Studies on the Reactions of ω-Carbethoxy Fatty Acid Sodioesters with Brominated Compounds

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ABSTRACT

Several ω-carbethoxy fatty acid sodioesters (C_2H_5-$O_2CCHNa(CH_2)_{n-1}$-$CO_2C_2H_5$ and C_2H_5-$O_2CCHNa(CH_2)_{n-2}$-$CHNaCO_2C_2H_5$ where n/6, 7, or 8) were condensed with ω-bromoaliphatic esters ($Br(CH_2)_zCO_2C_2H_5$ where z-5, 8 or 10), α,ω-dibromoalkanes ($Br(CH_2)_{n'}$-Br where n'=4, 6 or 8) and α,α'-dibromo m- or p-xylene. Tri- and tetraesters and several carbethoxy cycloheptanones which arose mainly from Dieckmann type condensations were isolated. The infrared spectra of the tri- and tetraesters were compared with those of their parent ω-carbethoxy fatty acid ester and additional peaks in the regions of $\nu_{C=O}$ and ν_{C-O-C} were observed. Reactions involving the formation of both the α-sodio and α,α'-disodiodiester salts are also discussed.

INTRODUCTION

Numerous references are listed in the literature for the synthesis of tri- and tetracarboxylic esters by the substitution of bromine from an appropriate substrate by either the diethyl malonate (1-8) or an α-substituted diethyl malonate carbanion (9-16). The required carbanion was generated by the action of sodium ethoxide on a malonate ester in absolute ethanol. Tri- and tetraesters containing one or more geminal carbethoxy groups were obtained in satisfactory yields. ω-Carbethoxy fatty acid ester carbanions, however, cannot be obtained in the same way, since the decreased acidity of the α-hydrogens, as compared to the hydroxyl hydrogen of ethanol (17), causes an exchange equilibrium (eq. 1) first described by Mignonac and Rambeck (18) and later by other workers (19). The reverse reaction is favored and adequately explains the stability of long chain esters.

$$H\text{-}\underset{|}{\overset{|}{C}}\text{-}\underset{O}{\overset{\|}{C}}\text{-} + OC_2H_5^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} :\underset{|}{\overset{|}{C}}\text{-}\underset{O}{\overset{\|}{C}}\text{-} + C_2H_5OH \qquad [1]$$

This paper describes a series of condensation reactions of ω-carbethoxy fatty acid sodioesters (II, III) with brominated aliphatic (VII-IX) or aromatic (XXIV-XXVIII) compounds to obtain several tri- and tetraesters with carbethoxy groups distributed at various positions along the aliphatic chain. The various reactions that have occurred are also discussed.

MATERIALS AND METHODS

General Methods

Long chain diesters which could not be purchased pure were prepared by the Fisher-Speir method (20,21). Carbon and hydrogen analyses were made by Micro-Tech Laboratories Inc., Skokie, Illinois. Infrared spectra (IR) were obtained on a Beckman instrument, model IR-10 and a Perkin Elmer, model 467. The proton magnetic resonance (PMR) spectra were recorded on a Varian T-60 using CCl_4 as a solvent and tetramethyl silane (TMS) as an internal standard. Mass spectra were determined by Morgan-Shaeffer Corp., Montreal, Que.

Gas liquid chromatographic (GLC) analyses were carried out on a Varian instrument, model 1520, using a 3% SE-30 on Chromosorb-W(AW-DMCS), 100/120 mesh 1/8" x 8' stainless steel (SS) column at 250 to 265C with helium as carrier gas (25 ml/min). Preparative gas liquid chromatography was performed on a Hewlett-Packard, model 5754, equipped with a 3% SE-30 on Chromosorb-W(AW-DMCS) 70/80 mesh 1/4" x 14' SS column. A Hewlett-Packard, model 5795B, automatic preparative attachment permitted automatic injection and fraction collection. Fractional distillation was carried out in a single stage rota-film molecular still and a Piros-Glover spinning band micro still operating at a reflux ratio of 120:1.

