[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, TOKYO INSTITUTE OF TECHNOLOGY]

Pyrolysis of Acid Amides. II. Pyrolysis of 2-Haloacetamides

TERUAKI MUKAIYAMA, MAKOTO TOKIZAWA, AND HISASHI TAKEI

Received May 29, 1961

The pyrolysis of 2-haloacetamides has been studied. The pyrolysis of 2,2,2-trichloroacetamides at a temperature range from 500° to 600° gave the corresponding isocyanates in low yields and, unexpectedly, nitriles were obtained in fairly good yields along with hydrogen chloride and phosgene. The pyrolysis of 2,2-dichloroacetamides and 2-chloroacetamide gave the corresponding nitriles and isocyanates.

In a previous paper,[1] a successful method for the conversion of acetoacetamides into isocyanates and acetone by a pyrolytic reaction was reported. The products obtained by this process are quite unreactive with each other and pure isocyanates can be separated easily. This reaction is considered to proceed through essentially the same cis-type elimination reaction as is usual in pyrolytic reactions of esters and xanthates.[2]

In the present study, the pyrolysis of acid amides was extended to 2-haloacetamides which are considered to be adducts of isocyanates and halomethanes. It is possible to produce isocyanate and chloroform by the pyrolysis of 2,2,2-trichloroacetamide *via* two fairly stable ions, $RNHCO^+$ and CCl_3^-, formed by the breaking of the carbon-carbon bond of the acid amide.

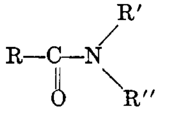
By use of the apparatus consisting of a quartz tube, 18 mm. in diameter and 120 cm. in length, the pyrolysis of 2,2,2-trichloroacetanilide was attempted at 520–530° under reduced pressure. Unexpectedly, a 61% yield of benzonitrile, a rearranged product, was obtained along with a 9% yield of phenyl isocyanate. Further study under various conditions also gave benzonitrile in a good yield and phenyl isocyanate was obtained only as a minor product (see Table II). The other products were chlorine, hydrogen chloride and phosgene, but chloroform could not be obtained. In each experiment, an increase in the pressure of the reaction system was noted, presumably due to carbon monoxide. The amount of undesirable char deposited in the reaction tube was greater than that found in the case of the acetoacetamides.

$$C_6H_5NHCOCl_3 \longrightarrow C_6H_5C{\equiv}N + C_6H_5N{=}C{=}O + COCl_2 + HCl + Cl_2 + (CO)$$

Under the same condition, the pyrolysis of various *para* substituted 2,2,2-trichloroacetanilides gave the corresponding nitriles and isocyanates. 2,2,2-Trichloro-4′-nitroacetanilide gave a 5% yield of *p*-nitrophenyl isocyanate which was not obtained in the case of 4′-nitroacetoacetanilide. On the other hand, *N*-benzyl-2,2,2-trichloroacetamide, an aliphatic *N*-substituted compound, gave benzyl cyanide in a 55% yield while the amount of benzyl isocyanate was very small (see Table III).

TABLE I

MELTING POINT OR BOILING POINT OF

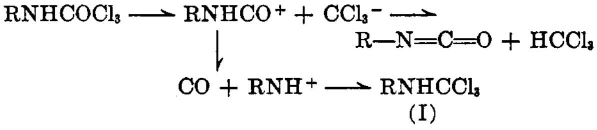


$$R{-}\underset{\underset{O}{\|}}{C}{-}N\begin{matrix}R' \\ R''\end{matrix}$$

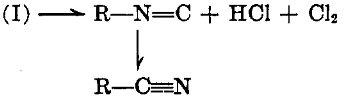
R	R′	R″	M. p. [b. p.]
CCl_3	C_6H_5	H	95 (95–97)[a]
CCl_3	p-$NO_2C_6H_4$	H	146 (146–147)[a]
CCl_3	p-$CH_3C_6H_4$	H	111–112 (111)[b]
CCl_3	$C_6H_5CH_2$	H	90–92 (90–91)[b]
$CHCl_2$	C_6H_5	H	118 (118–121)[a] (117.7)[c]
$CHCl_2$	p-$NO_2C_6H_4$	H	128–130 (127)[d]
$CHCl_2$	p-$CH_3C_6H_4$	H	155–156 (154)[e]
$CHCl_2$	p-$CH_3OC_6H_4$	H	131
$CHCl_2$	$C_6H_5CH_2$	H	94 (96.2)[c]
CH_2Cl	C_6H_5	H	135 (135)[a]
$CHCl_2$	C_6H_5	t-C_4H_9	82–83
CH_2Cl	C_6H_5	t-C_4H_9	[105–108/0.33 mm.]
CH_3	C_6H_5	t-C_4H_9	55 (55–56)[f]

