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CHLORINATED LONG-CHAIN FATTY ACIDS. THEIR PROPERTIES AND REACTIONS—VI

KINETICS AND MECHANISMS OF BASE-CATALYZED DEHYDROCHLORINATION OF SODIUM *THREO,THREO*-9,10,12,13-TETRACHLOROOCTADECANOATE

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Abstract—The base-catalyzed dehydrochlorination of sodium *threo,threo*-9,10,12,13-tetrachlorooctadecanoate has been carried out in aqueous ethylene glycol solutions. During the first reaction step two chlorine atoms are eliminated nearly simultaneously as hydrogen chloride whereas the third and fourth chlorine atoms are released separately. The relative rates of these three reaction steps at 130°C are 497, 41 and 1, respectively. The possible reaction mechanisms have been discussed in light of the kinetic results and product analyses which showed that the dehydrochlorination results mainly in conjugated diene-yne systems.

Our previous reports dealt with the base-catalyzed dehydrochlorination of various mono- and dichlorooctadecanoic acids.[1-3] For instance, dehydrochlorination of *threo*-9,10-dichlorooctadecanoic acid was found to occur in two steps.[1,2]

The catalytic vapour-phase dehydrochlorination of chlorinated linoleic acid at low pressure and high temperatures has been studied by Van Atta *et al.*[4] and the base-promoted removal of hydrogen bromide from the tetrabromo derivative of linoleic acid by Maruyama *et al.*[5] and later Khan.[6]

It is well known that linoleic acid is the main component in the fatty acid fraction of resins of soft and hard woods in chemical pulping.[7] Ewart and Hergert[8] have studied the composition of resinous wood extractives during the pulp bleaching process using chlorinated derivatives of oleic and linoleic acids as model compounds. However, in all previous investigations very little attention has been paid to kinetic and mechanistic aspects concerning the dehydrochlorination of polychlorinated long-chain fatty acids. In the following, the rate and mechanisms of the alkaline dehydrochlorination of sodium salt of *threo,threo*-9,10,12,13-tetrachlorooctadecanoic acid **1** will be considered.

RESULTS AND DISCUSSION

Kinetics of dehydrochlorination. On the basis of the results concerning the base-promoted dehydrochlorination of sodium *threo*-9,10-dichlorooctadecanoate[1,2] it was expected that the reactivities of the various chlorine atoms in sodium *threo,threo*-9,10,12,13-tetrachlorooctadecanoate **1** might be different. Preliminary kinetic runs showed that the amount of chlorine, removed readily, was about 50 per cent of the total chlorine content. Thereafter the reaction proceeded more slowly (Fig 1). If the reaction followed (apparent) first-order kinetics, the half-life time of the reaction should be about 170 min. The amount of the removed chlorine after threefold half-life time (about 500 min) should then be 87·5% of the total. The kinetic measurements showed, however, that only 60% of the total chlorine was released at this moment. This great difference is due to the fact that the four chlorine atoms in **1** are eliminated at unequal rates. Experiments at different temperatures revealed that the base-catalyzed dehydrochlorination of **1** occurs in three reaction steps. During the first reaction step two moles of HCl are removed nearly simultaneously (Fig 1). The last two chlorine atoms are split off at slower and distinct rates during the second and third reaction steps (Fig 2). Using suitable temperature ranges it was possible to follow each of the above-mentioned reaction steps separately. It is worth emphasizing that the two chlorine atoms, which are removed during the first reaction step, may also really have somewhat different rates, though in this work it is more practical to assume that they react at equal rates.

The values of the different rate coefficients at several temperatures are shown in Table 1 and the thermodynamic functions of activation derived from them with the method of least squares in Table 2. The Arrhenius plots were found to be linear in the temperature ranges used.

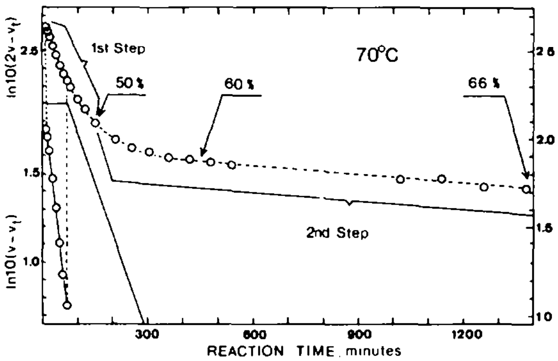


Fig 1. The base-catalyzed dehydrochlorination of sodium *threo, threo*-9, 10, 12, 13-tetrachlorooctadecanoate in aqueous ethylene glycol (x_{water} = 0·165) at 70°C. The molality of NaOH is 0·733. The amount of chlorine reacted shown as % chlorine content of substrate.

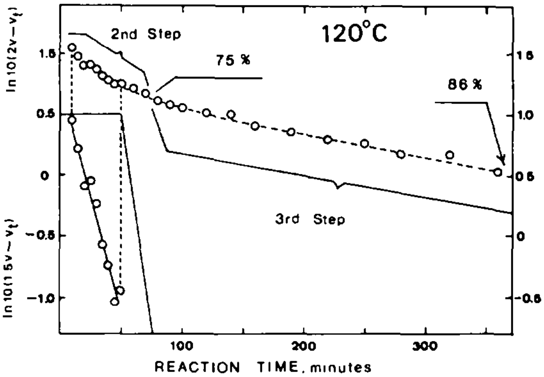


Fig 2. The base-catalyzed dehydrochlorination of sodium *threo, threo*-9, 10, 12, 13-tetrachlorooctadecanoate in aqueous ethylene glycol (x_{water} = 0·165) at 120°C. The molality of NaOH is 0·738. The amount of chlorine reacted shown as % chlorine content of substrate.

