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The Reaction of Isocyanides with Halogens or *N*-Halosuccinimides and Alcohols

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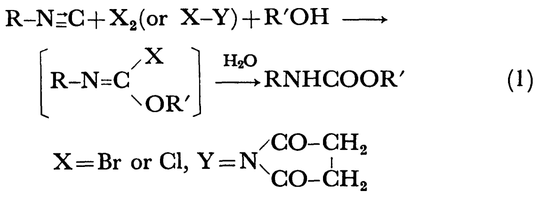
The reaction of aliphatic isocyanides with bromine or chlorine in primary alcohols, followed by hydrolysis, afforded the corresponding carbamates in moderate yields, together with various amounts of amines. Bromine was superior to chlorine as a halogen source for the formation of carbamates. unexpectedly, the addition of $HgCl_2$ resulted in a decrease in the carbamate yield. When *N*-halosuccinimides were used in the place of halogens, an additional formation of the succinimide-incorporated product was observed to some extent.

Previously we reported that the reactions of isocyanides with *t*-butyl hypochlorite and with wet *N*-bromo amides in chlorinated methanes in either the presence or absence of the $ZnCl_2$ catalyst, followed by treatment with water, gave *t*-butyl carbamates and acylureas respectively, although the yields were low.[1] In order to know whether or not the combined use of halogens and alcohols in the place of the alkyl hypohalite is feasible for the former reaction, and also to determine to what extent the formation of carbamates may compete in the latter reaction using alcohols as solvents, we have examined the reaction of isocyanides with halogens or *N*-halosuccinimides and alcohols. Taking into account the nucleophilic nature of isocyanides, the reaction was carried out with or without an acid catalyst. The present paper deals with these results.



$$R\text{-}N\equiv C + X_2(\text{or } X\text{-}Y) + R'OH \longrightarrow \left[R\text{-}N{=}C\begin{matrix}\diagup X\\ \diagdown OR'\end{matrix}\right] \xrightarrow{H_2O} RNHCOOR' \qquad (1)$$

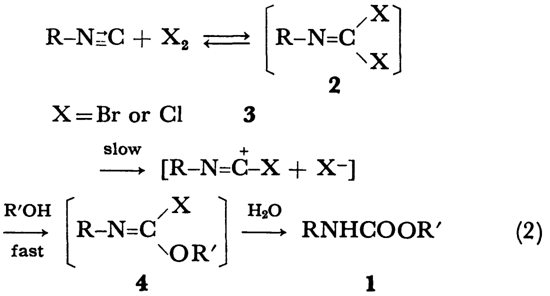
$$X = Br \text{ or } Cl,\ Y = N\begin{matrix}\diagup CO\text{-}CH_2\\ \diagdown CO\text{-}CH_2\end{matrix}$$

In this connection, the facile addition of chlorine or bromine to both aliphatic and aromatic isocyanides to afford the corresponding carbonimidoyl dihalides (isocyanide dihalides) is well-known, except for the case of unstable alkylcarbonimidoyl dibromides, but studies of the alcoholysis and hydrolysis of carbonimidoyl dihalides has been confined to the *N*-aryl compounds, which afford *N*-arylcarbamates and/or arylamines as final products under neutral or acidic conditions.[2,3]

Results and Discussion

The treatment of isocyanides with bromine or chlorine in various alcohols without a catalyst for several hours at room or a higher temperature, followed by a work-up procedure with water, gave the expected carbamates (**1**) in moderate yields, along with various amounts of amines, as is shown in Table 1. A controlled experiment indicated that the amines were formed by the hydrolysis of the unreacted imidoyl dihalides (**2**) during the work-up procedure and that iminocarobates [R–N=C(OR′)$_2$], if they are formed, did not give amines at least under the given work-up conditions.

When an equimolar reaction of cyclohexyl isocyanide with bromine was carried out in a small quantity of methanol, a yellowish-orange solid separated out in a considerable amount at an early stage of the reaction, leaving nearly a half equivalent amount of the isocyanide in the solution. Further, when a methanol solution of this solid was allowed to stand for several hours at room temperature, the expected **1** (R=cyclo-C_6H_{11}, R'=Me) was produced in a good yield (see Experimental). Based on these facts the solid was tentatively presumed to be a 1 : 1 molecular complex of **2** (R=cyclo-C_6H_{11}, X=Br) and bromine. The use of chlorine in place of bromine did not cause any formation of such a complex, but the conversion of **2** (R=cyclo-C_6H_{11}, X=Cl) into **1** (R=cyclo-C_6H_{11}, R'=Me) with methanol was also confirmed by another experiment. We may thus conclude that **2** is the initial intermediate of this reaction.



