addition product from I and piperidine under the conditions used for II were unsuccessful; the only product isolated was IV. The reaction of I with morpholine was carried out as previously described for piperidine,[1] except that the reaction time was shortened to five minutes. The yield was nearly quantitative. A sample of **3-(N-morpholino)-thianaphthene-1-dioxide** crystallized from dilute alcohol and benzene–Skellysolve "B" was light yellow in color and melted at 222–223° (dec.).

Anal. Calcd. for $C_{12}H_{11}O_3NS$: N, 5.57. Found: N, 5.49.

3-(N-Morpholino)-2-bromo-2,3-dihydrothianaphthene-1-dioxide.—The morpholino analog of V was prepared from II in alcohol solution under conditions similar to those used for V, except that a longer time was required. At the end of six hours II was still present in appreciable quantities; after thirty-six hours a 92% yield of product was obtained. Crystallization from dilute alcohol gave colorless plates, m. p. 156–157°.

Anal. Calcd. for $C_{12}H_{14}NSBr$: N, 4.21. Found: N, 4.10.

After four hours at 80° in benzene solution using a 6:1 molar ratio of amine to II, 50% of 3-(N-morpholino)-2-bromo-2,3-dihydrothianaphthene-1-dioxide and 16% of 3-(N-morpholino)-thianaphthene-1-dioxide were isolated.

3-Diethylamino-2-bromo-2,3-dihydrothianaphthene-1-dioxide.—The addition of diethylamine to II in alcohol solution was carried out in a manner similar to that used above except that the solution had to be warmed at intervals to redissolve the starting material. At the end of twelve days a 68% yield of the product was obtained. Crystallization from dilute alcohol gave colorless plates, m. p. 88–88.5°.

Anal. Calcd. for $C_{12}H_{16}O_2NSBr$: N, 4.40. Found: N, 4.15.

It is interesting that the addition compounds (V and its analogs) are colorless whereas the corresponding unsaturated compounds (IV and its analogs) are yellow.

Quantitative Determinations.—The liberated bromide ion was determined by the Volhard titration method. In alcohol the titration was run directly on the reaction mixture. When benzene was used as a solvent, the reaction mixture was diluted with water and the water layer was either separated and the determination made on aliquots of the combined water layer and washings, or the total sample was titrated without separation of the layers. The latter method was simpler and gave better results.

Summary

The reaction of 2,3-dibromo-2,3-dihydrothianaphthene-1-dioxide (III) with excess piperidine may be conducted so as to yield 2-bromothianaphthene-1-dioxide (II), 2-bromo-3-(1-piperidino)-2,3-dihydrothianaphthene-1-dioxide (V) or 3-(1-piperidino)-thianaphthene-1-dioxide (IV).

Any one of these three products may be obtained in high yield if the solvent (benzene or alcohol), time and temperature are properly chosen. It is possible also to obtain IV and V from II, and to obtain IV from V.

A study of the quantity of bromide ion released from II, III, V and also 3-bromothianaphthene-1-dioxide (I) in the reaction with excess piperidine in benzene and alcohol solutions has been made. The mechanism of these reactions has been discussed in the light of this information.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 10, 1948

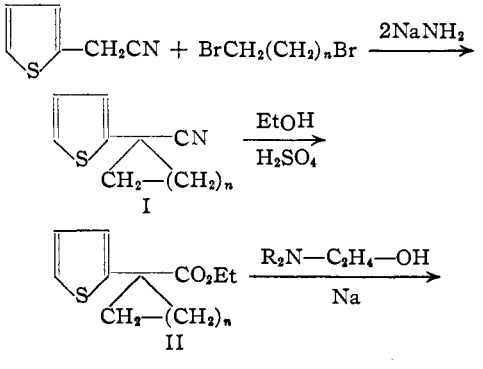
[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, RESEARCH LABORATORIES, THE WM. S. MERRELL COMPANY]

Aminoesters of 1-Substituted Alicyclic Carboxylic Acids[1]