[a] E. Votoček and J. Burda, *Ber.*, **48**, 1002 (1915). [b] J. Braun, F. Jostes, and W. Münch, *Ann.*, **453**, 133 (1927). [c] P. V. McKie, *J. Chem. Soc.*, **123**, 2215 (1923). [d] A. S. Wheelen and S. C. Smith, *J. Am. Chem. Soc.*, **45**, 1841 (1923). [e] H. W. Doughty, *J. Am. Chem. Soc.*, **47**, 1097 (1925). [f] W. J. Hickinbottom, *J. Chem. Soc.*, 947 (1933).

These results obtained by the gas phase decomposition of 2,2,2-trichloroacetamides suggest that there are two possible pathways in the reactions of ions, $RNHCO^+$ and CCl_3^-, initially formed by the breaking of the carbon-carbon bond of acid amide. When the anion preferentially accepts hydrogen atom from the cation, isocyanate and chloroform are produced. On the other hand, when the decomposition of the cation to form RNH^+ and carbon monoxide proceeds more rapidly than the preceding reaction, $RNHCCl_3$ (I) may be obtained. By eliminating hydrogen chloride and chlorine from I, isonitrile is formed, which in turn rear-



$$\begin{tikzcd}
RNHCOCl_3 \arrow[r] & RNHCO^+ + CCl_3^- \arrow[r] \arrow[d] & R{-}N{=}C{=}O + HCCl_3 \\
& CO + RNH^+ \arrow[r] & \underset{(I)}{RNHCCl_3}
\end{tikzcd}$$



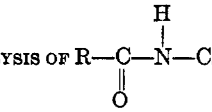
$$\begin{tikzcd}
(I) \arrow[r] & R{-}N{=}C + HCl + Cl_2 \arrow[d] \\
& R{-}C{\equiv}N
\end{tikzcd}$$

---

(1) T. Mukaiyama, M. Tokizawa, H. Nohira, and H. Takei, *J. Org. Chem.*, **26**, 4381 (1961).

(2) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

TABLE II

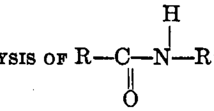


PYROLYSIS OF $\mathrm{R{-}C({=}O){-}N(H){-}C_6H_5}$ UNDER VARIOUS CONDITIONS

R	Material Charged, G.	Pyrolysis condition				Products		Material Recovered, G.
		Temp.	Press., mm.	Time, min.	Apparatus used	Nitrile, g. (%)	Isocyanate, g. (%)	
$\mathrm{CCl_3}$	5.0	520–530	6.0	70	[a]	1.3 (61)	0.2 (9)	
$\mathrm{CCl_3}$	5.0	530	7.0	40	[c]	0.4 (14)	0.05 (2)	2.1
$\mathrm{CCl_3}$	5.0	570	4.5–5.5	35	[b]	1.4 (66)	0.3 (13)	
$\mathrm{CCl_3}$	5.0	570	17.0	37	[b]	1.5 (67)	0.2 (8)	
$\mathrm{CHCl_2}$	5.0	560	5.0–10.0	70	[a]	1.1 (44)	0.1 (4)	
$\mathrm{CHCl_2}$	3.0	500	7.0–12.0	30	[a]	0.6 (40)	—	
$\mathrm{CH_2Cl}$	5.0	460	6.0	32	[a]	trace	—	
$\mathrm{CH_2Cl}$	5.0	520–530	1.5–3.5	51	[a]	0.4 (13)	0.03 (1)	
$\mathrm{CH_2Cl}$	5.0	570	15.0	14	[b]	trace	—	
$\mathrm{CH_2Cl}$	5.0	630	7.0	20	[a]	trace	—	

[a] Quartz tube is 120 cm. in length; *cf.* See Experimental. [b] Quartz tube is 60 cm. in length. [c] Quartz tube is 120 cm. in length without chips.

