Behavior of *N,N*-Dichloroamides and *N,N*-Dichlorocarbamates toward Nucleophiles[1]

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Abstract: Exposure of *N,N*-dichloroamides and *N,N*-dichlorocarbamates to sodium methoxide or potassium hydroxide in methanol gave moderate to high yields of the corresponding methyl esters and nitrogen gas. The reaction appears to involve chloronitrene (**4**) as an intermediate *via* dichloroamide ion (**3**). The low relative rate of nitrogen evolution from *N,N*-dichlorourethane (**10**) *vs. tert*-butyl *N,N*-dichlorocarbamate (**18**) suggests that the rate-determining step may be loss of chloride from **3**. *N*-Chloro-*N*-methylurethane reacted more sluggishly than its *N,N*-dichloro analogs, and the products were somewhat different. Reaction of **10** with benzylamine gave *N,N*-dichlorobenzylamine and urethane.

Our treatment of the historical background will be limited to the response of *N*-haloamides and *N*-halocarbamates toward nucleophiles. The most familiar reaction involving *N*-haloamides is the Hofmann degradation.[4] Studies with the sodium salt of *N*-bromoacetamide indicated that this type of species was involved as an intermediate during degradation.[5,6] Although an acidic amide proton is not available, *N*-bromosuccinimide on exposure to strong base yielded[4] a Hofmann rearrangement product. When an *N-tert*-butyl group was present, as in $C_6H_5CH_2CONCl$-*t*-C_4H_9, treatment with *tert*-butoxide afforded a product containing an α lactam structure.[7] Prior work most closely related to the present investigation involves *N,N*-dihaloamides. Hofmann observed that, in the presence of caustic, *N,N*-dibromoacetamide was converted to acetic acid, nitrogen, and hypobromite.[8] *N,N*-Dichlorobenzamide yielded sodium benzoate with sodium carbonate, and gave *N,N'*-diphenylurea with ammonia.[9] In the presence of sodium hydroxide, however, decomposition occurred with formation of nitrogen, phenyl isocyanate, benzonitrile, and benzoic acid.

The literature pertinent to the carbamate area is summarized elsewhere.[10]

The present work is concerned with the reaction of *N*-chloroamides and *N*-chlorocarbamates with various nucleophiles. Most of the studies involved the *N,N*-dichloro derivatives. Particular attention was given to the mechanistic features.

Results and Discussion

Preparation of Starting Materials. The desired substrates for this study were *N,N*-dichloroamides and *N,N*-dichlorocarbamates.

The *N,N*-dichloro derivatives were prepared from the amide or carbamate by chlorination with calcium hypochlorite,[10] rather than chlorine.[11] Compounds synthesized in this manner were the *N,N*-dichloro derivatives of valeramide, 5-chlorovaleramide, urethane, *tert*-butyl carbamate, and phenethyl carbamate. The *N*-monochloro derivative of *N*-methylurethane was also obtained by this method.

The requisite amides and carbamates were generated in various ways. Valeramide and 5-chlorovaleramide were prepared from the corresponding acid chlorides. Stannic chloride catalyzed condensation of phenethyl alcohol with urea[12] produced phenethyl carbamate in 34% yield. *N*-Methylurethane was obtained by treatment of ethyl chloroformate with methylamine.[13]

***N,N*-Dichlorovaleramide and Sodium Methoxide.** *N,N*-Dichlorovaleramide (**1**), a new compound, is a distillable, yellow liquid. Iodometry showed that the preparation contained 94% of the theoretical amount of active chlorine. The impurity may be in the form of valeramide (6%) or, more likely,[14] *N*-monochlorovaleramide (12%). Yields are based on the latter condition, with the further assumption that the *N*-monochloroamide may also react (see below).

Treatment of **1** with sodium methoxide in methanol at 0° resulted in immediate quantitative decomposition according to eq 1. The main organic product was methyl valerate (**2**),

$$\underset{\mathbf{1}}{2CH_3(CH_2)_3CONCl_2} + 3NaOMe \longrightarrow \underset{\mathbf{2}}{2CH_3(CH_2)_3CO_2Me} + N_2 + 3NaCl + MeOCl \quad (1)$$

identified by comparison (glpc, ir, nmr) with authentic material. A low yield of methyl formate was also present, which most likely arose from oxidation of methanol.[10] The inorganic materials, nitrogen and sodium chloride, occurred in good yields (Table I).