Ethyl Hydrogen Sebacate

This compound was prepared according to the literature

TABLE I

Reactions of ω-Carbethoxy Fatty Acid Esters with ω-Bromoesters

Reaction	$\overset{CO_2C_2H_5}{\underset{CO_2C_2H_5}{(CH_2)_n}}$[a]	Reaction time for sodio salt formation (hr)	Reaction temperature (C)	$\overset{CO_2C_2H_5}{(CH_2)_zBr}$[a]	Reflux time (hr)	Weight of reaction products (g)
A	n=6	1 1.5	130-135 145-150[b]	VIII z=8	12	26.0
B	n=6	1 1.25	100-120 145-155[b]	IX z=10	6	27.0
C[c]	n=7	3	130-135	VII z=5	16	29.0
D[c]	n=7	3	130-140	VIII z=8	12	29.1
E[c]	n=7	2.5	135-140	IX z=10	12	32.9
F[c]	n=8	3	135-140	VII z=5	16	21.7
G	n=8	3.5 1	130-135 140-145[b]	VIII z=8	6	27.0
H[c]	n=8	3	135-138	IX z=10	12	22.0

[a]0.13 mole.
[b]Reaction initiated at temperature range indicated.
[c]Reaction initiated with 1 ml of piperidine.

TABLE II

Reactions of ω-Carbethoxy Fatty Acid Esters with ω-Bromoesters. Products Isolated and Distillation Conditions

Reaction	Product Number	Product Name	Distillation temperature (C)	Pressure (μ)	Yield (g)	η_D^{20}
A	XX	2-carbethoxy-2(8-carbethoxyoctyl)-cycloheptanone	145-146	5	2.3	1.4645
	XII	1,6,14-tricarbethoxytetradecane	160-161	5	3.7	1.4489
B	XXI	2-carbethoxy-2(10-carbethoxydecyl) cycloheptanone	193-194	150	1.2	1.4626
	XIII	1,6,16-tricarbethoxyhexadecane	204-205	150	3.0[a]	1.4497
C[b]	X	N-(8-carbethoxyoctanoyl)piperidine	123-124	5	1.2	1.4748
	XIV	1,6,12-tricarbethoxydodecane	146-147	5	1.2	1.4486
D[b]	XV	1,7,15-tricarbethoxypentadecane	179-180	10	1.8	1.4500
E[b]	XVI	1,7,17-tricarbethoxyheptadecane	183-184	10	3.9	1.4508
F[b]	XI	N-(9-carbethoxynonanoyl)piperidine	142-143	10	1.3	1.4720
	XVII	1,6,13-tricarbethoxytridecane	159-160	10	1.6	1.4483
G	XVIII	1,8,16-tricarbethoxyhexadecane	172-173	5	3.1	1.4510
H[b]	XIX	1,8,18-tricarbethoxyoctadecane	188-189	10	0.7[c]	1.4511

[a]Yield, 38.9% calculated from the molecular still fraction by gas chromatography.

[b]Reaction initiated with 1 ml of piperidine.

[c]Yield, 22.1% calculated from the molecular still fraction by gas chromatography.

(22) in 50% yield: mp 36-39 C (lit. mp 34-36 C).

Ethyl 9-Bromononanoate

This compound was prepared by the method of Hunsdiecker et al. (23,24) in 59.5% yield: bp 104-108 C/0.44 mm (lit. bp 118 C/2 mm).

Reactions of Long Chain Diesters with ω-Bromoesters, α,ω-Dibromoalkanes and α,α′Dibromoxylenes, Respectively. Preparation of Tri- and Tetraesters

Method A: reactions A, B, G, K, L, N and O. Sodium metal (0.13 g atom), cut into small pieces, was added to the ω-carbethoxy fatty acid ester (0.13 mole; n=6, 7 or 8) in a round bottom flask fitted with a reflux condenser and a drying tube. The mixture was then heated and vigorously stirred. At about 100 C, a suspension resulted which was then further heated under conditions given in Tables I and V to give a very thick orange-yellow paste. The reaction mixture was cooled to 75 C and xylene (70 ml) was added. The thick paste was loosened with a spatula and the appropriate ω-bromoester (0.13 mole; z=8 or 10), or α,ω-dibromoalkane (0.065 mole; R=$(CH_2)_4$, $(CH_2)_6$ or $(CH_2)_8$), was added. The resulting mixture was then refluxed for the times given in Tables I and V during which time a precipitate of sodium bromide formed. After removal of the xylene under reduced pressure, the resulting thick, pale yellow paste was dissolved in water (500 ml) and acidified with 20% hydrochloric acid (20 ml). The mixture was extracted with ether (2 x 150 ml), and the combined ether extracts were treated with a saturated solution of barium hydroxide (100 ml) in order to precipitate any diacid present. The filtered ether layer was washed with water and dried.

