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SYNTHESIS OF α-CHLOROCARBOXYLIC ACIDS BY CHLORINATING COMPOUNDS CONTAINING THE CCl_2—CH GROUP IN ACID MEDIUM*

A. N. NESMEYANOV, R. KH. FREIDLINA, V. N. KOST, T. T. VASSILYEVA and B. V. KOPYLOVA
Institute of Organo-Element Compounds, U S S R Academy of Sciences, Moscow

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THE ready availability of α,α,α,ω-tetrachloroalkanes by telomerization of ethylene and carbon tetrachloride, their ability to react with nucleophilic, electrophilic and radical reagents made it possible for us to create on their basis a wide system of syntheses of bifunctional compounds.[1]

This paper reports on the results of our study to develop a method of synthesizing various tri- and poly-functional compounds according to the general scheme I.

I. $$Cl(CH_2)_nCH_2CCl_3 \begin{cases} \xrightarrow{a} X(CH_2)_nCH_2CCl_3 \\ \xrightarrow{a'} Cl(CH_2)_nCH\ \ CCl_2 \end{cases} \xrightarrow{b}$$

$$\longrightarrow X(CH_2)_nCH\ \ CCl_2 \xrightarrow{c} X(CH_2)_nCHClCO_2H \longrightarrow X(CH_2)_nCHYCO_2H.$$

where X and Y are substituents, and n odd numbers† from 1 to 15.

This system is new in that it involves a one stage conversion of dichlorovinyl compounds to α-chlorocarboxylic acids (stage c), first instances of syntheses following this scheme having been reported in the paper mentioned above (see ref. 1)

To synthesize α-chlorocarboxylic acids we have worked out "conjugated addition" of chlorine to compounds containing the CCl_2=CH group in acid medium according to scheme II.

II. $$X(CH_2)_nCH\ \ CCl_2 \xrightarrow[HOAc]{Cl_2} [X(CH_2)_nCHClCCl_2OAc] \xrightarrow{H_2O}$$

$$\longrightarrow X(CH_2)_nCHClCO_2H + HCl$$

with Ac being the remainder of any acid.

Conjugated addition of various addenda to unsaturated hydrocarbons in different media has been known for a long time and is being extensively investigated. It has recently been suggested that conjugated addition of halogens to olefines proceeds through intermediate π-complexes of different types.[2-4]

* Translated by A. L. Pumpiansky, Moscow.

† n being limited to odd numbers is essential only when dichlorovinyl compounds are synthesized directly from α,α,α,ω-tetrachloroalkanes. Other routes to these compounds are, however, known that do not involve this restriction.

[1] A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Quart. Rev.* **10**, 330 (1956).
[2] M. Dewar, *J. Chem. Soc* 406, 777 (1946).
[3] E. A. Shilov, *Soobschenya Vses. Khim. Obsch. imeni Mendeleyeva*, **2**, 36 (1947).
[4] A. I. Titov and F. I. Maklyayev, *Zh. Obsch. Khim* **24**, 1624 (1954).

Titov *et al*[5] have found conjugated addition of halogen to the double bond of the CH_2 CH group in strong acid media such as sulphuric, phosphoric and aryl-sulphonic acids, to form corresponding β-haloalkyl esters. Nothing was, however, known of conjugated addition of halogens to the dichlorovinyl group.

Conjugated addition of chlorine to $RCH{=}CCl_2$ in different acids was carried out at 10–30°. Under these conditions almost no hydrolysis of starting compounds to corresponding acids RCH_2CO_2H was to be observed even in concentrated sulphuric acid. Usually chlorine saturation was continued until no hydrogen chloride was evolved, the mixture was diluted with water and extracted with chloroform. Acid

Table 1. Chlorination of $CCl_2{=}CH(CH_2)_2Cl$ in different media

Medium	Yield $Cl(CH_2)_2CHClCO_2H$ (% of theory)	Yield $Cl(CH_2)_2CHClCCl_3$ (% of theory)	Refs.
HCl*	—	81	7
$HClO_4$ (70%)	36	Neutral products were not investigated	7
CH_3CO_2H – $Hg(OAc)_2$†	62	36	8
HCOOH (anhydrous)	69	23	9
H_2SO_4 (93%)	78	8	6

* Trichloropentene in a mixture of ether and hydrochloric acid was simultaneously saturated with chlorine and hydrogen chloride.

