

THE DECOMPOSITION REACTION OF *N*-NITROSO- ϵ -CAPROLACTAM WITH ACIDS

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SYNOPSIS

A solution of ϵ -caprolactam in aqueous hydrochloric acid was treated with sodium nitrite below 0°C, and the resulting *N*-nitroso compound was decomposed at 60°C. After the conversion of the acids in the reaction mixture into methyl esters, each component was separated by gas chromatography and identified by NMR and MS. As a result, the components were found to be 5- and 6-chlorocaproic, 5-hexenoic, 5, 6-dichlorocaproic, 6-hydroxy caproic acids, caprolactone, and a high boiling point mixture of which the main component was $\text{Cl}(\text{CH}_2)_5\text{COO}(\text{CH}_2)_5\text{COOH}$. When hydrobromic acid was used in place of hydrochloric acid, the corresponding bromo-compounds were obtained. The formation process and yield of these compounds, and the effect of the acids on these compounds were also examined.

1. INTRODUCTION

We have reported¹⁾ on the synthesis of ω -(*p*-carboxyphenoxy) alkanolic acids and their dimethyl esters by Williamson synthesis in one of the investigations for the application of *p*-hydroxybenzoic acid and then examined the various syntheses of ω -haloalkanoic acids in connection with this reaction. In these haloalkanoic acids, 6-halocaproic acid was prepared from the decomposition of *N*-nitroso- ϵ -caprolactam by hydrohalogenic acids with respect to the material and the operation. In this reaction, it was reported²⁾ that 5-hexenoic acid was formed as a by-product together with 6-chlorocaproic acid when hydrochloric acid was used as an acid. But it was found by gas chromatography that there exists some other by-products in addition to 5-hexenoic acid. The results of these tests examining these by-products by gas chromatography, NMR, MS and so on, are reported.

2. EXPERIMENT

2.1 The Decomposition Reaction of *N*-Nitroso- ϵ -caprolactam (NCL) with Acids.

One example is described in the following. A solution of 113 g (1 mole) of ϵ -caprolactam and 170 ml of water was maintained below 0°C. To this solution a prescribed amount of 35 % hydrochloric acid was added and then a solution of 150

ml of water and a prescribed amount of sodium nitrate was dropped. After that, the mixture was stirred for three minutes at below 0°C, and for a further ninety minutes at 60°C and the resulting NCL was decomposed. After the reaction, the mixture was cooled and the products (caproic acid derivatives) were extracted with ether. The ether was distilled off as much as possible, at atmospheric pressure.

2. 2 Esterification.

To 80 g of the ethereal extract obtained above, 10 ml of concentrated sulfuric acid and 300 ml of absolute methanol were added and the mixture was refluxed for three hours.

2. 3 Methyl 6-Hydroxycaproate.

A mixture of 50 g of methyl 6-chlorocaproate, 25 g of potassium hydroxide and 100 ml of methanol was heated in an autoclave at 130°C for three hours. Bp 118-119°C/10mmHg (lit. Bp 123°C/12mmHg³⁾).

2. 4 Methyl 6-Methoxycaproate.

Methyl 6-Methoxycaproate was obtained by Williamson's ether synthesis from sodium methoxide and methyl 6-chlorocaproate in methanol. Bp 101-102°C/19mmHg (lit. 58-61°C/2mmHg⁴⁾).

2. 5 Dichlorination and Dibromination.

The reaction mixture containing 9.0 g of 5-heptenoic acid was dissolved in 30 ml of tetrachloromethane and 22.0 g of sulfuryl chloride was added dropwise to this solution under reflux for 30 min, and the stirring was continued for another 1 hr.

The addition of bromine was conducted according to the method described in JIS J 2534-1965.

2. 6 Addition of Hydrogen Halide to a Double Bond

To 5-hexenoic acid, 35 % hydrochloric acid or hydrobromic acid, whose amount corresponds to six times moles of the former, was added and after stirring at 60-65°C for 1.5 hr it was esterified according to the method described in 2.2.

2. 7 Analysis.