TABLE III



PYROLYSIS OF $\mathrm{R{-}C({=}O){-}N(H){-}R'}$, BY USE OF THE APPARATUS OF (A)

R	R′	Material Charged, G.	Pyrolysis Condition			Products		Material Recovered, G.
			Temp.	Press., mm.	Time, min.	Nitrile, g. (%)	Isocyanate, g. (%)	
$\mathrm{CCl_3}$	$\mathrm{C_6H_5}$	5.0	520–530	6.0	70	1.3 (62)	0.2 (9)	
$\mathrm{CCl_3}$	$p\text{-}\mathrm{NO_2C_6H_4}$	5.0	550	6.0	15	Trace	0.1 (5)	
$\mathrm{CCl_3}$	$p\text{-}\mathrm{CH_3C_6H_4}$	3.2	570	8.0–10.0	22	0.5 (33)	Trace	
$\mathrm{CCl_3}$	$\mathrm{C_6H_5CH_2}$	4.0	550–560	4.5–5.0	43	1.0 (55)	Trace	
$\mathrm{CHCl_2}$	$\mathrm{C_6H_5}$	5.0	560	5.0–10.0	70	1.1 (41)	0.1 (4)	
$\mathrm{CHCl_2}$	$p\text{-}\mathrm{NO_2C_6H_4}$	5.0	530	5.0	46	Trace	0.8 (28)	
$\mathrm{CHCl_2}$	$p\text{-}\mathrm{NO_2C_6H_4}$	5.0	540	5.0	35	Trace	0.3 (10)	
$\mathrm{CHCl_2}$	$p\text{-}\mathrm{CH_3C_6H_4}$	3.9	500	4.0	23	Trace	—	1.5
$\mathrm{CHCl_2}$	$p\text{-}\mathrm{CH_2OC_6H_4}$	5.0	500	6.0–10.0	34	0.4 (15)	0.05 (2)	
$\mathrm{CHCl_2}$	$\mathrm{C_6H_5CH_2}$	5.0	530	5.0	40	0.6 (22)	Trace	0.8

ranges to give nitrile at high temperature. This rearrangement was established in a separate experiment with benzoisonitrile under the same conditions as in the pyrolysis of 2,2,2-trichloroacetanilide (shown in the Experimental).

In the next experiment, the pyrolysis of 2,2-dichloroacetanilide at 500° and 560° was tried; benzonitrile and phenyl isocyanate were obtained in somewhat reduced yield in comparison with the pyrolysis of 2,2,2-trichloroacetanilide.

$$\mathrm{C_6H_5NHCOCHCl_2 \longrightarrow C_6H_5C{\equiv}N + C_6H_5N{=}C{=}O + HCl + (CO)}$$

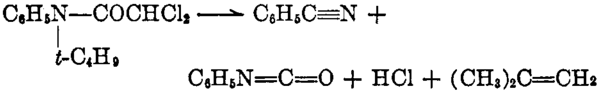
The pyrolysis of various *para* substituted 2,2-dichloroacetanilides also gave the corresponding nitriles and isocyanates under identical conditions. It is noteworthy that 2,2-dichloro-4′-nitroacetanilide gave exclusively *p*-nitrophenyl isocyanate in contrast to the other 2,2-dichloroacetanilides which gave nitriles in about 11 times higher yields than isocyanates (see Table II and III). Similarly, the pyrolysis of *N*-benzyl-2,2-dichloroacetamide as a model of an aliphatic compound gave a 22% yield of benzyl cyanide with a small amount of benzyl isocyanate.

In addition, the per cent conversion in the pyrolysis of 2-chloroacetanilide decreased markedly and gave only a 13% yield of benzonitrile and a 1% yield of phenyl isocyanate along with hydrogen chloride and a large amount of dark red tar under optimum condition.