After stripping the ether, the viscous residue was heated to 145 C under reduced pressure (0.2-1.5 mm) to remove the unreacted diester. The reaction conditions and weights of products obtained are listed in Tables I and V. After distillation, the product was passed through a spinning band micro still, and appropriate cuts were taken. After GLC analysis the purest fractions were analyzed. Products and yields are given in Tables II and VI. Elemental analyses and principal infrared absorption bands are shown in Table III.

Method B: reactions C, D, E, F, H, I and J. Sodium (0.13 g atom), cut into small pieces, was added to a solution comprised of xylene (80 ml), the ω-carbethoxy fatty acid ester (0.13 mole; n=6, 7 or 8) and piperidine (1 ml) in a round bottom flask fitted with a reflux condenser and a drying tube. The mixture was then refluxed (~ 140 C) with stirring for 4 hr. After cooling to ca. 50 C, the ω-bromoester (0.13 mole; z=5, 8 or 10), α,ω-dibromoalkane (R=$(CH_2)_4$ or $(CH_2)_6$) or α,α′-dibromo m- or p-xylene (0.065 mole) was added slowly. The resulting mixture was then slowly heated to reflux for the period indicated in Tables I and V. After removing the xylene under reduced pressure, the reaction products were then treated as described in Method A. Products obtained and respective yields are shown in Tables II and VI. Chemical analyses and characteristic IR bands are given in Table III.

1,7,17,24-Tetracarbethoxytetracosane (XXXIV)

This compound was prepared according to the procedure described in Method A (Tables V and VI). Although the product was distilled (25-215 C at 15μ), the tetraester could not be separated by fractional distillation in a spinning band column. Instead, a 4% w/v solution of the molecular distillation fraction in benzene was separated by preparative gas chromatography using 35 μl injections. The chromatogram showed five well resolved peaks. The second peak was identified as (XXXIV). Chemical analysis and characteristic IR absorption frequencies of the 31 mg collected are given in Table III.

RESULTS AND DISCUSSION

The nucleophilic substitution reactions of ω-bromoaliphatic esters (VII-IX) with ω-carbethoxy fatty acid esters (I) are outlined in Scheme I, while the reaction conditions are shown in Table I. Examination of both Scheme I and Tables II and III shows that all the reactions described gave triesters (XII-XIX) whose isolation was possible only by a combination of molecular and fractional distillations. The yields of these triesters are not high because α-sodio diesters showed a remarkable tendency to cyclize usually through an intramolecular loss of sodium ethoxide. 2-Carbethoxy-