$$R\text{-}N\equiv C + X_2 \rightleftarrows \underset{\mathbf{2}}{\left[R\text{-}N{=}C\begin{matrix}\diagup X\\ \diagdown X\end{matrix}\right]}$$

$$X = Br \text{ or } Cl \qquad \mathbf{3}$$

$$\xrightarrow{\text{slow}} [R\text{-}N{=}\overset{+}{C}\text{-}X + X^-]$$

$$\underset{\text{fast}}{\xrightarrow{R'OH}} \underset{\mathbf{4}}{\left[R\text{-}N{=}C\begin{matrix}\diagup X\\ \diagdown OR'\end{matrix}\right]} \xrightarrow{H_2O} \underset{\mathbf{1}}{RNHCOOR'} \qquad (2)$$

Relating to the transformation of **2** to **4**, it has been reported that both neutral and acidic hydrolyses of **2**, where R=aryl and X=Cl, in aqueous dioxane proceeds by means of the S_N1 mechanism, based on an aryl-substituent effect on the rate (the rate decreases in this order: *p*-Me>H>*p*-Cl>*m*-Cl).[3] This mechanism involving the rate-determining heterolysis to afford the cation, **3**, can be safely adapted for the case of R=alkyl; thus, the yields of **4**, and hence those of **1**, may be expected to decrease in this order: R=tertiary>secondary>primary and R=alkyl>aryl. The obtained data agree with this expectation. Further, the fact is known that the relative reactivity of acyl halides, the structure of which is similar to **2**, decreases in this order: X=Br>Cl in alcoholysis with ethylene glycol[4] and in the acylation of active aromatics.[5] A similar feature may be expected for the ionization of one C–X bond, since the effect of another X (being not ionized) may not be so important on the ground that only a slight difference in polar (both inductive and resonance) effect between Br and Cl is known. Thus, in the reaction with bromine, the better the yields of **1** compared with

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TABLE 1. REACTION OF ISOCYANIDES WITH HALOGENS AND ALCOHOLS
Isocyanides, 20 mmol; Br_2, 20 mmol; Cl_2, 60 mmol; alcohols, 20 ml.
Reaction conditions: near 5 °C, 1 h and 20—25 °C, 5 h.

RNC	X_2	R′OH	Additive (mol%)	Product and yield/%[a)]	
				1	Amine[b)]
cyclo-$C_6H_{11}NC$	Br_2	MeOH	—	76	4
cyclo-$C_6H_{11}NC$	Br_2	MeOH[c)]	—	74	—[d)]
cyclo-$C_6H_{11}NC$	Br_2	MeOH	$HgCl_2$ (10)	64	0
cyclo-$C_6H_{11}NC$	Br_2	EtOH	—	65	—[d)]
cyclo-$C_6H_{11}NC$	Br_2	*n*-PrOH	—	60	—[d)]
cyclo-$C_6H_{11}NC$	Br_2	*i*-PrOH	—	33	—[d)]
cyclo-$C_6H_{11}NC$	Br_2	*n*-BuOH	—	58	—[d)]
cyclo-$C_6H_{11}NC$	Br_2	$PhCH_2OH$	—	47	—[d)]
t-BuNC	Br_2	MeOH	—	70	—[d)]
n-BuNC	Br_2	MeOH	—	43	—[d)]
PhNC	Br_2	MeOH	—	3	55
cyclo-$C_6H_{11}NC$	Cl_2	MeOH[e)]	—	43[g)]	34
cyclo-$C_6H_{11}NC$	Cl_2	MeOH[f)]	—	54[g)]	27
cyclo-$C_6H_{11}NC$	Cl_2	MeOH[e)]	$HgCl_2$ (50)	25[g)]	11[h)]

a) Isolated yield (based on isocyanide). b) Isolated as its HCl salt. c) Reaction conditions: near 5 °C, 1 h and 20—25 °C, 1 h. d) Not determined, but it seems to be 5% or so. e) Reaction conditions: near 5 °C, 2 h and 20—25 °C, 7 h. f) Reaction conditions: near 5 °C, 2 h and 65 °C, 2 h. g) Determined by GLC. h) Other product, probably $C_6H_{11}N(HgCl)\,CCl_2(OMe)$, 38% (based on isocyanide).

the case of chlorine can be ascribed to the higher reactivity of **2** where X=Br, while the poorer yields of amine can be explained by the same reason.