BY CHARLES H. TILFORD, LEWIS A. DOERLE, M. G. VAN CAMPEN, JR., AND ROBERT S. SHELTON

The high spasmolytic activity of β-diethylaminoethyl 1-phenyl- and 1-cyclohexyl-cycloalkanecarboxylates has been previously reported.[2,3] More recently β-diethylaminoethyl 1-methylcyclohexanecarboxylate was investigated[4] as a spasmolytic agent. Further search has now led to the preparation of aminoesters of 1-(2-thienyl)-cycloalkanecarboxylic and 1-alkyl-cyclohexanecarboxylic acids. 1-Methyl-,[5] 1-ethyl-,[6] and 1-(*i*-propyl)-[7]cyclohexanecarboxylic acids and 1-methyl-,[8] 1-ethyl-,[9] and 1-propyl-cyclopentanecarboxylic[10] acids have been previously prepared. The most practical method reported[8] was the conversion of 1-methylcyclopentanol, obtained from cyclopentanone and methylmagnesium halide, to the corresponding chloride, which was converted to the Grignard reagent and allowed to react with carbon dioxide. Low yields of desired product are reported for the last two reactions.

The thienyl derivatives of the present study were prepared from thenyl cyanide and the appropriate alkylene dihalide in the presence of sodamide.[3]



(1) Presented at the 114th Meeting of the American Chemical Society, Medicinal Section, Washington, August 31, 1948.

(2) (a) Rubin and Wishinsky, THIS JOURNAL, **68**, 829 (1946); (b) Weston, *ibid.*, **68**, 2347 (1946); see U. S. Patent 2,404,588.

(3) Tilford, Van Campen and Shelton, *ibid.*, **69**, 2902 (1947).

(4) Levy and Tchoubar, *Compt. rend. soc. biol.*, **141**, 257 (1947).

(5) Tarbouriech, *Compt. rend.*, **150**, 1606-1607 (1910); Reichstein, *et al.*, *Helv. Chim. Acta*, **18**, 724 (1935); see also Gutt, *Ber.*, **40**, 2069 (1907); Meerwein, *Ann.*, **396**, 235 (1913).

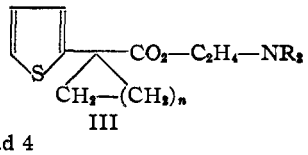
(6) Meerwein, *Ann.*, **419**, 168 (1919); Arnold and Liggett, THIS JOURNAL, **64**, 2875-2877 (1942); German Patent 620,903.

(7) Shive, Crouch and Lochte, THIS JOURNAL, **63**, 2979 (1941).

(8) Meerwein, *Ann.*, **405**, 171 (1914); **417**, 263 (1918); Petrov, *J. Russ. Phys.-Chem. Soc.*, **45**, 644 (1912).

(9) Meerwein, *Ann.*, **396**, 230 (1913); **419**, 121-175 (1919).

(10) Meerwein, *ibid.*, **419**, 165 (1919).

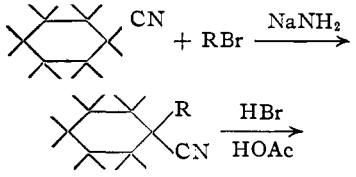


III

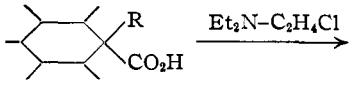
n = 3 and 4
R = methyl and ethyl

Alcoholysis[3] of the cyanides (I) followed by re-esterification[3] of the ethyl esters (II) with an aminoalcohol gave the desired aminoesters (III).

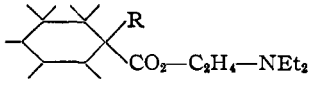
1-Alkylcyclohexyl cyanides (IV) were obtained in good yield from the reaction of cyclohexyl cyanide, the appropriate alkyl halide, and sodamide.



IV



V

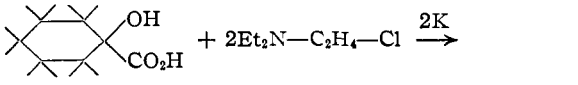


VI

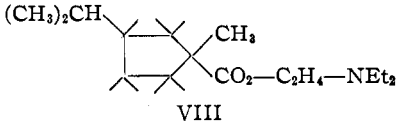
R = n-propyl, n-butyl, i-butyl, n-amyl, i-amyl, 1-methylbutyl, 2-methylbutyl, 1-ethylpropyl, n-hexyl, 2-ethylbutyl, 2-methylpentyl, n-heptyl, n-octyl and β-cyclohexylethyl.

Hydrolysis to the acids (V) was carried out by refluxing the cyanide with a mixture of hydrobromic acid and acetic acid.[1] The cyclohexanecarboxylic acids were then converted to the aminoesters (VI) using β-diethylaminoethyl chloride in isopropyl alcohol.[11] Δ^3-Cyclohexenyl cyanide was alkylated as above and the aminoesters of 1-cyclohexyl- and 1-(β-diethylaminoethyl)-Δ^3-cyclohexenecarboxylic acids were obtained.