The actual amounts of methyl valerate and nitrogen formed were greater than could possibly be produced by the *N,N*-dichloroamide (88%) present in the impure starting material. On the assumption that the *N*-monochloroamide also participates in a similar fashion, the yield figures are reasonable. The monochloro derivative is presumably converted into the reactive dichloro form as shown in eq 2. In

$$RCOCNHCl \xrightarrow{NaOMe} RCOCNCl^-Na^+ \xrightarrow{MeOCl} RCOCNCl_2 + NaOMe \quad (2)$$

this manner *N*-monochlorovaleramide can participate with resultant consumption of positive chlorine. Indeed, the data in Table I lend support to this premise. Only 5% of the original positive chlorine remained at the end of reaction, as opposed to 26% from the reaction of DCU with methoxide.[10]

Mechanism. The overall reaction suggests attack of methoxide on carbonyl, generating dichloroamide ion **3** (Scheme I). Loss of chloride from **3** would produce chloronitrene (**4**) which then dimerizes to dichlorodiazene (**5**). Ni-

Scheme I

$$RCONCl_2 + R'O^- \longrightarrow RCO_2R' + \underset{\mathbf{3}}{NCl_2^-}$$

$$\mathbf{3} \xrightarrow{-Cl^-} \underset{\mathbf{4}}{NCl} \xrightarrow{\text{dimerize}} \underset{\mathbf{5}}{ClN{=}{=}NCl} \xrightarrow[-Cl_2]{} N_2$$

trogen results from decomposition of **5**. A more detailed discussion and evidence for this mechanistic pathway are presented elsewhere with DCU as substrate.[10] Results from a related system indicate that this course is followed when the amide nitrogen contains two electron-withdrawing groups.

Table I. *N,N*-Dichloro Compounds with Sodium Methoxide

$RCONCl_2$, R =	Products, % yield				
	RCO_2Me	N_2[a]	NaCl[b]	Positive Cl[c]	Other
n-Bu[d]	89	102	81	5	6[e]
$Cl(CH_2)_4$[f]	83	62	78	30	2[g]
t-BuO[d]	54	79	39	13	24[h]
$PhCH_2CH_2O$[d]	69	102	61	5	7[i]

[a] Assuming all evolved gas is nitrogen. [b] Yield based on sodium. [c] % of original. [d] 25 mmol of NaOMe. [e] HCO_2Me, 6%. [f] Stoichiometric amount of NaOMe (18.7 mmol). [g] 5-Chlorovaleramide, 2%. [h] Isobutylene, 7%; *t*-BuOMe, 7%; HCO_2Me, 10%. [i] $PhCH_2CH_2OH$, 7%.

For example, *N*-bromosuccinimide with strong base yielded $MeO_2C(CH_2)_2NHCO_2Me$,[4] presumably through the intermediacy of $MeO_2C(CH_2)_2\bar{C}ONCl$ which then underwent Hofmann rearrangement.

An alternate mechanism, initial attack of methoxide at a chlorine atom, was also considered (Scheme II). The general approach of Scheme II is discussed in further detail elsewhere,[10] including evidence in opposition.

Scheme II

$$RCONCl_2 \xrightarrow[-R'OCl]{R'O^-} \underset{6}{RCO\bar{N}Cl} \xrightarrow[-Cl^-]{RCONCl_2} RCONClNClCOR \xrightarrow{-Cl_2} RCON{=}{=}NCOR \longrightarrow RCO_2R' + N_2$$

A third possibility involving radical intermediates is also conceivable. Thus, strong base might effect one-electron transfer[15] to the *N,N*-dichloro substrate, generating the *N*-chloro nitrogen radical **7** (Scheme III). Dimerization of **7** and loss of chlorine would give the diacyldiazene **8** which should react rapidly with base giving the ester and nitrogen.[16] Studies with DCU-^{15}N indicate that this pathway is unlikely.[10]

Scheme III

$$RCONCl_2 \longrightarrow \underset{7}{RCON\cdot}Cl$$

$$7 \xrightarrow{\text{dimerize}} RCONClNClCOR \xrightarrow{-Cl_2} RCON{=}{=}NCOR \longrightarrow RCO_2R' + N_2$$

$$\underset{8}{}$$

***N,N*-Dichloro-5-chlorovaleramide and Sodium Methoxide.** *N,N*-Dichloro-5-chlorovaleramide (**9**) was obtained in an impure state. It distilled with extensive decomposition giving material only slightly purer than the raw reaction product. Iodometry indicated 84% of the calculated amount of positive chlorine, with the impurity consisting of either free amide (16%) or *N*-monochloroamide (32%). Yields were calculated based on the latter assumption and on the hypothesis that the monochloro derivative enters the reaction as in eq 2.

