TABLE I

ESTERS OF LONG-CHAIN, HYDROXY ALIPHATIC ACIDS

Ester	Formula,	Yield,[a] %	M. p., °C.	Saponification no. Calcd.	Saponification no. Found	Carbon[b] Calcd.	Carbon[b] Found	Hydrogen[b] Calcd.	Hydrogen[b] Found
9,10-Dihydroxyoctadecyl 12-hydroxystearate	$C_{36}H_{72}O_5$	60	86-87	95.9	95.0	73.9	73.6	12.4	11.7
9,10-Dihydroxyoctadecyl 9,10,12-trihydroxystearate	$C_{36}H_{72}O_7$	40	103.5–104.2	90.9	90.2	70.1	70.5	11.8	11.7
Tetrahydrofurfuryl 9,10-dihydroxystearate	$C_{23}H_{44}O_5$	30	59.8- 60.6	140.1	142.7	69.0	68.8	11.1	11.3

[a] Purified products after at least three crystallizations from 95% ethanol. [b] Analyses were made by Mary Jane Welsh of this Laboratory.

waxy solids. The purified products were white, odorless solids with the same solubility characteristics as the esters previously reported.[1,5]

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(5) Swern, Jordan and Knight, THIS JOURNAL, **68**, 1673 (1946).

EASTERN REGIONAL RESEARCH LABORATORY, PHILADELPHIA 18, PA., ONE OF THE LABORATORIES OF THE BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE
H. B. KNIGHT
E. F. JORDAN, JR.
DANIEL SWERN

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New Compounds as Plant Growth Regulators

The compounds listed below were prepared for testing for plant growth regulating activity under a contract between the Chemical Warfare Service and the Ohio State University Research Foundation. The activity of some of these compound has been reported in the *Botanical Gazette*, **107**, June (1946).

Methods

A. The phenol was condensed with ethyl bromoacetate in ethanol in presence of an excess of concentrated aqueous potassium carbonate solution at room temperature. The ester formed was isolated and saponified in the usual way. The yield of acid reported is based on the original phenol used. In some cases the reaction mixture was saponified without any attempt at isolation of the ester.

B. *p*-Chlorophenol containing a catalytic amount of sodium *p*-chlorophenolate was treated at 130° with acrylonitrile.[1]

C. The halophenyl γ-bromopropyl ether was prepared from the sodium halophenolate in ethanol and 1,3-dibromopropane. An ethanol solution of the ether was converted to the nitrile[2] by sodium cyanide in the usual manner. The yield of nitrile reported is based on the original phenol used.

D. A solution of the nitrile in glacial acetic acid was hydrolyzed by boiling with aqueous sulfuric acid during six to eighteen hours.

E. A solution of the phenol in pyridine was treated with an equimolecular quantity of ethyl chlorocarbonate at 0°; followed by stirring while allowing to warm to room temperature during one to three hours.

F. (a) Esterification was carried out by refluxing the acid in benzene solution with an excess of the alcohol in presence of a little *p*-toluenesulfonic acid, while removing the water produced in the reaction as fast as formed. (b) Concentrated sulfuric acid was used as catalyst. (c) In the preparation of a methyl ester F(a) was followed, with omission of benzene.

G. A crude sample of 2,4-diiodophenol[3] was converted to the phenoxyacetic acid by Method S. The product was esterified by Method F(a) saponified and the resulting mixture of mono- and diiodophenoxyacetic acids separated by partial precipitation as the potassium salts. Pure 2,4-diiodophenoxyacetic acid was obtained by recrystallization of the free acid from benzene-Skellysolve-B. The yield of acid reported is based on the phenol used for iodination.

H. The corresponding allyl ester was chlorinated in carbon tetrachloride solution at 0°.

I. Reaction of alkali halophenolates with halogenated esters or alcohols. (a) The sodium halophenolate was refluxed with diethyl chlorofumarate in xylene and the resulting ester saponified.[4] (b) Dry potassium 2,4-dichlorophenolate was heated with an equimolecular quantity of ethylene bromohydrin in xylene at 150° for five hours. (c) The sodium halophenolate in ethanol was treated at 75° with ethyl α-bromoheptoate and heated at 75–100° for two hours. The resulting ester was then saponified.

J. A solution of the ketoxime in dioxane and a suspension of the calculated quantity of sodamide in dioxane

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(1) I. G. Farbenindustrie, French Patent 833,734; *Chem. Zentr.*, **110**, I, 1451 (1939).