An ether analog (VII) was prepared with 1-hydroxycyclohexanecarboxylic acid as the starting material.



VII



VIII

β-Diethylaminoethyl 1-methyl-3-isopropylcyclopentanecarboxylate (VIII) was readily prepared from the commercially available fencholic acid.

(11) Burtner and Cusic, THIS JOURNAL, **65**, 262 (1943).

Pharmacological Results

The *in vitro* spasmolytic activities are given in Table I. Aminoesters having the thienyl group were about equal in potency to those having the phenyl group (compare nos. 1, 17 and 21 with compounds in Table I of reference 3). The most potent aminoesters of this series were the 1-alkylcyclohexane derivatives, the peak of activity apparently being attained when the alkyl group has 5 carbon atoms. The isoamyl group (no. 9) engendered greater activity than the n-amyl group (no. 8).

In vivo tests have also shown the high activities of several of these compounds; no. 9 was effective in the anesthetized cat in a dosage of 0.5 mg./kg.

Acknowledgment.—The pharmacological data were furnished by Dr. Harold W. Werner, Miss Barbara B. Brown, and Mr. Emmett Peters of these laboratories. We also wish to acknowledge the assistance of Dr. J. L. Farmer in many phases of the work.

Experimental

1-Substituted Cycloalkyl Cyanides.—The results are summarized in Table II. The method reported for the preparation of 1-phenylcyclopentyl cyanide[3] was followed in preparing 1-(2-thienyl)-cyclopentyl and 1-(2-thienyl)-cyclohexyl cyanides; thenyl cyanide[12] was used in place of phenylacetonitrile. The remaining cyanides were obtained by the same procedure using 1 mole of cyclohexyl[13] or Δ^3-cyclohexenyl[14] cyanide, and 1.15 moles each of sodium and alkyl halide. Toluene was used as the solvent and the reaction mixture was finally refluxed six to ten hours. When t-butyl bromide was used in this reaction, none of the desired 1-(t-butyl)-cyclohexyl cyanide could be isolated. During one of the sodamide alkylation experiments (no. 11 of Table II), water accidentally entered the liquid ammonia reaction mixture shortly after the addition of the alkyl halide. Consequently the reaction mixture was not refluxed as stated above. However, the yield was 57%, giving evidence that the alkylation of cyclohexyl cyanide may occur to a large extent at temperatures below −35°.

2-Ethylbutyl,[15] 2-methylpentyl,[15] 2-methylbutyl[16] and 1-ethylpropyl[17] bromides were obtained from the corresponding alcohols; the remainder of the alkyl halides are commercially available. In one experiment (no. 4 of Table II), the alkyl iodide was used effectively.

1-Alkylcyclohexanecarboxylic Acids.—The reported hydrolysis procedure[1] using hydrobromic and acetic acids was followed and the data are given in Table II.

Aminoesters.—Table I summarizes the results obtained. The methods used are exemplified in the following procedures.

β-Diethylaminoethyl 1-(2-Thienyl)-cyclopentanecarboxylate (Method A).—The method[3] reported for the preparation of β-diethylaminoethyl 1-phenylcyclopentanecarboxylate was carried out using 1-(2-thienyl)-cyclopentyl cyanide.

(12) Blicke and Leonard, *ibid.*, **68**, 1934 (1946).

(13) See reference 3. A convenient method for the preparation of cyclohexyl cyanide from the corresponding acid was that of Oxley, Partridge and Robson, *J. Chem. Soc.*, 769 (1946), in which 1 mole of the acid was heated with 2 moles of p-toluenesulfonamide. A yield of 75% of product distilling at 72-75° (12 mm.) was obtained.

(14) U. S. Patent 2,217,632.

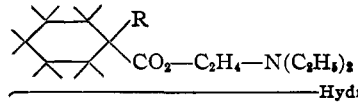
(15) Shonle, *et al.*, THIS JOURNAL, **58**, 586 (1936).

(16) Bartlett and Rosen, *ibid.*, **64**, 545 (1942).

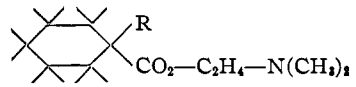
(17) Kharasch, *et al.*, *ibid.*, **61**, 1561 (1939).

