BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 480—484 (1966)

The Synthesis of α, ω-Disubstituted Higher Alkanes from $\alpha, \alpha, \alpha, \omega$-Tetrachloroalkanes

By Kazuo SAOTOME, Hiroshi KOMOTO and Toshiaki YAMAZAKI

Technical Research Laboratory, Asahi Chemical Industry Co., Itabashi-ku, Tokyo

(Received June 22, 1965)

Higher ω-chloroalkanoic acids than ω-chlorooctanoic acid were prepared in good yields (over 90%) by improved methods of the hydrolysis of $\alpha, \alpha, \alpha, \omega$-tetrachloroalkanes. The reactions were carried out in fuming nitric acid, with the addition of nitrogen dioxide during the reaction or in the presence of a small amount of phosphoric anhydride. α, ω-Dichloroalkanes were derived from the ω-chloroalkanoic acids by the Kolbe electrolytic synthesis. Various other novel α, ω-disubstituted alkanes with very long methylene chains, such as glycols, dinitriles, dicarboxylic acids, and diamines, were also prepared starting from the tetrachloroalkanes.

Many kinds of bifunctional derivatives have been prepared by several Russian authors¹⁾ from $\alpha, \alpha, \alpha, \omega$-tetrachloroalkanes which had been obtained by the telomerization of ethylene with carbon tetrachloride. Some of the lone-chained derivatives have also been synthesized. For example, α, ω-dodecanedioic and α, ω-hexadecanedioic acids were obtained through the dimeric compounds produced by the catalytic hydrogenation of these tetrachloroalkanes:²⁾

$$\mathrm{Cl(CH_2)_nCCl_3} \rightarrow \mathrm{[Cl(CH_2)_nCCl_2\text{-}]_2} \rightarrow$$
$$\mathrm{Cl(CH_2)_{2n+2}Cl} \rightarrow \mathrm{HOOC(CH_2)_{2n+2}COOH}$$

In the present work, α, ω-disubstituted derivatives with a long methylene chain have been prepared by the Kolbe electrolytic synthesis of the ω-substituted alkanoic acids derived from $\alpha, \alpha, \alpha, \omega$-tetrachloroalkanes.

The preparation of lower ω-chloroalkanoic acids from the tetrachloroalkanes with sulfuric acid was also well investigated by the previously-mentioned authors. Freidlina et al.³⁾ obtained higher ω-chloroalkanoic acids (C_9—C_{13}) in yields of 60—70% by treating the tetrachloroalkanes with fuming nitric acid. A careful hydrolysis of these higher tetrachloroalkanes in concentrated sulfuric acid also gave the acids in nearly the same yields.⁴⁾

We have found that the yield of these higher ω-chloroalkanoic acids (C_9–C_{15}) is remarkably affected by the density of fuming nitric acid, and that the

---

1) A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Quart. Rev.*, **10**, 330 (1956).

2) A. N. Nesmeyanov, L. I. Zakharkin and T. A. Kost, *Izv. Acad. Nauk S. S. S. R., Otd. Khim. Nauk*, **1955**, 657.

3) R. Kh. Freidlina and Ye. I. Vasil'eva, *Doklady Akad. Nauk S. S. S. R.*, **100**, 85 (1955).

4) Sh. A. Karapetyan and N. A. Semenov, *Zh. Prikl. Khim.*, **37**, 2003 (1964).

Table I. The preparation of higher ω-chloroalkanoic acids

$Cl(CH_2)_nCCl_3$		HNO_3	$Cl(CH_2)_nCCl_3$		$Cl(CH_2)_nCOOH$	
n	g.	g.	Recovered g.	Conversion %	g.	Yield, %*
8	130	350	6.0	95.5	87.0	96.0
10	120	400	19.0	84.0	74.0	97.5
12	120	450	31.0	74.0	66.5	96.5
14	100	450	30.0	70.0	51.0	92.0

* The yield was calculated by taking the recovered tetrachloroalkane into account.