(2) Lohmann, *Ber.*, **24**, 2631 (1891).

(3) Brenans, *Bull. soc. chim.*, [3] **25**, 629 (1901).

(4) Ruhemann, *Ber.*, **54**, 912 (1921).

TABLE I

FSA no.	Compound	Method	Yield, %	B. p., °C.	B. p., Mm.	M. p., cor., °C.	$t°$	n^t_D	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, halogen or neutral equivalent Calcd.	Nitrogen, halogen or neutral equivalent Found
80	3,5-Dichlorophenoxyacetic acid	A	50.7			117.5–118			$C_8H_6Cl_2O_3$	43.5	43.6	2.7	3.3	221	227
430	2,4-Dichloromandelic acid	O	15			119.5–120.5			$C_8H_6Cl_2O_3$					221	222
93	2-Bromo-4-chlorophenoxyacetic acid	T	27.9			139–140.5			$C_8H_6ClBrO_3$	36.2	36.5	2.3	2.5	266	267
94	2-Chloro-4-bromophenoxyacetic acid	T	60			144.5–146.5			$C_8H_6ClBrO_3$	36.2	36.4	2.3	2.4	266	270
142	2-Iodo-4-chlorophenoxyacetic acid	A	40.3[c]			136–140			$C_8H_6IClO_3$	30.7	30.7	1.9	2.2	313	314
150	2-Chloro-4-iodophenoxyacetic acid	A	[d]			138–141			$C_6H_6IClO_3$	30.7	30.8	1.9	2.2	313	310
71	2,4-Dibromophenoxyacetic acid	A	65[b]			151.8–153.5			$C_8H_6Br_2O_3$	31.0	30.8	1.9	2.0	310	309
145	2,4-Diiodophenoxyacetic acid	G	2			165–167			$C_8H_6I_2O_3$					404	402