TABLE I

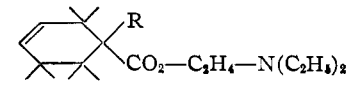
SPASMOLYTIC ACTIVITY

A. 

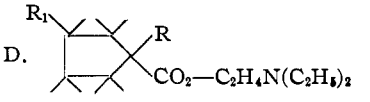
No.	R	Free base: Distilling range °C.	mm.	Yield, %	Method[a]	Hydrochloride: Formula	M. p. °C. (cor.)	Chlorine, % Calcd.	Found	Normal[b]	Acetyl[c] choline	Barium[d] chloride	Histamine[e] γ/ml.
1	2-Thienyl	[f]		33	A	$C_{17}H_{27}O_2NS\cdot HCl$	140–141	10.25	10.20	1.0	1.0	0.5	5.0
2	β-Cyclohexylethyl	135–140	0.01	69	B	$C_{21}H_{39}O_2N\cdot HCl$	137–139	9.48	9.50	0.5	0.25	0.25	1.0
3	*n*-Octyl	150–153	.03	74	B	$C_{21}H_{41}O_2N\cdot HCl$	114–115	9.43	9.35	2.0	0.01	0.10	20.0
4	*n*-Heptyl	143–147	.05	65	B	$C_{20}H_{39}O_2N\cdot HCl$	108–110	9.80	9.70	0.25	0.25	0.25	1.0
5	*n*-Hexyl	133–135	.1	74	B	$C_{19}H_{37}O_2N\cdot HCl$	112–115	10.19	10.08	.25	1.0	1.0	5.0
6	2-Methylpentyl	132–135	.03[g]	64	B	$C_{19}H_{37}O_2N\cdot HCl$	118–120	10.19	10.20	.2	0.2	0.2	10.0
7	2-Ethylbutyl	142–145	.3[h]	67	B	$C_{19}H_{37}O_2N\cdot HCl$	133–134	10.19	10.18	1.0	0.5	2.0	0.5
8	*n*-Amyl	[f]		50	B	$C_{18}H_{35}O_2N\cdot HCl$	120–121	10.62	10.73	2.5	2.5	1.6	5.0
9	*i*-Amyl	118–120	.1	67	B	$C_{18}H_{35}O_2N\cdot HCl$	144–146	10.62	10.58	2.0	10.0	1.0	5.0
10	1-Ethylpropyl	124–127	.08[i]	73	B	$C_{18}H_{35}O_2N\cdot HCl$	135–137	10.62	10.62	0.5	0.1	0.1	10.0
11	1-Methylbutyl	132–135	.2[j]	70	B	$C_{18}H_{35}O_2N\cdot HCl$	129–130	10.62	10.62	1.0	1.0	2.0	10.0
12	2-Methylbutyl	133–136	.2[k]	70	B	$C_{18}H_{35}O_2N\cdot HCl$	137–138	10.62	10.60	0.1	0.5	0.5	10.0
13	*n*-Butyl	114–116	.03	72	B	$C_{17}H_{33}O_2N\cdot HCl$	150–152	11.08	11.05	.5	1.0	1.0	0.1
14	*i*-Butyl	98–102	.03	78	B	$C_{17}H_{33}O_2N\cdot HCl$	144–146	11.08	11.20	.1	1.0	1.0	1.0
15	*n*-Propyl	100–103	.1	71	B	$C_{16}H_{31}O_2N\cdot HCl$	127–129	11.59	11.50	.25	0.5	0.5	0.2
16	β-Diethylaminoethoxy	140–150	.2	5	C	$C_{19}H_{38}O_3N_2\cdot 2HCl$	137–140	17.09	16.85	.1	0.01	0.01	20.0

B. 

17	2-Thienyl	[f]		25	A	$C_{15}H_{23}O_2NS\cdot HCl$	138–139	11.15	11.12	0.5	0.25	1.0	1.0
18	β-Cyclohexylethyl	[f]		64	B	$C_{19}H_{35}O_2N\cdot HCl$	142–143	10.25	10.20	0.1	1.0	0.25	2.0

C. 

19	Cyclohexyl	[f]		30	B	$C_{19}H_{33}O_2N\cdot HCl$	122–124	10.31	10.25	0.1	5.0	0.1	
20	β-Diethylaminoethyl	135–145	0.3	44	A	$C_{19}H_{36}O_2N_2\cdot 2HCl$[l]	159–161	17.09	17.10	0.01	0.01	.01	20.0

D. 