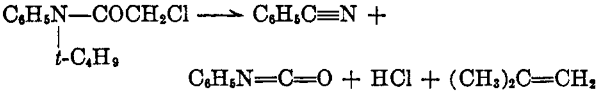
$$\mathrm{C_6H_5NHCOCH_2Cl \longrightarrow C_6H_5C{\equiv}N + C_6H_5N{=}C{=}O + HCl + (CO)}$$

The results of these experiments, together with the fact that acetanilide was shown not to undergo pyrolytic decomposition under the present experimental conditions, indicate that the per cent conversion in the pyrolysis of 2-haloacetamides and the ratio of isocyanate to nitrile, increase in proportion to the number of chlorine atoms with a large electronegativity value attached to the α-carbon of acid amides. This can be explained by the mechanism of the pyrolysis of 2,2,2-trichloroacetamides represented above.

Benzonitrile and phenyl isocyanate were obtained in nearly the same amount from the pyrolysis of *N*-*t*-butyl-2-haloacetanilides as from the 2-haloacetanilides along with isobutylene.

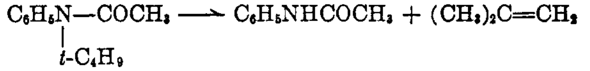


$$C_6H_5\underset{t\text{-}C_4H_9}{\underset{|}{N}}\text{—}COCHCl_2 \longrightarrow C_6H_5C{\equiv}N + C_6H_5N{=}C{=}O + HCl + (CH_3)_2C{=}CH_2$$



$$C_6H_5\underset{t\text{-}C_4H_9}{\underset{|}{N}}\text{—}COCH_2Cl \longrightarrow C_6H_5C{\equiv}N + C_6H_5N{=}C{=}O + HCl + (CH_3)_2C{=}CH_2$$

Since the pyrolysis of *N*-*t*-butylacetanilide gives only acetanilide and isobutylene under identical conditions, the chlorine atom substituted on the α-carbon of acid amides plays an important role in the production of nitrile and isocyanate.



$$C_6H_5\underset{t\text{-}C_4H_9}{\underset{|}{N}}\text{—}COCH_3 \longrightarrow C_6H_5NHCOCH_3 + (CH_3)_2C{=}CH_2$$

EXPERIMENTAL

Materials. 2,2,2-Trichloroacetamide, 2,2-dichloroacetamide, and 2-chloroacetanilide listed in Table I were prepared from the corresponding acid chlorides and amines in ether or benzene.

N-t-Butyl-2,2-dichloroacetanilide was prepared by the following procedure. A solution of 7.4 g. (0.05 mole) of dichloroacetyl chloride in ether was added dropwise with stirring to a solution of 7.5 g. (0.05 mole) of *t*-butylaniline, and 5.1 g. (0.05 mole) of triethylamine in ether. Triethylamine hydrochloride was separated from the reaction mixture and the ether was distilled. From the residue, 8.7 g. (67%) of *N*-*t*-butyl-2,2-dichloroacetanilide was distilled at 110–120°/0.33 mm. and could be recrystallized from methanol and a small amount of water, m.p. 82–83°.

Anal. Calcd. for $C_{12}H_{15}ONCl_2$: N, 5.38. Found: N, 5.39.

By the same procedure, 7.7 g. (68%) of *N*-*t*-butyl-2-chloroacetanilide was prepared from 5.7 g. (0.05 mole) of chloroacetyl chloride, 7.5 g. (0.05 mole) of *t*-butylaniline, and 5.1 g. (0.05 mole) of triethylamine, b.p. 105–108°/0.33 mm., n^{25}_{D} 1.4787.

Anal. Calcd. for $C_{12}H_{16}ONCl$: N, 6.21. Found: N, 6.45.

N-*t*-Butylacetanilide was prepared according to the method of Hickinbottom[3] from acetic anhydride and *t*-butylaniline, m.p. 55°.