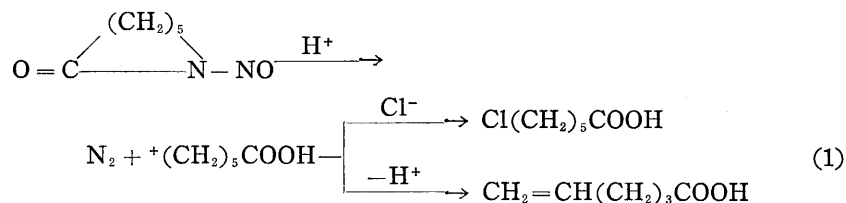
Gas chromatography: Yanagimoto GCG 550T; column, 2.25 m, PEG 20M; carrier gas, He; internal standard, diphenylether.

NMR analysis: Japan Electron Optics Lab.

Mass analysis: Hitachi Mass Spectrometer (RMU-6L)-HITAC 10; electron accelerating voltage of 70eV.

3. RESULTS AND DISCUSSION.

The mixture of 6-chlorocaproic acid (2a)⁵⁾ and 5-hexenoic acid (3a), the latter being a by-product, was mainly obtained when the hydrochloric acid solution of *N*-nitroso caprolactam (NCL) was heated. The outline of the reaction is shown in Equation (1).



First, this reaction product was converted to methyl ester and the composition was determined by gas chromatography. As the esterification is usually fairly good, the loss by esterification was ignored in the following.

An example of a gas chromatogram is shown in Fig. 1. To determine the structure of each component in the gas chromatogram, four components of the peaks A, C, D, and G were obtained separately by gas chromatography. The result of these NMR, MS, and elementary analysis are shown in Table 1.

It was considered from the mass data and elementary analysis that the peak A component is methyl 5-hexenoate (3m), this structure being also supported by NMR.

Both molecular weights of the peaks C and D components were 164 (Mass analysis) and the existence of chlorine was confirmed by a flame reaction. The ratios of the intensities of *m/e* 135 and 133 of both components in the mass

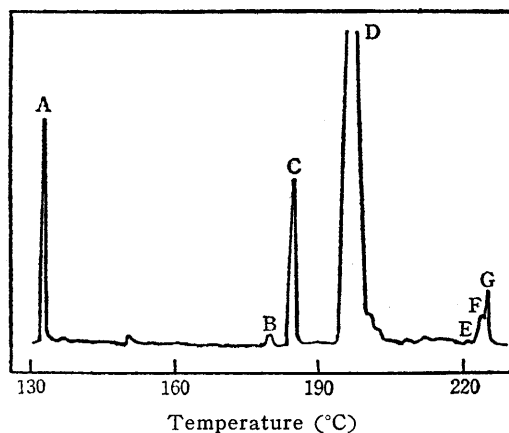


Fig. 1. Gas chromatogram of esterified mixture
 Condition : $x:y:z = 1:1:6$ (See Table 2)
 Heating rate : $6^\circ\text{C}/\text{min}$

Table 1 .NMR, Mass spectral, and elementary analyses.

Peaks ^{a)}	Data ^{b)}
A	Mass : 128(M ⁺ , 4.4), 97(25.6), 74(100), 69(32.0), 68(58.7), 59(24.7), 43(80.9), 41(77.1), 39(47.7), 27(30.7), 15(31.8). Analysis : Found C 65.24 %, H 9.65 % Calcd for C ₇ H ₁₂ O ₂ C 65.59 %, H 9.44 %
C	NMR(neat) : 6.0, m(1); 6.31, s(3); 7.7, m (2); 8.2 m(4); 8.43, d(3). Mass : 164(M ⁺ , 0.6), 135(6.5), 133(18.5), 97(36.3), 87(41.0), 74(72.9), 69(100), 68(99.1), 59(59.6), 55(38.8), 41(91.2), 27(50.3), 15(40.8). Analysis : Found C 50.66 %, H 7.99 % Calcd. for C ₇ H ₁₃ ClO ₂ C 51.07 %, H 7.96 %
D	NMR (in benzene) : 6.55, s(3); 6.76, t(2); 7.89, t ^{c)} (2); 8.6, m(6). Mass : 164(M ⁺ , 0.8), 135(5.9), 133(17.9), 87(28.2), 74(100), 69(44.8), 59(27.7), 55(19.2), 43(45.8), 41(54.6), 39(21.0), 27(25.3), 15(26.3) Analysis : Found C 50.53 %, H 8.11 % Calcd. for C ₇ H ₁₃ ClO ₂ C 51.07 %, H 7.96 %
G	Analysis : Found C 41.97 %, H 5.97 %, Cl 34.71 % Calcd for C ₇ H ₁₂ Cl ₂ O ₂ C 42.23 %, H 6.08 %, Cl 35.62 %
I	NMR (in CCl ₄) : 6.37, s(3); 6.62, t(2); 7.71, t(2); 8.3, m(6). Analysis : Found C 40.41 %, H 6.06 % Calcd for C ₇ H ₁₃ BrO ₂ C 40.21 %, H 6.27 %