In the presence of sodium methoxide, **9** was smoothly converted to methyl 5-chlorovalerate (identified by the ir spectrum),[17a] nitrogen, and sodium chloride. Yields are set forth in Table I. The reason for the discrepancy between the yields of nitrogen and ester is not clear, but it may be due to the impurity of the starting material.

Compound **9** has a chloromethyl group positioned favorably at the end of the hydrocarbon chain, permitting stereochemical interaction with the dichloroamino group. If dichloroamide were being generated, it might be able to effect displacement of chloride ion, at least to some extent. However, no methyl 5-aminovalerate or methyl 4-cyanobutyrate was formed according to glpc or tlc. Apparently, diffusion of NCl_2^- from the parent molecule is very rapid.

Table II. Reaction of *N,N*-Dichlorocarbamates with Potassium Hydroxide

RO_2CNCl_2, R =	Products, % yield[a]				
	$ROCO_2Me$	N_2[b]	KCl[c]	CO_2	Other
Et	42	103			7[d]
Et	36			9[e]	4[f]
Et	45	104	101		3[g]
Et	73[h]			6[h]	20[i]
$PhCH_2CH_2$	57	103	96		

[a] Yields not determined for blanks. [b] Assuming all evolved gas is nitrogen. [c] % yield based on potassium. [d] HCO_2Me, 2%; HCO_2Et, 1%; $MeOCO_2Me$, 3%; 1% unidentified. [e] Solution not acidified after reaction. [f] HCO_2Me, 2%, 2% unidentified. [g] HCO_2Me, 3%. [h] Solution acidified after reaction. [i] HCO_2Me, 9%; HCO_2Et, 6%; 5% unidentified.

DCU and Potassium Hydroxide. Addition of potassium hydroxide to a methanolic solution of DCU (**10**) at 0° resulted in vigorous evolution of nitrogen accompanied by precipitation of potassium chloride. The main organic product was ethyl methyl carbonate (**11**) (eq 3). Dimethyl carbonate, methyl formate, and ethyl formate were present as minor side products. Yield data for this system are summarized in Table II. Dimethyl carbonate was identified by means of its ir spectrum,[17b] whereas methyl and ethyl formate were characterized by comparison of glpc retention times with those of authentic materials. High yields of potassium chloride and nitrogen were produced. Ethyl methyl carbonate, on the other hand, was found in only 36–45% yield. The remaining 55–64% is probably in the form of potassium ethyl carbonate (**12**) for the most part. Since some carbon dioxide (9%) is produced, the indicated equilibrium,[18] eq 4, appears to be involved. In addition, the yield of ethyl methyl carbonate was increased to 73% when the mixture was acidified at the end of reaction, presumably *via* **13**. Ester **11** most likely arises from attack[10] of methoxide on $EtOCONCl_2$ (*cf.* Scheme I), by analogy to esterification of acyl halides with alcoholic caustic.[19]

$$\underset{10}{EtOCONCl_2} + 2KOH \xrightarrow{MeOH} \underset{11}{EtOCO_2Me} + \tfrac{1}{2}N_2 + KCl \quad (3)$$

$$\underset{12}{EtO_2CO^-K^+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{13}{EtO_2COH} \rightleftharpoons EtOH + CO_2 \quad (4)$$

DCU and Benzylamine. Addition of DCU to a solution of benzylamine in tetrahydrofuran produced an immediate reaction resulting in precipitation of benzylamine hydrochloride (33% yield). The volatile products determined by glpc were benzaldehyde (5% yield), benzonitrile (47% yield), and urethane (50% yield) (eq 5). In addition, iodometry revealed the presence of 34% of the original positive chlorine content. The products and their yields suggest that the initial reaction consists of transfer of chlorine from DCU to benzylamine, generating *N,N*-dichlorobenzylamine (**14**) (eq 6). Since Datta and Gupta demonstrated that *N*-monochlorourethane is able to chlorinate benzylamine,[20] this step is reasonable for DCU as well. Dehydrohalogenation of *N,N*-dichloramines by base, which is well established,[21] would in this case generate the *N*-chloroimine **15**. Hydrolysis by small amounts of water produces benzaldehyde. Since removal of a second mole of hydrogen chloride

$$EtO_2CNCl_2 + PhCH_2NH_2 \longrightarrow PhCHO + PhCN + EtO_2CNH_2 \quad (5)$$

from **15** is also facile,[21] rationale is provided for the major product, benzonitrile.