TABLE I *(Continued)*

FSA no.	Compound	Method	Yield, %	B. p., °C.	B. p., Mm.	M. p., cor., °C.	$t°$	n^t_D	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, halogen or neutral equivalent Calcd.	Nitrogen, halogen or neutral equivalent Found
	4-Methyl-4-trichloromethyl-2-chloro-2,5-cyclohexadiene-1-one oxime	X	52.6			182–183			$C_8H_7Cl_4NO$	34.9	35.0	2.6	2.7		
172	β-Hydroxyethyl 2,4-dichlorophenyl ether	Ib	44	121–128	1	57–58			$C_8H_8Cl_2O_2$	46.4	46.8	3.9	4.2		
437	S-2,4-Dichlorobenzylisothiourea hydrochloride	N	[h]			222–227			$C_8H_9Cl_3N_2S$	35.4	35.6	3.3	3.4		
427	2,4-Dichlorocinnamic acid	M	70			235–236[a]			$C_9H_6Cl_2O_2$					217	220
416	*m*-Trifluoromethylphenoxyacetic acid	S	64			93.5–94.0			$C_9H_7F_3O_3$					220	220
96	Ethyl 2,4-dichlorophenyl carbonate	E	66	98–99	1		20	1.5180	$C_9H_8Cl_2O_3$					30.2	30.5
164	Methyl 2,4-dichlorophenoxyacetate	Fc	74	119	1				$C_9H_8Cl_2O_3$	46.0	46.4	3.4	3.7		
426	2-Chloromethyl-4-chlorophenoxyacetic acid	U	73[b]			127–129			$C_9H_8Cl_2O_3$	46.0	46.2	3.4	3.5	235	233
438	1-(2,4-Dichlorophenoxy)-2,3-epoxypropane	P	10	107–109	1		25	1.5565	$C_9H_8Cl_2O_2$	49.3	49.2	3.7	3.8		
72	Methyl 2,4-dibromophenoxyacetate	A	65[b]	150	1				$C_9H_8Br_2O_3$	33.4	33.8	2.5	3.0		
140	Ethyl 2,4-dibromophenyl carbonate	E	79	135–136	2		20	1.5574	$C_9H_8Br_2O_3$					49.4	50.1
84	β-(*p*-Chlorophenoxy)propionitrile	B	40	dec.	2	46.4–47.0			C_9H_8ClNO					7.7	7.0[l] (*N*)
440	2,4-Dichlorobenzylcarboxymethyl sulfide	Z	35.5			73–75			$C_9H_8Cl_2SO_2$	43.1	43.1	3.2	3.5	251	248
441	2,4-Dichlorobenzylcarboxymethyl sulfone	R	80.8			181–182.5			$C_9H_8Cl_2SO_4$	38.2	38.7	2.8	3.1	283	280
434	1-(*p*-Chlorophenoxy)-2,3-epoxypropane	P	36	93–95	1		25	1.5430	$C_9H_9ClO_2$	58.5	58.3	4.9	5.1		
458	2-Methyl-4-fluorophenoxyacetic acid	S	51			147–148			$C_9H_9FO_3$					184	187
97	2-Methyl-4-bromophenoxyacetic acid	A	34.5			122–124			$C_9H_9BrO_3$	44.1	44.6	3.7	3.7	245	242
450	*p*-Chlorobenzylmercaptoacetic acid	Q	75			61–62			$C_9H_9ClSO_2$					217	218
451	*p*-Chlorobenzylsulfonylacetic acid	R	40			151.5–152.5			$C_9H_9ClSO_4$					249	247
428	Benzylcarboxymethyl sulfone	R				135–137			$C_9H_{10}SO_4$	50.5	50.7	4.7	4.9	214	216
158	2,4-Dichlorophenoxyfumaric acid	Ia	14			235–236[a] (dec.)			$C_{10}H_6Cl_2O_5$					139	138
432	2-Cyanomethyl-4-chlorophenoxyacetic acid	W	72[k]			156.5–159			$C_{10}H_8ClNO_3$	53.3	53.5	3.5	3.4	226	228
439	1-(*m*-Trifluoromethylphenoxy)-2,3-epoxypropane	P	23	80–83	1		25	1.4650	$C_{10}H_9F_3O_2$	55.1	55.5	4.2	4.2		
148	β-Chloroethyl 2,4-dichlorophenoxyacetate	Fa	69	157–158	1.5	39.0–39.6			$C_{10}H_9Cl_3O_3$	42.4	42.9	3.2	3.5		
100	β-Chloroethyl 2,4-dibromophenoxyacetate	Fb	89.8	182–184	0.5				$C_{10}H_9ClBr_2O_3$	32.2	32.6	2.4	2.8		
174	β-Bromoethyl 2,4-dichlorophenoxyacetate	Fa	89	166–168	2	33.6–34.2			$C_{10}H_9BrCl_2O_3$	36.6	37.0	2.8	3.0		
151	β-Bromoethyl 2,4-dibromophenoxyacetate	Fa	83.9			56–58			$C_{10}H_9Br_3O_3$	29.0	29.0	2.2	2.6		
414	2-Acetyl-4-chlorophenoxyacetic acid	A				174–176			$C_{10}H_9ClO_4$	52.5	52.4	4.0	4.2	229	232

TABLE I (*Continued*)