	R	R_1										
21	2-Thienyl	H[f]	45	A	$C_{16}H_{25}O_2NS\cdot HCl$	118–121	10.68	10.66	2.0	0.5	.25	5.0
22	Methyl	*i*-Propyl[f]	44	B[m]	$C_{16}H_{31}O_2N\cdot HBr$	109–111	22.81[n]	22.60	0.5	1.0	.5	20.0

E. Standards for comparison

23	Diocyl	(β-Diethylaminoethyl 1-cyclohexylcyclohexanecarboxylate hydrochloride)	0.1	10.0	.2	5.0
24	Trasentin	(β-Diethylaminoethyl diphenylacetate hydrochloride)	0.05	1.0	.2	5.0
25	Pavatrine	(β-Diethylaminoethyl 9-fluorenecarboxylate hydrochloride)	2.5	1.0	.5	5.0
26	Amethone	(3-β-Diethylaminoethyl-3-phenyl-2-benzofuranone hydrochloride)	0.5	5.0	.1	5.0
27	Atropine		10.0	80.0	.2	5.0
28	Papaverine		0.15	0.1	.1	
29	Benadryl	(β-Dimethylaminoethyl benzhydryl ether hydrochloride)				0.02

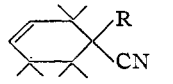
[a] Examples of these methods are given in the Experimental part. [b] Dilutions in million parts of water that gave a minimal but definite relaxation of the normal isolated rabbit jejunum. [c] Dilutions in million parts of water that gave complete relief of spasm on isolated rabbit jejunum induced by a 1 to 1 million concentration of acetylcholine. [d] Dilu-

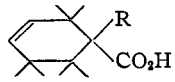
tions in million parts of water that gave complete relief of spasm on isolated rabbit jejunum caused by a 1 to 10 thousand concentration of barium chloride. [e] Minimal concentration of test compound necessary to antagonize 0.1 γ/cc. of histamine diphosphate on isolated guinea pig intestine. [f] The crude free base was converted directly to the hydrohalide. [g] M. p. 77–79°. [h] M. p. 92–95°. [i] M. p. 103–105°. [j] M. p. 96–97°. [k] M. p. 88–91°. [l] Contains 1 H_2O of crystallization. [m] Fencholic acid obtained from Dow Chemical Co. [n] Per cent. bromine.

TABLE II

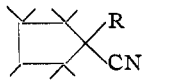
1-SUBSTITUTED CYCLOALKYL CYANIDES AND CARBOXYLIC ACIDS

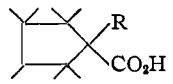
No.	R	Distillation range °C.	Mm.	Yield, %	Nitrogen, % Calcd.	Found	Distillation range °C.	Mm.	M. p. °C. (cor.)	Yield, %	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
1	2-Thienyl	102–103	1.0	29	[a]				145–147		210[b]	207		
2	β-Cyclohexylethyl	180–182	12.0	75	6.39	6.41	150–152	0.5	55–58	70	75.58	75.67	11.00	10.65
3	*n*-Octyl	163–166	16.0	94[c]	6.33	5.41[d]	162–165	.2		84	74.95	75.09	11.73	11.82
4	*n*-Heptyl	150–154	13.0	83	6.76	6.75	152–154	.05	35–36	92	74.28	74.68	11.58	11.72
5	*n*-Hexyl	138–142	13.0	80	7.25	6.99	135–139	.05		85	73.54	73.95	11.39	11.00
6	2-Methylpentyl	148–151	26.0	60	7.25	6.59[d]	139–142	.08		91	73.54	73.70	11.39	11.62
7	2-Ethylbutyl	138–142	22.0	62	7.25	7.26	139–143	.08		77	73.54	73.50	11.39	11.12
8	*n*-Amyl	100–102	1.0	86	[a]		124–126	.02		72	72.68	72.41	11.18	10.64
9	*i*-Amyl	118–122	10.0	62	[a]		126–128	.05		79	72.68	72.40	11.18	11.25
10	1-Ethylpropyl	140–144	27.0	55[c]	7.82	7.69	133–137	.03	91–92	84	72.68	72.74	11.18	10.93
11	1-Methylbutyl	137–139	27.0	57	7.82	7.71	138–141	.2	90–91	81	72.68	72.82	11.18	10.72
12	2-Methylbutyl	133–137	25.0	78[c]	7.82	6.39[d]	138–140	.2		69	72.68	72.57	11.18	10.74
13	*n*-Butyl	118–121	17.0	95[c]	8.48	7.60[d]	118–121	.06		78	71.69	71.69	10.94	10.75
14	*i*-Butyl	106–110	10.0	75	8.48	8.30	102–103	.01	91–92	87	71.69	71.91	10.94	11.25
15	*n*-Propyl	99–104	16.0	76[c]	9.26	6.94[d]	103–107	.03	57–58	51	70.55	70.31	10.66	10.66





