (**13**),[8] butyllithium in petroleum ether, and ethylmagnesium bromide in THF were prepared by the usual methods. The ureas, thioureas, carbon disulfide, 1, 2-dibromoethane, and THF were dried before use. All the reactions were carried out under a dry nitrogen atmosphere.

Reaction of Carbon Disulfide with N,N'*-Dilithio-*N,N'*-diphenylthiourea (**7**; R=Ph) (Direct Method).* In a flask equipped with a mechanical stirrer, a condencer, a dropping funnel, and a nitrogen inlet, butyllithium (60 mmol) was slowly introduced into a solution of the thiourea (**1**; R=Ph; 6.3 g, 27 mmol) in THF (50 cm^3) under cooling with a water bath to form, directly, **7** (R=Ph). Carbon disulfide (4.5 g; 60 mmol) was then added to the solution and the mixture was refluxed for 3 h. After the evaporation of the solvent, the residue was distilled in a vacuum to afford phenyl isothiocyanate (**2**: R=Ph) in a 72% yield (5.3 g, 39 mmol); bp 95—100 °C/15 Torr. The IR and NMR spectra coincided well with those of an authentic sample.[3] The results for other thioureas are summarized in Table 1.

Step-by-step Reaction of N,N'*-Di-*o*-tolylthiourea (**1**; R=*o*-$CH_3C_6H_4$) with Butyllithium and Carbon Disulfide (Step-by-step Method).* *N,N'*-Di-*o*-tolylthiourea (**1**; R=*o*-$\mathrm{CH_3C_6H_4}$; 6.3 g, 27 mmol in 50 cm^3 of THF) was allowed to react with butyllithium (30 mmol), accompanied by the evolution of butane (28 mmol). To the solution of the *mono*-lithio thiourea thus prepared, carbon disulfide (2.2 g, 30 mmol in 3 cm^3 of THF) was added slowly under cooling with an ice bath. The homogeneous reaction mixture was subsequently treated again with an additional amount of butyllithium (30 mmol) at room temperature, thus evolving more butane (25 mmol). The total amount of butane formed in the metallation reaction was twice the amount of thiourea used. However, the structure of the unstabe intermediate (or trandition state), **10a** or **10b**, could not be established even by spectroscopic methods such as IR and NMR. After the addition of butyllithium for 10 min, the reaction mixture became a heterogeneous solution to form **11** (R=*o*-$\mathrm{CH_3C_6H_4}$) and **9**,[4] the former being detected by the $\nu_{\mathrm{N=C=N}}$ band at 2145 cm^{-1} in the IR spectrum of the mixture. In the following step, carbon disulfide (2.2 g, 30 mmol) was added to the heterogeneous solution and the mixture was stirred for 30 min at room temperature to give a semi-transparent solution, which showed the $\nu_{\mathrm{N=C=S}}$ band of **2** (R=*o*-$\mathrm{CH_3C_6H_4}$) at 2070 cm^{-1} and the $\nu_{\mathrm{N=C=N}}$ band of **11** at 2145 cm^{-1}. The mixture was heated for further 3 h to convert the **11** to **2**. After the evaporation out of the solvent of THF and petroleum ether the residue was distilled under a vacuum to afford *o*-tolyl isothiocyanate in a 92% yield (6.8 g, 50 mmol).

*Reaction of **8** with **12** (R=*o*-$CH_3C_6H_4$) Prepared* in situ. A heterogeneous solution containing **11** and **9** was prepared from *N,N'*-di-*o*-tolylthiourea (**1**; R=*o*-$\mathrm{CH_3C_6H_4}$; 6.3 g; 27 mmol), butyllithium (30+30 mmol), and carbon disulfide (30 mmol) by the Step-by-step Method described above; when it was then heated for 3 h, the mixture became almost homogeneous. After evaporation of the solvent, the mixture was distilled to afford **2** (3.7 g, 25 mmol) and a residue containing **12** (R=*o*-$\mathrm{CH_3C_6H_4}$). After the residue had been treated with an excess of carbon disulfide with an exotherm, the distillation of the reaction mixture gave **2** (3.4 g, 23 mmol) and **9**. The latter was detected by the IR method ($\nu_{\mathrm{CS_3}}{}^{-2}$

935 cm^{-1}).

Detection of ***12*** *(R=*o*-$CH_3C_6H_4$).* The distillation residue containing **12**, prepared by the method described above, was treated with an excess of 1,2-dibromoethane to form 2-(*o*-tolylimino)-1,3-dithiolane, which was identified by a comparison of its IR and NMR spectra with those of an authentic sample.[9]

*Reaction of Carbodiimide (R=*o*-$CH_3C_6H_4$) with* ***9****.* Compound **11** (R=*o*-$CH_3C_6H_4$; 3.4 g) was allowed to react with powders of anhydrous dilithium trithiocarbonate (**9**; 30 mmol, 3.7 g) for 3 h under reflux of THF containing carbon disulfide (20 cm^3); the reaction mixture was then distilled to give **2** (R=*o*-$CH_3C_6H_4$) in an almost quantitative yield (6.1 g, 90%).