yield is much improved to over 90% by adding nitrogen dioxide to the reaction mixture during the course of the reaction. The yield has also been found to increase when the reaction is carried out in a fuming nitric acid solution containing a small amount of phosphoric anhydride. ω-Chloroalkanoic and ω-hydroxyalkanoic acids derived from the tetrachloroalkanes were subjected to the Kolbe electrolysis to afford α, ω-disubstituted long alkanes according to the following scheme;

$$\begin{tikzcd}
Cl(CH_2)_nCCl_3 \arrow[d] & \\
Cl(CH_2)_nCOOH \arrow[r] \arrow[d] \arrow[r, phantom, shift right=4ex, "\text{Kolbe electrolysis}"] & HO(CH_2)_nCOOH \arrow[d] \\
Cl(CH_2)_{2n}Cl \arrow[d] & HO(CH_2)_{2n}OH \\
CN(CH_2)_{2n}CN \arrow[r] \arrow[d] & H_2N(CH_2)_{2n+2}NH_2 \\
HOOC(CH_2)_{2n}COOH &
\end{tikzcd}$$

The Kolbe electrolytic syntheses of some ω-chloroalkanoic(5) and ω-hydroxyalkanoic(6) acids have been reported.(7) In this work, however, very long α, ω-dichloroalkanes (up to α, ω-dichlorotetracosane) were prepared. Dinitriles, dicarboxylic acids, and diamines were also derived from these long α, ω-dichloroalkanes.

Experimental and Results

δ-Chlorovaleric, ω-chloroenanthic and ω-chloropelargonic acids were prepared by hydrolyzing the corresponding tetrachloroalkanes in sulfuric acid according to the method in the literatures.(8)

The Preparation of Higher ω-Chloroalkanoic Acids in Fuming Nitric Acid with Nitrogen Dioxide Added.—A mixture of $\alpha, \alpha, \alpha, \omega$-tetrachloroalkane and fuming nitric acid (d=1.52) was stirred in a water bath. The reaction started at about 40°C with the generation of gas. When the initial generation of gas stopped (at 45—50°C, after 2—2.5 hr.), a stream of an excess of nitrogen dioxide was passed through the solution. Then the temperature was gradually raised to 70°C until the gas genaration practically ceased. 2—2.5 hr. were needed to complete the reaction under the flow of nitrogen dioxide. The reaction was carried out for about 5 hr. in all. A crystalline product was precipitated by adding ice-water to the reaction mixture. The precipitate was then filtered and washed several times with water. White crystals were obtained after recrystallization from ether - petroleum ether. From the mother liquor, the unreacted tetrachloroalkane was recovered by distillation under reduced pressure. The repeated recrystallization of the crystals from the same solvents afforded the following specimens: ω-chloropelargonic acid (a fraction of b. p. 140—143°C/2 mmHg was recrystallized), m. p. 30°C (lit. 30°C); ω-chloroundecanoic acid, m. p. 42°C (lit. 42°C); ω-chlorotridecanoic acid, m. p. 53°C (lit. 52°C); and ω-chloropentadecanoic acid, m. p. 62°C (lit. 62°C).

The details of the reaction are shown in Table I.

The Preparation of Higher ω-Chloroalkanoic Acids in Fuming Nitric Acid Containing Phosphoric Anhydride.—1) A mixture consisting of 55 g. of 1, 1, 1, 9-tetrachlorononane, 150 g. of fuming nitric acid (d=1.52) and 6 g. of phosphoric anhydride was stirred. The reaction started at 40°C with the generation of gas. The temperature was then gradually raised to 70°C as the reaction proceeded. After a 3 hr. reaction, the mixture was treated as above. Distillation under reduced pressure afforded a crystalline product without the unreacted tetrachloroalkane. Yield, 38.5 g. (96.5%).

2) A mixture consisting of 60 g. of 1,1,1,11-tetrachloroundecane, 180 g. of fuming nitric acid and 4 g. of phosphoric anhydride was treated as above. The reaction was carried out at temperatures between 40—60°C for 5 hr. Recrystallization from ether - petroleum ether gave white crystals. From the mother liquor, 3.5 g. of the unreacted tetrachloroalkane was recovered; conversion, 94%. Yield, 37.5 g. (89%).