† Mercuric acetate and trichloropentene were taken in equimolecular amounts.

products were isolated from chloroform with concentrated soda solution. By acidifying alkaline extracts acid reaction products were obtained. Fractionation of the residue after evaporation of chloroform gave rise to neutral products. In Tables 1–6 all yields are based on pure compounds. As a rule, all acids produced are characterized by their chloro anhydrides, anilides or other crystalline derivatives.

Taking 1,1,5-trichloropentene-1 as an example we have studied chlorination in different acid media (see Table 1).

It will be seen from the table that in all cases the two main reactions, that of conjugated addition, that is the introduction of the molecules from the medium, and that of usual chlorination of the double bond proceed concurrently. The latter reaction seems to be favoured by the appearance in the reaction mixture of hydrogen chloride. For the successful production of α-chlorocarboxylic acids it is therefore necessary to carry out the reaction under such conditions when hydrogen chloride is being bound (e.g. by adding mercuric acetate) or driven out of the medium (in anhydrous acids).

Chlorination in concentrated sulphuric acid can be recommended in all cases when starting compounds contain substituents that are not affected by this medium. (See Table 2). But when substituents are not inert to the action of sulphuric acid it is

[5] A. I. Titov and F. L. Maklyayev, *Zh. Obsch. Khim.* **24**, 1631 (1954).
[6] A. N. Nesmeyanov, V. N. Kost and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR* **103**, 1029 (1955).
[7] R. Kh. Freidlina, V. N. Kost and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1202 (1956).
[8] A. N. Nesmeyanov, V. N. Kost, T. T. Vassilyeva and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 152 (1958).
[9] V. N. Kost, T. T. Sidorova, R. Kh. Freidlina and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 2122 (1959).

better to synthesize α-chlorocarboxylic acids in acetic or formic acid. (See Tables 3 and 4). Thus in glacial acetic acid in the presence of mercuric acetate or in anhydrous formic acid we obtained corresponding α-chlorocarboxylic acids starting with compounds

$$R(CH_2)_nCH{=}CCl_2, \text{ where } R = C_6H_5, CH_3COO, HCOO, CH_3O, CN.$$

TABLE 2 CHLORINATION OF RCH=CCl$_2$ IN SULPHURIC ACID (d 1.8)

R	Yield RCHClCO$_2$H (% of theory)	Refs	R	Yield RCHClCO$_2$H (% of theory)	Refs.
$CH_3(CH_2)_3$–	71	6	$HOOC(CH_2)_3$–	77	6
$CH_3(CH_2)_4$	51	6	$HOOC(CH_2)_4$	73	6
$ClCH_2$	66	9	$HOOC(CH_2)_8$–	69	6
$Cl(CH_2)_3$	78	6	$C_6H_4\begin{matrix}CO\\CO\end{matrix}N(CH_2)_3$ –	92	11
$Cl(CH_2)_4$	70	6	$C_6H_4\begin{matrix}CO\\CO\end{matrix}N(CH_2)_4$–	84	10
$CCl_3(CH_2)_3$–	52	7	p-$ClC_6H_4CH_2$–	83	12

TABLE 3 HALOGENATION OF RCH= CCl$_2$ IN GLACIAL ACETIC ACID IN THE PRESENCE OF MERCURIC ACETATE

R	Yield RCHClCO$_2$H (% of theory)*	Yield RCHClCCl$_3$ (% of theory)	Refs
CH_3OCH_2	25	Neutral products were not investigated	8
CH_3COOCH_2–	27	55	8
$C_6H_5CH_2$ †	45 (54)	37	8
$Cl(CH_2)_3$	62	30	8
$CH_3COO(CH_2)_3$–	55	35	8
$CN(CH_2)_3$	54	30	8
$Cl(CH_2)_8$ ‡	24 (48)	32	8

* Yields calculated for the product that had reacted are listed in parentheses.
† With no mercuric acetate the acid was obtained in 30% yield [10]
‡ Bromine addition. $Cl(CH_2)_3CHBrCO_2H$ and $Cl(CH_2)_3CHBrCCl_2Br$ were produced.

We succeeded also in producing ω-chloro-α-bromopentanoic acid by making bromine react with 1,1,5-trichloropentene-1 in acetic acid in the presence of mercuric acetate.

