Pyrolysis of Acid Amides. III. Pyrolysis of Cyanoacetamides and 2-Phenylacetamides

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The pyrolyses of acetoacetamides and 2-haloacetamides to give isocyanates and acetone, and nitriles, isocyanates and hydrogen chloride, respectively, have been reported in preceding papers[1,2]. It has been shown there that carboxylic acid amides containing atomic groups which are stable as anion in their acyl groups can produce isocyanates or nitriles by vapor phase decomposition. For the present study, the pyrolyses of cyanoacetamides, 2-phenylacetanilide, 2,2-diphenylacetanilide and 2,2,2-triphenylacetanilide were carried out in order to confirm this finding.

The pyrolysis of cyanoacetamides, which have

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

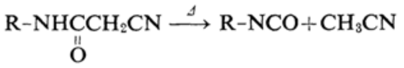
[2] T. Mukaiyama, M. Tokizawa and H. Takei, ibid., **27**, 803 (1962).

TABLE I. PYROLYSIS OF CYANOACETAMIDES

R-NHCOCH$_2$CN		Pyrolysis conditions				Products		
R	M. p. °C	Charge g.	Temp. °C	Press. mmHg.	Time min.	Acetonitrile g.	Isocyanate g.	Material recovered g.
C_6H_5-	198~199 (198~199)[d]	5.0	535~540	11.0	20	—	0.06	4.16
C_6H_5-		5.0	590~600	11.0	23	0.30	1.04	2.08
C_6H_5-		5.0	640~645	7.0	78	—	0.17	3.90
C_6H_5-		4.4	630~650	5.0	90	0.33	1.16	1.70
C_6H_5-		5.0	645~650	11.0	55	0.70	1.84	1.17
C_6H_5-[a]		5.0	710~720	7.0	20	—	0.06	about 2
p-$CH_3C_6H_4$-	183~184 (180)[d]	5.0	590~600	7.0	25	0.40	1.22	2.60
p-$CH_3C_6H_4$-		5.0	630~640	5.5~7.0	25	0.36	1.48	1.89
p-$CH_3C_6H_4$-		10.0	640~660	8.0	35	0.56	2.27	4.54
$C_6H_5CH_2$-[b]	122~123 (120)[d]	8.0	640~650	5.0	23	—	trace	2.66
p-$NO_2C_6H_4$-[a,c]	217~218 (decomp.)[e]	5.0	540~550	10.0~11.0	17	—	—	about 2

a) The char deposit in this reaction tube was much larger than in the others.
b) Unidentified by-products were obtained; 0.12 g, b. p., 90~110°C/15 mmHg; 1.29 g., b. p., 130~170°C/0.5~0.8 mmHg.
c) A trace of *sym-p, p'*-dinitrodiphenylurea was obtained.
d) K. G. Naik and Y. N. Baht, *J. Indian Chem. Soc.*, **4**, 547 (1927); *Chem. Abstr.*, **22**, 2353 (1928).
e) Found: C, 52.88; H, 3.50; N, 20.25. Calcd. for $C_9H_7O_3N_3$: C, 52.68; H, 3.44; N, 20.48%.

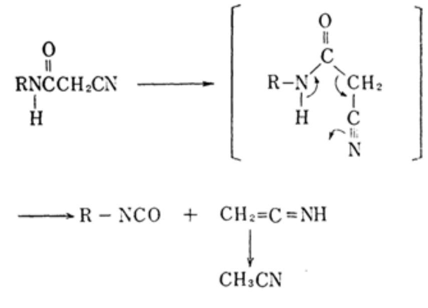
a structural possibility of forming $NCCH_2^-$ and $RNHCO^+$ ions at an elevated temperature, was tried first by using a quartz column packed with quartz chips; isocyanates and acetonitrile were obtained, as had been expected. The results of the experiments are summarized in Table I.



$$\text{R-NH}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{CH}_2\text{CN} \xrightarrow{\Delta} \text{R-NCO}+\text{CH}_3\text{CN}$$

The amounts of isocyanate and acetonitrile increase as the temperature rises, but they decrease markedly above 700°C, probably because of side reactions. The amount of undesirable char deposited in the reaction tube was larger than that found in the case of acetoacetamides. In addition, it was shown that the pyrolysis of cyanoacetamides has poor reproducibility, unlike the results obtained in the case of acetoacetamides (see Table I). In the case of 4'-nitrocyanoacetanilide, the char deposit in the reaction tube was much larger and *p*-nitrophenyl isocyanate could not be obtained, although it can be pyrolyzed at a relatively low temperature (550°C).