FSA no.	Compound	Method	Yield, %	B. p., °C.	mm.	M. p., cor. °C.	$t°$	n^t_D	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, halogen or neutral equivalent Calcd.	Nitrogen, halogen or neutral equivalent Found
433	2-Carboxymethyl-4-chlorophenoxyacetic acid	D	40.6			167.8–169.5			$C_{10}H_9ClO_5$	49.1	49.4	3.7	3.8	122	124
98	γ-(2,4-Dichlorophenoxy)-butyronitrile	C	35	136.5–137.5	*ca.* 1	46–48[g]	20	1.5472	$C_{10}H_9Cl_2NO$					6.1	5.9 (N)
91	γ-(*p*-Chlorophenoxy)-butyronitrile	C	31			44.5–45.3			$C_{10}H_{10}ClNO$					7.2	7.4 (N)
90	γ-(2,4-Dichlorophenoxy)-butyric acid	D	72						$C_{10}H_{10}Cl_2O_3$					249	251
146	β-Chloroethyl *p*-chlorophenoxyacetate	Fa	60	156–157	2.5	41.5–42.5			$C_{10}H_{10}Cl_2O_3$	48.2	48.7	4.1	4.1		
147	β-Bromoethyl *p*-chlorophenoxyacetate	Fa	80	182–184	4.5	39.6–40.4			$C_{10}H_{10}ClBrO_3$	40.9	41.4	3.4	3.6		
154	β-Hydroxyethyl 2,4-dichlorophenoxyacetate	Fa	20	177–180	1.5				$C_{10}H_{10}Cl_2O_4$	45.3	45.6	3.8	3.9		
66	4-Methyl-4-trichloromethyl-2,5-cyclohexadien-1-one-O-carboxymethyl oxime	J	11.7			118.5–120			$C_{10}H_{10}Cl_3O_3N$	40.2	39.7	3.4	3.4	299	304
435	1-(2-Methyl-4-chlorophenoxy)-2,3-epoxypropane	P	32	103–105	1		25	1.5385	$C_{10}H_{11}ClO_2$	60.5	60.7	5.6	5.8		
424	2-Ethyl-4-chlorophenoxyacetic acid	A	40.5			109–112			$C_{10}H_{11}ClO_3$	56.0	56.0	5.1	5.1	215	211
153	β-Hydroxyethyl *p*-chlorophenoxyacetate	Fa	23	163–166	1.5	29–30			$C_{10}H_{11}ClO_4$	52.1	52.2	4.8	4.9		
408	N-(2-Hydroxyethyl)-α-(2,4-dichlorophenoxy) acetamide	La	86			121.5–122.0			$C_{10}H_{11}Cl_2NO_3$	45.5	45.7	4.2	4.3		
423	N-(2-Hydroxyethyl)-α-(*p*-chlorophenoxy)-acetamide	La	79.3			94.5–96			$C_{10}H_{12}NClO_3$	52.3	52.0	5.2	5.0		
199	Isopropyl O-phenylcarbamate	Lb	43.8			81.8–83.5			$C_{10}H_{13}NO_2$	67.1	67.3	7.3	7.6		
185	2-Methyl-4-chlorophenoxyfumaric acid	Ia	15			223–227[a] dec.			$C_{11}H_9ClO_5$					128	128
156	Allyl 2,4-dichlorophenoxyacetate	Fa	75	134–134.5	2		25	1.5395	$C_{11}H_{10}Cl_2O_3$	50.6	50.9	3.9	3.9		
163	β-Trichloroethyl 2-methyl-4-chlorophenoxyacetate	Fa	66.3	179–180	1				$C_{11}H_{10}Cl_4O_3$	39.8	40.1	3.0	3.4		
176	2,3-Dichloropropyl 2,4-dichlorophenoxyacetate	H	49	183–185	2		19.4	1.5530	$C_{11}H_{10}Cl_4O_3$	39.8	40.0	3.0	3.1		
165	β,γ-Dichloropropyl-2,4-dibromophenoxyacetate	H	38.9	190–195	0.5				$C_{11}H_{10}Cl_2Br_2O_3$	31.4	31.4	2.4	2.6		
404	2-Allyl-4-chlorophenoxyacetic acid	A	36.3			104–106			$C_{11}H_{11}ClO_3$	58.3	58.2	4.9	5.0	227	229
155	Allyl *p*-chlorophenoxyacetate	Fa	82	122–124	2		25	1.5255	$C_{11}H_{11}ClO_3$	58.3	58.7	4.9	5.1		
175	2,3-Dichloropropyl *p*-chlorophenoxyacetate	H	34	169–171	2		20	1.5418	$C_{11}H_{11}Cl_3O_3$	44.4	43.8	3.7	3.7		
167	Isopropyl 2,4-dichlorophenoxyacetate	Fa	83.6	139–140	1				$C_{11}H_{12}Cl_2O_3$	50.2	50.3	4.6	4.6		
177	Ethyl-2-chloromethyl-4-chlorophenoxyacetate	V	73[b]	140–142	1				$C_{11}H_{12}Cl_2O_3$	50.2	50.5	4.6	4.7		
160	β-Bromoethyl 2-methyl-4-chlorophenoxyacetate	Fa	75	153–155	1				$C_{11}H_{12}ClBrO_3$	42.9	42.7	3.9	4.0		

TABLE I (*Continued*)

