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THE REACTION OF ISOCYANIDE—MERCURIC CHLORIDE COMPLEXES WITH AMINES. PREPARATION OF GUANIDINES

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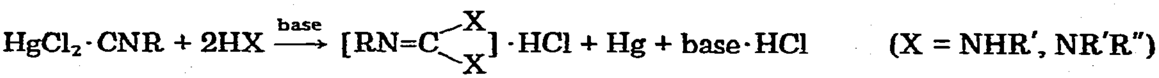
Summary

Isocyanide—mercuric chloride complexes react readily with an excess of primary and secondary amines to give guanidines and metallic mercury in high yields through a redox decomposition reaction. In the presence of triethylamine, isocyanide—mercuric chloride complexes react with an equimolar amount of a primary amine to give a carbodiimide and metallic mercury. An intermediate organomercuric compound was isolated in the reaction of the isocyanide—mercuric chloride complex with pyrrolidone.

Introduction

A wide variety of isocyanide—metal complexes has been reported [1], and reactions of the coordinated isocyanide in metal complexes have recently attracted widespread interest. However, little has been reported about isocyanide—mercury(II) complexes. Only two isocyanide complexes of mercury(II) have been reported [2,3]. We have prepared some isocyanide—mercuric chloride complexes, and have studied some of their reactions. The complexes react with nucleophiles such as amines, active methylene compounds and hydroxide ion, undergoing a redox decomposition reaction to give various products.



$$HgCl_2\cdot CNR + 2HX \xrightarrow{base} [RN{=}C(X)_2]\cdot HCl + Hg + base\cdot HCl \qquad (X = NHR', NR'R'')$$

$$HgCl_2\cdot CNR + H_2Y \xrightarrow{base} RN{=}C{=}Y + Hg + 2\ base\cdot HCl$$

$$\downarrow$$

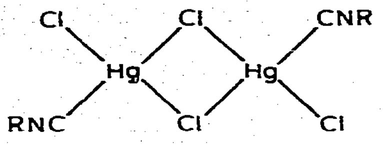
$$\text{final products} \qquad (Y = O, NR', CR'R'')$$

In the present paper we report the preparation of isocyanide—mercuric chloride complexes and the redox decomposition reaction of the complexes with amines.

Results and discussion

Isocyanide—mercuric chloride complexes

Complexes of the formula $HgCl_2 \cdot CNR$ (II) were prepared as white precipitates by reaction of mercuric chloride with an excess of the isocyanide (I) in cold ether. The phenyl and benzyl isocyanide complexes are too unstable to be isolated and turn to yellow gummy substances at room temperature. The t-butyl and 2,6-dimethylphenyl isocyanide complexes show a ν(N$\equiv$C) band at 2218 and 2245 cm^{-1}, respectively, characteristic of the coordinated isocyanide [1]. Molecular weight determinations of the complexes were unsuccessful due to their insolubility or instability in solution. The coordination number of mercury(II) is usually two or four and dimeric mercuric chloride complexes having a chloro-bridged structure are known in the case of sulfide, arsine and phosphine complexes [4]. Therefore the structure of the isocyanide—mercuric chloride complexes could be dimeric as shown below:

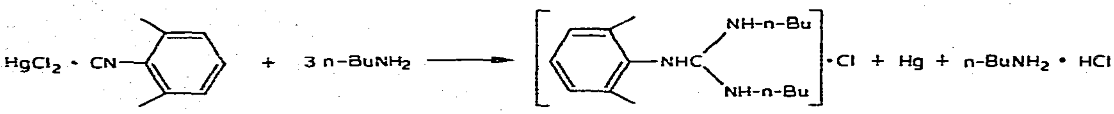


IIa R = 2,6-dimethylphenyl
IIb R = t-butyl

(II)

Reaction of isocyanide—mercuric chloride complexes with an excess of primary amine

The 2,6-dimethylphenyl isocyanide—mercuric chloride complex (IIa) reacted with an excess of n-butylamine in dry tetrahydrofuran (THF) at reflux for 0.5 h to yield *N,N'*-di-n-butyl-*N''*-2,6-dimethylphenylguanidine hydrochloride (IIIa), n-butylamine hydrochloride and metallic mercury in nearly quantitative yields:



(IIa) (IIIa)

Neutralization of the guanidine hydrochloride by aqueous sodium hydroxide gave the free guanidine. Similarly, reactions of other isocyanide—mercuric chloride complexes with primary amines gave the corresponding guanidines as shown in Table 1.