TABLE III

Chemical Analysis and Infrared Absorption Data

Compound	Formula	Percent calculated		Percent found		CH_3	CH_2	C=O	CH def modes		C-O-C		$(CH_2)_n$ def mode
		C	H	C	H	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}		cm^{-1}		cm^{-1}
X	$C_{16}H_{29}O_3N$[a]	67.80	10.31	67.16	10.49	2980	2930 2860	1735 1645[b]	1465 1440	1375	1250 1220 1180		725
XI	$C_{17}H_{31}O_3N$[c]	68.65	10.51	67.40	10.43	2980	2930 2860	1735 1645[b]	1465 1445	1370	1250 1220 1180		720
XII	$C_{23}H_{42}O_6$	66.63	10.21	66.02	10.25	2980	2930 2860	1740 1730	1465 1420	1375	1250 1220 1180 1160	1110	720
XIII	$C_{25}H_{46}O_6$	67.84	10.48	67.90	10.50	2980	2930 2850	1740 1730	1460 1415	1370	1250 1230 1190 1160	1110	720
XIV	$C_{21}H_{38}O_6$	65.25	9.91	64.90	9.95	2980	2930 2857	1745 1725	1460 1445	1370	1245 1220 1190 1160	1110	720
XV	$C_{24}H_{44}O_6$	67.25	10.35	66.67	10.36	2980	2930 2860	1740 1730	1465 1420	1375	1245 1220 1175 1165	1110	722
XVI	$C_{26}H_{48}O_6$	68.38	10.60	68.67	10.68	2980	2920 2860	1740 1730	1465 1420	1375	1245 1180 1160	1110	720
XVII	$C_{22}H_{40}O_6$	65.97	10.07	64.84	10.17	2980	2930 2860	1740 1730	1465 1420	1375	1240 1180 1160	1105	720
XVIII	$C_{25}H_{46}O_6$	67.84	10.48	68.04	10.48	2980	2930 2857	1740 1725	1465 1445	1370	1240 1175 1160	1112	720
XIX	$C_{27}H_{50}O_6$	68.90	10.71	69.03	10.76	2980	2930 2860	1740 1730	1462 1420	1375	1240 1180 1160	1110	720
XX	$C_{21}H_{36}O_5$	68.44	9.85	67.74	10.00	2980	2940 2860	1730 1710[d]	1460 1420	1370	1220 1170	1112	720
XXI	$C_{23}H_{40}O_5$	69.66	10.17	69.49	10.26	2980	2920 2850	1730 1710[d]	1440 1410	1360	1200 1160	1110	720
XXX	$C_{30}H_{54}O_8$	66.39	10.03	65.52	10.20	2980	2940 2860	1740 1730	1460 1445 1420	1375	1250 1190- 1170	1110	720
XXXI[e]	$C_{32}H_{50}O_8$	68.30	8.96	68.90	9.05	2980	2940 2860	1740 1730	1465 1445 1420	1375	1250 1170 1160	1110	725
XXXII[f]	$C_{32}H_{50}O_8$	68.30	8.96	68.94	9.26	2980	2940 2860	1740 1730	1465 1445 1420	1375	1250 1180 1160	1110	725
XXXIII	$C_{32}H_{58}O_8$	67.33	10.24	67.17	10.44	2980	2940 2920 2860	1740 1730	1420	1375	1245 1180- 1160	1110	720
XXXIV	$C_{36}H_{66}O_8$	68.97	10.61	68.14	10.81	2980	2940 2860	1740 1730	1420	1375	1250 1180 1160	1115	720
XXXV	$C_{34}H_{62}O_8$	68.19	10.44	67.41	10.83	2980	2930 2860	1740 1735	1460 1420	1370	1245 1180- 1160	1115	720
XXXVI	$C_{18}H_{32}O_4$	69.19	10.32	68.62	10.33	2980	2940 2860	1740 1720	1460 1420	1375	1250 1225 1180 1145	1110	720
XXXVII	$C_{20}H_{36}O_4$	70.55	10.66	70.05	10.65	2980	2940 2860	1740- 1735	1460 1420	1375	1250 1220 1170 1145	1115	720

[a]Calculated for N: 4.94%. Found 4.73%.
[b]Amide C=O.
[c]Calculated for N: 4.71%. Found 4.59%.
[d]Ketonic C=O.
[e]Phenyl absorption of 3030, 1610, 1505, 890, 780, 740 and 698 cm^{-1}.
[f]Phenyl absorption at 3050, 1610, 1505, 855 and 810 cm^{-1}.

cycloheptanone (VI), identified by mass spectrographic analysis, was formed by a Dieckmann cyclization of α-sodiodiester II. Compound VI then reacted first with sodium and subsequently with ω-bromoesters VIII and IX to yield ketodiesters XX and XXI as shown earlier for 2-carbethoxy-5-methylcyclopentanone (25). Structural evidence for XX and XXI was obtained by examining their proton magnetic resonance (PMR) spectrum, which lacked a characteristic absorption for either a tertiary (δ4.25 to δ5.0) or an enolic (δ≅15) hydrogen, the latter possibly arising from a keto-enol tautomerization. This observation also shows that XX and XXI could not have formed through a Dieckmann condensation of α-sodio salts of triesters XII and XIII. α-Sodio salts of XII and XIII could have resulted from the possible monocarbethoxyalkylation of III by VIII and IX. These salts either cyclize to give substituted cycloheptanones or react with ω-bromo fatty acid esters to give tetraesters (XXII). The products (Reaction B, Table II) separated by preparative GLC (Fig. 1) were identified as 2-carbethoxy-2-(10-carbethoxydecyl)cycloheptanone (XXI), an isomer of XXI, 2-carbethoxy-7-(10-carbethoxydecyl)cycloheptanone, and a trace of the triester 1,6,16-tricarbethoxyhexadecane (XIII). Little or no tetraester was formed as shown in Fig. 1.

The formation of XII and XIII could not have occurred through ring opening of ketodiesters XX and XXI by sodium ethoxide, since any remaining ethoxide would have been scavanged by the ω-bromoester.