16	Cyclohexyl	160–163	18.0	70	[a]				154–155	88	208[b]	204		
17	β-Diethylaminoethyl	152–156	15.0	51	14.60[e]	14.55			[f]					





18	2-Thienyl	95–98	0.3	33	[a]				143–145		196[b]	197		

[a] Identified by acid. [b] Neutral equivalent. [c] Based on recovery of unchanged cyclohexyl cyanide, usually about 10%. [d] Evidently contaminated with products such as corresponding amide or acid not easily removed by fractional distillation but identified by its derived acid. [e] Identified as hydrochloride; per cent. chlorine. [f] Acid not isolated.

β-Diethylaminoethyl 1-(β-Cyclohexylethyl)-cyclohexanecarboxylate (Method B).—The procedure of Burtner and Cusic[11] was employed. A mixture of 38 g. (0.16 mole) of 1-(β-cyclohexylethyl)-cyclohexanecarboxylic acid, 5 g. (0.21 mole) of sodium dissolved in 200 ml. of 2-propanol, and 36 g. (0.21 mole) of β-diethylaminoethyl chloride hydrochloride dissolved in 150 ml. of 2-propanol was heated at 75° in a closed container for about thirty-six hours. The solvent was removed under a water pump vacuum on the steam-bath. The residue was made alkaline with a slight excess of 10% potassium hydroxide, and the crude aminoester extracted with a 1:1 petroleum ether and diethyl ether mixture. At this point the ether extract could be fractionally distilled (b. p. 135–140° at 0.1 mm.; yield, 39 g.) or converted directly to the hydrochloride with a slight excess of alcoholic hydrochloric acid. The salt was recrystallized twice from butanone, sometimes crystallizing from the solvent as a difficult-to-filter gel; m. p. 137–139°.

β-Diethylaminoethyl 1-(β-Diethylaminoethoxy)-cyclohexanecarboxylate (Method C).—To a solution of 51 g. (0.35 mole) of 1-hydroxycyclohexanecarboxylic acid[18] in 400 ml. of dry toluene was added 27 g. (0.7 mole) of potassium, and the mixture was refluxed with stirring until most of the potassium had reacted. A solution of 107 g. (0.7 mole) of β-diethylaminoethyl chloride in 200 ml. of dry toluene was added during a period of one and a half hours. The reaction mixture was refluxed with stirring for sixteen hours. The mixture was washed with 300 ml. of water, and the toluene solution was fractionally distilled. At 140–150° (0.2 mm.), 6.5 g. (5%) of product was collected. The white crystalline hydrochloride melted

(18) Bucherer, *Ber.*, **27**, 1231 (1894).

at 137–140° when recrystallized from a butanone–ether mixture.

Summary

A series of twenty-two new aminoesters of 1-substituted cycloalkanecarboxylic acids has been prepared, and their spasmolytic activity reported. The substituents were 2-thienyl, β-cyclohexylethyl, cyclohexyl, *n*-octyl, *n*-heptyl, *n*-hexyl, 2-methylpentyl, 2-ethylbutyl, *n*-amyl, *i*-amyl, 2-methylbutyl, 1-ethylpropyl, 1-methylbutyl, *n*-butyl, *i*-butyl, *n*-propyl, β-diethylaminoethyl and β-diethylaminoethoxy.

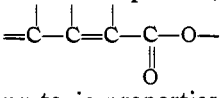
CINCINNATI 15, OHIO RECEIVED NOVEMBER 5, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

The Preparation and Properties of Esters Related Structurally to Certain Insecticides

BY HENRY M. WOODBURN AND CYRUS E. SROOG[1]

The commercial introduction of four chlorobenzoic acids, following close on the outstanding success of D.D.T. as an insecticide, suggested the possibility that the chloroethanol esters of these acids might possess useful toxic properties. Trichloroethyl *p*-chlorobenzoate, $ClC_6H_4CO_2CH_2CCl_3$, for example, contains two of the structural units of D. D. T. The presence of the ester link might also be helpful, since Läuger,[2,3] from a study of natural substances and certain related compounds, concluded that the grouping



was very important in conferring toxic properties on such compounds.