Aliphatic primary amines are more reactive than aromatic amines due to their greater basicity. IIa can react with ethylenediamine to afford the cyclic guanidine, but in lower yield. The formation of a stable complex of ethylenediamine with mercuric chloride suppresses the redox reaction. The n-butylamine—mercuric chloride complex also reacts readily with Ia to give IIIa and metallic mercury in high yield. This result suggests that a mixed ligand complex is an intermediate in the reaction.

In these reactions, oxidation of isocyanides by Hg^{II} took place giving guan-

TABLE 1

REACTIONS OF ISOCYANIDE COMPLEXES WITH PRIMARY AMINES

Isocyanide	Amine	Temp. (°C)	Time (h)	Yield (mol % based on Hg^{II})	
				Hg	Guanidine
t-Bu	n-Bu	66	1	96	39
	Ph	66	1	56	47
$PhCH_2$	n-Bu	66	0.5	99	90
Ph	n-Bu	30	1	99	98
	C_6H_{11}	30	1	96	95
	Ph	66	5	46	42
$2,6\text{-}Me_2C_6H_3$	n-Bu	66	0.5	100	97
	C_6H_{11}	66	1	99	48
	Ph	66	5	42	41
	$H_2NCH_2CH_2NH_2$	66	5	16	16
	n-Bu	66	1	100	94[a]
	C_6H_{11}	66	1	96	59[a]

[a] Reaction of amine complex with isocyanide. $HgCl_2$, 2.5 mmol; RNC, 5 mmol; RNH_2, 1 ml; THF, 10 ml.

idines. Isocyanides are oxidized to the corresponding isocyanates by various types of oxidizing agents [6]. Little has been reported about oxidation of isocyanides to guanidines. Group IB and IIB metal compounds, especially copper, have strong catalytic activity in the simple α-addition of isocyanides [5,6]. Mercuric chloride is found to cause only oxidative α-addition of isocyanides through redox reactions, but has no catalytic activity for the simple α-addition of primary amines to isocyanides.

Reactions of isocyanide—mercuric chloride complexes with secondary amines (Table 2)

Complex IIb reacts with diethylamine to yield *N,N,N',N'*-tetraethyl-*N''*-t-butylguanidine(IVb) and *N,N*-diethyl-*N'*-t-butylformamidine(Vb). Reaction of IIa with diethylamine gives *N,N*-diethyl-*N'*-2,6-dimethylphenylurea. IIa reacts with *N*-methylaniline to give only the formamidine VIa in nearly quantitative yield, and no redox reaction takes place at all. The reaction of IIa with diphenylamine gives neither guanidine nor formamidine.

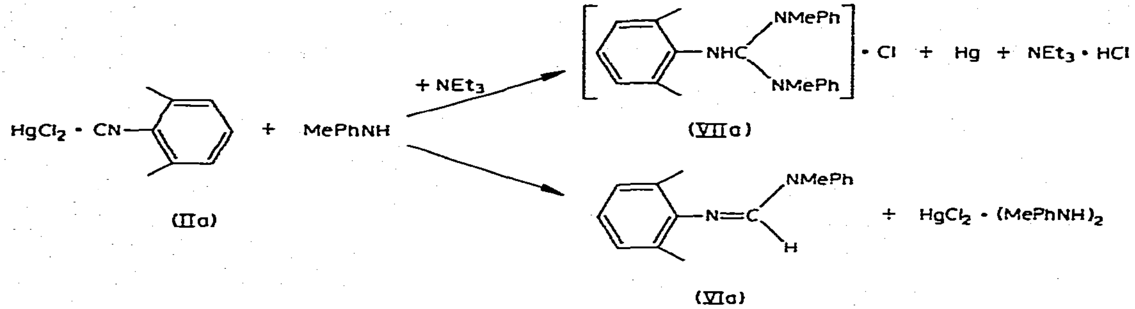
TABLE 2

REACTIONS OF ISOCYANIDE COMPLEXES WITH SECONDARY AMINES

Isocyanide	Amine	Temp. (°C)	Time (h)	Yield (mol % based on Hg^{II})	
				Hg	Guanidine
t-Bu	Et, Et	30	0.5	77	70
$2,6\text{-}Me_2C_6H_3$	Et, Et	66	1	82	80[a]
	Me, Ph	66	5	0	0
	Ph, Ph	66	5	0	0
	Me, Ph	66	5	86	77[b]

[a] *N,N*-diethyl-*N'*-2,6-dimethylphenylurea. [b] In the presence of 1 ml triethylamine. Hg^{II}, 2.5 mmol; RNC, 5 mmol; Amine, 1 ml; THF, 10 ml.