In five of the reactions listed (Tables I and II), the addition of piperidine as an initiating reagent (Method B) gave a marked improvement in the amount of reaction products obtained. In Reactions C and F, compounds X (Scheme I) and XI containing both a piperidine and an ester moiety were isolated. The IR spectrum of these compounds (Table III) shows a strong band at 1645 cm^{-1} attributed to the amide stretching vibration (26,27). Mass spectroscopic

TABLE IV

Proton Magnetic Resonance Spectral Data in CCl_4

Compound	Group	Chemical Shift p.p.m.	Multiciplity[a]	Coupling constant Hz	Number of protons
N-(8-carbethoxyoctanoyl)-piperidine (X)	Ester CH_2	4.05	q	8.0	2
	α-, α'-CH_2	2.2	t	6.0	4
	Ester CH_3	1.2	t	8.0	3
	α, α-H[b]	3.4	t	6.0	4
	β,γ-H[b]	1.3	s	—	6
N-(9-carbethoxynonanoyl)-piperidine (XI)	Ester CH_2	4.0	q	8.0	2
	α-, α'-CH_2	2.1	t	6.0	4
	Ester CH_3	1.2	t	8.0	3
	α, α-H[b]	3.35	t	6.0	≅4
	β,β,γ-H[b]	1.3	s	—	6

[a]s=singlet; t=triplet; q=quadruplet.

[b]Hydrogens in piperidine moiety.

TABLE V

Reactions of ω-Carbethoxy Fatty Acid Esters with Dibromo Compounds

Reaction	$\begin{matrix}CO_2C_2H_5\\(CH_2)_n\\CO_2C_2H_5\end{matrix}$[a]	Reaction time for sodio salt formation (hr)	Reaction temperature (C)	$BrCH_2RCH_2Br$[a]		Reflux time (hr)	Products (g)
I[b]	n=6	4.5	137-140	XXVIII	R=p-phenyl	16	26.7
J[b]	n=6	4	130-135	XXVII	R=m-phenyl	16	19.8
K	n=6	2	135-140	XXIV	$R=(CH_2)_4$	19	21.4
L	n=6	2.5	130-135	XXV	$R=(CH_2)_6$	19	23.8
		0.75	160-165[c]				
M	n=7	3.5	130-135	XXIV	$R=(CH_2)_4$	17	23.2
		0.5	160-165[c]				
N	n=7	2	135-140	XXVI	$R=(CH_2)_8$	17	29.6
		0.5	150-160[c]				
O	n=8	2	130-135	XXIV	$R=(CH_2)_4$	17	18.1
		1	150-160[c]				

[a]0.13 mole.

[b]Reaction initiated with 1 ml of piperidine.

[c]Reaction initiated at the temperature range indicated.

TABLE VI

Reactions of ω-Carbethoxy Fatty Acid Esters with Dibromo Compounds. Products isolated and Distillation Conditions

Reaction	Product		Distillation temperature (C)	Pressure (μ)	Yield (g)	η_D^{20}
	Number	Name				
I[a]	XXXII	1,4-bis(2,7-dicarbethoxyheptyl)benzene	154-155	5	1.9[b]	1.4815
J[a]	XXXI	1,3-bis(2,7-dicarbethoxyheptyl)benzene	153-154	5	2.0	1.4822
K	XXXVI	1,6-dicarbethoxycyclododecane	106-107	5	0.8	1.4642
	XXX	1,6,13,18-tetracarbethoxyoctadecane	125-126	5	1.3[c]	1.4484
L	XXXVII	1,6-dicarbethoxycyclotetradecane	120-121	5	0.7	1.4652
M	XXXIII	1,7,14-20-tetracarbethoxyeicosane	134-135	5	1.1	1.4458
N	XXXIV	1,7,17,24-tetracarbethoxytetracosane[d]	---	---	---	1.4493
O	XXXV	1,8,15-22-tetracarbethoxydocosane	141-147	5	0.6	1.4483

[a]Reaction initiated with 1 ml of piperidine.

[b]Yield, 25.8% calculated from the molecular still fraction by gas chromatography.