To bolster these proposals, a reverse addition experiment was conducted. Benzylamine was added to DCU so that at no time were appreciable concentrations of the free amine available to promote dehydrohalogenation. At the end of reaction, the mixture was diluted with water, precipitating the organic product. Benzylamine and urethane, being water soluble, were left in solution. The yellow oil which separated gave ir and nmr spectra consistent with those of structure **14,** and iodometric titration indicated that 91% of

$$\mathrm{EtO_2CNCl_2} + \mathrm{PhCH_2NH_2} \longrightarrow \underset{\mathbf{14}}{\mathrm{PhCH_2NCl_2}} + \mathrm{EtO_2CNH_2} \quad (6)$$

$$\mathrm{PhCH_2NCl_2} \xrightarrow{-\mathrm{HCl}} \underset{\mathbf{15}}{\mathrm{PhCH{=}NCl}} \xrightarrow{\mathrm{H_2O}} \mathrm{PhCHO}$$

$$\mathrm{PhCH{=}NCl} \xrightarrow{-\mathrm{HCl}} \mathrm{PhCN}$$

the calculated quantity of positive chlorine was present. As further structural confirmation, authentic **14** was prepared by treating benzylamine with excess calcium hypochlorite. The product gave an ir spectrum identical with that of material from the DCU reaction.

The reaction of DCU with benzylamine is completely different from its reaction with the more active nucleophiles, OH^- and MeO^-. Therefore, the reaction of *N,N*-dichlorocarbamates with nucleophiles obviously does not proceed through the same mechanism in all cases. Klopotek[22] observed attack of benzylamine at the carbonyl group of isopropyl *N,N*-difluorocarbamate, in contrast to the present finding. The change in behavior may be rationalized on the basis of the difference in polarity of the N–F *vs.* the N–Cl bond, the steric bulk of chlorine relative to fluorine, the presumed greater stability of NF_2^-, and the inductive effect of halogen on the positive nature of the carbonyl carbon.

Phenethyl *N,N*-Dichlorocarbamate and Sodium Methoxide or Potassium Hydroxide. Since phenethyl *N,N*-dichlorocarbamate (**16**) could not be readily purified, the reactions were carried out with the crude material, which was about 90% pure. Yields are based on the purity indicated by iodometry. Carbamate **16** gave with sodium methoxide a good yield of methyl phenethyl carbonate (**17**) and essentially quantitative evolution of nitrogen (Table I). The authentic carbonate for comparison was synthesized by pyridine-catalyzed condensation of phenethyl alcohol with methyl chloroformate. A low yield of phenethyl alcohol was also present, presumably from transesterification of **17.**

With potassium hydroxide, the reaction was analogous to the one observed with DCU; yields are given in Table II. The main product was methyl phenethyl carbonate (**17**), in somewhat higher yield than the carbonate from DCU. No other volatile materials were observed.

The aromatic nucleus of **16** should be susceptible to attack by chloronitrene. For example, cyanonitrene, formed by thermal decomposition of cyanoazide, yields ring expansion products (azepines) with aromatics of various types. Upon acid hydrolysis, the isolated product is a substituted aniline[23] derived from rearrangement. Likewise, phenyl azidoformate underwent thermolysis to a nitrene which cyclized by insertion involving the aromatic nucleus.[24] However, neither sodium methoxide nor potassium hydroxide provided basic products corresponding to this type of reaction, *e.g., o-* or *p*-aminophenethyl methyl carbonate. Thus, **4,** if formed, does not react rapidly with the aromatic nucleus but instead quickly diffuses away.

***tert*-Butyl *N,N*-Dichlorocarbamate and Sodium Methoxide.** *tert*-Butyl *N,N*-dichlorocarbamate (**18**), a new compound, was obtained as a stable, distillable, yellow liquid. It reacted vigorously with sodium methoxide, but the yield of *tert*-butyl methyl carbonate (**19**) was substantially lower (54 *vs.* 89%) than the corresponding yield from **1** (Table I). The amount of nitrogen was also diminished. However, two new types of products, isobutylene and *tert*-butyl methyl ether, were discovered, which were identified by comparison of their glpc retention times with those of the authentic compounds. Characterization of **19** was accomplished through comparison (glpc, ir, nmr) with a sample of ester obtained from potassium *tert*-butoxide and methyl chloroformate.