Table 1. Rate coefficients of the dehydrochlorination of sodium *threo,threo*-9,10,12,13-tetrachlorooctadecanoate in aqueous alkaline ethylene glycol (x_{water} = 0·165) at different temperatures[a]

Run	Temp[b] °C	OH^- Molality	10^5k (s^{-1})	10^5k_{OH} ($kg\ mol^{-1}\ s^{-1}$)	The released Cl as % from the total
The first reaction step					
1	50	0·730	2·50 ± 0·04[c]	1·72 ± 0·03[c]	9–22
2	60	0·741	8·46 ± 0·29	5·71 ± 0·20	10–26
3	60	0·729	7·39 ± 0·06	5·07 ± 0·04	10–36
4	70	0·742	20·4 ± 0·5	13·7 ± 0·4	7–18
5	70	0·725	18·4 ± 0·7	12·7 ± 0·5	12–31
6	75	0·735	35·0 ± 0·3	23·8 ± 0·2	10–40
7	80	0·735	58·1 ± 0·8	39·5 ± 0·6	11–36
8	80	0·730	59·3 ± 1·3	40·6 ± 0·9	19–40
The second reaction step					
8	80	0·730	1·63 ± 0·18	2·24 ± 0·24	54–59
9	90	0·730	4·35 ± 0·12	5·96 ± 0·17	56–68
10	100	0·740	12·4 ± 0·6	16·8 ± 0·8	62–68
11	110	0·738	30·1 ± 0·2	40·8 ± 0·2	59–71
12	120	0·738	62·0 ± 4·7	84·0 ± 6·3	62–72
The third reaction step					
11	110	0·738	2·18 ± 0·31	2·96 ± 0·40	77–81
12	120	0·738	2·91 ± 0·24	3·93 ± 0·33	81–86
13	130	0·738	3·76 ± 0·18	5·09 ± 0·24	82–90
14	145	0·735	4·80 ± 0·38	6·53 ± 0·50	91–94

[a] The substrate concentration was 0·0028 mmole per g of solvent.
[b] ± 0·1°C at 50–90°C and ± 0·2°C at 100–145°C.
[c] Standard deviation.

Determination of the rate coefficients. The alkaline dehydrochlorination reactions studied in this work were second-order and had the rate equation

$$\text{Rate} = k_{OH}[OH^-][S]$$

where [S] is the concentration of the reacting substrate. The NaOH concentration in the reaction mixtures was initially 250 times greater than that of the substrate and hence the first-order rate coefficients could be determined graphically by plotting

Table 2. Values of the thermodynamic functions of activation at 90°C and the relative rates at 90° and 130°C for the alkaline dehydrochlorination of sodium *threo,threo*-9,10,12,13-tetrachlorooctadecanoate **1** in aqueous ethylene glycol containing 16·5 mole per cent of water

	Reaction step	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	Rel. rate 90°C	130°C
1	I	95·2 ± 2·6[a]	− 42·3 ± 7·6[a]	110·5 ± 0·19[a]	53	497
	II	103·1 ± 2·4	− 43·4 ± 6·5	118·8 ± 0·11	3·4	41
	III	27·2 ± 2·3	− 262·4 ± 5·7	122·5 ± 0·22	1	1
DCO[b]	I	93·8 ± 0·4	− 55·3 ± 1·2	113·9 ± 0·02	17	155
	II	108·1 ± 1·8	− 64·3 ± 4·3	131·5 ± 0·2	0·051	0·73

[a] Standard deviation.

[b] Sodium *threo*-9,10-dichlorooctadecanoate; see Refs. 1 and 2.

the logarithm of the concentration of chloride ion formed in the reaction against the time

$$\ln C = -kt + \text{constant}.$$

The slopes (− k) were obtained by the method of least squares. The substrate concentration is proportional to the titrant consumption and can be replaced by the latter, the magnitude of which depends on the reaction step. The final consumption of the titrant after removal of all four chlorine atoms from **1** (2v in ml/g) was determined after the reaction mixture was left at 145°C for 24 h. If v_t is the consumption at time t, the quantity C for the three successive reaction steps may be replaced with the following terms

Reaction step	C
1	$v-v_t$
2	$1{\cdot}5v-v_t$
3	$2v-v_t$

It can be seen from Figs 1 and 2 that the linearity of the curves for the first and second reaction steps became much better when the total concentration (2v) was replaced with v and 1·5v, respectively. This procedure assumes that the isomeric compounds formed either in the first or in the second reaction step, which operate as reacting species in the second and third dehydrochlorination steps, respectively, decompose further by equal rates. Experimentally, the contribution of the three separate reaction steps on each other could be mainly avoided by selecting suitable conditions to follow them separately (Table 1 and Figs 1 and 2). Moreover, in comparison with errors originating from other sources, this simplified treatment introduced only minor inaccuracies on the rate coefficients.

To obtain the second-order rate coefficients (k_{OH}) the first-order rate coefficients were divided by the base concentration and in the case of the first reaction step also by statistical factor two. The last mentioned is a consequence of the simplifying assumption that the removal of each four chlorine atoms is almost equally probable at this reaction stage and two of them react simultaneously and at nearly equal rates.

Product analyses. The dehydrochlorination products of **1** obtained after the various reaction steps were protected against autoxidation with gaseous nitrogen and the products were analyzed rapidly after their separation from reaction mixtures.

The reaction products of all three stages of the alkaline dehydrochlorination of **1** had more intense yellow colour than the dehydrochlorination products of sodium *threo*-9,10-cichlorooctadecanoate.[1] Especially, the product of the second reaction step of **1** had very intense yellow-green colour probably due to the conjugated triene systems containing an auxochromic chlorine atom.

Gas liquid chromatography. The alkaline dehydrochlorination of **1** yields complex product mixtures as shown by GLC (Fig 3). All three reaction steps followed kinetically produce their own principal products (Figs 3A, 3B and 3E). Peaks 1 and 2 in Fig 3A are due to the first-step products (**3**–**6**). Peaks 6 and 7 in Figs 3B and 3C represent the major reaction products after the second reaction step (**9**–**14**). The large size of the peak 6 in the gas chromatogram of the first-step product (Fig 3A) is probably due to the transformation of allylic dichlorides (**3b**, **3c**) into the allenic monochlorides (**9**, **10**) during a GLC analysis. Peak 8 in Fig 3E exhibits the reaction products (**15**, **16**) after the total dehydrochlorination of **1**. It is worth noting that the elution time of the major component becomes shorter in every dehydrochlorination step in agreement with previous observations.[9] The retention times (relative to that of methyl stearate) of methyl esters of *threo*-9,10-dichloro- and *threo,threo*-9,10,12,13-tetrachlorooctadecanoic acids under the conditions used in this work were 6 and 33, respectively. Peaks