The Preparation of ω-Hydroxyalkanoic Acids.—A mixture of ω-chloroalkanoic acid and its two moles of sodium hydroxide (a 5% aqueous solution) was refluxed for 6 hr. The solution was

---

5) F. L. M. Pattison, J. B. Stothers and R. G. Woolford, *J. Am. Chem., Soc.*, **78**, 2255 (1956).

6) G. E. Svadkovskaya, S. A. Voitkevich, Y. K. Smol'yaninova and V. N. Belov, *Zh. Obsch. Khim.*, **27**, 2146 (1957).

7) B. C. L. Weedon, "Advances in Organic Chemistry (Methods and Results), I," Interscience Publisher, New York (1960), p. 1.

8) R. M. Joyce, W. E. Hanford and J. Harmon, *J. Am. Chem. Soc.*, **70**, 2529 (1948).

TABLE II. THE KOLBE ELECTROLYSIS OF ω-SUBSTITUTED ALKANOIC ACIDS

$X(CH_2)_nCOOH$			MeOH	Na	$X(CH_2)_{2n}X$	
X,	n,	g.	ml.	g.	g.	Yield, %*
Cl	4	137	500	2.3	51.5	56.0 (51.5)**
Cl	5	150	500	1.1	68.0	65.0 (55.0)
Cl	6	165	500	1.1	66.0	55.0
Cl	8	190	500	1.1	76.5	52.5
Cl	10	220	500	1.2	75.5	43.0
Cl	12	120	400	0.8	48.0	49.0
OH	8	170	500	1.1	34.5	27.5
OH	10	100	400	0.8	9.3	12.0

* A large part of the by-products was found to be the methyl ester of the initial carboxylic acid.

** Yields in ( ) are cited from the literature.[5]

TABLE III. CHARACTERISTICS AND ANALYTICAL RESULTS OF α, ω-DISUBSTITUTED ALKANES

Formula	B. p. (lit.) °C/mmHg	n_D^{25} or M. p. (lit.) °C	Elementary Analysis, % Found C	Found H	Found Cl	Calcd. C	Calcd. H	Calcd. Cl
$Cl(CH_2)_8Cl$	75—76/2 (115—116/10)	1.4568 (1.4570)						
$Cl(CH_2)_{10}Cl$	101—102/1 (140—142/11)	1.4580 (1.4585)						
$Cl(CH_2)_{12}Cl$	170—172/10	27—28	60.20	9.86	29.57	60.25	10.11	29.65
$Cl(CH_2)_{16}Cl$		52—53	64.98	10.59	24.32	65.07	10.92	24.01
$Cl(CH_2)_{20}Cl$		60—61	68.17	11.49	20.46	68.35	11.47	20.18
$Cl(CH_2)_{24}Cl$		69—70	70.53	11.92	17.18	70.73	11.87	17.40
$HO(CH_2)_{16}OH$		89—90 (90.5)						
$HO(CH_2)_{20}OH$		102—103	76.32	13.38		76.37	13.46	

then acidified with sulfuric acid while being cooled with ice-water in order to separate the product. The precipitate was filtered, washed with water, and dissolved in ether-petroleum ether. The crystals which were separated after the evaporation of a large part of the solvents were again recrystallized from ethyl acetate. The following ω-hydroxyalkanoic acids were thus obtained: ω-hydroxypelargonic acid, m. p. 51°C (lit. 51.5°C); yield 86%; ω-hydroxyundecanoic acid, m. p. 69°C (lit. 70°C); yield 89%; ω-hydroxyundecanoic acid, m. p. 69°C (lit. 70°C); yield 89%; ω-hydroxytridecanoic acid, m. p. 79°C (lit. 79°C); yield 83%; and ω-hydroxypentadecanoic acid, m. p. 82°C (lit. 82°C); yield 78%.