The basicity and steric characteristics of amines affect their activity in this redox reaction. The addition of triethylamine, which does not react with the isocyanide—mercuric chloride complexes, enhanced the redox reaction. Thus *N,N'*-dimethyl-*N,N'*-diphenyl-*N''*-dimethylphenylguanidine (VIIa) was obtained in high yield from IIa with *N*-methylaniline in the presence of triethylamine.



Synthesis of carbodiimides by reactions of isocyanide—mercuric chloride complexes with n-butylamine

IIb reacts with an equimolar amount of n-butylamine in the presence of triethylamine to yield n-butyl-t-butylcarbodiimide (VIIIb), with the formation of metallic mercury and triethylamine hydrochloride. Similarly, n-butyl-2,6-dimethylphenylcarbodiimide (VIIIa) is formed from IIa with n-butylamine. This carbodiimide formation does not take place at all in the absence of triethylamine.

$$HgCl_2 \cdot CNR + n\text{-}BuNH_2 \xrightarrow{+NEt_3} RN{=}C{=}N\text{-}n\text{-}Bu + Hg + 2NEt_3 \cdot HCl$$

(II)	(VIII)
(IIa) R = 2,6-dimethylphenyl	(VIIIa) 32.5%; 77% (66°C, 5 h)
(IIb) R = t-butyl	(VIIIb) 8.5%; 39% (66°C, 2 h)

Reaction of Ia with n-butylamine in the presence of mercuric salts

Various mercuric salts undergo the redox reaction. However, an intermediate isocyanide—mercuric salt complex cannot be isolated from the reaction of Ia with mercuric salts except mercuric chloride. In situ reaction of the mercuric salt Ia with n-butylamine gives IIIa or the urea [7] as shown in Table 3. Mercurous chloride reacts in the same manner. The reactivity of the salts in the redox reaction is in the following order: $Hg(OAc)_2 \approx Hg(NO_3)_2 > HgBr_2 > HgCl_2 > Hg_2Cl_2 > Hg(SCN)_2 > HgSO_4 > Hg(CN)_2$.

Reaction of IIa with pyrrolidone

Compound IIa does not react with pyrrolidone at 66°C. However, in the presence of triethylamine an amidino type complex IXa can be isolated in 25% yield. The IR spectrum of IXa shows ν(C=O) and ν(C=N) bands at 1672 and 1578 cm^{-1}, respectively, and no absorptions at 3200-3500 cm^{-1} due to ν(NH), indicating that IXa is not a carbene type complex, but rather an amidino complex. The NMR spectrum and the elemental analysis of IXa also support the

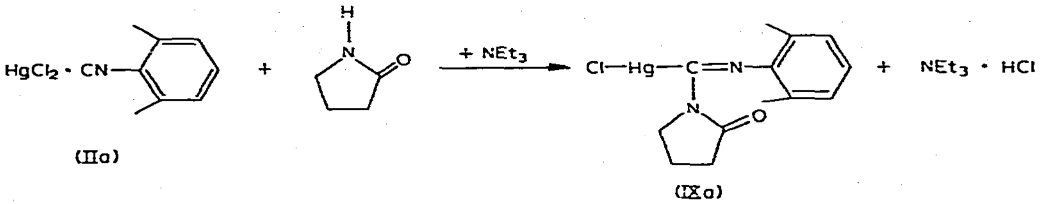
TABLE 3

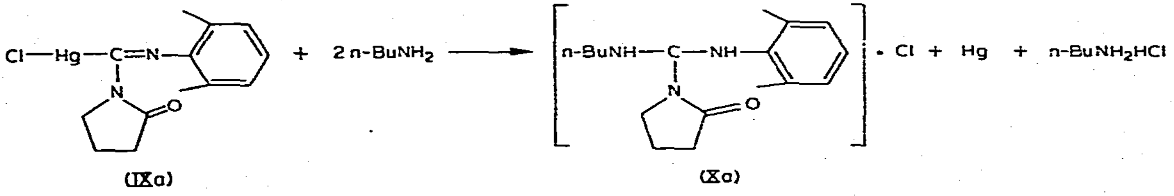
REACTIONS OF 2,6-DIMETHYLPHENYL ISOCYANIDE AND n-BUTYLAMINE WITH MERCURIC SALTS[a]

X	Temp. (°C)	Time (h)	Yield (mol %)	
			Hg	Guanidine(urea)
OAc	25	0.5	97	(88)
NO_3	25	1	99	43 (13)
Br	25	1	71	63
	66	0.5	100	95
Cl	25	1	0	0
	66	0.5	100	97
SCN	66	0.5	37	25
SO_4	66	0.5	6	trace
CN	66	0.5	3	0

[a] HgX_2, 2.5 mmol; RNC, 5 mmol; $n\text{-}BuNH_2$, 1 ml.