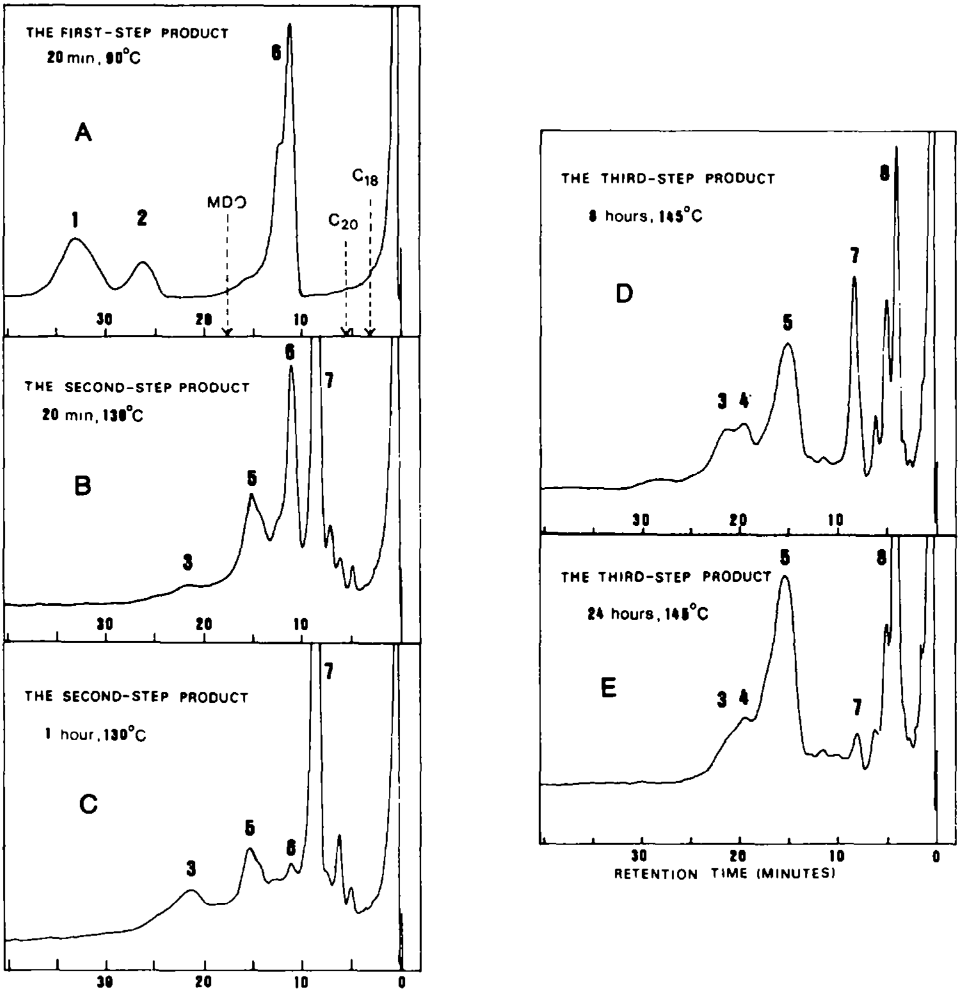


Fig. 3. Gas–liquid chromatograms of the dehydrochlorination products of sodium *threo,threo*-9,10,12,13-tetrachlorooctadecanoate. C_{18}: Methyl stearate, C_{20}: Methyl arachidate, MDO: Methyl *threo*-9,10-dichlorooctadecanoate.

3, 4 and 5 in the chromatograms may be due to the secondary reaction products. Peak 5 is of further interest. The chlorine content of this component is negligible since the total chlorine content of the third-step product has been found to be less than one per cent (Fig 3E). Obviously, this peak corresponds to the compounds formed by the addition of ethylene glycol to a triple bond.

The first-step product. To obtain the reaction products after the first dehydrochlorination step 1 was kept in the alkaline aqueous ethylene glycol for 20 min at 90°C. The separated reaction product showed the IR absorption bands (Fig 4) at 3020 (CH═CH), 1710 (COOH), 1660 (C═C), 970 (CH═CH, *trans*), 956 (CH═CH, conjugated), 648 and 620 cm^{-1} (C—Cl). The strong absorptions at 788 and 760 cm^{-1} may be due to the trisubstituted alkenes, e.g., vinylic chlorides formed in the dehydrochlorination reaction.

The product gave the following ^{1}H NMR signals (Fig 5): 0·91 ppm for $C\underline{H}_3$—, 1·37 ppm for —$(CH_2)_n$—, 2·10 ppm for —$C\underline{H}_2$—CH═, 2·30 ppm for —$C\underline{H}_2$—COOH, 2·80 ppm for ═CH—$C\underline{H}_2$—CH═, 3·2 ppm for ═CCl—$C\underline{H}_2$—CCl═, 3·65 ppm for ═CCl—$C\underline{H}_2$—CH═CCl—, 4·1 ppm for —C$\underline{H}$Cl—, and 5·2–7·0 ppm for the protons of conjugated double bonds. The poorly-resolved triplet (J = 6·7 c/s) at 5·50 ppm is due to the proton in the grouping —CCl═CH—. The corresponding signal for 9(10)-chloro-*trans*-9-octadecenoic acid has been earlier found to be at 5·42 ppm (triplet, J = 6·7 c/s).[1] The carboxyl proton, which usually locates at 10–12 ppm, appears in the NMR spectra of all dehydrochlorination pro-

