RADICAL ADDITIONS TO OLEFIN DERIVATIVES. V.*

PREPARATION OF β,ω-DIHALOGENALKANOIC ACIDS AND SOME OF THEIR REACTIONS

S. DOLEŽAL

Department of Organic Chemistry,
Institute of Chemical Technology, Prague 6

Received October 2nd, 1971

Under the effect of sulfuric acid on acetates of tetrachloroalkanols *I* dichloroalkane acids *II* were formed from which *trans-trans*-alkadiene acids *III* were formed on heating with an alcoholic potassium hydroxide solution, and corresponding ω-hydroxy-*trans*-2-alkenoic acids *IV* on boiling with potassium acetate at elevated temperature.

During our study of the utilisation of radical reactions for the synthesis of substituted unsaturated acids[1-3] we followed the acid hydrolysis of acetylated tetrachloroalkanols *I* which are formed on addition of tetrachloromethane to corresponding alkenol acetates[2]. Under the effect of 95% sulfuric acid on acetates of tetrachloroalkanol *I* dichloroalkanoic acids *II* are formed which may be isolated either free or in the form of esters. The acetoxyl group of the starting compound *I* is thus substituted by chlorine under the effect of hydrogen chloride liberated in the reaction medium. In this manner 3,6-dichlorohexanoic acid (*IIa*) and its methyl ester (*IIa*, $R^2 = CH_3$), 3,7-dichloroheptanoic acid (*IIb*) and 3,5-dichlorohexanoic acid (*IId*) were prepared, not yet described in the literature. In the case of higher homologs (with 10 C-atoms and more) of dichloroalkanoic acids and their ester *II* a molecule of hydrogen chloride is easily split off on distillation. The substances are purified with difficulty and the analysis of compounds *IIc*, *IIe*, and *IIf* are characterised by a lower content of chlorine. Therefore, for subsequent reactions, these homologs were used in crude state, and the products were identified only in the next reaction step.

From dichloroalkanoic acids or their esters *II* alkadienoic acids *III* were formed on heating with ethanolic potassium hydroxide solution, *i.e.* 2,5-hexadienoic acid (*IIIa*), 2,6-heptadienoic acid (*IIIb*), and 2,11-dodecadienoic acid (*IIIc*). 2,4-Alkadienoic acids were isolated in the form of esters, *i.e.* ethyl ester of 2,4-hexadienoic acid (sorbic acid) (*IIId*, $R^2 = C_2H_5$), methyl ester of 2,4-decadienoic acid (*IIIe*, $R^2 = CH_3$), and ethyl ester of 2,4-undecadienoic acid (*IIIf*, $R^2 = C_2H_5$). After the elimination reaction of the dichloroalkanoic acid *IIa* a product of substitution

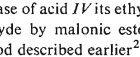
* Part IV: This Journal *35*, 1932 (1970).

was also isolated in low yield in addition to acid *IIIa*, *i.e.* 6-hydroxy-*trans*-2-hexanoic acid (*IVa*). According to the known mechnism of *trans* elimination reactions, to which the method used also belongs, we assign the double bonds formed *trans* configuration, *i.e.*, for 2,4-alkadienoic acids configuration *trans-trans*.

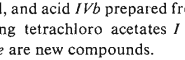
Esters *IIId* ($R^2 = C_2H_5$)[4], *IIe* ($R^2 = CH_3$) (ref.[5,12]) and *IIIf* ($R^2 = C_2H_5$) (ref.[6,7]) were already described in the literature. Acid *IIIa* is known in the form of its *cis*-isomer[8] or in the form of ester[2,9]. Acid *IIIe* is also known in the form of its butylamide as a component of the natural insecticide pellitorine[10].

Further experiments were carried out in order to transform β,ω-dichloroalkanoic acids *IIa*, *IIb*, and *IIc* to corresponding ω-hydroxy-*trans*-2-alkenoic acids *IV*. Heating with a solution of sodium carbonate or potassium acetate did not lead to pure products. Hydrolysis almost did not take place, only elimination, and the isolated substances contained a variable amount of chlorine. Only when the reaction was carried out in the presence of potassium acetate in diethylene glycol at elevated temperature and in a closed vessel could ω-hydroxy-2-alkenoic acids *IV* be isolated in satisfactory purity, except for acid *IVc* which would not crystallise after isolation.