a) See Fig. 1.

b) NMR : τ Value, peak (intensity).

Mass : m/e (relative intensity, %).

c) Triplet, but with some distortion, not clear.

spectra were about 1 : 3. This indicates that both are monochloro compounds. The elementary analysis value was almost consistent with the calculated one for C₇H₁₃ClO₂. It was considered from NMR that the peak C component is methyl 5-chlorocaproate (4m) and the peak D is methyl 6-chlorocaproate (2m).

On the other hand, it has been reported⁶⁾ that when a compound with an ethylenic double bond is treated with sulfuryl chloride, the corresponding dichloro-compound is obtained. When the ester mixture containing (3m) was treated with sulfuryl chloride, the peak A completely disappeared and the intensity of the peak G increased. Therefore, the peak G component is methyl 5,6-dichlorocaproate (5m). Both the elementary analysis and NMR supported this structure.

The peaks B, F, and E were considered to be methyl 6-methoxycaproate (6a), ϵ -caprolacton (7), and methyl 6-hydroxycaproate respectively, by comparing the retention times of these components with authentic samples.

NCL was decomposed by hydrobromic acid instead of hydrochloric acid and after the esterification the components were analyzed by gas chromatography. As a result, the new peaks H, I, and J were detected in addition to the peaks A, B,

E, and F seen in Fig. 1. Then, the mixture was analyzed by gas chromatography after treatment with hydrobromic acid and esterification. As a result, the intensity of the peak H increased. So that, the peak H component is considered to be methyl 5-bromocaproate (9m). From NMR data (Table 1) the peak A component is considered to be methyl 6-bromocaproate (10m), This was in accordance with the elementary analysis.

When the ester mixture containing (3m) was treated with bromine, the peak A completely disappeared and the intensity of the peak J increased. So that the peak J component was considered to be methyl 5, 6-dibromocaproate (11m).

It may be concluded from the above results that the reaction mixture obtained by the decomposition of NCL with hydrochloric acid or hydrobromic acid, at least, consists of six components (3a), (2a) or (10a), (4a) or (9a), (5a) or (11a), (7) and (8a). In addition, (6m) may be produced from (8a) under the esterification. The results obtained by gas chromatography is shown in Table 2. However, in (8a) the hydroxy group was determined by the acetylation method.

Table 2 Results of quantitative analysis by a gas chromatograph.

Condition ^{a)}			Yield (%)					Ratio (%)
x	y	z	(2m)	(4m)	(3m)	(5m)	(8e ^{b)})	(2m)/(4m)
1	1	2	15.6	2.5	9.1	0.2	2.6	6.2
1	1	3	21.2	2.6	6.0	0.5	2.4	8.2
1	1	4	25.2	2.8	2.0	1.0	2.1	9.0
1	1	6	29.8	3.2	0.3	1.0	1.0	9.3
1	2	4	28.7	3.9	0.7	2.2	2.0	7.4
1	2	6	37.1	4.4	0.0	1.9	0.8	8.4
x	y	w	(10m)	(9m)	(3m)	(11m)	—	(10m)/(9m)
1	1	2	14.4	1.4	0.6	4.2	—	10.3
1	1	3	16.2	0.63	0.2	3.4	—	25.7
1	1	6	12.7	0.12	0.1	2.2	—	105.8

a) ϵ -Caprolactam: NaNO_2 : HCl (or HBr) = x : y : z (or w) (molar ratio)

b) General formula: $\text{R}(\text{CH}_2)_3\text{COOR}'$

(2m) $\text{R}=\text{Cl}(\text{CH}_2)_2-$, $\text{R}'=\text{CH}_3$

(4m) $\text{R}=\text{CH}_3\text{CHCl}-$, "