The results listed in Table I show that the temperature required for the pyrolysis of cyanoacetamides is about 100°C higher than that needed for the pyrolysis of acetoacetamides. This may be attributed to the relative stabilities of the anions[3], $NCCH_2^-$ and $CH_3COCH_2^-$, which determine the ease of the carbon-carbon bond breaking of the acid-amide linkage. Assuming six-membered cyclic intermediates for the pyrolysis, as has been mentioned in the case of acetoacetamides, the result can be explained by the linear nature of the nitrile group, because of which the formation of the cyclic intermediate is more difficult.



Pyrolyses of 2-phenylacetanilide and 2,2-diphenylacetanilide were next attempted on the assumption that carbon-carbon bond breaking may also be facilitated by the introduction of phenyl groups which stabilize $C_6H_5CH_2^-$ or $(C_6H_5)_2CH^-$ ions by the resonance effect. These amides were expected to produce phenyl isocyanate and toluene, and phenyl isocyanate

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[3] The pK_a values of acetone and acetonitrile are about 20 and 25 respectively.

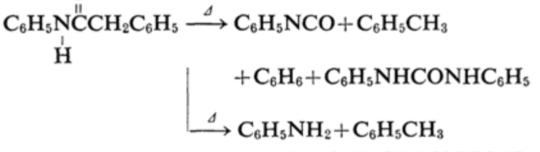
Table II. Pyrolysis of 2-phenylacetanilides[a)]

R-$CONHC_6H_5$ R	M. p. °C	Pyrolysis conditions Charge g.	Temp. °C	Press. mmHg	Time min.	Products Phenyl isocyanate g.	Aniline g.	R-H g.	*sym*-Di-phenylurea g.	Material recovered g.
								(toluene)		
$C_6H_5CH_2$-	115~116 (116)c)	5.0	500	3.0~4.0	25		trace	—	—	4.26
$C_6H_5CH_2$-		5.0	600	5.0	20	0.03		trace	—	3.31
$C_6H_5CH_2$-		5.0	620	8.0	20	0.76		1.27	0.80	—
$C_6H_5CH_2$- b)		15.0	680~690	7.0	55		0.94	0.62f)	1.65	—
$C_6H_5CH_2$- b)		5.0	700~710	3.0	43		trace	0.39g)	0.44	—
								(diphenyl-methane)		
$(C_6H_5)_2CH$-	179~181 (180)d)	5.0	490~500	8.0~11.0	30	trace		0.50	0.60	0.80
$(C_6H_5)_2CH$-		5.0	490~520	9.0	20	0.14		0.73	1.01	—
$(C_6H_5)_2CH$-		5.0	550~570	5.0~7.0	37	0.34		1.23	0.34	—
$(C_6H_5)_2CH$-		5.0	600~610	6.0	25	0.54		1.32	0.25	—
$(C_6H_5)_2CH$-		4.2	640~650	7.0	20	0.46		1.20	0.14	—
								(triphenyl-methane)		
$(C_6H_5)_3C$- b)	169~170 (173.5~174.5)e)	5.0	450~460	3.0	18	—	trace	trace	trace	—
$(C_6H_5)_3C$- b)		4.0	500~520	12.0	20	—	0.28	—	trace	0.50
$(C_6H_5)_3C$- b)		5.0	570~600	4.0~11.0	15	—	0.13	0.68	0.02	—

a) The pyrolyses were so complicated that various by-products not listed in this table were also obtained.
b) The char deposit in this reaction tube was much larger than in the others.
c) C. A. Bischoff and P. Walden, *Ann.*, **279**, 125 (1894).
d) F. Klingemann, ibid., **275**, 84 (1893).
e) J. Schmidlin and H. H. Hodgson, *Ber.*, **41**, 446 (1908).
f) Gas chromatographic analysis showed that crude toluene was 15% benzene.
g) Gas chromatographic analysis showed that crude toluene was 11% benzene.