FSA no.	Compound	Method	Yield, %	B. p., °C.	B. p., Mm.	M. p., cor., °C.	t°	n^t_D	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, halogen or neutral equivalent Calcd.	Nitrogen, halogen or neutral equivalent Found
178	2-Propyl-4-chlorophenoxyacetic acid	A	30.9			115–118			$C_{11}H_{13}ClO_3$	57.8	57.9	5.8	5.9	229	230
183	Ethyl 2-methyl-4-chlorophenoxyacetate	Fa	75	115–117	1		23	1.5150	$C_{11}H_{13}ClO_3$	57.9	58.0	5.7	6.0		
406	N-(2-Hydroxyethyl)-α-(2-methyl-4-chlorophenoxy) acetamide	La	81			98–99			$C_{11}H_{14}ClNO_3$	54.2	54.3	5.8	5.6		
78	7-Chloro-1-naphthoxyacetic acid	A	50			169.0–169.6			$C_{12}H_9ClO_3$					237	243
455	Methallyl 2,4-dichlorophenoxyacetate	Fa	80	130–132	2				$C_{12}H_{13}ClO_3$	59.8	60.2	5.4	5.8		
195	2-Nitro-2-methylpropyl 2,4-dichlorophenoxyacetate	Fa	65			45.0–45.6			$C_{12}H_{13}Cl_2NO_5$	44.7	44.8	4.1	3.7		
456	Crotyl *p*-chlorophenoxyacetate	Fa	68.4	141–142	2				$C_{12}H_{14}ClO_3$	59.6	59.5	5.8	5.8		
143	*n*-Butyl 2,4-dichlorophenoxyacetate	Fa	92	146–147	1				$C_{12}H_{14}Cl_2O_3$					25.6	26.1
171	Isobutyl 2,4-dichlorophenoxyacetate	Fa	86.8	133–134	1				$C_{12}H_{14}Cl_2O_3$	52.0	52.3	5.0	5.3		
184	*n*-Propyl 2-methyl-4-chlorophenoxyacetate	Fa	81	109.5–111.5	0.5		23	1.5100	$C_{12}H_{15}ClO_3$	59.4	59.2	6.2	6.6		
402	2-*s*-Butyl-4-chlorophenoxyacetic acid	A	50			124–125.5			$C_{12}H_{15}ClO_3$	59.4	59.7	6.2	6.2	243	240
81	2-Bromo-4-*t*-butylphenoxyacetic acid	A	19			110.8–111.2			$C_{12}H_{15}BrO_3$					287	285
182	Isopropyl 2-methyl-4-chlorophenoxyacetate	Fa	73	99–101	<1		20	1.5070	$C_{12}H_{15}ClO_3$	59.4	59.7	6.2	6.5		
407	N-(2-Hydroxyisopropyl)-α-(2-methyl-4-chlorophenoxy)-acetamide	La	95			80.0–80.5			$C_{12}H_{16}ClNO_3$	55.9	55.8	6.3	6.1		
168	Amyl 2,4-dichlorophenoxyacetate	Fa	69.3	164	2				$C_{13}H_{16}Cl_2O_5$	53.6	53.9	5.5	5.7		
169	Isoamyl 2,4-dichlorophenoxyacetate	Fa	81.8	136–138	1				$C_{13}H_{16}Cl_2O_3$	53.6	54.0	5.5	5.8		
198	β-Chloroethyl 2-propyl-4-chlorophenoxyacetate	Fa	73	173–175	4				$C_{13}H_{16}Cl_2O_3$	53.6	53.8	5.5	5.9		
422	α-(2,4-Dichlorophenoxy)-heptylic acid	Ic	79			100.0–100.5			$C_{13}H_{16}Cl_2O_3$					291	291
194	2-Nitro-2-methylpropyl 2-methyl-4-chlorophenoxyacetate	Fa	80			60.6–61.6			$C_{13}H_{16}ClNO_5$	51.8	52.0	5.3	5.0		
179	Ethyl 2-propyl-4-chlorophenoxyacetate	Fa	80	134–136	1				$C_{13}H_{17}ClO_3$	60.8	61.1	6.6	7.0		
425	2-Amyl-4-chlorophenoxyacetic acid	A	10.6			127.5–129.5			$C_{13}H_{17}ClO_3$	60.8	61.2	6.6	6.8	257	256
418	α-(*p*-Chlorophenoxy)-heptylic acid	Ic	78			79.5–80			$C_{13}H_{17}ClO_5$					257	257
89	α-(*p*-Chlorophenyl)-2,4-dichlorophenoxyacetic acid	A	48.6			145–146			$C_{14}H_9Cl_3O_3$	50.7	51.0	2.7	3.0	332	332
442	Bis-(2,4-dichlorobenzyl) sulfide	Z	32.1	197.5–199	2				$C_{14}H_{10}Cl_4S$	47.8	47.8	2.8	3.0		
448	Bis-2,4-dichlorobenzyl disulfide	Y	94.3[k]			69–71			$C_{14}H_{10}Cl_4S_2$	43.8	43.3	2.6	2.8		
88	α-(*p*-Chlorophenyl)-*p*-chlorophenoxyacetic acid	A	68.7			138.5–140.5			$C_{14}H_{10}Cl_2O_3$	56.6	56,9	3.4	3.8	297	300