Twelve esters were prepared without difficulty by the interaction of 2-chloro-, 2,2-dichloro- and 2,2,2-trichloroethanol with the acid chlorides of *p*-chloro-, *o*-chloro-, 2,4-dichloro- and 3,4-dichlorobenzoic acids. They were either white crystalline solids melting between 30 and 65°, or high boiling colorless liquids. The solids were soluble in acetone and benzene and easily recrystallized from hot 95% ethanol. Liquids were miscible with acetone and benzene, partially miscible with 95% ethanol.

In toxicity tests compounds 1, 2, 3, 9, 10 and 12 (Table I) formulated as 5% dusts proved to be inactive in a simple walk-around test against the confused flour beetle (*Tribolium confusum*), the German cockroach, and the large milkweed bug.

TABLE I

ESTERS OF CHLOROBENZOIC ACIDS

	Yield, %	M. p., °C., uncor.	B. p. °C.	Mm.	$n^{25}D$	Chlorine, % Calcd.	Found[a]
2,2,2-Trichloroethyl *p*-chlorobenzoate	84	49–49.5				49.3	49.2 49.4
2,2,2-Trichloroethyl *o*-chlorobenzoate	84	39–40.5				49.3	49.4 49.8
2,2,2-Trichloroethyl 2,4-dichlorobenzoate	75	33–34				55.0	54.9 55.1
2,2,2-Trichloroethyl 3,4-dichlorobenzoate	65		208–209	38	1.564	55.0	55.2 55.3
2,2-Dichloroethyl *p*-chlorobenzoate	78	60–62				42.0	41.6 41.8
2,2-Dichloroethyl *o*-chlorobenzoate	86		150–154	8–9	1.549	42.0	42.1 41.8
2,2-Dichloroethyl 2,4-dichlorobenzoate	85		180–182	10		49.3	49.3 49.1
2,2-Dichloroethyl 3,4-dichlorobenzoate	89	64–65				49.3	49.1 49.1
2-Chloroethyl *p*-chlorobenzoate	79	38–38.5				32.4	32.2 32.2
2-Chloroethyl *o*-chlorobenzoate	74	30–31				32.4	32.3 32.7
2-Chloroethyl 2,4-dichlorobenzoate	80		198–199	35	1.561	42.0	41.6 41.6
2-Chloroethyl 3,4-dichlorobenzoate	89	47–48.5				42.0	42.3 42.1

[a] Rauscher, *Ind. Eng. Chem., Anal. Ed.*, 9, 296 (1937).

Compounds 4, 5, 6, 7, 8 and 11, also as 5% dusts, were inactive against the Mexican bean beetle on potted bean plants and against greenhouse spider. The toxicity tests were admittedly limited and on a specific type of formulation. Insecticidal activity against other types of insects might develop on further examination.

Experimental

Acids.—The following acids were furnished by the Heyden Chemical Co., to whom grateful acknowledgment is made: *p*-chlorobenzoic, *o*-chlorobenzoic, 3,4-dichlorobenzoic, and 2,4-dichlorobenzoic.

Acid Chlorides.—Acid chlorides were prepared by the reaction at elevated temperatures (100–135°) of a 100% excess of thionyl chloride on the appropriate acid. The products were recovered and purified by vacuum distillation; yields 72–90%; *p*-chlorobenzoyl chloride b. p. 127–129° (32 mm.); *o*-chlorobenzoyl chloride b. p. 133–137° 45 mm.); 3,4-dichlorobenzoyl chloride b. p. 153–155° (42 mm.) low melting solid; 2,4-dichlorobenzoyl chloride b. p. 146–149° (28 mm.).

Chloroalcohols. 2-Chloroethanol.—C. P. ethylene chlorohydrin obtained from the Eastman Kodak Co. was redistilled before use.

(1) From the thesis submitted by C. E. Sroog in partial fulfillment of the requirements for the M.A. degree, June, 1948.

(2) Läuger, *Helv. Chim. Acta*, **27**, 71 (1944).

(3) Läuger, Martin and Muller, *Helv. Chim. Acta*, **27**, 892 (1944).