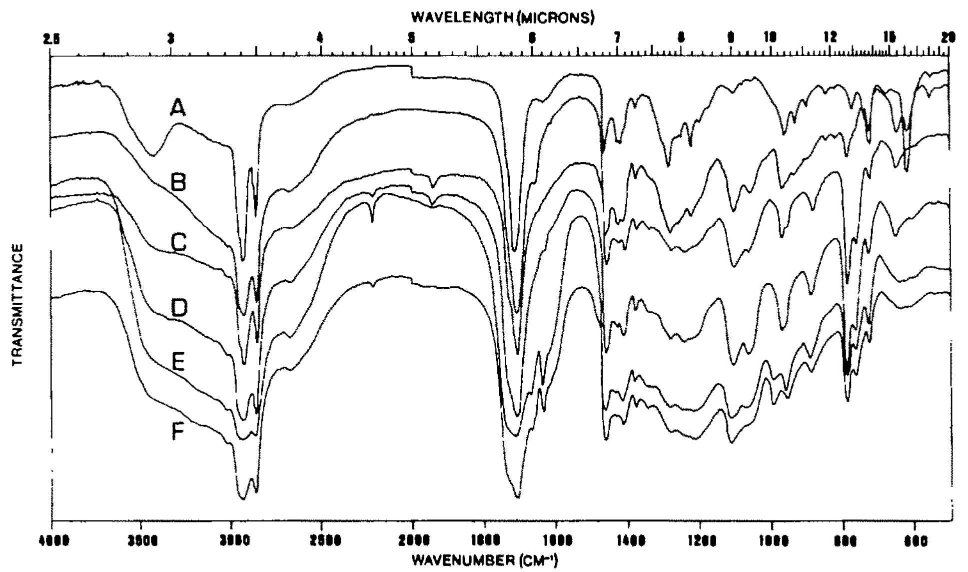


Fig 4. Infrared absorption curves of (A) *threo, threo*-9, 10, 12, 13-tetrachlorooctadecanoic acid and its reaction products formed in the alkaline dehydrochlorination: (B) the first-step product (20 min, 90°C), (C) the second-step product (20 min, 130°C), (D) the second-step product (1 h, 130°C), (E) the third-step product (8 h, 145°C), and (F) the third-step product (24 h, 145°C).

ducts of **1** at a higher field (8–9 ppm) indicating the presence of changeable protons.

The strong UV maxima located at 238 and 244 nm may be caused by the conjugated dienes including one or two chlorine atoms. The weak absorptions at 271 and 278 nm are probably due to a minor contribution of some conjugated trienes.

The mass spectrum of the first-step product showed the base peak at *m/e* 80 and two very weak peaks at 422 (M^+ of **1**, **1** in acid form) and at *m/e* 385 ($M\text{-}HCl^+$ from **1**). M^+ of the first-step product (*m/e* 349) is good agreement with the molecular weight (349·4) of $C_{18}H_{30}O_2Cl_2$. Two large fragment peaks at *m/e* 314 (76% from the base peak) and at *m/e* 278 (92%) were assigned to be due to $M\text{-}Cl^+$ and $M\text{-}2Cl^+$ fragments of the latter compound.

The second-step product. The second-step dehydrochlorination products obtained after the alkaline treatment of **1** for 20 min at 130°C had the IR bands (Fig 4) at 3020 (CH═CH), 1942 (C═C═C), 1710 (COOH), 1655 (C═C), 1635 (C═C, conjugated with a triple bond), 970 (CH═CH, *trans*), 956 (conjugated double bonds) and 650 cm⁻¹ (C—Cl).

NMR data (Fig 5): 0·90 ppm for C$\underline{H}_3$—, 1·35 ppm for —$(CH_2)_n$—, 2·1 ppm for —C$\underline{H}_2$—CH═ or —C$\underline{H}_2$—C≡, 2·30 ppm for —C$\underline{H}_2$—COOH, 3·65 ppm for —C≡C—C$\underline{H}_2$—CH═CCl— or —CH═CCl—C$\underline{H}_2$—CH═C═CH— and 5·2–6·8 ppm for the protons in the conjugated double bonds. The conjugation of the allenic group with a double bond is likely to shift the proton resonance of the grouping —C$\underline{H}$═C═C$\underline{H}$— from the value (4·93 ppm) reported by Gunstone *et al.*[10] to lower field. This signal and that due to the grouping —CH═C$\underline{H}$—C≡C— (lit.[11] 5·4 ppm) are covered by the multiplets due to the protons of the conjugated double bonds. The signal at 3·65 ppm may again be indicative for a product formed by the addition of ethylene glycol to a triple bond. According to the results of Cross and Mackay[12] the protons in the grouping —OC$\underline{H}_2$—C$\underline{H}_2$O— resonate at the region 3·0–3·9 ppm.

The UV absorption maxima at 238, 244, 271 and 278 nm also show the presence of conjugation. Two last maxima may be due to the conjugated trienes including one chlorine atom.

The mass spectrum has a small peak at *m/e* 375, which may be due to the molecular ion of the above-mentioned ethylene glycol adduct (313 + 62). The peak at *m/e* 349 is due to the remaining first-step product. The large peak at *m/e* 313 represents the molecular ion of the second-step product in agreement with the molecular weight (312·9) of $C_{18}H_{29}O_2Cl$. This peak has an intensity of 39% of the base peak at *m/e* 92. The other large peak (33%) at *m/e* 278 was assigned to correspond the fragment formed from the second-step product by the loss of Cl or HCl.

The continued heating of **1** in alkaline ethylene glycol (60 min at 130°C) caused the band at 1655 cm⁻¹ (C═C) to vanish and a new one to appear at 2220 cm⁻¹ (C≡C).

The third-step product. The product obtained after the dehydrochloroination of **1** for 8 h at 145°C gave the IR bands (Fig 4) at 3020 (CH═CH), 2220 (C≡C), 1942 (C═C═C), 1730 (ketonic C═O), 1710