and diphenylmethane, respectively. The reactions, however, were complicated, and the isocyanate and toluene or diphenylmethane formed was accompanied with a considerable amount of by-products. Since the reaction pathway is markedly influenced by even a minor change in the reaction conditions, the pyrolytic reactions also have poor reproducibility in both cases. The results of several runs are listed in Table II.

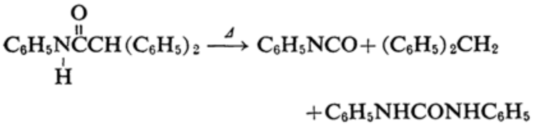
In the case of 2-phenylacetanilide, generalizations may be made as follows. Below 600°C, most of the starting material was recovered. In temperature range from 600 to 650°C, phenyl isocyanate was obtained along with toluene, benzene and *sym*-diphenylurea. However, it was shown that there was another reaction, the formation of aniline instead of phenyl isocyanate, under nearly the same conditions. At a more elevated temperature (670~680°C), the reaction became more complicated and the char deposit in the reaction tube was much larger. Phenyl isocyanate could not be obtained from the pyrolyzate, although aniline, toluene, benzene and *sym*-diphenylurea were obtained, along with various unidentified by-products.



$$C_6H_5\underset{H}{N}\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow{\Delta} C_6H_5NCO + C_6H_5CH_3 + C_6H_6 + C_6H_5NHCONHC_6H_5$$

$$\xrightarrow{\Delta} C_6H_5NH_2 + C_6H_5CH_3 + C_6H_6 + C_6H_5NHCONHC_6H_5$$

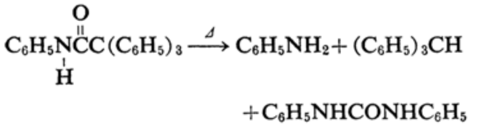
When 2,2-diphenylacetanilide was pyrolyzed with the temperature range from 490 to 650°C, phenyl isocyanate, diphenylmethane and *sym*-diphenylurea were obtained.



$$C_6H_5\underset{\overset{|}{H}}{N}\overset{\overset{O}{\|}}{C}CH(C_6H_5)_2 \xrightarrow{\varDelta} C_6H_5NCO + (C_6H_5)_2CH_2 + C_6H_5NHCONHC_6H_5$$

As was mentioned in a previous report[2)], the percentage of conversion in the pyrolysis of 2-haloacetamides increases in proportion to the number of halogen atoms, with a large electronegativity value being attached to the α-carbon of acid amides. Similarly, the finding that 2, 2-diphenylacetanilide decomposed more easily than 2-phenylacetanilide indicates that the number of phenyl groups attached to the α-carbon of acid amides plays an important role in this type of pyrolysis.

Unexpectedly, phenyl isocyanate could not be obtained by the pyrolysis of 2, 2, 2-triphenylacetanilide, only a large amount of tarry product resulted, although it decomposed at a relatively low temperature (450°C). From the tarry pyrolyzate, traces of aniline, triphenylmethane and *sym*-diphenylurea were obtained. The reason why phenyl isocyanate could not be obtained by the pyrolysis of 2, 2, 2-triphenylacetanilide remains unexplained.



$$C_6H_5\underset{\overset{|}{H}}{N}\overset{\overset{O}{\|}}{C}C(C_6H_5)_3 \xrightarrow{\varDelta} C_6H_5NH_2 + (C_6H_5)_3CH + C_6H_5NHCONHC_6H_5$$

Contrary to the cases of the pyrolyses of acetoacetamides and cyanoacetamides, which yield only isocyanates through the cyclic intermediate, the pyrolyses of 2-phenylacetamides gave various products. These results indicate that the pyrolyses of 2-phenylacetamides does not involve cyclic intermediates, but rather proceeds through radical intermediates, benzyl-type radicals, formed by the homolytic breaking of the carbon-carbon bond or the carbon-hydrogen bond.