The effect of the alcohol component on the yields of **1** was not so significant, except for one case. In the reaction with isopropyl alcohol, the considerable decrease in the yield of **1** may be due mostly to the decreased stability of the corresponding **4** (R=cyclo-C_6H_{11}, R′=*i*-Pr, X=Br). In connection with this, we previously observed a considerable formation of cyclohexyl isocyanate, which probably arose from the initially formed **4** (R=cyclo-C_6H_{11}, R′=*t*-Bu, X=Cl), in the reaction of cyclohexyl isocyanide with *t*-butyl hypochlorite.[1)] Besides, in the hydrolysis of alkyl chloroformates (ClCOOR″) where R″=secondary alkyls, such as *i*-Pr and cycloalkyls, their relatively sacile ionization by means of the S_N1 mechanism and the succeeding rapid decomposition leading to olefins and/or secondary alcohols have been cited, in contrast to the cases of R=primary alkyls.[6,7)] Thus, a partial loss of **4** (R=cyclo-C_6H_{11}, R′=*i*-Pr, X=Br) by a limilar process is highly probable.

We also have to note the effect of a Lewis-acid catalyst on the reaction. When 10 mol% of $HgCl_2$ was added as a catalyst in the cyclohexyl isocyanide-bromine-methanol reaction, a 12% decrease in the yield of **1** (R=cyclo-C_6H_{11}, R′=Me) was observed. This result is somewhat surprising in view of our previous information that $HgCl_2$ is the most efficient catalyst for the formation of **1** from isocyanides and halogens in cyclic ethers.[9)] Further, the addition of a larger amount of $HgCl_2$ resulted in the formation of another product, besides considerable decreases in the yields of both **1** and amine. That is, when 50 mol% of $HgCl_2$ was added, 18 and 23% drops in the yields of **1** and cyclohexylamine respectively were observed, while a white, solid product was formed in a considerable quantity. In this case, it was observed that the reaction mixture became homogeneous by the dissolution of $HgCl_2$ at an earlier stage, and that then a white solid separated out gradually. Here, the existence of an equilibrium (Eq. 3) may be presumed for the homogeneous system, because a marked solubility of $HgCl_2$ in alcohols and the existence of a similar equilibrium between $HgCl_2$ and HgCl(OH) in an aqueous $HgCl_2$ solution has been known.[10)]

$$HgCl_2 + MeOH \rightleftharpoons HgCl(OMe)\ HCl + HCl \qquad (3)$$

The same solid was also obtained by the reaction of **2** (R=cyclo-C_6H_{11}, X=Cl) with equimolar $HgCl_2$ in methanol. On the contrary, we previously observed that a similar treatment in tetrahydrofuran did not afford any product and that most of the **2** was recovered.[7)] The above solid was soluble in dil. hydrochloric acid and was reprecipitated by adding aqueous potassium carbonate. This suggests the presence of a basic nitrogen other than the C=N group. The absence of this group was also confirmed by the IR spectrum. The result of the elemental analysis of the solid corresponded to that for $C_8H_{14}NCl_3Hg$. Based on these facts, it was supposed that the product was a 1 : 1 adduct of either **2** (R=cyclo-C_6H_{11}, X=Cl) and HgCl(OMe) or **4** (R=cyclo-C_6H_{11}, R′=Me, X=Cl) and $HgCl_2$ (see Experimental). Considering both the substantial decrease in the amine yield and the probably high reactivity of HgCl(OMe) compared with $HgCl_2$, the former structure, *i.e.*, $C_6H_{11}N(HgCl)CHCl_2(OMe)$, is highly probable. An analogous example which involves an electrophilic attack of $HgOAc^+$ on the methine N of aromatic aldehyde arylhydrazone has been reported in a recent article.[11)]

Next, when *N*-bromo- and *N*-chlorosuccinimide (NBS and NCS respectively) were used as halogen sources, the yields of **1** were generally not so good as in the case of halogens, even when a large excess of alcohol was used. Besides, the formation of *N*-carbamoylsuccinamates (**7**), a succinimide-incorporated product,