(3m) $\text{R}=\text{CH}_2=\text{CH}-$, "

(5m) $\text{R}=\text{ClCH}_2\text{CHCl}-$, "

(10m) $\text{R}=\text{Br}(\text{CH}_2)_2-$, "

(9m) $\text{R}=\text{CH}_3\text{CHBr}-$, "

(11m) $\text{R}=\text{BrCH}_2\text{CHBr}-$, "

(8a) $\text{R}=\text{HO}(\text{CH}_2)_2-$, $\text{R}'=\text{H}$

Considering the formation processes of these products, NCL was decomposed by acids into (1). (1) will change into 6-halosubstituted product or (8a) by reacting with a halogen anion or water, or into (3a) by the elimination of the hydrogen

on the fifth carbon atom. If the cation on the sixth carbon atom isomerizes to the fifth position, a 5-substituted compound will be formed. However, the addition reaction of hydrogen halide to (3a) can be also considered as a formation process of a 5-halo substituted product. A mixture of (3a) and 35 % of hydrochloric acid was kept between 60° and 65°C for 1.5 hr and after esterification the mixture was analyzed by gas chromatography. As a result, only 6 % of (3a) was changed into (4a) when hydrochloric acid was used. Therefore, this process is not of importance as a formation process. However, most of the (3a) was changed into (9a) when hydrobromic acid was used. In addition, as is shown in Table 2, the yield of (9a) [\div (9m)] is considerably low and is decreased with the yield of 3a [\div (3m)], this indicating that all or most of the (9a) was formed by the addition of hydrogen bromide to (3a). On the other hand, chloride anions and bromide anions are oxidized by nitrous acid to give chlorine and bromine, which react with (3a) to give (5a) and (11a) respectively.

Large amount of residue was obtained in the distillation of ester mixture or acid decomposed compounds of NCL. In order to examine the components of the residue, the reaction mixture obtained with caprolactam: NaNO_2 : HCl =1: 1: 3 was divided into the following four fractions, and each IR absorption of the carbonyl group were measured. The absorption was recognized at 1704 (shoulder on 1716) cm^{-1} for both the first fraction (80-128°C/5mmHg, 10.4 wt %) and the main fraction (128-135°C/5mmHg, 43.1 wt %), at 1735 and 1710 cm^{-1} (separated at the top) for the last fraction (135-180°C/5 mmHg, 19.3 wt %) and at 1734-1728 cm^{-1} for the residue.

The absorption of the residue apparently suggested the existence of ester. Furthermore, the analytical values of the residue obtained higher than 135°C under 5 mmHg were C, 53.57 %; H 7.60 % Cl, 12.15 %, and N, 1.57 %, whose values are close to the calculated ones for $\text{Cl}(\text{CH}_2)_5\text{COO}(\text{CH}_2)_5\text{COOH}$, that is, C, 54.44 %; H, 8.00 %, and Cl, 13.39 %. Therefore, the residue would be the dimeric mixtures of caproic acid derivative and the main component is a condensation product of (2a) and (8a) which was formed by attacking of carboxylate anions on (1) and not the polymer of (8a) as reported earlier.

Regarding the influence of the kinds of halogens, we recognized a great difference in the yields of dihalo compounds and the ratio of 6-halo compound to 5-halo compound. The reactions may be due to the bromide anions changing to bromine much more during the reaction, since the bromide anion is more easily oxidized than the chloride anion and has a strong nucleophilicity. Especially, when hydrobromic acid was used, the quantity of (9a) formed during the substitution reaction was almost negligible, so that the bromide anion was considered to attack before the $\text{C}_6\text{-N}$ bond of NCL was completely broken.

This reaction could be compared with that of deamination of alkylamines be-

cause of the similarity of the type of reaction. For example, when the 1 N hydrochloric solution of *n*-butylamine was treated with sodium nitrate, the compounds corresponding to (2a), (4a), (3a), and (8a) were formed.⁷⁾ In this way a similar result was obtained. Whereas, dichloro compounds corresponding to (5a) could not be detected. Therefore, it is considered that in the dilute hydrochloric acid solution, the oxidation of chloride anion by nitrous acid may be difficult and that dichloro compounds may not be formed either.

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