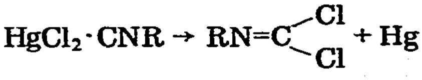
amidino type structure. IXa is stable at room temperature; it reacts with n-butylamine at 66°C for 5 h giving the corresponding guanidine Xa and metallic mercury in 18% yield.





Reaction scheme

Guanidines are formed from isonitrile dichlorides and amines [8]. Isocyanides react with cupric chloride to afford isonitrile dichlorides and cuprous chloride [6]. Consequently, in the reaction of isocyanide—mercuric chloride complexes with amines, guanidines could be formed via isonitrile dichlorides as follows:



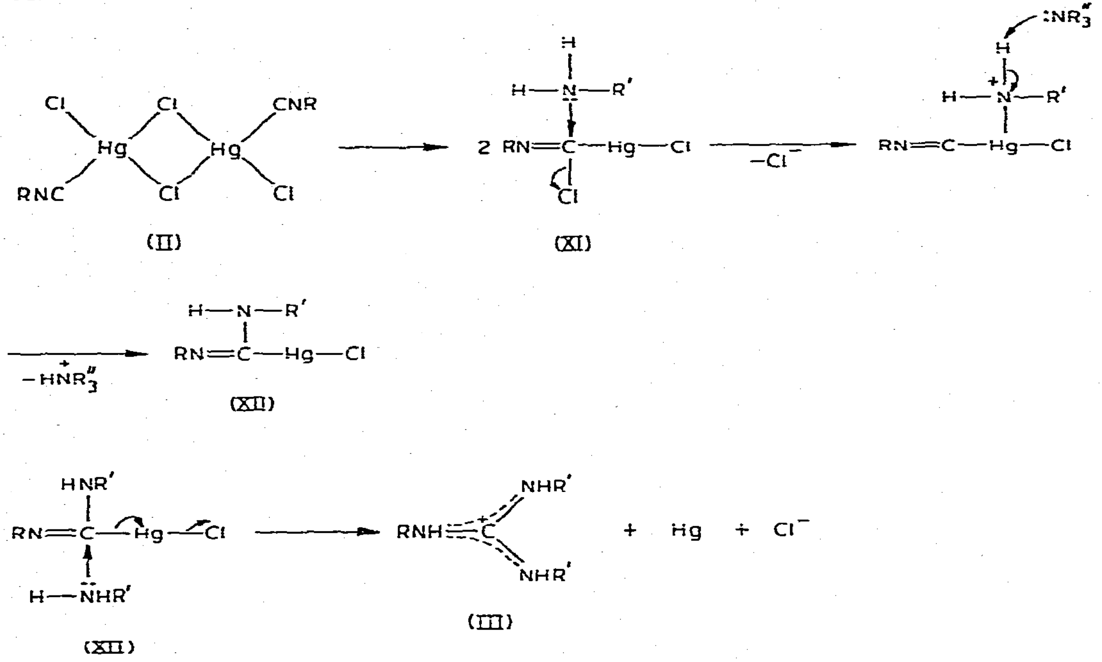
$$HgCl_2 \cdot CNR \rightarrow RN{=}C\genfrac{}{}{0pt}{}{Cl}{Cl} + Hg$$

$$RN{=}C\genfrac{}{}{0pt}{}{Cl}{Cl} + 3R'NH_2 \rightarrow RNHC\genfrac{}{}{0pt}{}{NHR'}{NHR'} \cdot Cl + R'NH_2 \cdot HCl$$

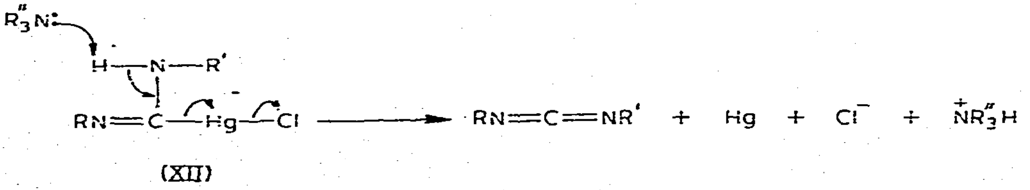
However, this possibility is excluded by the following results: *(i)* no isonitrile dichloride nor metallic mercury was formed upon heating the isocyanide—mercuric chloride complex in the absence of primary amines; *(ii)* addition of triethylamine in this system also did not cause isonitrile dichloride formation.