In conclusion, it can be said of the pyrolysis of acid amides that: 1) The reactivity of amides toward the pyrolytic decomposition depends on the easiness of the carbon-carbon bond breaking of the amide linkage. This suggests that amides containing atomic groups which are stable as anion or free radical in their acyl groups decompose readily.

2) Since acetoacetamides and cyanoacetamides can form the cyclic intermediates, the pyrolytic decomposition takes place in the direction of forming isocyanate. However, such amides as 2-haloacetamides and 2-phenylacetamides, which form the cyclic intermediate only with difficulty, gave a small amount of isocyanate along with various by-products probably through radical intermediates. These results show that the greater the chance of forming cyclic intermediates, the greater the proportion of isocyanate.

Experimental

Materials.—Cyanoacetamides were prepared from corresponding amines and ethyl cyanoacetate. Their melting points are listed in Table I.

2-Phenylacetanilide, 2,2-diphenylacetanilide and 2,2,2-triphenylacetanilide were prepared from aniline and corresponding acid chlorides, and their melting points are listed in Table II.

Pyrolysis of Cyanoacetanilide.—The apparatus used consisted of a vertical quartz tube, 18 mm. in diameter and 120 cm. in length, equipped with a standard taper joint and a side-inlet tube near the top for the replacement of air with nitrogen. This tube was packed with quartz chips and externally heated with an electric furnace. The temperature was measured by a pyrometer with a thermocouple attached to the outside of the pyrolysis tube. During the pyrolysis, a slow stream of dry nitrogen was introduced through the capillary under reduced pressure. By the use of this apparatus, 5.0 g. (0.031 mol.) of cyanoacetanilide was pyrolyzed at 645～650°C over a period of 55 min. under the reduced pressure of 5.0 mm. The pyrolyzate was collected in a flask cooled in a dry ice-ethanol bath, and a 71% (0.70 g.) yield of acetonitrile and a 65% (1.84 g.) yield of phenyl isocyanate were obtained by fractional distillation. From the residue, 1.17 g. (23%) of cyanoacetanilide was recovered; m. p., 196°C.

Pyrolyses of cyanoacetanilide under various conditions and of other derivatives of cyanoacetamides are listed in Table I.

Pyrolysis of 2, 2-Diphenylacetanilide.—With the same apparatus as was employed in the case of cyanoacetamides, 5.0 g. (0.017 mol.) of 2, 2-diphenylacetanilide was pyrolyzed at 550～570° under the reduced pressure of 5.0～7.0 mmHg. The precipitate was collected from the dark brown pyrolyzate and washed with benzene. After recrystallization from ethanol, *sym*-diphenylurea (0.34 g.; m. p., 237°C) was obtained. When the filtrate was distilled, a 42% (1.23 g.) yield of diphenylmethane and a 15% (0.31 g.) yield of phenyl isocyanate were obtained, along with considerable amounts of unidentified by-products.

The results of the pyrolyses of 2,2-diphenylacetanilide under other conditions and of 2-phenylacetanilide and 2,2,2-triphenylacetanilide are listed in Table II.

Summary

The pyrolyses of cyanoacetamides, 2-phenylacetanilide, 2, 2-diphenylacetanilide and 2, 2, 2-triphenylacetanilide have been studied. The pyrolysis of cyanoacetamides gave the corresponding isocyanates and acetonitrile. On the other hand, the pyrolysis of 2-phenylacetanilide and 2, 2-diphenylacetanilide gave a small amount

of phenyl isocyanate, along with various by-products. The pyrolysis of 2, 2, 2-triphenylacetanilide, however, against expectation, did not give isocyanate; only a tarry product resulted.

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