TABLE I (*Concluded*)

FSA no.	Compound	Method	Yield, %	B. p., °C.	B. p., Mm.	M. p., cor. °C.	$t°$	n^t_D	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, halogen or neutral equivalent Calcd.	Nitrogen, halogen or neutral equivalent Found
443	Bis-2,4-dichlorobenzyl sulfone	R	85			197–199			$C_{14}H_{10}Cl_4SO_2$	43.8	43.8	2.6	2.9		
28	2-(2′-Chlorophenyl)-phenoxyacetic acid	S	47.5[j]			123.5–125.5			$C_{14}H_{11}ClO_3$	64.0	63.8	4.2	4.2	263	258
29	2-(4′-Chlorophenyl)-phenoxyacetic acid	S	85[j]			109.5–110.5			$C_{14}H_{11}ClO_3$	64.0	64.2	4.2	4.3	263	262
429	2-Cyclohexyl-4-chlorophenoxyacetic acid	A	[f]			167.5–170.5			$C_{14}H_{17}ClO_3$	62.6	62.6	6.3	6.3	269	269
400	2,2-Dimethyl-1,3-dioxalane-4-methanyl-*p*-chlorophenoxyacetate	K	71	160	1		25	1.5108	$C_{14}H_{17}ClO_5$	55.9	55.9	5.7	5.9		
35	β-Diethylaminoethyl 2,4,5-trichlorophenoxyacetate	Lc	89	176–178	1.5				$C_{14}H_{18}Cl_3NO_3$	47.4	47.1	5.1	4.9	4.0	3.9 (N)
180	Isopropyl 2-propyl-4-chlorophenoxyacetate	Fa	83.8	155–157	5				$C_{14}H_{19}ClO_3$	62.1	62.3	7.0	7.4		
403	Ethyl 2-*s*-butyl-4-chlorophenoxyacetate	Fa	89.9	128–129	1				$C_{14}H_{19}ClO_3$	62.2	62.3	7.0	7.4		
420	α-(2-methyl-4-chlorophenoxy)-heptylic acid	Ic	91			72.5–73			$C_{14}H_{19}ClO_3$					271	271
465	N-(*m*-Trifluoromethylphenyl)-α-(2,4,5-trichlorophenoxy)-acetamide	La	73			191.5–192.5			$C_{15}H_9Cl_3F_3NO_2$					3.5	3.5 (N)
463	N-(*m*-Trifluoromethylphenyl)-α-(2,4-dichlorophenoxy)-acetamide	La	96			148.6–149.2			$C_{15}H_{10}Cl_2F_3NO_2$					3.9	4.1 (N)
464	N-(*m*-Trifluoromethylphenyl)-α-(*p*-chlorophenoxy)-acetamide	La	100			94–95			$C_{15}H_{11}ClF_3NO_2$					4.3	4.6 (N)
401	2,2-Dimethyl-1,3-dioxolane-4-methanyl-2-methyl-4-chlorophenoxy-acetate	K	82	151–152	1		25	1.5100	$C_{15}H_{19}ClO_5$	57.2	57.1	6.1	6.1		
421	Ethyl α-(2,4-dichlorophenoxy)-heptoate	Ic	74	131.5–133	1		25	1.5038	$C_{15}H_{20}Cl_2O_3$	56.4	56.7	6.3	6.4		
417	Ethyl α-(*p*-chlorophenoxy)-heptoate	Ic	65	121–123	1		25	1.4938	$C_{15}H_{21}ClO_3$	63.3	63.0	7.4	7.7		
462	N-(*m*-Trifluoromethylphenyl)-α-(2-methyl-4-chlorophenoxyacetamide	La	88			138–139			$C_{16}H_{13}ClF_3NO_2$					4.1	4.3 (N)
144	2-Ethylhexyl 2,4-dichlorophenoxyacetate	Fa	76.5	173–174	0.5				$C_{16}H_{22}Cl_2O_3$					21.3	21.7
170	Octyl 2,4-dichlorophenoxyacetate	Fa	60	173–174	1				$C_{16}H_{22}Cl_2O_3$	57.7	58.0	6.6	6.8		
419	Ethyl α-(2-methyl-4-chlorophenoxy)-heptoate	Ic	42	126–127	1		26	1.4930	$C_{16}H_{23}ClO_3$	64.3	64.3	7.8	7.7		