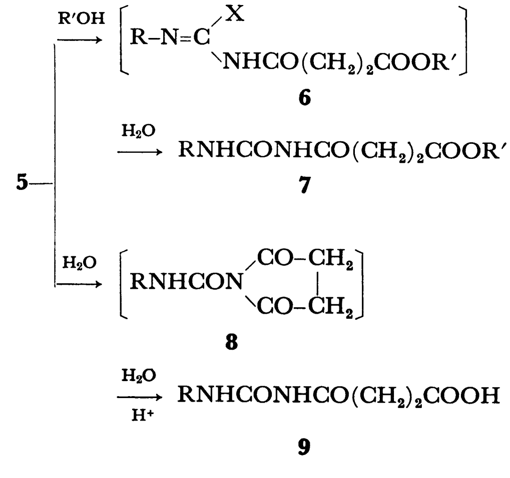
Table 2. Reaction of cyclohexyl isocyanide with *N*-halosuccinimides and alcohols

Isocyanide, 20 mmol; NBS or NCS, 20 mmol; alcohols, 10 ml. Reaction conditions: near 5 °C, 1 h and 20—25 °C, 1 h.

Halide	R′OH	Product and yield/%[a]		
		1($R=C_6H_{11}$)	**7**($R=C_6H_{11}$)	**9**($R=C_6H_{11}$)
NBS	MeOH	49	22	2
NBS	MeOH[b]	51	12	3
NBS	MeOH[c]	45	26	0
NBS	EtOH	40	29	1
NBS	*i*-PrOH	10	9	16[d]
NBS	$PhCH_2OH$	38	0	0
NCS	MeOH	34	26	10
NCS	EtOH	27	39	7
NCS	*n*-PrOH	29	39	6

a) Isolated yield (based on isocyanide). b) Thirty ml of MeOH was used. c) Reaction conditions: near 5 °C, 1 h and 20—25 °C, 6 h. d) Other product, *N*-(cyclohexylcarbamoyl)succinimide (**8**), 18%.

in lower yields was observed. In the cyclohexylamine–NBS–methanol reaction, a change in the amount of methanol from 10 ml (*ca.* 10 equiv.) to 30 ml (*ca.* 30 equiv.) resulted in a slight increase (only 2%) in the yield of **1** and a considerable decrease in that of **7**. Some results are shown in Table 2. The reaction proceeded readily even in the dark. Further, it is generally accepted that *N*-halo imides act as electrophiles in polar media. Thus, a pathway *via* the haloimidoyl cation, **3**, formed by the electrophilic attack of X^+ (or the highly polarized halo imide), may be suggested (Eq. 4). Here, both **8** and **9** are products formed from **5** during the work-up procedure.



(4)

In the cyclohexyl isocyanide–NBS–isopropyl alcohol reaction, the marked decrease in the yield of the corresponding **1** is due to the lower stability of the corresponding **4** described above, and a steric hindrance in the ring-opening alcoholysis of the isocyanide–NBS adduct, **5**, resulted in a poor yield of the corresponding **7**. The reaction in benzyl alcohol appears to be somewhat complex, and none of products derived from **5** are found. The reason for this is not clear, but the competitive consumption of NBS for the oxidation of benzyl alcohol may be postulated, at least in part, since its facile oxidation with *N*-bromoacetamide is known.[12]

It is obvious from Table 2 that NBS is more effective than NCS as a halogen source for the formation of **1** from isocyanides, but no sufficient explanation of the observed different selectivities of the cation **3** (X=Br and Cl) can be offered at the present time, since the mechanistic details of the **3**-forming stage(s) and the relative stabilities of **3** are not yet available.

Experimental

The GLC analyses were carried out on a Shimadzu 5APTF apparatus, using EGSS-X(30%)-Chromosorb W(1 m) (with N_2 as the carrier gas). The ^1H NMR, IR, and mass spectra recorded on Varian A-60, Hitachi EPI-S2, and JEOL-01SG spectrometers respectively. The isocyanides (RNC) were prepared by the method of Ugi *et al.*[13] R=*n*-Bu, bp 119—120 °C (lit,[13] bp 116—117 °C/730 Torr); R=cyclo-C_6H_{11}, bp 69—71 °C/22 Torr (lit,[13] bp 56—58 °C/11 Torr); R=*t*-Bu, bp 91—92 °C (lit,[13] bp 91—92 °C/730 Torr); R=Ph, bp 60 °C/19 Torr (lit,[13] bp 50—51 °C/11 Torr). Commercial organic materials were used after distillation or recrystallization. Commercial inorganic materials were used without further purification.