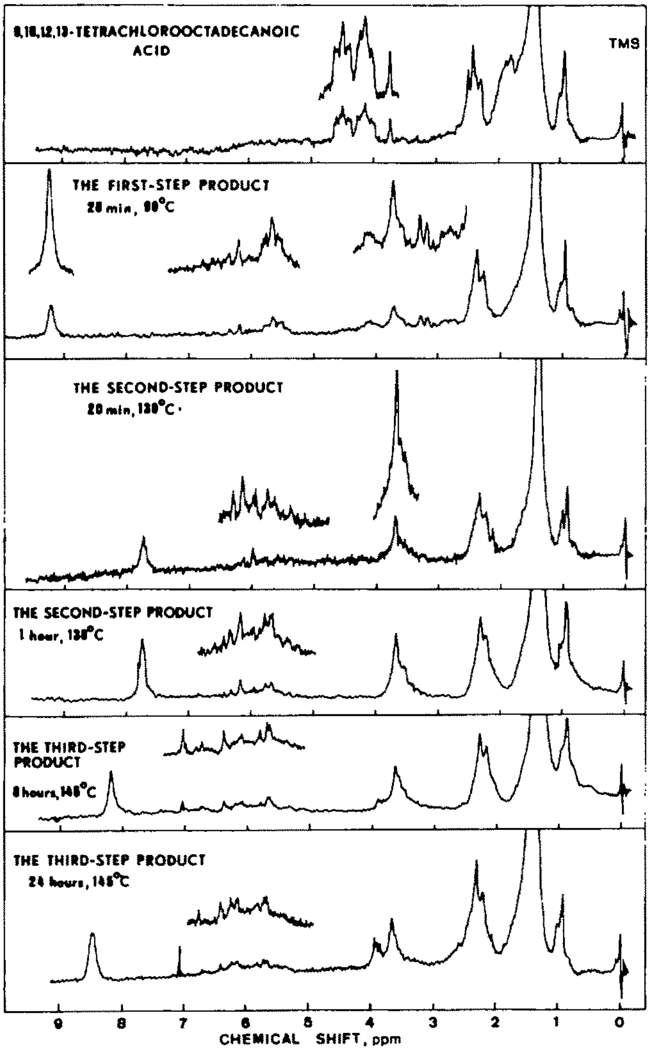


Fig 5. NMR spectra of *threo*, *threo*-9, 10, 12, 13-tetrachlorooctadecanoic acid and its dehydrochlorination products.

(COOH), 1668 (C═C), 1635 (C═C, conjugated with a triple bond) and 991 and 956 cm^{-1} (conjugated unsaturation). The C—Cl stretching vibration at 650 cm^{-1} was absent. The bands at 788 and 760 cm^{-1} may be due to trisubstituted alkenes.

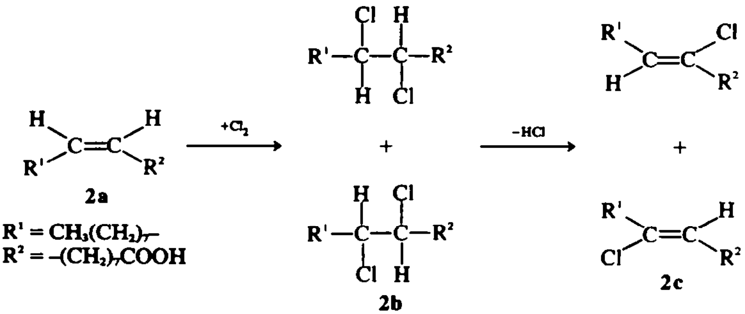
The NMR spectrum showed the following signals (Fig 5): 0·90 ppm for $C\underline{H}_3$—, 1·35 ppm for —$(C\underline{H}_2)_n$—, 2·08 ppm for —$C\underline{H}_2$—CH═ or —$C\underline{H}_2$—C≡, 2·29 ppm for —$C\underline{H}_2$—COOH and 5·2–7·2 ppm for the protons of the conjugated double bonds. The group of peaks at the region 3·2–3·9 ppm are likely to be due to the secondary reaction products, which may be formed by addition of ethylene glycol to a triple bond.

The UV absorption maxima at 233, 238, 257, 267, 275, 298 and 315 nm also reveal conjugated unsaturation.

In the mass spectrum the peaks at *m/e* 339 and 295 may correspond the molecular ions of the products formed when the third-step product adds to ethylene glycol and water, respectively. The peak at *m/e* 277 represents the molecular ion of the third-step product in agreement with the molecular weight (276·4) of $C_{18}H_{28}O_2$.

Further treatment of **1** with alkali (for 24 h at 145°C) caused the disappearance of the IR absorption band at 1942 cm^{-1} (C═C═C) and the decrease of the intensity of the band at 2220 cm^{-1} (C≡C).

Mechanism of dehydrochlorination. It is well known that addition of chlorine to linear olefins preponderantly proceeds in the *trans*-sense.[13] Thus the addition of chlorine to oleic acid (*cis*-9-octadecenoic acid, **2a**) gives two enantiomeric *threo*-dichlorides (**2b**):



On the other hand a bimolecular elimination mechanism (E2) is stereospecific and the elimination of HCl from **2b** leads to two isomeric *trans*-chloro alkenes (**2c**).[14] The chlorination of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid) yields four enantiomeric tetrachlorides, of which **1** had the least solubility and the highest melting point.[15]

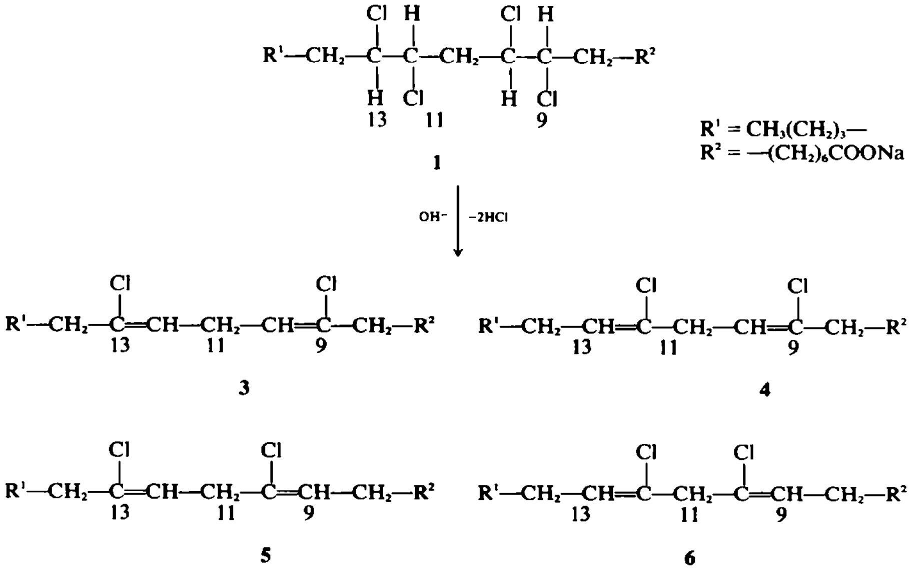
As shown by GLC (Fig 3) many reaction products are formed in all three of the dehydrochlorination steps of **1**. Secondary reaction products, especially in the third reaction step, make the interpretation of the analytical results more difficult. In the following the principal reaction paths of the alkaline dehydrochlorination of **1** are discussed in light of the kinetic and spectroscopic results.