A plausible scheme for the reaction is shown in Scheme 1. The base catalyzed rearrangement of complex II to XI, followed by nucleophilic displacement of chlorine by amine could give the intermediate complex XII. Strong base promotes the formation of XII by helping to remove H$^+$. Thus, triethylamine is necessary in the reaction of II with weak bases such as *N*-methylaniline and pyrrolidone. Nucleophilic attack of the amine to the amidino carbon of XII causes the redox decomposition of the complex forming the guanidine. The formation of the carbodiimide proceeds similarly through the redox decomposition reaction of amidino complex XII as shown in Scheme 2. In the reaction of II with amines, intermediate amidino complexes could not be isolated because of their instability. However, the corresponding amidino complex, which reacts with n-butylamine giving the guanidine, was isolated from the reaction of IIa with pyrrolidone.

SCHEME 1.

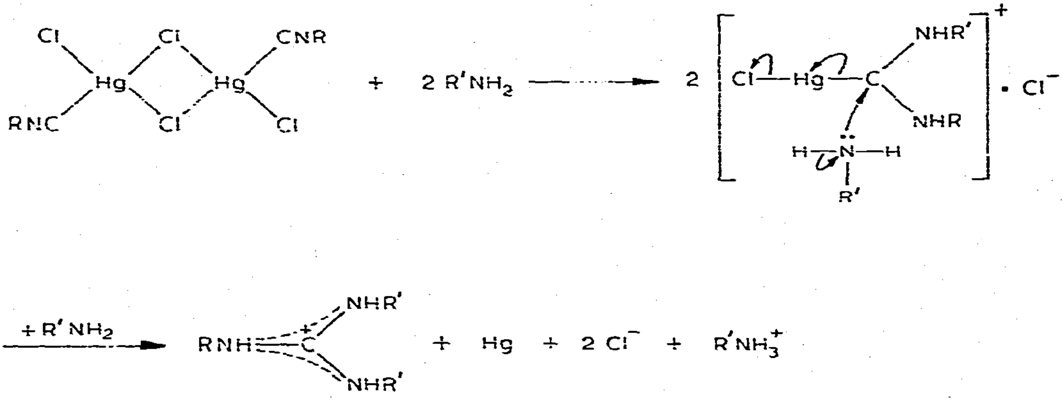


SCHEME 2.



Reactions of isocyanide—metal complexes with amines give diaminocarbene complexes in the case of Pd^{II}, Pt^{II} and Fe^{III} [9,10]. The in situ reaction of mercuric acetate, methyl isocyanide and secondary amines gives bis(diaminocarbene) complexes [11]. Therefore, another reaction scheme of guanidine formation via an intermediate carbene complex could be proposed (Scheme 3).

SCHEME 3.



Under the same conditions isocyanide—palladium(II) chloride complexes react with primary and secondary amines to form stable diaminocarbene complexes. An attempt to conduct the redox decomposition reaction of the diaminocarbene—palladium(II) chloride complex was unsuccessful in spite of the greater activity of palladium chloride in the carbonylation of amines which gives ureas [12].

Experimental

Isocyanides were prepared according to the method of Ugi and coworkers [13]. All chemicals were reagent grade. Tetrahydrofuran (THF) was dried over lithium aluminum hydride and distilled before use. IR spectra were measured with a JASCO DS 402 instrument. NMR spectra were measured using a Nihondenshi JMN-TS-100 spectrometer.

Preparation of isocyanide—mercuric chloride complexes

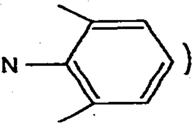
A solution of mercuric chloride (271 mg, 1 mmol) in 10 ml of THF was stirred for 10 min and treated with 4 mmol of the isocyanide in 5 ml of dry ether while cooling with Dry-Ice/methanol. The reaction product precipitated immediately. The precipitation was completed by adding 10 ml of dry ether. The product, washed with ether several times, did not require further purification. Analytical and some other data of the complexes are shown in Table 4.