[10] R. Kh. Freidlina, V. N. Kost, T. T. Vassilyeva and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 826 (1959).
[11] A. N. Nesmeyanov, R. Kh. Freidlina and R. G. Petrova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 451 (1957).
[12] R. Kh. Freidlina, N. A. Semenov and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 652 (1959).

In many instances, however, the yields of α-halo-carboxylic acids obtained in acetic acid still leave much to be desired. Curiously enough, bromination of fluoro-olefines containing the $\rangle C{-}{=}CF_2$ group in glacial acetic acid and in the presence of mercuric acetate or sulphate proceeds essentially with conjugated addition to form corresponding acetates of α,α-difluorosubstituted alcohols $CH_3CO_2CF_2\overset{|}{C}\overset{|}{B}r$.[13]

In anhydrous formic acid conjugated addition of chlorine to $CCl_2{=}CH$ gives rise to a high yield of α-chlorocarboxylic acids even with no mercuric acetate present. This synthetic alternative is rather convenient and applicable to many instances (see Table 4).

Table 4. Chlorination of $RCH{=}CCl_2$ in formic acid

R	Yield $RCHClCO_2H$ (% of theory)*	Yield $RCHClCCl_3$ (% of theory)	Refs.
CH_3OCH_2	60	Neutral compounds were not investigated	10
$HCOOCH_2$	73	16	10
$C_6H_5CH_2$—	63	29	9
$ClCH_2$ —	52 (60)	31	10
$HCOO(CH_2)_2$	82	9	10
$Cl(CH_2)_3$—	69	23	10
$Cl(CH_2)_4$ —	76 (85)	9	10
$Cl(CH_2)_5$	71 (82)	6	10
p-$C_6H_4(CH_2CH{=}CCl_2)_2$	30†		14

* Yields calculated for the product that had reacted are listed in parentheses.
† Dicarboxylic acid p-$C_6H_4(CH_2CHClCO_2H)_2$ was obtained

With formic acid as reaction medium we succeeded in effecting the synthesis of almost not investigated α-chloro-ω-sulphocarboxylic acids by chlorinating isothiourea salts $HCl.NH_2(NH{=})CS(CH_2)_nCH{=}CCl_2$ according to scheme III.

III. $HClNH_2(NH{=})CS(CH_2)_nCH{=}CCl_2 \xrightarrow[HCOOH]{Cl_2}$ (1) $\rightarrow HO_3S(CH_2)_nCHClCO_2H$

(2) $\rightarrow HO_3S(CH_2)_nCHClCCl_3$

Chlorination of alkylisothiourea hydrochlorides in aqueous medium is known to have been suggested as a method to obtain alkylsulphochlorides.[15,16,17] But the report[18] about the reaction mixture exploding when treated made limited its usefulness. Chlorinating in anhydrous formic acid without heating we observed no violent processes. Separation of acids (1) and (2) was based on the latter being less soluble in water. The former were isolated as their bis-benzylisothiouea salts, the latter as sodium salts. (See Table 5.)

[13] I. L. Knunyants, L. Ja. Pervova and V. V. Tukneva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 843 (1956).
[14] A. N. Nesmeyanov, R. Kh. Freidlina and N. A. Semenov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1969 (1960).
[15] C. Ziegler and J. M. Sprague, *J. Org. Chem.* **16**, 621 (1951).
[16] J. M. Sprague and T. B. Johnson, *J. Amer. Chem. Soc.* **59**, 1837, 2439 (1937).
[17] T. B. Johnson and J. M. Sprague, *J. Amer. Chem. Soc.* **58**, 1348 (1936).
[18] K. Folkers, A. Russell and R. W. Bost, *J. Amer. Chem. Soc.* **63**, 3530 (1941).

It is to be noted that we were not concerned with optimum yields of α-chlorocarboxylic acids in all the instances under investigation. In a number of cases the yields might be probably increased. We did not deem it possible, therefore, to discuss the relationship existing between the structure of starting dichlorovinyl derivatives and the yield of corresponding reaction products.

The reactions under study showed that compounds containing CCl_2=CH— with a relatively weak nucleophilic bond (that is a bond that does not seem to form readily π-complexes with halogens) can also undergo reactions of "conjugated addition" by a mechanism which has not yet been investigated and is of a special interest.