The Kolbe Electrolysis of ω-Substituted Alkanoic Acids.—The apparatus used for the electrolysis was as follows. In a glass cell (10×10×1 cm³), electrodes of titanium plates plated with platinum (8×8×0.3 cm³) were settled 2 mm. apart. The cell was then placed in a cooling bath, and a sample solution was vigorously circulated through it. Commercial absolute methanol was used as the solvent, and small amounts of metallic sodium were added. The current density was maintained between 0.10 and 0.12 amp./sq. cm. throughout the reaction. The temperature in the cell was controlled below 50°C (30—40°C), while the solution outside the cell was cooled with ice-water in order to deposit crystalline products. A glass filter was placed between the outer section and the cell in order to protect the circulation pump from the solid precipitate. The reaction was continued until the solution was just alkaline to litmus; the time needed for this to occur was usually 100—150% longer than that calculated. The product, after being acidified with hydrochloric acid, was condensed almost to dryness, then the residue was extracted with ether. The ether extract was washed with a dilute solution of sodium carbonate in order to remove the unreacted acid, and then dried. The product which was obtained after the evaporation of the ether was recrystallized from ethanol. In the cases of α, ω-dichloroalkanes, in which carbon atoms in a molecule are less than 16, however, the products were purified by distillation under reduced pressure.

The details of the reaction and the characteristics of the products are shown in Tables II and III.

The Preparation of Dinitriles from α, ω-Dichloroalkanes.—α, ω-Dicyanoalkanes were prepared by treating these dichloroalkanes with potassium cyanide in the solvent of dimethylformamide (DMF). The reaction products were filtered to remove precipitated potassium chloride, and the filtrates were condensed by heating under reduced

Table IV. The cyanation of α,ω-dichloroalkanes

$Cl(CH_2)_nCl$		DMF	KCN	Reaction		$CN(CH_2)_nCN$	
n	g.	ml.	g.	Temp. °C	Time hr.	g.	Yield, %
8	60	200	50	120—130	8	44.0	82.0
10	60	200	45	110—115	8	40.5	74.5
12	65	250	40	130—140	10	43.5	73.0
16	85	300	40	140—150	12	55.0	70.0
20	35	100	15	140—150	15	17.2	55.0

Table V. Characteristics and analytical results of α,ω-dicyanoalkanes

Formula	B. p. (lit.) °C/mmHg	n_D or M. p. (lit.) °C	Elementary analysis N%	
			Found	Calcd.
$CN(CH_2)_8CN$	153—155/2 (199—200/15)	n_D^{16} 1.4528 (n_D^{20} 1.4474)		
$CN(CH_2)_{10}CN$	145—146/2	n_D^{16} 1.4550	14.60	14.57
$CN(CH_2)_{12}CN$	164—166/1.5	n_D^{16} 1.4578	12.75	12.71
$CN(CH_2)_{16}CN$		45—46	10.20	10.13
$CN(CH_2)_{20}CN$		56—57	8.25	8.42

pressure in order to evaporate the solvent. The lower dinitriles were separated and purified by distillation under reduced pressure, while the higher ones were obtained as white crystals after repeated recrystallizations from ethanol. The yields in Table IV are the values after the first distillation or recrystallization. The characteristics and the analytical results are shown in Table V.

The Preparation of α, ω-Alkanedioic Acids.—1) The oxidation of ω-hydroxyalkanoic acids. ω-Hydroxyundecanoic, ω-hydroxytridecanoic and ω-hydroxypentadecanoic acids were oxidized with nitric acid. For example, a mixture of 11 g. of ω-hydroxytridecanoic acid and 150 g. of nitric acid (98%) was stirred at room temperature for 1.5 hr. Then the temperature was gradually raised to 60°C over a 1-hr. period and then maintained between 60 and 70°C for 5 more hours. The mixture was diluted with water, and a crystalline product was filtered, washed with water and recrystallized from ethyl acetate. The pure crystals were obtained after repeated recrystallization from benzene.

2) The oxidation of glycols. Hexadecamethylene and eicosamethylene glycols were oxidized with potassium permanganate in acetone-water. For example, 5 g. of hexadecamethylene glycol was added to a solution of acetone (200 ml.) and water (20 ml.) containing 10 g. of potassium permanganate. The mixture was then heated at 70°C for 8 hr. while being stirred. After being allowed to stand overnight, the mixture was acidified with hydrochloric acid; then an aqueous solution of sodium hydrogen sulfite was added in order to dissolve precipitated manganese dioxide. The separation and the purification of a crystalline product were carried out as above.

3) The hydrolysis of dinitriles. Into a mixture consisting of 25 ml. of sulfuric acid (96%), 20 ml. of water and to 80 ml. of acetic anhydride, 25 g. of the dinitrile shown in Table V was added and the mixture was then refluxed for 15 hr. The reaction mixture was cooled and diluted with water to afford a crystalline precipitate, which was then separated and purified much above.