Isobutylene and *tert*-butyl methyl ether evidently result from solvolysis of the *N,N*-dichloro substrate (eq 7). This

$$\underset{\mathbf{18}}{(\mathrm{CH_3})_3\mathrm{CO_2CNCl_2}} \longrightarrow (\mathrm{CH_3})_3\mathrm{C^+} + \underset{\mathbf{20}}{^-\mathrm{O_2CNCl_2}} \quad (7)$$

$$(\mathrm{CH_3})_3\mathrm{C^+} \xrightarrow{-\mathrm{H^+}} (\mathrm{CH_3})_2\mathrm{C{=}CH_2}$$

$$(\mathrm{CH_3})_3\mathrm{C^+} \xrightarrow[-\mathrm{H^+}]{\mathrm{MeOH}} (\mathrm{CH_3})_3\mathrm{COCH_3}$$

reaction involves the novel dichlorocarbamate leaving group **20.** Concerning the fate of this ion, one can only speculate. It may be stable as the sodium salt at moderate temperatures; on the other hand, it could conceivably fragment into carbon dioxide and dichloroamide ion (NCl_2^-). Since this process was only a minor side reaction, it was not pursued further.

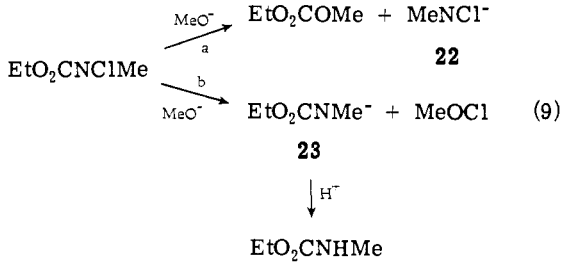
Our principal interest in **18** related to its reaction rate *vs.* that of DCU (**10**). The rates of nitrogen evolution were measured for the reaction of **10** and of **18** with sodium methoxide at 2°. Second-order rate constants[25] were calculated from the data,[3] giving values of 2.6×10^{-1} and 1.5×10^{-1} l. mol^{-1} sec^{-1} for **10** and **18,** respectively. The relative rate ($k_{Et}/k_{t\text{-}Bu}$) is only 1.7, which may not represent a significant difference considering the experimental error. In contrast to this, ethyl acetate underwent saponification (water, 20°) 57 times faster than *tert*-butyl acetate.[26] The rate difference was ascribed to steric hindrance associated with the *tert*-butyl group. The conclusion to be drawn from this experiment is that attack of methoxide on the carbonyl is not involved in the rate-determining step of the overall conversion of dichlorocarbamate to nitrogen. However, this may mean either that there is no attack at carbonyl, or, more likely, that some other reaction in the mechanistic pathway is the slow step, *e.g.*, loss of chloride from NCl_2^-. In an analogous system, loss of chloride from the trichloromethyl carbanion to give dichlorocarbene appears to be the rate-determining step in the basic hydrolysis of chloroform.[27]

***N*-Chloro-*N*-methylurethane and Sodium Methoxide.** *N*-Chloro-*N*-methylurethane (**21**), a colorless, distillable liquid, was selected for examination in order to determine the structural requirements of the reaction between *N*-chlorocarbamates and base. Another desire was to obtain mechanistic insight into the reactive intermediate which serves as precursor to nitrogen gas. However, **21** reacted with sodium methoxide only sluggishly at 0°, giving a mixture of compounds, dimethyl carbonate (12%), ethyl methyl carbonate (1%), methyl *N*-methylcarbamate (17%), and *N*-methylurethane (10%), eq 8. No gas evolution was noted, and at the

$$\underset{\mathbf{21}}{\mathrm{EtO_2CNClMe}} + \mathrm{NaOMe} \longrightarrow \mathrm{MeO_2COMe} + \mathrm{EtO_2COMe} + \mathrm{MeO_2CNHMe} + \mathrm{EtO_2CNHMe} \quad (8)$$

end of the reaction period, 73% of the original positive chlorine content was still present. This substrate is much less reactive than the *N,N*-dichloro derivatives, indicating a large effect from substitution of methyl for chlorine.