TABLE 5. CHLORINATION OF HCl·NH$_2$(NH=)CS(CH$_2$)$_n$CH=CCl$_2$ IN FORMIC ACID

n	Yield of compound I* (% of theory)	Yield of compound II† (% of theory)
3	42-5	19
5	33-5	28-7
7	13-23	42
9	11-14-5	

* Compound I is HOOCCHCl(CH$_2$)$_n$SO$_3$H.2C$_6$H$_5$CH$_2$SC(=NH)NH$_2$.
† Compound II is CCl$_3$CHCl(CH$_2$)$_n$SO$_3$Na.H$_2$O.

As seen from instances given in Tables 1–5, α-chlorocarboxylic acids containing in ω-position different substituents can be readily obtained in high yield starting with compounds X(CH$_2$)$_n$CH=CCl$_2$. α-Chloroacids produced by this method are readily freed from by-products that consist of neutral substances or acids much less soluble in water. This makes this method superior to direct chlorination of carboxylic and dicarboxylic acids that often gives rise to a product mixture that is difficult to separate.

Many of the compounds obtained are useful as starting compounds for further synthesis.

Starting with a number of α-chlorocarboxylic acids produced by the above method we have, in particular, synthesized corresponding α-aminoacids including racemates of natural amino acids, as well as their analogues and homologs.

The available data on ammonolysis of α-halo carboxylic acids mostly refer to α-bromoderivatives whereas only isolated instances of α-chloroderivatives have been reported. This seems to be accounted for by the latter being less available and the difficulty to obtain them pure.

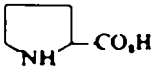
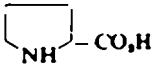
In some instances the yields of aminoacids are claimed to be substantially lower than using α-bromoderivatives.[19,20] This is likely to be due to chloroacids not being pure enough and the reaction conditions not well known. Our high yields of aminoacids on ammonolysis of α-chloroacids show that the yield of aminoacids seems to be little affected by the nature of the halogen in α-position. (See Table 6.)

Owing to the availability of starting compounds and high yields of products at all stages following scheme 1 this synthetic route to a number of α-amino acids must be considered superior to other methods known.

The method is illustrated below by representative syntheses of α-chloro acids under different conditions.

[19] R. Goudry, *Canad. J. Res.* **23 B**, 88 (1945).
[20] R. Goudry and L. Berlinguet, *Canad. J. Res.* **27 B**, 282 (1949).

TABLE 6. AMMONOLYSIS OF α-CHLOROCARBOXYLIC ACIDS WITH 25% AQUEOUS AMMONIA

Starting α-chloroacids	α-aminoacids	Yield (% of theory)	Refs
$C_6H_5CH_2CHClCO_2H$	$C_6H_5CH_2CH(NH_2)CO_2H$*	77	9
p-$ClC_6H_4CH_2CHClCO_2H$	*p*-$ClC_6H_4CH_2CH(NH_2)CO_2H$*	70	9
$C_6H_5OCO(CH_2)_2CHClCO_2C_2H_5$	$HOOC(CH_2)_2CH(NH_2)CO_2H$†	70	9
$C_6H_5OCO(CH_2)_2CHClCO_2C_2H_5$	$HOOC(CH_2)_2CH(NH_2)CO_2H$‡	80	9
$HOOC(CH_2)_4CHClCO_2H$	$HOOC(CH_2)_4CH(NH_2)CO_2H$§	80	9
$HOOC(CH_2)_4CHClCO_2H$	$HOOC(CH_2)_4CH(NH_2)CO_2H$§	85	9
	$NH_2(CH_2)_4CH(NH_2)CO_2H \cdot 2HCl$	74	9
$Cl(CH_2)_3CHClCO_2H$		50	11 conf (20)
	$NH_2(CH_2)_3CH(NH_2)CO_2H \cdot HCl$	30	11
	+ 	21	
$CH_3OCH_2CHClCOOH$	$CH_3OCH_2CH(NH_2)COOH$	84	
$ClH_2OCH_2CHClCOOH$	$HOCH_2CH(NH_2)COOH$	80	
$HCOOCH_2CHClCOOH$	$NH_2CH_2CH(OH)COOH$	83	