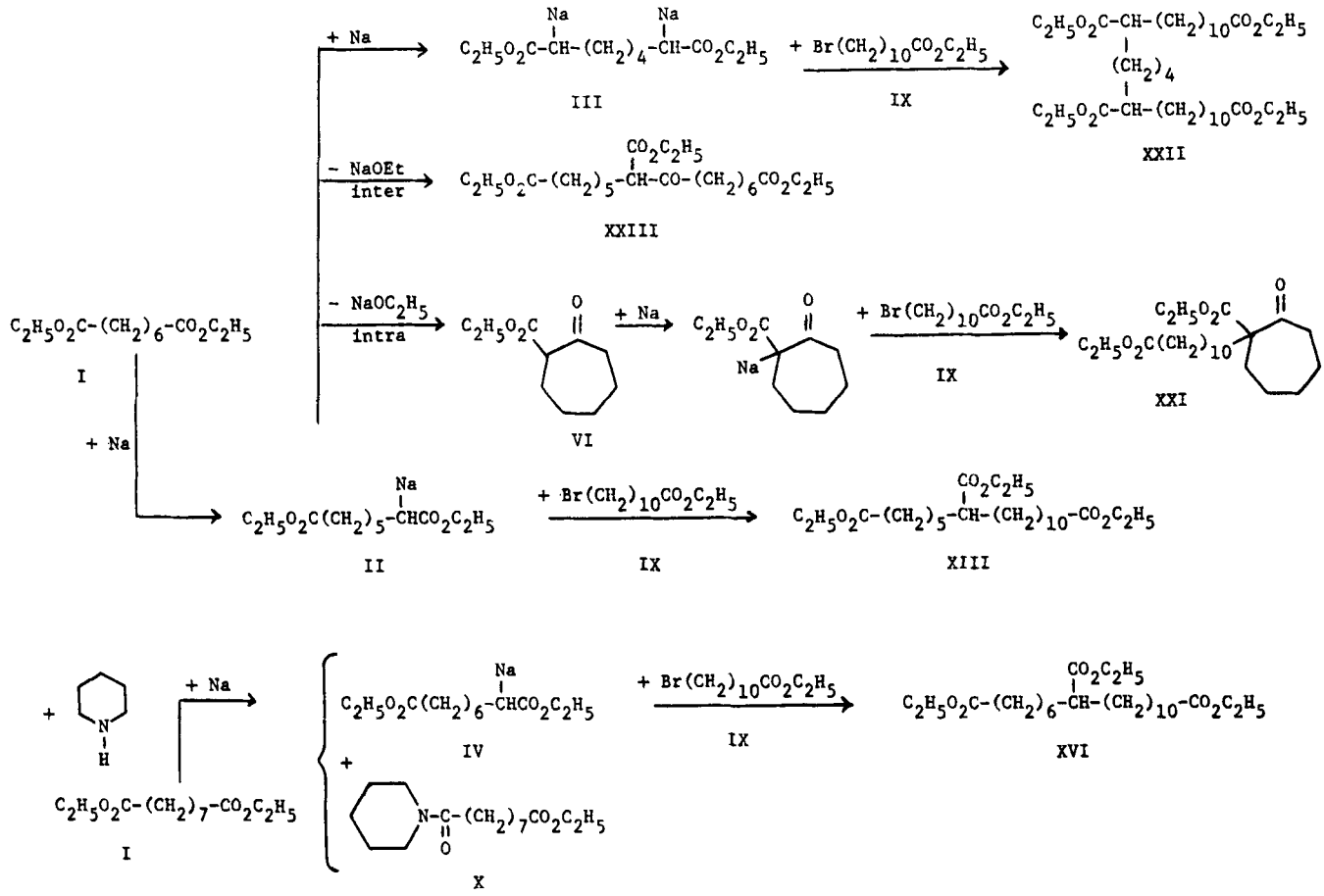
[c]Yield, 17.3% calculated from the molecular still fraction by gas chromatography.

[d]Compound separated by preparative gas chromatography.