The carbonate products may result from attack of methoxide ion at carbonyl to displace methylchloroamide ion **22** (eq 9, path a). The fate of **22** is unknown. Alternatively,



methoxide may attack at the chlorine atom, displacing the anion of *N*-methylurethane (**23**) (eq 9, path b). With both the carbonate- and carbamate-type products, transesterification might occur in the presence of strong base.

Experimental Section

Materials. In general, high purity commercial chemicals were used without further purification. Urethane and *tert*-butyl carbamate were obtained from Aldrich Chemical Co.

Analytical Procedures. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer with neat samples or with potassium bromide pellets using the 1601.8-cm^{-1} band of polystyrene for calibration. Nmr spectra were taken with a Varian T-60 instrument and are reported in parts per million relative to tetramethylsilane as internal standard. Gas chromatography was conducted on a Varian Aerograph 1720 by means of the indicated columns (0.25 in., copper), (column number, packing): (1) 20% Carbowax 20M on Chromosorb W (45–60 mesh), 10 ft; (2) molecular sieve 5A (30–60 mesh), 5 ft.

Quantitative glpc was accomplished by comparison of peak areas of solutions of crude products with those of solutions of authentic materials. Positive chlorine content of preparations of *N*-chloro compounds was determined by standard iodometric titration.[28] Melting and boiling points are uncorrected.

Valeramide. A brisk stream of ammonia was passed into a solution of valeryl chloride (20 g, 166 mmol) in tetrahydrofuran (200 ml) at 20° until reaction was complete. After the precipitated ammonium chloride was removed, the filtrate was evaporated, leaving a white solid. The crude amide was recrystallized once from chloroform–hexane (1:10), yielding 14.4 g (86%) of mica-like flakes, mp 103–106° (lit.[29a] mp 106°).

5-Chlorovaleramide. The procedure used for preparation of valeramide was employed. The product was obtained in 76% yield, mp 76–78° (lit.[30] mp 78°).

Phenethyl Carbamate. A previously described procedure[12] was used with modifications. A mixture of urea (60 g, 1 mol), phenethyl alcohol (122 g, 1 mol), and stannic chloride (10 g) was heated at 140–160° for 16 hr. Water (200 ml) was added, and the suspension was shaken vigorously. After the solid was removed by filtration and boiled with benzene (500 ml), the insoluble residue was collected. The cooled filtrate precipitated a mass of crystals. Crystallization from benzene afforded 56.6 g (34%) of phenethyl carbamate as white flakes, mp 88–90°. A small sample was recrystallized from benzene: mp 90–92° (lit.[31] mp 91–91.5°); ir (KBr) 3290 (NH), 1670 (C=O), 1325, 1114, 1082, 1072, 1042, 966, 910, 783, 767, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 2.87 (t, 2 H, $PhCH_2$), 4.23 (t, 2 H, OCH_2), 5.00 (broad s, 2 H, NH_2), and 7.20 (s, 5 H, C_6H_5).

***N*-Methylurethane.** A previous method[13] was used to afford 30 g (58%) of product: bp 69–72° (11 mm); $n^{28}D$ 1.4167 [lit.[13] bp 55–60° (12 mm)].

***N,N*-Dichloro Compounds.** The following procedure was used for all *N*-chloro compounds except DCU. To a suspension of the carbamate or amide (20 mmol) and calcium hypochlorite (40 mmol) in methylene chloride (50 ml) at 0° was added enough dilute hydrochloric acid (12%, 26 ml) during 25 min to dissolve the calcium hypochlorite. The two-phase, translucent yellow mixture was stirred at 0° for 1 hr, and then the layers were separated. The organic phase was washed with water and dried with sodium sulfate. Removal of solvent provided a mobile liquid which was distilled.

***N,N*-Dichlorovaleramide.** The dichloroamide was obtained in 69% yield as a yellow oil: bp 38° (0.3 mm); $n^{23}D$ 1.4722; purity by iodometry, 94%; ir (neat) 1730 (C=O), 1134, 1079, 752, and 693 cm^{-1}; nmr (CCl_4) δ 0.93 (t, 3 H, CH_3), 1.2–2.0 (m, 4 H, CH_2), and 2.63 (t, 2 H, $COCH_2$).

Anal. (iodometric titration). Calcd for $C_5H_9Cl_2NO$: Cl, 41.70. Found: Cl, 39.30.