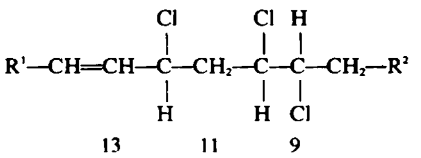
The preliminary kinetic experiments pointed out that the base-promoted dehydrochlorination of **1** involves roughly three distinct reaction steps owing to the different reactivity of the chlorine atoms.

Reaction step 1. The previous results dealing with the alkaline dehydrochlorination of sodium *threo*-9,10-dichloro- **2b** and *threo*-9(10)-chloro-10(9)-hydroxyoctadecanoates[1-3] enable one to assume that the dehydrochlorination of **1**, also, occurs principally through bimolecular elimination (E2). Accordingly, the first reaction step may yield four isomeric dichloro-*trans*-9,*trans*-12-octadecadienoates which may contain two chlorine atoms at positions 9, 13 (**3**), 9, 12 (**4**), 10, 13 (**5**) and 10, 12 (**6**). Their double bonds contain, of course, two vinylic hydrogen atoms but the NMR analysis of the first-step product showed, however, that the total relative number of double bond hydrogens was 2·7. This means that the sodium dichlorooctadecadienoates formed should include approximately three double bond hydrogens. Probably the vinylic and isolated double bonds, formed initially during the first reaction step, become partly conjugated like linoleic acid in similar media. Spectroscopic analyses of the first-step reaction products are consistent with this assumption.

The reaction scheme below presupposes that both the first and second chlorine atoms are released as HCl at equal rates from the two methylene-interrupted *vic*-dichloride groupings in **1**. At first sight it seemed to be possible that also monoenes like **7** and **8** could be formed from **1**.

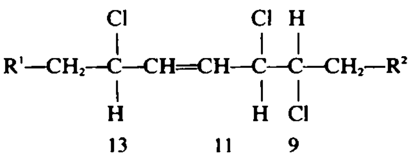
However, **7** contains one and **8** two chlorine





$R^1-CH=CH-CHCl-CH_2-CHCl-CHCl-CH_2-R^2$

7



$R^1-CH_2-CHCl-CH=CH-CHCl-CHCl-CH_2-R^2$

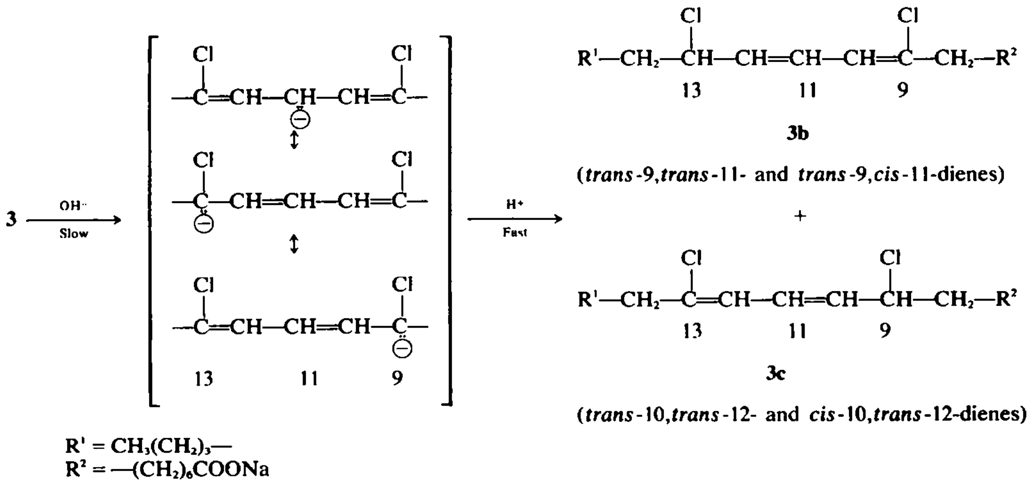
8

atoms in very reactive allylic positions. Thus the formation of **8** in the first dehydrochlorination step should lead to the release of three chlorine atoms nearly simultaneously. The experimental findings, however, do not support this view. After the formation of **7** the spontaneous release of the allylic chlorine may, of course, explain the observation that in the first reaction step two chlorine atoms are split off at nearly equal rates. This means, however, that the two closely related *vic*-dichloride groupings should have greatly different reactivities. Experimentally, the rate of the first dehydrochlorination step at 90°C was about 15 times greater than that of the second (Table 1). A rate difference of this order of magnitude can not be explained with the different reactivities of the two vicinal dichloride groupings but the occurrence of **7** and **8** as the reaction intermediates in the dehydrochlorination of **1** is only of minor importance.