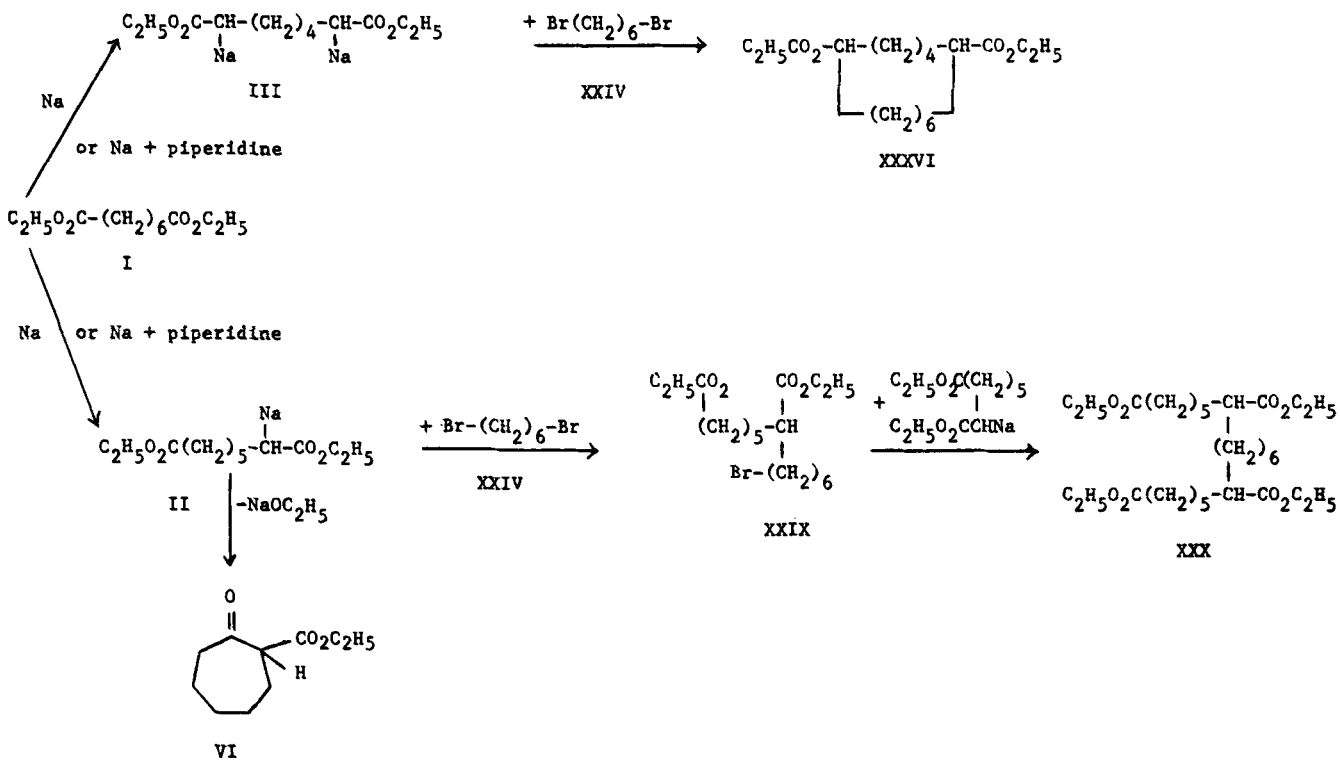
analysis of these compounds indicated their respective molecular masses to be 283 and 297. PMR spectral data (Table IV) showed two ester methylene, four α,α'-methylene and three ester methyl protons in these molecules. Thus, compounds X and XI are substituted amides of piperidine.

The expected ketotriesters resulting from a Claisen type condensation of diesters with their corresponding α-sodio salts were not isolated. However, the ketotriester XXIII was identified by mass spectroscopic analysis as the principal component in a fraction from Reaction A.

1,10-Dicarbethoxydecane (n=10) behaved differently from the other diesters when treated according to Method A. Its α-sodio salts could be obtained only at a higher temperature (185-200 C), and subsequent addition of ω-bromoester IX or α,α'-dibromo-p-xylene (XXVIII)



SCHEME I



SCHEME II

yielded little or no corresponding triesters, but rather 1,10-dicarboxydecane and diethyl ether, both of which were identified. Once the elimination of sodium ethoxide via the usual Dieckmann condensation is initiated, a preferential nucleophilic displacement on the methylene carbon of the ethyl group occurs in a manner analogous to the formation of sodium benzoate from methyl benzoate and sodium methoxide (28-30). This latter reaction at 100 C also gives a 74% yield of dimethyl ether (30).

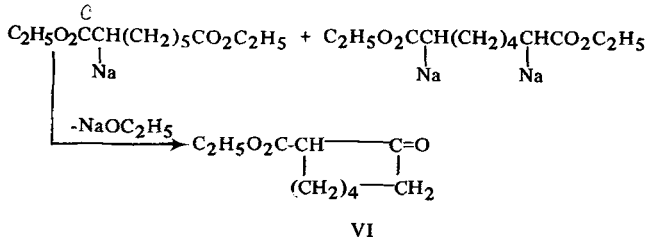
A number of tetraesters (XXX-XXXV) have likewise been prepared from diesters (I) and α,ω-dibromo compounds (XXIV, XXVI-XXVIII). These reactions are outlined in Scheme II. Since the intermediate ω-bromodiesters (XXIX) were less thermally stable than their corresponding tetraesters, purification by distillation was more difficult. Consequently, only those reactions yielding sufficiently pure compounds are listed in Table V. The IR data and the elemental analysis are given in Tables III and VI. The aromatic tetraesters (XXXI and XXXII) reported were synthesized using Method B. Reaction K yielded a cyclic diester, 1,6-dicarbethoxycyclododecane (XXXVI), in addition to tetraester XXX, while reaction L gave only the homologous cyclotetradecane diester XXXVII. Although the cyclic intermediate VI was not isolated, mass spectroscopic evidence for its existence in Reactions I, J and K was obtained.