Reaction of IIa with n-butylamine

Mercuric chloride (680 mg, 2.5 mmol) 2,6-dimethylphenyl isocyanide (660 mg, 5 mmol) and THF (10 ml) were mixed in a 30 ml conical flask and stirred for 10 min under nitrogen to prepare IIa. One ml of n-butylamine was added to

TABLE 4

ISOCYANIDE—MERCURIC CHLORIDE COMPLEXES

Complex	M.p. (dec.) (°C)	ν(N≡C) (cm^{-1})	Elemental analysis found (calcd.) (%)		
			C	H	N
$HgCl_2$·(t-BuNC)	72-74	2245 (2127)^a	16.22 (16.9)	2.14 (2.55)	3.72 (3.95)
$HgCl_2$ · (CN )	185-187	2218 (2120)^a	26.64 (26.8)	2.39 (2.24)	3.51 (3.48)
$HgCl_2$·(C_6H_5NC)	dec. at r.t.				
$HgCl_2$·($C_6H_5CN_2NC$)	dec. at r.t.				

^{a} Free isocyanide.

this reaction mixture gradually with stirring. The reaction mixture was heated to 66°C, refluxed for 30 min with stirring, and then filtered and washed with THF to give the filtrate A, and then with methanol to give filtrate B. The residue was metallic mercury. Concentration of the filtrate B gave white crystals of n-butylamine hydrochloride. Filtrate A was concentrated under reduced pressure to a few ml and poured into n-hexane to separate the guanidine hydrochloride as an oily residue. This oily substance was treated with aqueous sodium hydroxide, extracted with ether, dried over anhydrous sodium carbonate and purified by chromatography on silica gel. The purified colorless oily product was confirmed to be *N,N'*-di-n-butyl-*N''*-2,6-dimethylphenylguanidine by comparison of the IR spectrum and melting point of the picrate with those of an authentic sample prepared by Kühle's method [8].

The procedure used for the reaction of the isocyanide—mercuric chloride complexes with primary amines were virtually identical with that used in the reaction of IIa with n-butylamine. The crystalline guanidines were recrystallized from ether/n-hexane or methylene chloride/ether. The guanidines prepared in this reaction are listed in Table 5 together with the melting points and analytical data. The IR and NMR spectra of these guanidines are consistent with their structure.

Reaction of the n-butylamine—mercuric chloride complex with 2,6-dimethylphenyl isocyanide

In a 30 ml conical flask, mercuric chloride (680 mg, 2.5 mmol) was treated with n-butylamine (1 ml) in THF (10 ml) with stirring to give the n-butylamine—mercuric chloride complex as a white precipitate. To this suspension, 2,6-dimethylphenyl isocyanide (660 mg, 5 mmol) was added gradually and stirred for 30 min at 66°C. The reaction of the cyclohexylamine—mercuric chloride complex with 2,6-dimethylphenyl isocyanide was carried out in the same manner. The separation and identification of the products were carried out by the same techniques as described in the reaction of IIa with n-butylamine.

TABLE 5

GUANIDINES OBTAINED FROM REACTIONS OF ISOCYANIDE COMPLEXES WITH PRIMARY AMINES

Guanidine			M.p. (°C)	IR (cm^{-1})	Elemental analysis found (calcd.) (%)		
N	*N*'	*N*''			C	H	N
2,6-$Me_2C_6H_3$[a]	n-Bu	n-Bu	123-125	1610	54.74 (54.65)	6.39 (6.36)	16.62 (16.63)
2,6-$Me_2C_6H_3$[b]	C_6H_{11}	C_6H_{11}	208.5-209.5	1615	69.16 (69.20)	9.30 (9.38)	11.27 (11.07)
2,6-$Me_2C_6H_3$	2,6-$Me_2C_6H_3$	Ph	169-171	1650	80.56 (80.34)	12.24 (12.24)	7.30 (7.34)
2,6-$Me_2C_6H_3$	—CH_2—CH_2—		155.5-156.5	1665	69.57 (69.81)	7.98 (7.99)	22.00 (22.20)
Ph	n-Bu	n-Bu	oily (120-121)[a]	1620			
Ph	C_6H_{11}	C_6H_{11}	172-174	1610	76.40 (76.20)	9.62 (9.76)	14.10 (14.03)
Ph	Ph	Ph	144-146(145)[c]	1630	79.64 (79.41)	14.45 (14.62)	6.04 (5.96)
t-Bu	n-Bu	n-Bu	oily (115-116)[a]	1625			
t-Bu	Ph	Ph	95-97	1630	76.56 (76.39)	7.85 (7.92)	15.74 (15.72)
$PhCH_2$[b]	n-Bu	n-Bu	55-60(54-64)[d]	1612	67.32 (67.85)	8.06 (8.09)	12.47 (12.44)

[a] Picrate. [b] Hydrochloride. [c] Ref. 14. [d] Ref. 15.