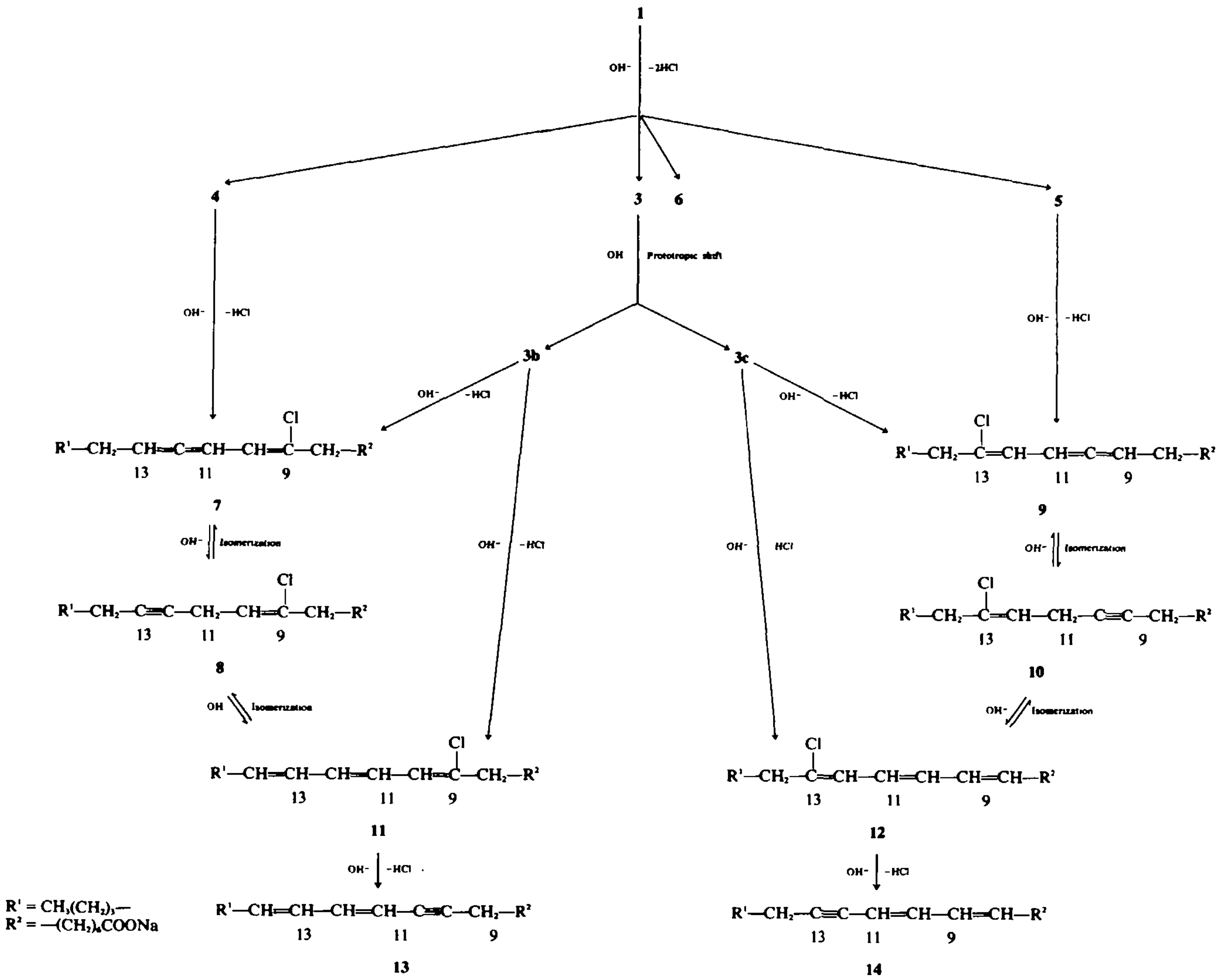
Reaction step 2. Scheme 2 presents the reaction paths proposed for the further dehydrochlorination of **1** the first-step products **3**, **4** and **5**. The fourth possible intermediate **6** seems to be of less importance. The dehydrochlorination of **3** is likely to be preceded by conjugation-isomerization whereas **4** and **5** may directly release HCl. In both cases the reaction leads to two allenes **9** and **10**, which may further isomerize *via* **11** and **12** to conjugated monochloro trienes **13** and **14**. The overall reaction rates measured for the second dehydrochlorination include both the direct elimination of HCl from **4** and **5** and the removal of HCl after the base-catalyzed prototropic shifts. The reactivity of allylic chlorides is very much greater than those of alkyl or vinyl chlorides.[16] Therefore the rate determining step in the second dehydrochlorination stage of **3** is the alkaline conjugation-isomerization followed by the rapid elimination of the allylic chlorine as HCl. The dehydrochlorination of the first-step products **4** and **5** may also occur through a prototropic shift-elimination which results in the same final products **15** and **16** after the third reaction step. It is, however, more likely that HCl is removed directly from **4** and **5** because of the presence of the central methylene group being activated by vinylic double bonds.

It is well known that allylic compounds easily undergo allylic isomerization.[17] It may be shown that the allylic rearrangement of **3b** and **3c** followed by a spontaneous elimination of HCl leads to the allenes **9** and **10** and thereafter to the same final products **15** and **16** as shown in Scheme 2.

The base-catalyzed conjugation-isomerization occurs in two steps (Scheme 1). After a slow deprotonation stage the base attacks on the central methylene group and a fast protonation step follows.[18] The carbanion formed from the first-step product **3** is stabilized by resonance as shown in Scheme 1. The prototropic shift gives two pairs of geometric isomers from all of the first-step products. It has been reported that the isomerization of methyl *trans*-9,*trans*-12-octadecadienoate in al-



SCHEME 1. The prototropic shifts of the first-step product 3.



SCHEME 2. Proposed reaction paths of dehydrochlorination of 1.

kaline ethylene glycol yielded 56% of *trans,trans*-conjugated dienes, 39% of *cis,trans*-conjugated dienes but not at all *cis,cis*-conjugated dienes.[19] The double bonds in the *trans,trans*-conjugated dienes located mainly (89%) at positions 9, 11 and 10, 12.[19] Similarly, during the treatment of *cis*-9,*cis*-12-octadecadienoic acid (linoleic acid) under mild alkaline conditions, the double bond migrates towards the central methylene group.[17,18,20,21]

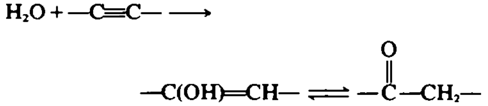
Blekkingh *et al.*[21] could not find secondary migrations in the conjugated dienes formed from linoleic acid. However, Koritala[19] stated that secondary reaction products—8,10- and 11,13-isomers of methyl *trans*-9,*trans*-12-octadecadienoate—are formed *via* prolonged heating. It has been reported earlier that the conjugation reactions occur, also, in alkaline water solutions, the most important factor being temperature.[22]

The formation of conjugated double bonds in the elimination reactions of **1** increases the tendency to polymerization and cyclization reactions. According to Sagredos *et al.*[23] conjugated octadecatrienoic acids including a *cis* central double bond are very sensible to produce disubstituted cyclohexadienes in alkaline ethylene glycol. The second dehydrochlorination step of **1** may produce *trans,cis,trans*- and *trans,trans,trans*-conjugated double bond systems which should thus be capable of ring formation. Any cyclohexadiene derivatives cannot, however, be detected, indicative for a minor formation of these compounds under conditions used in this work. The characteristic NMR shifts of the double bond protons of 1,3- and 1,4-cyclohexadienes are located at 5·83 and 5·78 ppm, respectively.[24] If these signals were very weak they might be obscured by the aliphatic double bond proton signals locating at the same region.