***N,N*-Dichloro-5-chlorovaleramide.** Distillation of the crude product, which occurred with extensive decomposition, afforded 39% of the dichloroamide: bp 85–110° (0.25–0.35 mm); purity by iodometry, 84%; ir (neat) 1721 (C=O), 1107, and 751 cm^{-1}; nmr (CCl_4) δ 1.83 (m, 4 H, CH_2), 2.70 (t, 2 H, $COCH_2$), and 3.53 (t, 2 H, $ClCH_2$).

***tert*-Butyl *N,N*-Dichlorocarbamate.** The dichloro compound was isolated as a yellow oil (78% yield): bp 43.5–44° (2.5 mm); $n^{23}D$ 1.4510; ir (neat) 1765 (C=O), 1400, 1373, 1274, 1240, 1143, 1045, 994, 882, 820, 785, and 753 cm^{-1}; nmr (CCl_4) δ 1.53 (s, CH_3).

Anal. (iodometric titration). Calcd for $C_5H_9Cl_2NO_2$: Cl, 38.11. Found: Cl, 38.47.

Phenethyl *N,N*-Dichlorocarbamate. The crude material was used directly without further purification. Iodometric titration of an aliquot indicated 90% conversion to the desired product.

***N*-Chloro-*N*-methylurethane.** The above procedure (20 mmol of calcium hypochlorite) yielded 87% of the colorless *N*-chloro derivative: bp 52–53° (14.5 mm) [lit.[32] bp 57° (30 mm)]; $n^{23}D$ 1.4349; ir (neat) 1724 (C=O), 1318 (CO), 1181 (CO), 1028, 875, and 753 cm^{-1}; nmr ($CDCl_3$) δ 1.28 (t, 3 H, CH_2CH_3), 3.32 (s, 3 H, NCH_3), and 4.22 (q, 2 H, OCH_2).

Anal. (iodometric titration). Calcd for $C_4H_8ClNO_2$: Cl, 25.77. Found: Cl, 25.54.

***N,N*-Dichlorourethane.** A published procedure[10] yielded the dichloro derivative.

***N,N*-Dichloro Compounds with Sodium Methoxide.** The following procedure, with *N,N*-dichlorovaleramide as an example, was used in all cases. A solution of sodium methoxide (15 mmol) in methanol (14 ml) was added during 45 min to a solution of *N,N*-dichlorovaleramide (1.07 g, 10 mmol) in methanol (10 ml) at 0°. Volume changes were monitored with a gas buret. The reaction mixture was stirred for 20 min, and then volatile products were analyzed by glpc (column 1). The off-gas was analyzed by gc (column 2).

***N,N*-Dichlorocarbamates with Potassium Hydroxide.** The following procedure, with DCU as an example, was used in all cases. To a solution of DCU (3.95 g, 25 mmol) in methanol (35 ml) was added a solution of potassium hydroxide (3.3 g, 50 mmol) in methanol (25 ml) at about 0° during 1 hr. Volume changes were monitored with a gas buret. After gas evolution ceased, the reaction mixture was diluted with methanol to 100 ml, and volatile products were analyzed by glpc (column 1). In experiments in which carbon dioxide was to be measured, a slow flush of nitrogen was maintained through the system, and the off-gases were passed through calcium chloride and then through a tube filled with solid potassium hydroxide.

Kinetic Runs. A solution of sodium methoxide (4.00 mmol) in methanol (5 ml) was rapidly mixed with a solution of the *N,N*-dichlorocarbamate (2.00 mmol) in methanol (95 ml) at 2°. Nitrogen evolution was immediately monitored by means of a gas buret.

DCU to Benzylamine. A. DCU to Benzylamine. DCU (10.1 g, 64 mmol) was added during 50 min to a solution of benzylamine (13.7 g, 128 mmol) in tetrahydrofuran (40 ml) at 5–10°. After the reaction mixture had been stirred for an additional 25 min, the precipitated benzylamine hydrochloride was filtered off, washed with ether, and dried to yield 6 g (33%) of white powder, mp 245–250° (lit.[29b] mp 255–258°). Iodometric titration of the filtrate indicated 34% of the original positive chlorine content. Subsequent gas chromatography of the filtrate demonstrated the presence of benzaldehyde (5% yield) and benzonitrile (47% yield).

B. Benzylamine to DCU. A solution of benzylamine (6.1 g, 57 mmol) in methanol (20 ml) was added to DCU (9 g, 57 mmol) at 0° during 30 min. After the clear yellow solution had warmed to room temperature, water (50 ml) was added, and the organic layer was separated. Iodometric titration of the crude *N,N*-dichlorobenzylamine (6.8 g, 68%) indicated 91% of the theoretical positive chlorine; the ir spectrum was identical with that of material prepared from benzylamine and calcium hypochlorite.