Reaction of Carbon Disulfide with N,N′*-Dilithio-*N,N′*-di-*t*-butyl)thiourea (****7****; R=$(CH_3)_3C$).* Compound **7** (R=$(CH_3)_3C$); 25 mmol), prepared *in situ* by the Direct Method, was allowed to react with carbon disulfide (4.0 g, 55 mmol) in THF under reflux, after which the mixture was distilled to afford *t*-butyl isothiocyanate (2.5 g, 43%) and di-*t*-butylcarbodiimide (1.0 g, 25%); bp 70—72 °C/10 Torr; IR (neat) 2094 cm^{-1} ($\nu_{N=C=N}$); NMR (CCl_4) δ=1.20 ppm (s, 18, CH_3).

Reaction of Dithiolan-2-thione with N,N′*-Dilithio-*N,N′*-Diphenylthiourea (****7****; R=Ph).* Compound **7** (R=Ph; 45 mmol) was allowed to react with 1,3-dithiolan-2-thione (**13**; 6.1 g, 45 mmol) for 5 h in THF under reflux, after which the mixture was distilled to afford **2** (R=Ph) in a 67% yield 8.0 g, 60 mmol).

After the treatment of the distillation residue with dilute hydrochloric acid, 1, 2-ethandithiol was detected in the residue by gas-chromatographic analysis.

Thermal Decomposition of N,N′*-Bis(bromomagnesio)-*N,N′*-diphenylthiourea (****15****; R=Ph).* Compound **15** (R=Ph), prepared from *N,N′*-diphenylthiourea (5.8 g, 25 mmol) and ethylmagnesium bromide (55 mmol) in THF, was pyrolyzed in a flask at about 140 °C; the mixture was then distilled to afford phenyl isothiocyanate in a 35% yield (1.2 g); bp 95—97 °C/10 Torr. The distillation residue was allowed to react exothermically with excess carbon disulfide (6 cm^3) in 20 cm^3 of THF, and then heated for 2 h at 140 °C; The mixture was subsequently distilled to afford phenyl isothiocyanate in a 38% yield (1.3 g); bp 95—99 °C/10 Torr.

Hydrogen sulfide gas was vigorously evolved when the residue of the second distillation was treated with dilute acid.

Reaction of N,N′*-Bis(bromomagnesio)-*N,N′*-di-*p*-tolylthiourea (****15****; R=*p*-$CH_3C_6H_4$) in the Presence of Carbon Disulfide.* *(A)* Compound **15** (R=Ph), prepared *in situ* from *N,N′*-di-*p*-tolylthiourea (6.4 g, 25 mmol) and ethylmagnesium bromide (55 mmol), was treated with an excess of carbon disulfide (3.8 g, 50 mmol) in THF for 1 h under reflux; the reaction mixture was then distilled to afford *p*-tolyl isothiocyanate in a 33% yield (2.5 g). The residue was treated again with carbon disulfide (6 cm^3) for 2 h under reflux, and then distilled to afford *p*-tolyl isothiocyanate in a 16% yield (1.2 g). *(B)* Compound **15** (20 mmol), prepared as has been described above, was treated with an excess of carbon disulfide (10 cm^3) in THF under reflux. After the evaporation of the solvent and an excess of carbon disulfide, the residue was distilled in a vacuum to afford the corresponding isothiocyanate. The results are summarized in Table 2.

Reaction of Carbon Disulfide with the N,N′*-Dilithiourea (****18****).* *(A) Using Butyllithium*: Compound **18** (R=Ph) was prepared *in situ* from *N,N′*-diphenylurea (**17**, R=Ph; 6.4 g, 30 mmol) and butyllithium (66 mmol) in 50 cm^3 of THF under cooling by ice-water, and subsequently reacted with carbon disulfide (6 cm^3) for 30 min at room temperature The reaction mixture showed the $\nu_{N=C=S}$ band at 2070 cm^{-1} in the IR spectrum. After refluxing for 3 h, phenyl isothiocyanate was isolated by distillation in an 80% yield (6.5 g); bp 94—96 °C/15 Torr.

In the same manner described above, ethyl isothiocyanate was obtained in a 44% yield (1.2 g, 13 mmol) from a reaction using *N,N′*-diethylurea (**17**, R=Et; 3.5 g, 30 mmol); 78—91 °C/90 Torr; IR (neat) 2090 cm^{-1} ($\nu_{N=C=S}$); NMR (CCl_4) δ=1.36 (t, 3, J=7.1 Hz, CH_3) and 3.60 ppm (q, 2, J=7.1 Hz, CH_2). The distillation residue showed the band at 1745 ($\nu_{C=O}$) and at 1690 cm^{-1} in the IR spectrum.

(B) Using Ethylmagensium Bromide: *N,N′*-Bis(bromomagnesio)-*N,N′*-diphenylurea prepared *in situ* from the urea (**17**, R=Ph; 6.4 g, 30 mmol) and ethylmagnesium bromide (66 mmol) was allowed to react with an excess of carbon disulfide (12 cm^3) for 1 h at 45 °C; the mixture was then distilled to give phenyl isothiocyanate in a 44% yield (3.5 g).

Reaction of Phenyl Isocyanate with Dilithium Trithiocarbonate. Phenyl isocyanate (2.4 g, 20 mmol) reacted with dilithium trithiocarbonate powders (2.7 g, 22 mmol) in THF (50 cm^3) with stirring for 4 h under reflux; it was subsequently distilled to afford phenyl isothiocyanate in a 65% yield (1.8 g).

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