Reaction step 3. As shown in Scheme 2 the dehydrochlorination of the second-step products **13** and **14** give dienynes **15** and **16**, which contain two double bonds and one triple bond in conjugated sequence. The final products **15** and **16** are, also, composed of geometric isomers and the both double bonds can have *cis*- and/or *trans*-configurations (Scheme 1). The strongly alkaline ethylene glycol used in this work is very suitable for the geometric isomerization of these double bonds.

The third dehydrochlorination step could occur directly from the intermediates **11** and **12** (Scheme 2) yielding the identical diacetylenic acids. However, diynes which should be formed through this reaction path cannot be detected among the final reaction products in the total dehydrochlorination of **1**. Khan[6] reported that the alkaline dehydrobromination of 9,10,12,13-tetrabromooctadecanoate produced polymers containing bromine but no diacetylenic derivatives. In the present case, the average molecular weight of the dehydrochlorination products of **1** determined by mass spectrometry excludes the formation of polymeric byproducts.

It is well known that alkoxides can catalyze the addition of alcohols to a triple bond.[25] In this work the reaction mixtures containing alkoxide ions, anion of ethylene glycol, which were formed by the equilibration of the ethylene glycol and hydroxide ion: $ROH + OH^- \rightleftharpoons RO^- + H_2O$. The analytical results showed that the addition of ethylene glycol to a triple bond formed in dehydrochlorination of **1** is appreciable under conditions used. Also water can add to a triple bond:



$$H_2O + \text{—C}\equiv\text{C—} \longrightarrow$$
$$\text{—C(OH)}=\text{CH—} \rightleftharpoons \text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—CH}_2\text{—}$$

The evidence for this reaction is given by the IR analysis of the dehydrochlorination products (Fig 4). The ketonic carbonyl produced a new absorption band at 1730 cm^{-1} forming a broad peak in the region 1730–1710 cm^{-1} with the acid carbonyl absorption.

CONCLUSIONS

The proposed routes for the alkaline dehydrochlorination of **1** are shown in Scheme 2. The results of the kinetic experiments and the product analysis lead to the conclusion that at first two chlorine atoms, one from both *vic*-dichloride groupings, are eliminated nearly simultaneously. Accordingly, two vinylic double bonds are formed corresponding to the behaviour of a single *vic*-dichloride grouping in similar media.[1,2] The reaction rate increases with increasing number of the methylene-separated *vic*-dichloride groupings, the rate ratio of **1** and **2b** being 3·2 at 90°C (Table 2). After the first reaction step the dehydrochlorination products from **1** are like linoleic acid capable of isomerization. After the prototropic shift one of the remaining chlorine atoms is in an allylic position with respect to the migrated double bond and is thus released spontaneously. According to the earlier study[1,2] the alkaline dehydrochlorination of 9(10)-chloro-*trans*-9-octadecanoate **2c** produces 9-octadecynoic acid but no indication of the formation of allenic intermediate could be found. On the other hand the free energy of activation for the second-step dehydrochlorination of **1** is much lower than that for the triple bond formation (Table 2). Therefore the direct elimination of HCl from the first-step products without the prototropic rearrangement is unreal. In fact, the base-promoted conjugation is the rate-determining step of the second dehydrochlorination stage of **1**. The removal of the last chlorine atom as HCl during the third reaction step produces a triple bond conjugated with two double bonds. The fact that the free energy of activation for this reaction step is markedly lower than that for the triple bond formation in the second dehydrochlorination stage of sodium salt of *threo*-

9,10-dichlorooctadecanoic acid **2b** (Table 2) is in accordance with the increasing conjugation in the former case. In otherwords, the formation of a triple bond conjugated with respect to the double bond system is also observable in the increased stability of the transition state.

EXPERIMENTAL

threo,threo-9,10,12,13-*Tetrachlorooctadecanoic acid* has been synthesized previously.[15] It was converted to sodium salt **1** to increase its solubility into aqueous ethylene glycol. The conversion was carried out in alkaline methanol.

The kinetic measurements were made as reported earlier.[1,2]

The gas–liquid chromatographic analysis of the reaction products were carried out under isothermal conditions at 185°C with a Perkin-Elmer F11 gas chromatograph equipped with a flame ionization detector and a 200 cm stainless steel column (i.d. 1/8 in) packed with Chromosorb G (60/80 mesh), and coated with 5% XE-60.

Proton resonance spectra were recorded on a Perkin-Elmer R10 NMR spectrometer (60 MHz) using CCl_4 as solvent and tetramethyl silane (TMS) as internal reference. The sample concentrations varied between 5–10% (w/v). IR absorption spectra were obtained with a Perkin-Elmer Model 180 IR Spectrophotometer using potassium bromide pellets or a thin liquid film between potassium bromide windows. UV absorption spectra were recorded on a Unicam SP 800 Spectrophotometer using absolute ethyl alcohol (the State Alcohol Monopoly, Grade AaS, for Spectrophotometry) as solvent. The mass spectra were taken with a Perkin-Elmer M 270 Mass Spectrometer. The samples were introduced into the mass spectrometer as solid.

Isolation of the dehydrochlorination products. The reaction products in the alkaline dehydrochlorination of **1** were separated from the reaction mixtures and analyzed by spectroscopic methods. The reaction mixtures composed of 2 g of **1** and 200 g of aqueous alkaline ethylene glycol containing 5·4 wt.% of water and 0·73 moles of NaOH per kg of solvent. They were kept 20 min at 90° and 130°, and 24 h at 145°C to obtain (mainly) the reaction products of the first, second and third dehydrochlorination steps, respectively. In addition, two other reaction products obtained by the alkali treatment of **1** for 1 h at 130° and for 8 h at 145°C, were separated and studied.

The reaction mixtures were acidified ($pH < 2$) with 2·5 N aqueous HNO_3 and diluted by adding 200 ml of water. The acid solutions were then extracted six times with 100 ml of CCl_4. The combined extracts were dried with anhydrous Na_2SO_4 in dark for 20 h and then filtered. The solvent was evaporated from the filtrate in a rotating vacuum evaporator (Heidolph-Elektro KG, Germany). The temperature of the surrounding water bath was held at 50–55°C. The amounts of the viscous residues varied from 1·2 to 1·4 g. Attempts to crystallize the residues from acetone at − 75° and from acetonitrile at − 40°C were not successful.

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