***N*-Chloro-*N*-methylurethane with Sodium Methoxide.** A solution of sodium methoxide (14.5 mmol) in methanol (10 ml) was added during 15 min to a solution of *N*-chloro-*N*-methylurethane (2 g, 14.5 mmol) in methanol (20 ml) at 0°. The mixture was stirred at 0° for 1 hr; volume changes were monitored with a gas buret. The sodium chloride was filtered off, and an aliquot of the filtrate was titrated for positive chlorine. Finally the filtrate was analyzed by glpc (column 1).

N,N-Dichlorobenzylamine. A solution of benzylamine (10 g, 93 mmol) in water (55 ml) containing concentrated hydrochloric acid (34 ml) was added during 30 min to an ice-cold suspension of calcium hypochlorite (70%, 38 g, 186 mmol) in water (150 ml). After the viscous yellow-green suspension was stirred for another 10 min, the layers were separated. The crude yellow oil (bottom layer) weighed 11 g (67%): ir (neat) 1456, 755, and 702 cm^{-1}.

Anal. (iodometric titration). Calcd for $C_7H_7NCl_2$: Cl, 40.3. Found: Cl, 39.3.

Ethyl Methyl Carbonate. The ester was obtained according to a published procedure.[10]

Methyl Phenethyl Carbonate. A solution of methyl chloroformate (9.5 g, 0.1 mol) in ether (20 ml) was added slowly to a solution of phenethyl alcohol (12.2 g, 0.1 mol) and pyridine (7.9 g, 0.1 mol) in ether (50 ml). The resulting mixture was heated under reflux for 2 hr. Dilute hydrochloric acid was added, and the layers were separated. The organic layer was washed with water and dried with magnesium sulfate. Removal of solvent and distillation through a short Vigreux column provides 10.8 g (60%) of ester: bp 90-92° (0.35 mm), $n^{20}D$ 1.4962 [lit.[33] bp 85° (0.6 mm), $n^{20}D$ 1.4952]; ir (neat) 1736 (C=O), 1263 (CO), 986, 965, 934, 851, 794, 750, and 700 cm^{-1}; nmr (CCl_4) δ 2.90 (t, 2 H, $PhCH_2$), 3.63 (s, 3 H, OCH_3), 4.23 (t, 2 H, OCH_2), and 7.18 (s, 5 H, C_6H_5).

***tert*-Butyl Methyl Carbonate.** The procedure of Pozdnev and Chaman[34] gave a mixture of carbonates in low yield. The desired ester was isolated in pure form by preparative glpc (column 1): ir (neat) 1748 (C=O), 1397, 1370, 1282 (CO), 1258, 1161 (CO), 1104, 943, 867, 796, and 767 cm^{-1}; nmr (CCl_4) δ 1.45 (s, 9 H, $C(CH_3)_3$) and 3.63 (s, 3 H, OCH_3).

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Stable Acylpalladium(II) Complexes from Carbon Monoxide Insertion into Alkylpalladium(II) Complexes

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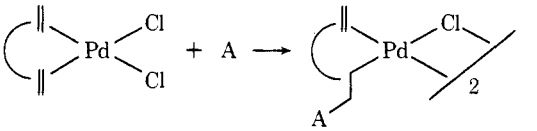
Abstract: Treatment of the unstable σ-alkylpalladium(II) complexes (**1**) resulting from nucleophilic attack of diethylamine on the palladium(II) chloride complexes of ethene, propene, and 1-butene (eq 4) with carbon monoxide results in the formation of stable acylpalladium(II) complexes (**2a–c**). These complexes are isolated in good yield and are well characterized. Treatment with Tl(AcAc) converts them to the corresponding acylpalladium(II) acetylacetonate complexes (**3a–c**).

Olefin palladium(II) complexes undergo facile nucleophilic attack upon the metal-complexed olefin, producing σ-alkylpalladium(II) complexes. With chelating diolefin complexes, the resulting σ-alkyl complexes (eq 1) are stable. Both the mechanism and stereochemistry of this reaction, as well as the physical and chemical properties of the σ-alkyl complexes, have been the subject of much study. Olefin-palladium(II) complexes in which the olefin is part



(1)

A = MeO^-,[1] R_2NH,[2] $\bar{C}H(COOR)$[3]

of a chelating system containing another ligand such as an