* Accompanied by dehydrochlorination of α chloroacids.
† Ammonolysis with alcohol ammonia; glutamic acid and ammonium chloride separation is effected on cationite KU-2.
‡ Ammonolysis with alcohol ammonia
§ Amino acid is purified from ammonium chloride with cationite KU-2

EXPERIMENTAL

Chlorination of 1,1,5-*trichloropentene*-1 *in sulphuric acid*

Through a mixture of trichloropentene (90 g) and 93% sulphuric acid (130 g) chlorine was passed with stirring at 15–20° till no hydrogen chloride was evolved. After dilution with water the mixture was extracted with chloroform. Acid products were isolated from the chloroform layer, and washed with 10% sodium hydroxide solution. Acidification of alkaline extracts gave α,δ-dichlorovaleric acid, b.p. 106–107°/1 mm; n_D^{20} 1.4825, d_4^{20} 1.3421. (Found: MR, 36.37. Calc.: MR, 36.56). Yield of pure acid 68 g (78% of theory). Lit.[81] for α,δ-dichlorovaleric acid: b.p. 129–131°/5 mm; n_D^{20} 1.4835; d_4^{20} 1.3421.

Acidechloride: b.p. 80°/5 mm, n_D^{20} 1.4840, d_4^{20} 1.3513 (Found: MR, 40.12. Calc. for $C_5H_7Cl_3O$: MR, 40.27).

Anilide: m.p. 58–59° (from petroleum ether plus benzene). (Found: C, 53.67, 53.69; H, 5.35, 5.50. $C_{11}H_{13}NCl_2O$ requires: C, 53.67; H, 5.32%.)

In addition, 16.5 g of neutral products were obtained boiling at 60–75°/1 mm. Repeated distillation gave the starting trichloropentene (4 g) and 1,1,1,2,5-pentachloropentane (10 g), b.p. 86–87°/2 mm, n_D^{20} 1.5100, d_4^{20} 1.4806 (Found: MR, 49.39. Calc.: MR, 49.62). Lit.[82] b.p. 121–122°/12 mm; n_D^{20} 1.5135, d_4^{20} 1.4807.

Chlorination of 1,1-*dichloro*-5-*cyanopentene*-1 *in acetic acid in the presence of mercuric acetate*

Through a mixture of dichlorocyanopentene (32.8 g), mercuric acetate (63.6 g), and glacial acetic acid chlorine was passed at 50° with stirring till its decoloration was no more observed. The precipitate was filtered off, acetic acid from the filtrate evaporated and the residue dissolved in ether with the mercuric salt precipitate filtered off. Acid products from ether solution were isolated with concentrated soda solution, the soda extracts acidified, repeatedly extracted with ether and dried over calcium chloride. Distillation gave 54% α-cloro-δ-cyanovaleric acid (17.4 g), b.p. 150° (1 mm), 162° (3 mm), n_D^{20} 1.4770, d_4^{20} 1.2660 (Found: MR, 36.06. Calc.: MR, 36.13.) (Found: C, 44.47, 44.27; H, 5.09, 5.05; Cl, 22.24. $C_6H_8NClO_2$ requires: C, 44.60; H, 4.98; Cl, 21.95%. Acidechloride: b.p. 110° (2 mm), n_D^{20} 1.4830, d_4^{20} 1.3072 (Found: MR, 39.33. Calc.: MR, 39.47.)

Sulphuric acid hydrolysis gave α-chloroadipinic acid, m.p. 102°. The melting point of the mixture with authentic α-chloroadipinic acid proved to be 102°.

In addition, 16.5 g of neutral products were obtained such as the starting 1,1-dichloro-5-cyanopentene (2.5 g), 1,1,1,2-tetrachloro-5-cyanopentane (14 g, 30%), b.p. 116° (2 mm); n_D^{20} 1.5045; d_4^{20} 1.4087 (Found: MR, 49.43. Calc.: MR, 49.19.) (Found: C, 31.09, 31.04; H, 3.03, 3.17. $C_6H_7NCl_4$ requires: C, 30.67; H, 3.00%.)

Chlorination of 1,1-*dichloro*-3-*formoxypropene*-1 *in formic acid*

Through a mixture of 1,1-dichloro-3-formoxypropene-1 (40 g) and anhydrous formic acid (80 g) at 30° chlorine was slowly passed with stirring till no hydrogen chloride was evolved. After removal of formic acid and distillation *in vacuo*, α-chloro-β-formoxypropionic acid was obtained. Yield 29.6 g (73% of theory), m.p. 66–67° (from benzene). (Found: C, 31.68, 31.70; H, 3.34, 3.30. $C_4H_5ClO_4$ requires: C, 31.49; H, 3.34%.)