Reaction of IIa with diethylamine

The complex IIa was prepared from 2,6-dimethylphenyl isocyanide (660 mg, 5 mmol) and mercuric chloride (680 mg, 2.5 mmol) in THF (10 ml) under nitrogen. Diethylamine (1 ml) was added to the reaction mixture which stirred for 2 h at 66°C. After the reaction, metallic mercury and the white crystalline precipitate were removed by filtration. The precipitate was confirmed to be diethylamine hydrochloride, m.p. 230-232°C, by a mixture with an authentic sample. The filtrate was concentrated under reduced pressure, neutralized with aqueous sodium hydroxide and extracted with ether. The organic layer was washed with water, dried over sodium carbonate and evaporated to dryness. Recrystallization from benzene/chloroform gave white, crystalline *N,N'*-diethyl-*N''*-2,6-dimethylphenylurea (530 mg, 96%), m.p. 177-178°C. (Found: C, 70.72; H, 8.99; N, 12.63. $C_{13}H_{20}N_2O$ calcd.: C, 70.87; H, 9.15; N, 12.72%.) IR (cm^{-1}) 3250, 1625.

Reaction of IIb with diethylamine

t-Butyl isocyanide (830 mg, 10 mmol), mercuric chloride (680 mg, 2.5 mmol) and THF (10 ml) were stirred in a 30 ml conical flask for 10 min to prepare IIb. Diethylamine (1 ml) was added gradually and the mixture was stirred for 30 min at 30°C. After the reaction was complete, the metallic mercury and diethylamine hydrochloride were removed by filtration. The filtrate was concentrated, poured into aqueous sodium hydroxide and extracted with ether. The extract was washed with water, dried over sodium carbonate, evaporated to dryness and distilled under reduced pressure to give a colorless oil, *N*,*N*,*N'*,*N'*-tetraethyl-*N''*-t-butylguanidine (394 mg, 77%), b.p. 76-79°C/1.5 Torr. (Found: C, 68.48; H, 12.95; N, 18.64. $C_{13}H_{29}N_3$ calcd.: C, 68.66; H, 12.86; N, 18.48%.) IR and NMR spectra are consistent with the structure.

Reaction of IIa with N-methylaniline

(a). In the absence of triethylamine. The complex IIa was prepared from 2,6-dimethylphenyl isocyanide (660 mg, 5 mmol) and mercuric chloride (680 mg, 2.5 mmol) in THF (10 ml). *N*-Methylaniline (1 ml) was added and the mixture stirred for 5 h at 66°C. No metallic mercury formation occurred. A white precipitate, which was confirmed to be the *N*-methylanilinemercuric chloride complex, was removed by filtration. The filtrate was concentrated under reduced pressure and chromatographed on silica gel. White crystalline *N*-methyl-*N*-phenyl-*N'*-2,6-dimethylphenylformamidine was obtained by using n-hexane/ether as an eluent, yield 518 mg, m.p. 41.5-42.5°C. (Found: C, 80.66; H, 7.64; N, 11.70. $C_{16}H_{18}N_2$ calcd.: C, 80.63; H, 7.61; N, 11.76%.)

(b). In the presence of triethylamine. The reaction procedure was identical with that described above, except that 1 ml of triethylamine was added with 1 ml of *N*-methylaniline. Metallic mercury (430 mg) and a white precipitate which was confirmed to be triethylamine hydrochloride were removed by filtration. The filtrate was concentrated, neutralized with aqueous sodium hydroxide and extracted with ether. The extract was dried over sodium carbonate, concentrated and chromatographed on silica gel. *N*-Methyl-*N*-phenyl-*N'*-2,6-dimethylphenylformamidine (662 mg) was obtained by using n-hexane/ether (10/1) as an eluent. White crystals were obtained by using n-hexane/ether (8/2) as an eluent. Recrystallization from n-hexane gave purified *N*,*N'*-dimethyl-*N*,*N'*-diphenyl-*N''*-2,6-dimethylphenylguanidine (679 mg, 77%), m.p. 135-136°C. (Found: C, 80.48; H, 6.90; N, 12.22. $C_{23}H_{25}N_3$ calcd.: C, 80.43; H, 7.34; N, 12.24%.)