Attempted preparation of tetraesters by treatment of sodio salts of diesters I with α,α'-dibromo-*o*-xylene resulted in recovery of the original diester.

Some deductions regarding the reaction scheme for the formation of α-sodio- and α,α'-disodiodiester salts can be made.

$$C_2H_5O_2C(CH_2)_6CO_2C_2H_5 + Na \rightarrow H_2 + \quad [2]$$

$$\text{or} + NaOC_2H_5 \rightarrow C_2H_5OH +$$



VI

First, the solvent free reaction of sodium on diesters that continuously evolves hydrogen and ethanol is produced early in the reaction. The sodio salt formation is initiated by the direct substitution of sodium for the hydrogen atom (equation [2]). A Dieckmann condensation forms VI with the elimination of sodium ethoxide, which in turn reacts with the diester via an ionic reaction to give the corresponding sodiodiester salts and ethanol.

Reactions involving the preparation of sodiodiester salts in xylene in the presence of small amounts of piperidine are exclusively ionic. In the initial stage, sodium hydroxide formed from the water (0.10%) in piperidine promotes base aminolysis, and ethanol and amide are produced. The sodium ethoxide subsequently formed likewise catalyzes aminolysis (31-33). The formation of the sodiodiester salts then proceeds in the usual manner. Here again a Dieckmann cyclization eliminates sodium ethoxide which then reacts with more diester to yield the sodiodiester salts.

The Infrared Spectra of Tri- and Tetraesters

The infrared data on tri- and tetraesters are shown in Table III. All spectra were obtained on neat liquids at room temperature.

In general, the characteristic carbonyl stretching frequency found at 1730 cm^{-1} in a diester was observed also in its derivatives: tri-, tetra- and cyclic ketodiesters. The tri- and tetraesters show an additional strong carbonyl absorption at 1740 cm^{-1}, while the cyclic ketodiesters XX and XXI reveal the normal ketonic absorption at 1720 cm^{-1}.

In the region of the C-O-C stretching vibration (1200-1100 cm^{-1}), the triesters gave broadened C-O-C absorption bands with a maximum between 1190 and 1175 cm^{-1} and an additional peak at 1160 cm^{-1} instead of a single peak at 1180 cm^{-1} shown by ω-carbethoxy fatty acid esters. The C-O-C absorption bands of tetraesters are broadened further in the region 1190-1160 cm^{-1}. All tri- and tetraesters gave an additional weak peak around 1110 cm^{-1} which cannot be assigned to any particular vibrational mode.

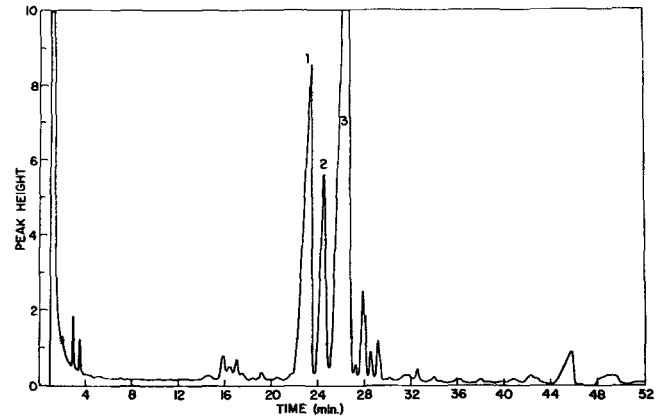


FIG. 1. Preparative gas chromatogram of products obtained from the reaction of sodio salts of diethylsuberate and ethyl 11-bromoundecanoate (Reaction B). 35 $\mu\ell$ injections of a 7% w/v benzene solution were introduced into a 1/4 in. x 14 ft column filled with 3% SE-30 on Chromosorb-W(AW-DMCS) 70:80 mesh and programmed from 225 C to 300 C at 4C/min. Carrier gas flow rate was 100 ml/min. 1. 2-Carbethoxy-2(10-carbethoxydecyl)cycloheptanone (XXI). 2. 2-Carbethoxy-7(10-carbethoxydecyl)cycloheptanone. 3. 1,6,16-Tricarbethoxyhexadecane (XIII).

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