The yields and the melting points of these dicarboxylic acids are shown in Table VI.

The Preparation of Diamines.—The dinitriles shown in Table V were hydrogenated in the presence of the Raney cobalt or nickel (recipe W-7) under hydrogen pressures of 110—130 atm. The reaction was carried out for 2 hr. in 200 ml. of methanol containing 20 g. of ammonia. The absorption of hydrogen generally reached the theoretical amount after 1 hr. From the reaction mixture, the catalyst was filtered off, and the filtrate

Table VI. The preparation of α,ω-alkanedioic acids

$HOOC(CH_2)_n$-COOH n	Process	Yield %	M. p., °C	
			Found	Lit.
8	3	96	134—134.5	134.5
9	1	94	111—111.5	111
10	3	87	127—127.5	128
11	1	86	113—113.5	113.5
12	3	79	125—126	127
13	1	83	114—115	114.5
14	2	78	123—124	124
16	3	82	124—125	125
18	2	72	121—122	123
20	3	78	124—125	124

TABLE VII. THE PREPARATION OF α,ω-DIAMINOALKANES

$CN(CH_2)_nCN$		Catalyst		Temp.	$H_2N(CH_2)_{n+2}NH_2$					
n	g.		g.	°C	Yield g.	Yield %	B. p. °C/mmHg	M. p. °C	N% (HCl salt) Found	N% (HCl salt) Calcd.
8	25	Co	10	100—105	17.5	72.0	128—130/2	59—59.5 (60—61)*		
10	20	Ni	8	100—110	13.8	70.5	145—148/2	65.5—66 (66—67)		
12	20	Ni	10	130—140	13.5	66.0	154—156/2	70.5—71	9.30	9.30
16	15	Ni	8	140—150	9.5	64.0	193—195/2	85—85.5	7.62	7.84

* The values in ( ) show the melting points of the literature.

was condensed by evaporating the solvent and ammonia. A fraction with a higher boiling point was again distilled under reduced pressure to give a product with a constant boiling point.

The details of the reaction and the products are summarized in Table VII.

Discussion

In the hydrolysis of the higher tetrachloroalkanes in fuming nitric acid, the yields of ω-chloroalkanoic acids were much improved by the addition of either nitrogen dioxide or phosphoric anhydride. The hydrolysis of the trichloromethyl group is denoted by:

$$RCl_3 + 2H_2O \rightarrow RCOOH + 3HCl$$

The hydrogen chloride produced is immediately oxidized by an attack of nitric acid to give 3 mol. of water:

$$3HCl + 3HNO_3 \rightarrow 3NO_2 + 3/2Cl_2 + 3H_2O$$

As a matter of fact, the gas generated from the reaction mixture is a mixture of nitrogen dioxide and chlorine. The actual reactions taking place in the nitric acid solution may be summarized as:

$$RCCl_3 + 3HNO_3 = RCOOH + 3NO_2 + 3/2Cl_2 + H_2O$$

According to the above equation, one mole of water is produced to dilute the nitric acid when one mole of the tetrachloroalkane is converted. The facts that the yield is greatly affected by the density of the fuming nitric acid and that relatively poor yields are obtained in a simple treatment with fuming nitric acid, reveal the prohibiting effect of dilution by the produced water. Moreover, the reaction is actually interrupted by the small addition of water into the system. It is obvious that the nitrogen dioxide and the phosphoric anhydride in the reaction mixture catch the water, thus maintaining the system free from the dilution. The characteristic feature of these acidic media with regard to the progress of the reaction is much affected by the dilution with water. The remarkable improvements in the yields of the higher ω-chloroalkanoic acids in these experiments may be explained by the above explanation.

On the other hand, the hydrolysis of the lower tetrachloroalkanes ($<C_9$) in fuming nitric acid proceeds smoothly enough to give a high conversion even without the addition of these dehydrating agents. The products, however, are somewhat yellow, and this color could not be removed even by repeated distillations. The infrared spectra of the colored products denote the presence of some nitro-compounds as impurities.