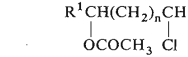
In the case of acid *IV* its ethyl ester[2] has been described, and acid *IVb* prepared from 5-hydroxy-valeraldehyde by malonic ester synthesis[11]. The starting tetrachloro acetates *I* were prepared by a method described earlier[2], while homologs *Ib* and *Ie* are new compounds.



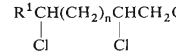
I



II



III



IV

a, $R^1 = H$, $n = 2$
b, $R^1 = H$, $n = 3$
c, $R^1 = H$, $n = 8$

d, $R^1 = CH_3$, $n = 1$
e, $R^1 = C_5H_{11}$, $n = 1$
f, $R^1 = C_6H_{13}$, $n = 11$

$R^2 = H, CH_3, C_2H_5$

EXPERIMENTAL

IR spectra were measured in chloroform on a Zeiss UR-10 spectrophotometer.

Starting Compounds

The acetates of tetrachloroalkanol *I* were prepared by a known method[2], except for homologs *Ib* and *Ie*, which were not described so far. 5,7,7,7-*Tetrachloro*-1-*heptanol acetate* (Ib), b.p. 103°C/0·4 Torr was prepared in 69% yield. For $C_9H_{14}Cl_4O_2$ (296·0) calculated: 36·52% C, 4·77% H,

47·91% Cl; found: 46·67% C, 4·87% H, 47·41% Cl. 1,1,1,3-*Tetrachloro-5-dekanol acetate* (Ie), b.p. 130–133°C/0·6 Torr was prepared in 66·5% yield. For $C_{12}H_{20}Cl_4O_2$ (338·1) calculated: 42·63% C 5·96% H, 41·94% Cl; found: 42·92% C, 6·09% H, 42·03% Cl.

Dichloroalkanoic Acids and Esters *II*

0·1 mol of tetrachloro acetate *I* was added dropwise and under stirring to 100 ml of 95% sulfuric acid. The addition was carried out at −10°C to 0°C over 90 min. The reaction mixture was allowed to stand at room temperature for 60–70 h, under occasional stirring and bubbling through with nitrogen which took off the formed hydrogen chloride from the reaction mixture. (In the case of the hydrolysis of substance *Ib* the reaction mixture was allowed to stand at 20°C for 24 hours and it was then heated at 30–35°C for another 8 h; the yield was lower). Then the solution was poured onto 1 kg of crushed ice and the product was extracted with ether, washed with water, and acid *II* was reextracted with 10% sodium carbonate solution. The neutral components were eliminated by washing with ether. By acidification of the alkaline solution with 10% HCl the acid was liberated and then extracted with ether. After washing the extract with water and drying over magnesium sulfate ether was distilled off and the product submitted to fractional distillation under reduced pressure. In the case of products *IIc*, *IIe*, and *IIf* the crude acid was esterified with methanol in the presence of acetyl chloride[14]. The corresponding methyl esters *II* formed (R^2 = $= CH_3$), had however (according to elemental analysis) a lower content of chlorine. Therefore crude acids *IIc*, *IIe*, and *IIf* or their esters were used for the preparation of acids *III* by elimination reaction without isolation and further purification. Yields, analyses and physical constants of substances are listed in Table I.

TABLE I

Preparation of β,ω-Dichloroalkanoic Acids

Starting compound	Product (yield, %)	B.p. °C/Torr	Formula (mol. w.)	Calculated/Found % C	% H	% Cl	IR spectrum cm^{-1}
Ia	*IIa*[a], $R^2 = H$ (64·5)	115–116 0·6	$C_6H_{10}Cl_2O_2$ (185·0)	38·94 38·97	5·45 5·40	38·32 38·13	1 720
Ib	*IIb*, $R^2 = H$ (25)	94–96 0·2	$C_7H_{12}Cl_2O_2$ (149·2)	42·21 42·57	6·07 6·32	35·61 35·20	1 720
Ic	*IIc*, $R^2 = CH_3$ (35)	185–190 0·01	$C_{13}H_{23}Cl_2O_2$ (283·2)	— —	— —	25·04 16·70	1 665, 1 735
Id	*IId*, $R^2 = H$ (42)	109–111 0·8	$C_6H_{10}Cl_2O_2$ (185·05)	38 94 39·30	5·45 5·49	38·32 38·30	1 730
Ie	*IIe*, $R^2 = CH_3$ (25)	110–115 0·6	$C_{11}H_{20}Cl_2O_2$ (255·2)	51·77 56·21	7·90 7·90	27·79 21·91	1 660, 1 730
If	*IIf*, $R^2 = CH_3$) (30)	116–120 0·5	$C_{12}H_{22}Cl_2O_2$ (269·2)	— —	— —	26·34 20·70	1 655, 1 735

[a] Methyl ester *IIa*, $R^2 = CH_3$, was prepared using dimethylacetal of acetone[13], b.p. 81°C/1 Torr, in 85% yield. For $C_7H_{12}Cl_2O_2$ (199·2) calculated: 42·33% C, 6·08% H, 35·62% Cl; found: 42·47% C, 6·22% H, 35·53% Cl. IR-Spectrum: 1 745 cm^{-1}.

Alkadienoic Acids and Esters *III*

To 0·1 mol of dichloroalkanoic acid or ester *II* 140 ml of a 18% ethanolic KOH were added and the mixture was refluxed for 12 h. After cooling the separated potassium chloride was filtered off and the filtrate evaporated under reduced pressure. The residue was worked up in two ways. Acids *IIIa*, *IIIb*, and *IIIc* were isolated by acidification of the residue with 5% HCl in the cold and extraction of the product with ether. After washing the extract with water and drying over magnesium sulfate ether was evaporated and the crude alkadienoic acid was vacuum distilled. In addition to acid *IIIa* 6% of a by-product were also isolated to which structure *IVa* ($R^2 = H$) was assigned on the basis of elemental analysis and infrared spectra. Other acids *III* were isolated in the form of their esters as *IIId* $R^2 = C_2H_5$, *IIIe* $R^2 = CH_3$, and *IIIf* $R^2 = C_2H_5$. Saturated alcoholic hydrogen chloride solution was added to the residue and the mixture boiled for 30 min. After cooling the separated potassium chloride was filtered off and the filtrate was diluted with 100 ml of benzene. The mixture was concentrated under normal pressure almost to dryness. Saturated hydrogen chloride solution in corresponding alcohol (100 ml) was then added again and the mixture refluxed for 4 h. After evaporation of the bulk of the alcohol the residue was dissolved in 150 ml of ether, the solution washed with water saturated sodium hydrogen carbonate solution, and water, and then dried over magnesium sulfate. After evaporation of ether the residual ester was distilled under reduced pressure. Yields, analyses and constants of acids and esters *III* are listed in Table II.

TABLE II

Preparation of Alkadienoic Acids and Esters *III* and ω-Hydroxy-2-alkenoic Acids *IV*

Starting compound	Product (yield, %)	B.p., °C/Torr (ref.)	Formula (mol. w.)	Calculated/Found % C	Calculated/Found % H	IR-Spectrum cm^{-1}
IIa ($R^2 = H$)	*IIIa*, $R^2 = H$ (33)	135/15 —	$C_6H_8O_2$ (112·1)	64·27 63·98	7·19 7·31	980, 1 628 w, 1 652, 1 740
IIa ($R^2 = H$)	*IVa*, $R^2 = H$) (6)	165–170/9 —	$C_6H_{10}O_3$ (130·1)	55·38 55·73	7·74 7·89	975, 1 650, 1 735, 3 465
IIb ($R^2 = H$)	*IIIb*, $R^2 = H$) (50)	134–135/12 —	$C_7H_{10}O_2$ (126·2)	66·64 66·80	7·99 7·97	985 w, 1 662 1 735
IIc ($R^2 = CH_3$)[a]	*IIIc*, $R^2 = H$ (29)	155–160/0·02 —	$C_{12}H_{20}O_2$ (196·3)	73·43 73·71	10·27 10·25	985 w, 1 660, 1 735
IId ($R^2 = H$)	*IIId*, $R^2 = C_2H_5$ (42·5)	78–79/12 (82·5/13)[4]	$C_8H_{12}O_2$ (140·2)	68·58 68·30	8·63 8·62	950, 1 628 w, 1 650, 1 720
IIe ($R^2 = H$)[a]	*IIIe*, $R^2 = CH_3$ (45)	110–115/0·8 (69–70/0·25)[5]	$C_{11}H_{18}O_2$ (182·3)	72·49 72·23	9·94 10·31	990, 1 645, 1 725
IIf ($R^2 = H$)[a]	*IIIf*, $R^2 = C_2H_5$) (39)	105–110/0·2 (155–160/4)[7]	$C_{13}H_{22}O_2$ (210·3)	74·24 74·01	10·55 10·72	980 w, 1 650, 1 730
IIa ($R^2 = H$)	*IVa*, $R^2 = H$ (46)	125–135/0·15 —	$C_6H_{10}O_3$ (130·1)	55·38 55·27	7·74 7·59	980, 1 645, 1 730, 3 480,
IIb ($R^2 = H$)	*IVb*, $R^2 = H$ (40)	138–142/0·1 (152/0·1[11]	$C_7H_{12}O_3$ (144·2)	58·31 58·13	8·39 8·32	970, 1 650, 1 730, 3 450

[a] Crude product was taken into the reaction.

ω-Hydroxy-2-alkenoic Acids *IV*

A mixture of 0·02 mol of dichloroalkanoic acid *II*, 15 ml of diethylene glycol, 0·04 mol of anhydrous potassium acetate, and 0·10 mol of water was heated in a glass vessel (inserted in a metallic pressure vessel) at 170°C (bath temperature) for 4 h. This temperature was then maintained for 30 h. After opening of the reaction vessel the mixture was diluted with 100 ml of water and boiled for 2 h. The solution was then saturated with ammonium sulfate and extracted with ether, the extract was washed with water (in the case of lower homologs with saturated sodium chloride solution) and dried over magnesium sulfate. After distillation off of ether the residue was distilled at reduced pressure. The yields, physical constants, and analyses of the isolated ω-hydroxy-2-alkenoic acids *IV* are listed in Table II.

The analyses were carried out in the analytical department, Central Laboratories, Institute of Chemical Technology, Prague, by Mrs B. Dědková, E. Bukáčková, H. Ráblová and J. Pechová. The IR spectra were measured by Dr E. Janáčková and Dr A. Kohoutová, Department of Instrumental Analysis, Central Laboratories, Institute of Chemical Technology, Prague.

REFERENCES

1. Doležal S.: This Journal *30*, 2638 (1965).
2. Doležal S.: This Journal *31*, 3765 (1966).
3. Doležal S.: This Journal *35*, 1932 (1970).
4. Rigg M. W., Rosenthal R.: J. Am. Chem. Soc. *71*, 2865 (1949).
5. Crombie L.: J. Chem. Soc. *1955*, 1007.
6. Anschütz R., Pictet A.: Ber. *13*, 1175 (1880).
7. Shigehiro Abe, Kikumasa Sato: J. Chem. Soc. Japan, Pure Chem. Sect. *75*, 953 (1954).
8. Chiusoli G. P.: Angew. Chem. *72*, 74 (1960).
9. Chiusoli G. P., Agner G., Geselli C. A., Merzoni S.: Chim. Ind. (Milan) *46*, 21 (1964); Chem. Abstr. *60*, 10539 (1964).
10. Crombie L.: J. Chem. Soc. *1955*, 995.
11. Kennedy J., Corkindale N. J., Raphael R. A.: J. Chem. Soc. *1961*, 3813.
12. Crossley A., Hilditch T. P.: J. Chem. Soc. *1949*, 3355.
13. Lorette N. B., Brown J. H. jr: J. Org. Chem. *24*, 261 (1959).
14. Baker B. R., Schaub R. E., Querry M. V., Williams J. H.: J. Org. Chem. *17*, 84 (1952).

Translated by Ž. Procházka.