Reaction of IIa and IIb with an equimolar amount of n-butylamine in the presence of triethylamine

(a). IIa with n-butylamine. The complex IIa was prepared from 2,6-dimethylphenyl isocyanide (2.6 g, 20 mmol) and mercuric chloride (2.71 g, 10 mmol) in THF (40 ml) under an atmosphere of nitrogen. n-Butylamine (730 mg, 10 mmol) and triethylamine (4 ml) were added and the mixture was stirred for 5 h at reflux. The reaction mixture was filtered to remove metallic mercury and triethylamine hydrochloride. The filtrate was concentrated in vacuo with sublimation of 2,6-dimethylphenyl isocyanide and distilled under reduced pressure to yield *N*-n-butyl-*N'*-2,6-dimethylphenylcarbodiimide (658 mg, 32.5%), b.p. 85-90°C/15 Torr. (Found: C, 77.35; H, 9.01; N, 13.60. $C_{13}H_{18}N_2$ calcd.: C, 77.18; H, 8.97; N, 13.85%.) IR, 2150 cm^{-1} $\nu(N{=}C{=}N)$. From the residue, 78 mg of *N*-n-butyl-*N'*-2,6-dimethylphenylurea was obtained.

(b). IIb with n-butylamine. The complex IIb was prepared from t-butyl isocyanide (4.15 g, 50 mmol) and mercuric chloride (6.79 g, 25 mmol) in THF (50 ml) under an atmosphere of nitrogen. n-Butylamine (1.83 g, 25 mmol) and triethylamine (10 ml) were added and the reaction mixture stirred for 2 h under reflux. The precipitated metallic mercury and triethylamine hydrochloride were removed, and the solution concentrated under reduced pressure and distilled to

yield *N*-n-butyl-*N'*-t-butylcarbodiimide (330 mg, 8.5%), b.p. 58-63°C/20 Torr. (Found: C, 70.10; H, 11.58; N, 17.95. $C_9H_{18}N_2$ calcd.: C, 70.30; H, 11.76; N, 18.16%.) IR, 2140 cm^{-1} ν(N=C=N).

From the residue, 168 mg of *N*-n-butyl-*N'*-t-butylurea was obtained.

Reaction of 2,6-dimethylphenyl isocyanide and mercuric salt with n-butylamine

2,6-Dimethylphenyl isocyanide (660 mg, 5 mmol), mercuric salt (2.5 mmol) and THF (10 ml) were stirred for 10 min in a 30 ml conical beaker. n-Butylamine was added and the mixture stirred at the given temperature (Table 4). The isolation and identification of the products were carried out by the method described in the reaction of IIa with n-butylamine. In the case of mercuric acetate, *N*-n-butyl-*N'*-2,6-dimethylphenylurea was obtained instead of the guanidine [7].

Reaction of IIa with pyrrolidone

Pyrrolidone (1 ml) and triethylamine (1 ml) were added to a stirred solution of IIa which was prepared from mercuric chloride (680 mg, 2.5 mmol) and 2,6-dimethylphenyl isocyanide (660 mg, 5 mmol) in THF (10 ml). The reaction mixture was heated at reflux for 5 h with stirring. The grayish precipitate (32 mg) and triethylamine hydrochloride (159 mg) were removed by filtration. The filtrate was concentrated under reduced pressure and chromatographed on silica gel. White crystals were obtained by using n-hexane/ether as an eluent. Recrystallization from n-hexane/methylene chloride gave the purified adduct IXa (285 mg, 25%), m.p. 205-206°C. (Found: C, 34.71; H, 3.30; N, 6.25. $C_{13}H_{15}N_2OClHg$ calcd.: C, 34.65; H, 3.30; N, 6.20%.) IR, 1672 ν(C=O), 1578 ν(C=N), 1380 cm^{-1}.

The adduct (260 mg) was treated with n-butylamine (730 mg) in THF (10 ml) with stirring for 10 h at reflux. Metallic mercury (33 mg, 27%) then was removed by filtration, and the reaction mixture was concentrated under reduced pressure, neutralized with aqueous sodium hydroxide and extracted with ether. The extract was dried over sodium carbonate and chromatographed on silica gel. Recrystallization of the resultant solid from n-hexane/methylene chloride gave *N*-butyl-*N'*-2,6-dimethylphenyl-*N''*-pyrrolidonylguanidine as white crystals (30 mg, 18%), m.p. 136-140°C. (Found: C, 70.65; H, 9.18; N, 14.37. $C_{17}H_{25}N_3O$ calcd.: C, 71.04; H, 8.77; N, 14.62%.) IR, 3320, 1660 and 1640 cm^{-1}.

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