In addition we obtained the starting formoxydichloropropene (2 g), 1,1,1,2-tetrachloro-3-formoxypropane (8.8 g, 18% of theory), b.p. 93–94° (7 mm); n_D^{20} 1.4932; d_4^{20} 1.5622 (Found: MR, 42.04. Calc.: MR, 41.79). (Found: C, 21.18, 21.30; H, 1.88, 1.92. $C_4H_4Cl_4O_2$ requires: C, 21.26; H, 1.78%.)

Ammonolysis of α-chloro-β-formoxypropionic acid with 25% aqueous ammonia when heated at 70° for 10 hr in an autoclave gave isoserin. Yield 83% of theory, m.p. 239–240° (from water). Lit.[83] m.p. 237°. (Found: C, 34.02, 34.18; H, 6.93, 6.71; N, 13.20, 13.27. $C_3H_7NO_3$ requires: C, 34.29; H, 6.72; N, 13.32%.)

Chlorination of $HCl\cdot NH_2(NH_2)CS(CH_2)_2CH_2CCl_3$ *in formic acid*

Through isothiourea chloride (5.5 g), produced from 1,1,5-trichloropentene-1, in anhydrous formic acid (25 ml) at 35° chlorine was slowly passed at the rate of about 50 ml/min till no hydrogen chlorine

[81] R. Kh. Freidlina and E. I. Vassilyeva, *Dokl. Akad. Nauk SSSR* **100**, 85 (1955).
[82] A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR* **56**, 87 (1954).
[83] H. Rinderknecht and C. Niemann, *J. Amer. Chem. Soc.* **75**, 6322 (1953).

TABLE 7

	Compound	m.p.(°C)	b.p.(°C)	n_D^{20}	d_4^{20}	Refs
1.	$ClCH_2CHClCOOH$	52–53	75/1.5			9
2.	$ClCH_2CHClCCl_3$		110–111/30	1.5108	1.6121	9
3.	$CH_3OCH_2CHClCOOH$*		79/1.5	1.4569	1.3216	8,9
	Acidechloride*		63–65/24	1.4590	1.3216	8
4.	$HCOOCH_2CHClCOOH$*	66–67	—	—		9
5.	$HCOOCH_2CHClCCl_3$*		93–94/7	1.4932	1.5622	9
6.	$CH_3COOCH_2CHClCOOH$*		112/1.5	1.4570	1.3496	8
	Acidechloride*		90–91/17	1.4565	1.3671	8
7.	$CH_3COOCH_2CHClCCl_3$		117–118/24	1.4860	1.4899	8
8.	$C_6H_5CH_2CHClCOOH$*	51	132/2			8,10,12
	Acidechloride*		74/2	1.5430	1.2647	8
	amide	93		—	—	8
	anilide*	125	—	—		8
	ethyl ester*		110/8	1.5092	1.1312	8
9.	$C_6H_5CH_2CHClCCl_3$		122/3	1.5555	1.3875	8
10.	$p\text{-}ClC_6H_4CH_2CHClCOOH$	99.5				12
11.	$C_6H_5OOCCHCl(CH_2)_3COOC_2H_5$*		93–94/1	1.4439	1.1388	10
12.	$CH_3(CH_2)_5CHClCOOH$		93–94/5	1.4442	1.4445	6
	Acidechloride*		61–62/28	1.4465	1.1765	6
	anilide*	63–64	—	—		6
13.	$Cl(CH_2)_5CHClCOOH$		107/1	1.4825	1.3421	6,7,8,9
	Acidechloride*		80/5	1.4840	1.3513	6
	anilide*	58–59			—	6
14.	$Cl(CH_2)_5CHClCCl_3$		86–87/2	1.5100	1.4806	6,7
15.	$HOOC(CH_2)_5CHClCOOH$	104–105				6
16.	$CCl_3CH_2CH_2CHClCOOH$	82–83	—			7
17.	$Cl(CH_2)_5CHBrCOOH$		106–107/0.5	1.5070	1.6215	8
18.	$Cl(CH_2)_5CHBrCCl_2Br$		84–85/1	1.5562	1.9322	8
19.	$HCOO(CH_2)_5CHClCOOH$*		138/1.5	1.4671	1.3148	9
20.	$HCOO(CH_2)_5CHClCCl_3$*		101/2	1.4973	1.4503	9
21.	$CH_3COO(CH_2)_5CHClCOOH$*		126–127/1	1.4640	1.2630	8
	Acidechloride*		133/18	1.4668	1.2765	8
22.	$CH_3COO(CH_2)_5CHClCCl_3$*		100–101/1.5	1.4870	1.3834	8
23.	$NC(CH_2)_5CHClCOOH$*		150/1	1.4770	1.2660	8
	Acidechloride*		110/2	1.4830	1.3072	8
24.	$NC(CH_2)_5CHClCCl_3$*		116/2	1.5045	1.4087	8
25.	$H_2N(CH_2)_5CHClCOOH$*	138	—	—		11
26.	$C_6H_4(CO)_2N(CH_2)_5CHClCO_2H$	118–119				11
27.	$C_6H_4(CO_2)N(CH_2)_5CHClCO_2H$	132	—	—	—	10
28.	$CH_3(CH_2)_5CHClCOOH$*		92–93/1	1.4485	1.0830	6
	Acidechloride		76–77/13	1.4498	1.1006	6
29.	$Cl(CH_2)_5CHClCOOH$	22–24	128–131/1	1.4804	1.2441	6,9
	Acidechloride*		104/2	1.4817	1.2557	6
	anilide	42–43	—	—	—	6
30.	$Cl(CH_2)_5CHClCCl_3$		102/2.5	1.5036	1.3715	9