Reaction of Isocyanides with Halogens and Alcohols. Some typical examples are shown below.

a): Into a stirred solution of bromine (3.20 g, 20 mmol) in methanol (16 ml), a solution of cyclohexyl isocyanide (2.18 g, 20 mmol) in methanol (4 ml) was added over a 0.5-h period, the temperature being maintained at near 5 °C by cooling with ice water. The mixture was stirred for an additional 0.5 h at that temperature and for 5 h at room temperature, and then added to a stirred suspension of $CaCO_3$ (4 g) in water. After the mixture had been stirred for 2 h at room temperature, the precipitated inorganic substance was filtered off and the filtrate was extracted with ether. Then the organic layer separated from the aqueous one washed with aqueous K_2CO_3 and water, and dried over anhydrous $MgSO_4$, and most of the solvent was evaporated. Distillation afforded crude methyl cyclohexylcarbamate (**1**, R=cyclo-C_6H_{11}, R′=Me) (2.40 g, 76% yield). The pure compound was obtained by redistillation; bp 82 °C/3 Torr, mp 72—74 °C (lit,[14] mp 75 °C); IR (KBr), 3380, 1530 (NH), 1690 (CO), and 1220, 1052 cm^{-1} (C–O–C); ^1H NMR ($CDCl_3$), $\delta=4.50$ (1H, b), 3.50 (3H, s), 3.30 (1H, b), 2.1—0.9 (10H, m). The filtrate was made basic (pH *ca.* 10) with aqueous K_2CO_3 and steam-distilled. The aqueous distillate was made acidic with concd. HCl and dried up to afford cyclohexylamine hydrochloride (0.11 g, 4% yield) (mp 208—209 °C), which was identified by the mixed-melting-point method.

When the amount of methanol was reduced to a half volume (total 10 ml) in the above reaction, a yellowish-orange solid separated out from the reaction mixture during an early stage of the reaction, and finally the stirring became difficult. After all the isocyanide had been added, the solid was filtered off, washed with a small amount of methanol, and dried. The solid weighed 1.93 g. From the filtrate, the unreacted isocyanide (9 mmol) was recovered. Assuming that the above solid is a 1 : 1 complex of **3** (R=cyclo-C_6H_{11}, X=Br) and Br_2, the yield of the solid is estimated to be 82% (based on the isocyanide consumed). In addition, when the solid (0.43 g, 1 mmol) was dissolved in methanol (2 ml) and this solution was allowed to stand for 5 h at room temperature, the above carbamate (0.11 g, 70% yield) was obtained after the usual work-up procedure.

b): Chlorine gas (4.26 g, 60 mmol) was bubbled into a stirred solution of cyclohexyl isocyanide (2.18 g, 20 mmol) in methanol (20 ml) over a period of 1.5 h at near 5 °C. After being maintained for 0.5 h at the same temperature and for 7 h at room temperature with stirring, the mixture was poured into water. The resulting mixture was stirred for 2 h at room temperature and then worked-up as has been described in *a*). A GLC analysis of the evaporation residue, using bibenzyl as the internal standard, showed the formation of the expected carbamate (1.35 g, 43% yield). From the acidic aqueous layer, cyclohexylamine hydrochloride (0.92 g, 34%) was isolated.

When this reaction was carried out in the presence of $HgCl_2$ (2.72 g, 10 mmol), a light brown solid was separated out by pouring the reaction mixture into ice water. This solid was dissolved in dil. HCl, and the subsequent neutralization of this acidic solution afforded a white precipitate (3.41 g), which was soluble in acetic acid, but insoluble in ether, chloroform, and methanol. This solid gave analytical figures corresponging to a 1 : 1 adduct of either **2** (R=cyclo-C_6H_{11}, X=Cl) and HgCl(OMe) or **4** (R=cyclo-C_6H_{11}, R′=Me, X=Cl) and $HgCl_2$. Found: C, 20.77; H, 3.72; N, 3.88%. Calcd for $C_8H_{14}NC_{13}Hg$. C, 21.49; H, 3.16; N, 3.13%. The IR spectrum revealed the absence of any C=N bond.