[a] M. p. taken in copper block (Bergstrom, *Ind. Eng. Chem., Anal. Ed.*, **9,** 340 (1937). [b] Part isolated as acid and part as ester. [c] Yield based on ethyl ester isolated. [d] No yield reported because impure iodinated chlorophenol was used. [e] No yield reported because crude phenol was used. [f] Exact yield not determined; yield in 40–50% region. [g] Solidified after standing for some time. [h] No yield reported since only part was isolated, the remainder being converted to mercaptan. [i] No yield reported because of accidental loss owing to vigorous reaction. [j] Isolated as ethyl ester—yield based on unrecovered phenol. [k] Crude yield. [l] Low analysis for nitrogen but acid prepared by hydrolysis was identical with known acid, Chakravorti and Dutta, *J. Ind. Chem. Soc.*, **16,** 639 (1944).

were boiled until evolution of ammonia had ceased. An excess of methyl bromoacetate was added and the mixture refluxed for three hours.

K. The acid chloride dissolved in dry benzene was added to a slight excess of isopropylidene glycerol and of collidine in dry benzene at 0°, followed by heating of the mixture at 50° for one hour.

L. Reaction of acid chlorides with aminoalcohols. (a) The acid chloride in dry benzene was added, with cooling, to an excess of the aminoalcohol in dry benzene, followed by heating to 50° for one-half hour and allowing to come to room temperature. (b) The acid chloride was added to an excess of the amino alcohol in benzene. (c) A 30% excess of the aminoalcohol was added to the acid chloride in benzene. After two hours the reaction mixture was worked up.

M. Perkin reaction using 2,4-dichlorobenzaldehyde.

N. 2,4-Dichlorobenzylisothiourea hydrochloride was prepared from the corresponding chloride and thiourea.[5]

O. 2,4-Dichlorobenzaldehyde was converted to the nitrile by way of the bisulfite addition compound. The nitrile was hydrolyzed by heating with concentrated hydrochloric acid for five hours at 100°.[6]

P. The epoxypropane compound was formed by reaction of the phenol with epichlorohydrin in presence of aqueous sodium hydroxide solution for forty-eight hours at room temperature.[7]

Q. *p*-Chlorobenzyl mercaptan dissolved in aqueous sodium hydroxide was treated with chloroacetic acid.[8]

R. The corresponding mercapto compound dissolved in a mixture of equal volumes of acetic anhydride and glacial acetic acid was oxidized by hydrogen peroxide.

S. The phenol was condensed with chloroacetic acid in presence of aqueous sodium hydroxide.[9]

T. The chlorophenoxyacetic acid was brominated at 80° for six hours with excess bromine in presence of aluminum chloride.

U. The ester was hydrolyzed by refluxing for one and one-half hours with a mixture of concentrated hydrochloric acid and glacial acetic acid.

V. Dry hydrogen chloride was passed into a mixture of ethyl *p*-chlorophenoxyacetate, paraformaldehyde and anhydrous zinc chloride, heated at 60°, for one hour.

W. Ethyl 2-chloromethyl-4-chlorophenoxyacetate in acetone was refluxed for six hours with an aqueous solution of potassium cyanide, using sodium iodide as a catalyst. The cyanomethyl acid was obtained by acidification of the mixture after removal of acetone.

X. The oxime was formed by addition of an excess of hydroxylamine hydrochloride in concentrated aqueous solution to a solution of the ketone in alcohol.[10]

Y. The mercaptan was converted to the disulfide by an excess of hydroxylamine hydrochloride in alcoholic solution.[11]

Z. A solution of the mercaptan in absolute ethanol was refluxed with a 10% excess of sodium methylate for one-half hour.

(a) A slight excess of ethyl bromoacetate was added and the mixture refluxed for one hour. Saponification was accomplished by alcoholic sodium hydroxide solution and the acid isolated in the usual manner.

(b) A slight excess of benzyl chloride was added and the mixture refluxed for one hour.

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(5) Urquhart, Gates and Connor, "Organic Syntheses," **21**, 36 (1941).

(6) Gnehm and Schüle, *Ann.*, **299**, 347 (1898).

(7) Marle, *J. Chem. Soc.*, **101**, 305 (1912).

(8) Gabriel, *Ber.*, **12**, 1639 (1879).