TABLE 7 (*continued*)

Compound	m.p. (°C)	b.p. (°C)	n_D^{20}	d_4^{20}	Refs.
31. $HOOC(CH_2)_4CHClCOOH$	98–99	—			6
32. $Cl(CH_2)_3CHClCOOH$*		142–143·0·5	1·4768	1·1694	9
Acidechloride*		130·1	1·4785	1·1899	9
anilide*	62–63				9
33. $Cl(CH_2)_3CHClCCl_3$*		120–121·1·5	1·4980	1·2947	9
34. p-$C_6H_4(CH_2CHClCOOH)_2$	199–200	—			14
35. $HOOCCHCl(CH_2)_2SO_3H$ $2C_6H_4CH_2SC(=NH)NH_2$	111–111·5				24
36. $HOOCCHCl(CH_2)_4SO_3H$ $2C_6H_4CH_2SC(=NH)NH_2$	132–133				24
37. $HOOCCHCl(CH_2)_5SO_3H$ $2C_6H_4CH_2SC(=NH)NH_2$	124–125				24
38. $HOOCCHCl(CH_2)_6SO_3H$ $2C_6H_4CH_2SC(=NH)NH_2$	143				24

was evolved. Treatment of the reaction mixture with warm water resulted in the product of chlorine addition to the double bond obtained as oil with α-chlorocarboxylic acid remaining in the solution. The organic layer (1·5 g) was separated, treatment with concentrated soda solution gave sodium salt (CCl_3-$CHCl(CH_2)_2SO_3Na \cdot H_2O$). Yield 1·35 g (19% of theory). (Found: C, 18·13, 17·95; H, 2·98, 2·76. $C_3H_4O_4Cl_4SNa$ requires: C, 18·18; H, 2·72%).

Evaporation of water layer *in vacuo* at 30–35° led to α-chlorocarboxylic acid (4·4 g). Treatment with aqueous soda and benzylthiourea chloride solution gave the salt of bis-benzylthiourea ($HOOCCHCl(CH_2)_2SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2$). Yield 5·1 g (42·5% of theory), m.p. 111–111·5° (after three crystallizations from water). (Found: C, 45·63, 45·53; H, 5·35, 5·32. $C_{31}H_{38}O_6ClS_3N_4$ requires: C, 45·94; H, 5·29%).

In Table 7 are listed several constants of substances obtained by conjugated chlorination of compounds containing the dichlorovinyl group. Substances previously not reported are marked with an asterisk.

[24] R. Kh. Freidlina, B. V. Kopylova and A. N. Nesmeyanov. In press.