Pyrolysis of 2,2,2-trichloroacetanilide. The apparatus used for pyrolysis consisted of a vertical quartz tube, 18 mm. in diameter and either (a) 120 cm. or (b) 60 cm. in length, equipped with standard taper joint and a side-inlet tube near the top for the exchange of air with nitrogen and for the steady flow of the nitrogen. This tube was packed with quartz chips and externally heated with an electric furnace. The temperature was determined by a pyrometer with the thermocouple attached to the outside of the pyrolysis tube. During pyrolysis, a slow stream of dry nitrogen was introduced through the capillary under reduced pressure. By use of the apparatus of (a) described above, 5.0 g. (0.021 mole) of 2,2,2-trichloroacetanilide was pyrolyzed at 520–530° over a period of 70 min. under a reduced pressure of 6.0 mm. Hydrogen chloride and phosgene in the pyrolysate were led into a solution of aniline in ether and 1.8 g. of aniline hydrochloride and 0.6 g. of *sym*-diphenylurea, the latter being equivalent to 0.3 g. (0.003 mole) of phosgene, were obtained. By distillation 1.5 g. of a mixture of phenyl isocyanate and benzonitrile was obtained (b.p. 50–74°/18 mm.), from which 0.4 g. of *sym*-diphenylurea was precipitated by addition of aniline; this is equivalent to 0.2 g. (9%) of phenyl isocyanate.

Pyrolysis of 2,2,2-trichloroacetanilide under other conditions and of other derivatives of 2,2,2-trichloroacetamides is tabulated in Table II and III.

Pyrolysis of 2,2-dichloroacetanilide. By use of the apparatus of (a) described above, 5.0 g. (0.025 mole) of 2,2-dichloroacetanilide was pyrolyzed at 560° under a reduced pressure of 5.0–10.0 mm. A 44% yield (1.1 g.) of benzonitrile and a 4% yield (0.1 g.) of phenyl isocyanate were obtained along with hydrogen chloride.

Pyrolysis of 2,2-dichloroacetanilide under other conditions and of other derivatives of 2,2-dichloroacetamides is listed in Table II and III.

Pyrolysis of 2-chloroacetanilide. In a similar way, 5.0 g. (0.029 mole) of 2-chloroacetanilide was fed to a reaction zone which was kept at 520–530° under reduced pressure 1.5–3.5 mm. A 13% yield (0.4 g.) of benzonitrile and a 1% yield (0.03 g.) of phenyl isocyanate were obtained along with hydrogen chloride and a large amount of dark red tar. Pyrolysis of 2-chloroacetanilide under other conditions is listed in Table II.

Pyrolysis of N-t-butyl-2,2-dichloroacetanilide. By use of the apparatus of (a), 4.3 g. (0.017 mole) of *N*-*t*-butyl-2,2-dichloroacetanilide was pyrolyzed at 550° under a reduced pressure of 4.0–6.0 mm. By the introduction of isobutylene into the pyrolysate, an acetic acid solution of bromine was decolorized. A 50% yield (0.8 g.) of benzonitrile and a 4% yield (0.08 g.) of phenyl isocyanate were obtained.

In a similar way, 5.0 g. (0.022 mole) of *N*-*t*-butyl-2-chloroacetanilide was fed to a reaction zone which was kept at 550° under a reduced pressure of 5.0–11.0 mm. Isobutylene and hydrogen chloride were obtained and the residue was dark red tar from which only two drops of liquid was obtained by distillation. It proved to be a mixture of benzonitrile and phenyl isocyanate.

Pyrolysis of N-t-butylacetanilide. By use of the apparatus of (a), 3.0 g. (0.016 mole) of *N*-*t*-butylacetanilide was pyrolyzed at 550° under a reduced pressure of 5.0–50 mm. A (89%) (1.9 g.) of acetanilide was obtained, m.p. 114–115° after recrystallization.

Rearrangement of benzoisonitrile. By use of the same apparatus as employed in the case of the pyrolysis of 2-haloacetamides, 1.4 g. (0.014 mole) of benzoisonitrile was treated at 540° under a reduced pressure of 3.0–5.0 mm. A 79% (1.1 g.) yield of benzonitrile, a rearranged product, was obtained and none of the odor of benzoisonitrile could be detected in the product.

OOKAYAMA, MEGURO-KU
TOKYO, JAPAN

---

[3] W. J. Hickinbottom, *J. Chem. Soc.*, 947 (1933).