The physical properties and analytical data of other pure **1** substances are as follows. cyclo-C_6H_{11}NHCOOR′: R′=Et, bp 87 °C/3 Torr, mp 54—55 °C (lit,[15] bp 123 °C/11 Torr, mp 56 °C). R′=*n*-Pr, bp 96—98 °C/3 Torr, mp 39—40 °C (lit,[16] mp 40—41 °C). R′=*i*-Pr, bp 84—85 °C/3 Torr, mp 65—66 °C (lit,[17] mp 66.5—67 °C). R′=*n*-Bu, bp 110—112 °C/3 Torr, mp 50—52 °C (Found: C, 66.19; H, 10.59; N, 6.62%. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03%). ^1H NMR ($CDCl_3$) δ=4.40 (1H, b), 3.90 (2H, t, J=6.0 Hz), 3.35 (1H, b), 1.8—1.05 (4H, m), 0.9 (3H, t, J=6.0 Hz), 2.05—0.9 (10H, m). R′=CH_2Ph, mp 85—87 °C (from 50% aq. EtOH) (Found: C, 71.73; H, 8.32; N, 5.96%; M+, 233 Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00%; M, 233). ^1H NMR ($CDCl_3$) δ=7.05 (5H, s), 4.90 (2H, s), 4.40 (1H, b), 3.40 (1H, b), 2.1—0.8 (10H, m). RNHCOOMe: R=*n*-Bu, bp 96 °C/20 Torr (lit,[18] bp 92 °C/15 Torr). R=*t*-Bu, bp 64 °C/20 Torr (lit,[18] bp 63.3 °C/17 Torr). R=Ph, bp 125—126 °C/10 Torr, mp 44—46 °C (lit,[19] mp 47 °C).

Reaction of Isocyanides with N-*Halosuccinimides and Alcohols*. A typical example is given below. A solution of cyclohexyl isocyanide (2.18 g, 20 mmol) in methanol (4 ml) was stirred into a solution of NBS (3.56 g, 20 mmol) in methanol (6 ml) over a 0.5-h period at near 5 °C. After the mixture had been stirred for an additional 0.5 h at the same temperature and for 1 h at room temperature, the reaction mixture was poured into water and allowed to stand for 2 h at room temperature with stirring. The work-up procedure was the same as above. Distillation gave the expected carbamate (1.54 g, 49% yield), leaving a solid residue of crude methyl *N*-(cyclohexylcarbamoyl)succinamate (**7**, R=cyclo-C_6H_{11}, R′=Me) (1.13 g, 22% yield). The recrystallization of this residue from 50% aq EtOH afforded the pure compound; mp 95—96 °C (Found: C, 56.37; H, 8.09; N, 10.89%; M+, 256. Calcd for $C_{12}H_{20}N_2O_4$: C, 56.24; H, 7.87; N, 10.93%; M, 256. IR (KBr) 3300, 3150, 1550 (NH), 1740 (ester CO), 1710 (urethane CO), 1685 (amide CO), 1220, 1175 cm^{-1} (C–O–C). ^1H NMR ($CDCl_3$) δ=9.70 (1H, s), 8.05 (1H, d, J=7.0 Hz), 3.60 (3H, s), 3.45 (1H, b), 2.70 (4H, s), 2.1—0.9 (10H, m). When the aqueous layer was allowed to stand for a few days, needles of crude *N*-(cyclohexylcarbamoyl)succinamic acid (**9**, R=cyclo-C_6H_{11}) (0.09 g, 2% yield) separated out. A pure compound was obtained by recrystallization; mp 170—173 °C (lit,[1] mp 162—164 °C).

The ^1H NMR ($CDCl_3$) data of other **7** and **8** substances are as follows. cyclo-$C_6H_{11}NHCONHCO(CH_2)_2COOR'$: R′=Et, δ=9.70 (1H, s), 8.10 (1H, d, J=8.0 Hz), 4.05 (2H, q, J=7.0 Hz), 3.55 (1H, b), 2.60 (4H, s), 1.25 (3H, t, J=7.0 Hz), 2.1—0.9 (10H, m). R′=*n*-Pr, δ=9.80 (1H, s), 8.10 (1H, d, J=8.0 Hz), 3.90 (2H, t, J=6.0 Hz), 3.55 (1H, b), 2.60 (4H, s), 1.60 (2H, m, J=6.0 Hz), 0.90 (3H, t, J=6.0 Hz), 2.1—0.9 (10H, m). R′=*i*-Pr, δ=9.20 (1H, s), 8.05 (1H, d, J=7.8 Hz), 4.80 (1H, m, J=6.0 Hz), 3.55 (1H, b), 2.60 (4H, m), 1.20 (6H, d, J=6.0 Hz), 2.0—0.9 (10H, m). **8** (R=cyclo-C_6H_{11}); δ=7.0 (1H, s), 3.65 (1H, b), 2.70 (4H, s), 2.1—1.0 (10H, m).

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