(9) Hayes and Branch, This Journal, **65**, 1555 (1943).

(10) Zincke and Suhl, *Ber.*, **39**, 4148 (1906).

(11) Fasbender, *ibid.*, **21**, 1470 (1888).

Department of Chemistry Melvin S. Newman
The Ohio State University William Fones
Columbus 10, Ohio Mary Renoll

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Derivatives of Fluorene

Tetrabiphenylene-butane.—A solution of 4 g. of 1-bromodibiphenylene-ethane[1] in 75 cc. of purified benzene containing freshly prepared copper powder was heated in a carbon tetrachloride bath for ten hours, and since the reaction appeared to be rather sluggish the heating was continued on a steam-bath for an additional eight hours. The reaction mixture was filtered, the filtrate removed by distillation, and the residue consisting of dibiphenylene-ethylene and tetrabiphenylene-butane was crystallized from ethyl acetate; yield of butane derivative, 1.1 g. This was recrystallized from acetic acid yielding glistening needle-like prisms, m. p. 291°.

Anal. Calcd. for $C_{52}H_{34}$: C, 94.80; H, 5.20. Found: C, 94.90; H, 5.49.

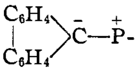
The compound is soluble in benzene, pyridine, ethyl acetate, carbon tetrachloride and ether.

Fluorenyl-9-ethylcarboxylate-9-dimethyloxide.—This compound was prepared by the reaction of 6.5 g. of fluorenyl-9-ethylcarboxylate, 0.75 g. of sodium and 3 cc. of chloromethyl ether in anhydrous ether by the method of Wislicenus and Mocker.[2] The reaction product was extracted with ether and distilled at 262-268° at 1 mm. pressure, yield 5 g., crystallized from ligroin as large prisms, m. p. 64–65°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.56; H, 6.43. Found: C, 76.51; H, 6.35.

Various attempts to hydrolyze or to decarboxylate the ester were unsuccessful. The compound was practically unaltered after fifteen minutes heating at 270° and ten minutes at 360° in a sealed tube. No change was effected after letting it stand in alcoholic ammonium hydroxide for several weeks or by heating an alcoholic solution of the ester in presence of hydrochloric acid. By heating it in an alcoholic solution of sodium hydroxide at 150° for six hours, less than 10% of the ester was converted to 9-methylfluorene,[2] m. p. 45°, which was isolated by two sublimations and recrystallization from methyl alcohol.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.28; H, 6.72. Found: C, 93.45; H, 6.69.

Triphenylphosphine Fluorenylidenide,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>\overset{-}{C}—\overset{+}{P}\text{-}(C_6H_5)_3$.—Staudinger and Meyer,[3] attempted to prepare triphenylphosphine fluorenylidenide by pyrolyzing triphenylphosphazine fluorenylidenide and obtained a resinous product which could not be purified. We found that this compound could be prepared in the following manner. To a solution of 3 g. of 9-bromofluorene in about 40 cc. of nitromethane was slowly added 3.21 g. of triphenylphosphine. As the last portion was added, fluorenyl-9-triphenylphosphonium bromide began to crystallize. The reaction was exothermic, evidenced by a 10° rise in temperature of the solution. After two hours, 5.75 g. of the bromide was removed, m. p. 303° (dec.). Triphenylphosphine fluorenylidenide was obtained by dissolving 3 g. of the salt in 150 cc. of boiling alcohol and making the solution alkaline with about 8 cc. of ammonium hydroxide. Yellow glistening plates crystallized as the solution cooled, weight 2.4 g., m. p. 253°.

Anal. Calcd. for $C_{31}H_{23}P$: C, 87.28; H, 5.44; P, 7.28. Found: C, 87.15; H, 5.66; P, 7.25, 7.26.

The compound remained unaltered when refluxed with aniline, phenol and hydrazine hydrate in alcohol.

Bureau of Plant Industry, Soils and
Agricultural Engineering
U. S. Department of Agriculture Louis A. Pinck
Beltsville, Maryland Guido E. Hilbert[4]

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(1) Grignard and Courtot, *Compt. rend.*, **152**, 1494 (1911); Courtot, *Ann. chim.*, (9) **4**, 165 (1915).

(2) Wislicenus and Mocker, *Ber.*, **46**, 2772 (1913).

(3) Staudinger and Meyer, *Helv. Chim. Acta.*, **2**, 619 (1919).

(4) Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois.