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THE GAS–LIQUID CHROMATOGRAPHIC PROPERTIES OF TEN SYNTHETIC CHLOROACETYLENES

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SUMMARY

Two series of chloroacetylenes, $CH_3(CH_2)_mC \equiv C(CH_2)_nCl$, where $m = 0$–4 and $n = 1$–4, were prepared and their gas-liquid chromatographic behaviour studied on polar (diethylene glycol succinate polyester) and non-polar (Apiezon L) stationary phases.

INTRODUCTION

The methods for the preparation of cyclic and acyclic acetylenic halides have been extensively reviewed by Viehe[1]. Gunstone and co-workers[2,3] and others[4-7] have employed numerous straight-chain acetylenic halides as intermediates in the synthesis of unsaturated fatty acids.

EXPERIMENTAL AND RESULTS

In the present work, two homologous series of chloroacetylenes were prepared:

Series 1: $CH_3(CH_2)_4C \equiv C(CH_2)_nCl$

1-chloroundec-5-yne	$n = 4$	$C_{11}\Delta^{5a}$–Cl
1-chlorodec-4-yne	$n = 3$	$C_{10}\Delta^{4a}$–Cl
1-chloronon-3-yne	$n = 2$	$C_9\Delta^{3a}$–Cl
1-chlorooct-2-yne	$n = 1$	$C_8\Delta^{2a}$–Cl

Series 2: $CH_3(CH_2)_mC \equiv C(CH_2)_3Cl$

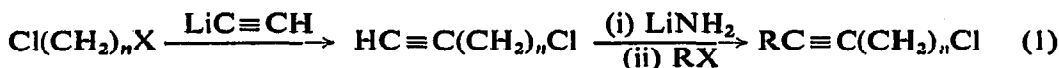|		
1-chlorodec-4-yne	$m = 4$	$C_{10}\Delta^{4a}$–Cl
1-chloronon-4-yne	$m = 3$	$C_9\Delta^{4a}$–Cl
1-chlorooct-4-yne	$m = 2$	$C_8\Delta^{4a}$–Cl
1-chlorohept-4-yne	$m = 1$	$C_7\Delta^{4a}$–Cl
1-chlorohex-4-yne	$m = 0$	$C_6\Delta^{4a}$–Cl
1-chloropent-4-yne	$HC \equiv C(CH_2)_3Cl$	$C_5\Delta^{4a}$–Cl

The gas–liquid chromatographic (GLC) properties of these chloroacetylenes were studied on polar (diethylene glycol succinate polyester, DEGS) and non-polar (Apiezon L, ApL) stationary phases. Castello and D'Amato[8] have analyzed the GLC

behaviour of alkyl halides and were able to correlate their molecular structures with their retention times.

In our study of the retention values of chloroacetylenes, both methyl esters of straight-chain fatty acids and n-chloroalkanes were used as internal reference standards to determine the equivalent chain length (ECL)[9] of the available chloroacetylenes.
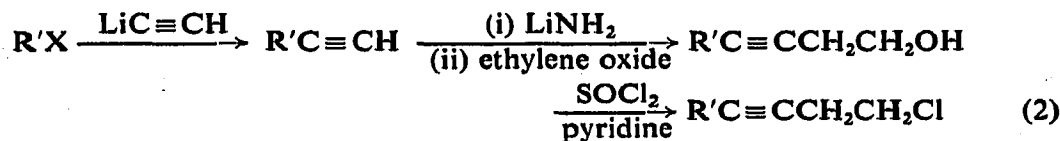
Preparation of chloroacetylenes

Most of the chloroacetylenes were prepared by a single multi-stage reaction. One general method sufficed for seven chloroacetylenes (namely C_5, C_6, C_7, C_8, C_9, $C_{10}\Delta^{4n}$–Cl and $C_{11}\Delta^{5n}$–Cl), as shown in eqn. 1.

$$Cl(CH_2)_nX \xrightarrow{LiC\equiv CH} HC\equiv C(CH_2)_nCl \xrightarrow[\text{(ii) RX}]{\text{(i) } LiNH_2} RC\equiv C(CH_2)_nCl \quad (1)$$

where n = 3 or 4, X = Br or I and R = n-alkyl.

This method cannot be used to prepare $C_9\Delta^{3n}$–Cl (n = 2) because reaction of $HC\equiv C(CH_2)_2Cl$ with lithamide gives mainly the elimination product[10] $HC\equiv C\cdot CH=CH_2$ and hardly any of the desired $LiC\equiv C(CH_2)_2Cl$ for further reaction with RX. We therefore used a procedure (eqn. 2) in which the acetylenic alcohol was first prepared by chain extension of a terminal acetylene by two carbon atoms by reaction with ethylene oxide, followed by chlorination of this intermediate with thionyl chloride using pyridine as catalyst:

$$R'X \xrightarrow{LiC\equiv CH} R'C\equiv CH \xrightarrow[\text{(ii) ethylene oxide}]{\text{(i) } LiNH_2} R'C\equiv CCH_2CH_2OH$$
$$\xrightarrow[\text{pyridine}]{SOCl_2} R'C\equiv CCH_2CH_2Cl \quad (2)$$

where R' = n-amyl.

The methylene-interrupted chloroacetylene was prepared by alkylation of the dilithium derivative[6] of propargyl alcohol and then chlorination of the intermediate with thionyl chloride in the usual way (eqn. 3):

$$HC\equiv CCH_2OH \xrightarrow[\text{(ii) R'X}]{\text{(i) } 2LiNH_2} R'C\equiv CCH_2OH \xrightarrow[\text{pyridine}]{SOCl_2} R'C\equiv CCH_2Cl \quad (3)$$
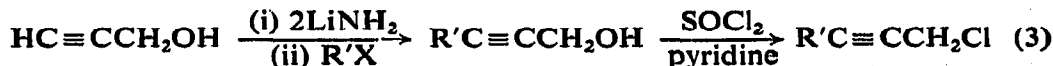
where R' = n-amyl.

1-Chloropent-4-yne ($C_5\Delta^{4a}$–Cl). Lithium acetylide was prepared by bubbling dry acetylene through lithamide (from 7 g of lithium) suspended in liquid ammonia (2 l) for 45 min. An ethereal solution (200 ml) of 1-bromo-3-chloropropane (157 g) was added dropwise and the mixture stirred overnight. The resulting 1-chloropent-4-yne was extracted with diethyl ether and distilled through a 50-cm Fenske column (60 g, 59% yield; b.p. 114–118°; ref. 11: 107–112°/709 mm).

1-Chlorodec-4-yne ($C_{10}\Delta^{4a}$–Cl). Lithium acetylide was prepared by the titration method[12] as follows. Dry acetylene was bubbled through stirred liquid ammonia (2 l) at the rate of 4–5 bubbles per second and lithium (7 g) cut into suitably small pieces was added to the liquid, each piece being added after the blue colour produced by the preceding piece had disappeared. The acetylene flow was stopped 3 min after the blue colour produced by the last piece of lithium had disappeared completely.

1-Chloro-3-bromopropane (157 g) in sodium-dried tetrahydrofuran (200 ml) was added slowly to the lithium acetylide suspension and the mixture stirred for 90 min. Lithamide (from 7 g of lithium, 2 g of iron(III)nitrate and 900 ml of ammonia) was carefully added to the reaction mixture and allowed to react for 1 h.

1-Bromopentane (149 g) in tetrahydrofuran (150 ml) was added to the reaction mixture, which was then stirred overnight. The product was extracted and distillation gave 1-chlorodec-4-yne (93 g, 54% yield; b.p. 113–116°/18 mm; ref. 3: 114–116°/15 mm).

$C_{11}\Delta^{5a}$–Cl; C_9, C_8, C_7 and $C_6\Delta^{4a}$–Cl. These chloroacetylenes were prepared as described above for 1-chlorodec-4-yne. The experimental results were:

	Yield	B.p.
1-chloroundec-5-yne	61%	76–80°/ 2 mm; ref. 13: 90–92°/1.5 mm
1-chloronon-4-yne	60%	82–85°/20 mm; ref. 14: 117°/40 mm
1-chlorooct-4-yne	58%	76–80°/22 mm; ref. 15: 87°/23 mm
1-chlorohept-4-yne	52%	110–114°/70 mm; ref. 16: 74.5°/31 mm
1-chlorohex-4-yne	44%	49–52°/25 mm

1-Chlorooct-2-yne ($C_8\Delta^{2a}$–Cl). Propargyl alcohol (56 g, 1 mole) in dry diethyl ether (200 ml) was added to a suspension of lithamide (from 15 g lithium, 2 g of iron(III) nitrate and 2 l of ammonia) and the mixture stirred for 1 h. 1-Bromopentane (96 g, 0.6 mole) in diethyl ether (200 ml) was added to the reaction mixture, which was then stirred overnight. Distillation gave oct-2-ynol (60 g, 80% yield; b.p. 86–89°/6 mm, ref. 3: 96–99°/12 mm).

Oct-2-ynol (30 g) was mixed at 0–5° with thionyl chloride (47 g) and pyridine (2 g) and the mixture heated for 3 h at 50°. Water was added and the extract on distillation gave 1-chlorooct-2-yne (29 g, 85% yield; b.p. 58–60°/4 mm, ref. 17: 40–41°/0.5 mm).

1-Chloronon-3-yne ($C_9\Delta^{3a}$–Cl). 1-Bromopentane (151 g) in anhydrous diethyl ether (200 ml) was added to a suspension of lithium acetylide (from 7 g of lithium, 2 g of iron(III) nitrate, 2 l of ammonia and acetylene) prepared by the titration method. The mixture was stirred for 90 min and lithamide (from 7 g of lithium, 2 g of iron(III) nitrate and 900 ml of ammonia) was added and allowed to react for a further 1 h. Ethylene oxide (60 g) in dry diethyl ether (100 ml) was added dropwise to the suspension and the mixture stirred overnight. Dilute hydrochloric acid was added and the ethereal extract on distillation gave non-3-ynol (110 g, 79% yield; b.p. 105–108°/20 mm).

Non-3-ynol (30 g) was treated at 0–5° with thionyl chloride (50 g) and pyridine (5 ml), and heated for 3 h at 60°. Water was added and the extract on distillation yielded 1-chloronon-3-yne (28 g, 87% yield; b.p. 46–48°/2 mm).

Gas–liquid chromatography
GLC was carried out on a Pye 104 gas chromatograph with a flame ionization detector, nitrogen as carrier gas at a flow-rate of 40 ml/mm. The column length was 5 ft. and the I.D. ¼ in.

The results indicated that *n*-alkyl halides produced not only a straight-line plot for the log t_R values (t_R = retention time) for a homologous series, but also a parallel relationship for the ECL values with methyl esters of fatty acids. The

TABLE I

ECL$_{RCOOMe}$ VALUES OF n-ALKYL HALIDES

Alkyl group	Chlorides		Bromides		Iodides	
	20% DEGS	5% ApL	20% DEGS	5% ApL	20% DEGS	5% ApL
n-Heptyl	5.0	6.8	6.4	7.8	7.7	8.9
n-Octyl	6.0	7.8	7.4	8.8	8.7	9.9
n-Nonyl	7.0	8.8	8.4	9.8	9.7	10.9
n-Decyl	8.0	9.8	9.4	10.8	10.7	11.9

TABLE II

ECL VALUES OF CHLOROACETYLENES $CH_3(CH_2)_mC \equiv C(CH_2)_nCl$

Compound	DEGS		ApL	
	ECL$_{RCOOMe}$*	ECL$_{RCl}$**	ECL$_{RCOOMe}$*	ECL$_{RCl}$**
Series 1				
$C_{11}\Delta^{5a}$–Cl	11.10	13.10	10.80	11.00
$C_{10}\Delta^{4a}$–Cl	10.10	12.10	9.80	10.00
$C_9\Delta^{3a}$–Cl	9.10	11.10	8.80	9.00
$C_8\Delta^{2a}$–Cl	8.60	10.60	8.00	8.20
Series 2				
$C_{10}\Delta^{4a}$–Cl	10.10	12.10	9.80	10.00
$C_9\Delta^{4a}$–Cl	9.10	11.10	8.70	8.90
$C_8\Delta^{4a}$–Cl	8.40	10.40	7.80	8.00
$C_7\Delta^{4a}$–Cl	7.30	9.30	6.90	7.10
$C_6\Delta^{4a}$–Cl	7.20	9.20	6.10	6.30
$C_5\Delta^{4a}$–Cl	6.40	8.40	4.60	4.80

* ECL$_{RCOOMe}$: methyl esters of fatty acids used as reference standards.
** ECL$_{RCl}$: n-chloroalkanes used as reference standards.

ECL$_{RCOOMe}$ (methyl esters as reference standards) for n-alkyl halides are recorded in Table I.

In measuring the ECL values of the chloroacetylenes, we employed n-chloroalkanes as well as methyl esters of fatty acids as internal reference standards. As we have already observed a parallel relationship between the ECL values of methyl esters and alkyl halides, the results obtained (Table II) exhibited a consistent and reproducible ECL value irrespective of which of the two standards was used in each chloroacetylene analysis.

Comments on equivalent chain lengths

A number of interesting comments can be made on the values in Table II.

Results on the polar stationary phase (DEGS). In series 1, $C_8\Delta^{2a}$–Cl, when $n = 1$ (one methylene interrupted), the ECL value of this compound exceeds by 0.5 ECL number its extrapolated value as a member of the homologous series. A similar effect was reported by Gunstone et al.[18] for cis-methyl octadec-3-enoate, where the carboxymethoxy group is also separated from the double bond by a single methylene group.

In series 2, the effect of the approach of the methyl group towards the triple bond slightly increased the retention times of C_7 and $C_8 \Delta^{4a}$–Cl, where $m = 1$ and 2, respectively, but strongly increased the retention time by 1.10 ECL number when the methyl group was directly attached to the triple bond, as in $C_6 \Delta^{4a}$–Cl. In the terminal chloroacetylene, the ECL value was again increased. Such a deviation from the normal extrapolated values of a homologous series was also noted in the ECL determination[18] of methyl octadec-16-enoate and octadec-17-enoate.

Results on the non-polar stationary phase (Apiezon L). The effect of the position of the chloro- or methyl group relative to the triple bond on the ECL values was similar to that on the polar phase, but less pronounced. $C_5 \Delta^{4a}$–Cl gave an unexpectedly low ECL value on Apiezon L.

CONCLUSION

As the conversion of hydroxy groups is relatively easy by treatment with thionyl chloride, these results open another approach to the GLC analysis (as the chloro derivatives) of hydroxy-compounds. Most hydroxy-compounds have long retention times on polar columns and, moreover, give very unsymmetrical peaks on non-polar columns. The parallel relationship between alkyl halides and methyl esters provides an easy conversion of ECL values for comparative purposes.

ACKNOWLEDGEMENT

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