distillation and the distillate collected until the odor of piperidine was no longer evident. The distillate was made strongly alkaline with sodium hydroxide and extracted with ether. After drying over sodium hydroxide, the solvent was removed and the piperidine was distilled; b. p. 104–105°; $n^{20}D$ 1.4532; yield 17 g. (81%) (identified as the benzenesulfonamide, mixed m. p. 93–94°).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

RECEIVED JUNE 6, 1946

NEW COMPOUNDS

Some Substituted Anthranilic Acids

N-(2′,4′-Dinitrophenyl)-5-methoxyanthranilic Acid.—This compound was prepared from 5-methoxyanthranilic acid and 2,4-dinitrochlorobenzene by a procedure analogous to that described by Jourdan.[1] The yield was 88% of bright red needles, m. p. 290–291°. Recrystallization of a sample from phenol–acetic acid did not change the melting point.

It was not found possible to prepare a chloroacridine from this acid. Compare the work of Albert and Linnell.[2]

Anal. Calcd. for $C_{14}H_{11}O_7N_3$: C, 50.45; H, 3.33. Found: C, 50.39, 50.49; H, 3.58, 3.50.

The acid chloride was prepared by refluxing a mixture of 9.0 g. of the acid, 10.0 g. of phosphorus pentachloride, and 45 cc. of benzene for thirty minutes. The clear, red solution was diluted with an equal volume of hot heptane, and cooled. It deposited 7.8 g. (82%) of large, orange crystals of the acid chloride, m. p. 153–155°. Further recrystallization raised the melting point to 155–156°.

Anal. Calcd. for $C_{14}H_{10}O_6N_3Cl$: C, 47.81; H, 2.87. Found: C, 47.93, 47.97; H, 3.00, 3.05.

3-Diethylaminopropylamide of N-(2′,4′-Dinitrophenyl)-5-methoxyanthranilic Acid Hydrochloride Dihydrate.—Six grams of the acid chloride was dissolved in 60 cc. of warm benzene, and a solution of 2.3 g. of 3-diethylaminopropylamine in 20 cc. of benzene was added slowly. The mixture was refluxed for thirty minutes, and the benzene was removed by distillation. The residual red gum was purified by dissolving it in hot ethanol (which contained an excess of hydrogen chloride), cooling the solution, and diluting it with ether. After several hours 3.9 g. (44%) of large, orange crystals of the hydrochloride dihydrate separated. A final recrystallization from propanol–dibutyl ether was carried out. The anhydrous form (red, very hygroscopic), prepared by heating a sample of the dihydrate (orange) at 100° for twenty minutes, melted at 139°.

Anal. Calcd. for $C_{21}H_{28}O_6N_5Cl\cdot 2H_2O$: C, 48.70; H, 6.23. Found: C, 48.97, 48.90; H, 6.28, 6.35.

N-(3′-Trifluoromethylphenyl)-4-chloroanthranilic Acid.—A mixture of 35 g. of the potassium salt of 2,4-dichlorobenzoic acid, 28 g. of *m*-aminobenzotrifluoride, 14 g. of potassium carbonate, 110 cc. of amyl alcohol and 0.5 g. of copper powder was heated at 125–130° for nine hours. The crude product was isolated by a procedure similar to that used for the naphthylanthranilic acid derivatives.[3] One recrystallization from ethanol gave 9.5 g. (20%) of a white, microcrystalline product, m. p. 205–208°. Further recrystallization raised the melting point to 208–209.5°.

Anal. Calcd. for $C_{14}H_9O_2NClF_3$: C, 53.26; H, 2.87. Found: C, 53.00, 53.12; H, 2.80, 2.88.

This acid reacted with phosphorus oxychloride in the usual way to give a 70% yield of the two possible, isomeric chloroacridines. These were not separated in a degree of purity sufficient for accurate characterization.

(1) Jourdan, *Ber.*, **18**, 1448–1449 (1885).
(2) Albert and Linnell, *J. Chem. Soc.*, 25 (1938).
(3) Bachman and Picha, THIS JOURNAL, **68**, 1599 (1946).

PURDUE UNIVERSITY G. BRYANT BACHMAN
LAFAYETTE, INDIANA GEORGE M. PICHA

RECEIVED JUNE 8, 1946

Preparation and Reactions of 2,4-Dichlorophenoxyacetyl Chloride[1]

We have found that the use of phosphorus pentachloride in the preparation of 2,4-dichlorophenoxyacetyl chloride is unsatisfactory, but that this substance may be prepared in the conventional manner employing thionyl chloride.

Procedure.—A mixture of 10 g. of 2,4-dichlorophenoxyacetic acid and 15 cc. of thionyl chloride was refluxed on a steam-bath for one hour. The excess thionyl chloride distilled off at atmospheric pressure. The product was then distilled at 180 mm. from a Claisen flask connected directly to a water-cooled receiver. The acyl halide crystallized out in the receiver in white needle-like crystals; m. p. 44.5–45.5°; yield 7.9 g. (67%).

Anal. Calcd. for $C_8H_5Cl_3O$: Cl (ionizable), 14.78. Found: Cl, 14.71.

This substance, as well as the methyl ester derivative of the parent acid, may be supercooled after melting without crystal formation. In its reactions it resembles more nearly aromatic rather than aliphatic acyl halides; *e. g.*, it undergoes the Schotten–Baumann reaction; it does not react with water, alcohol or amines in the cold. It reacts smoothly with sodium alkoxides to form esters. This substance has been found advantageous in the preparation of esters of alcohols that are affected by normal esterifying catalysts.

(1) Published as Technical Paper No. 493 with the approval of the Director of the Oregon Agricultural Experiment Station. Contribution of the Department of Farm Crops.

FARM CROPS DEPARTMENT
OREGON AGRICULTURAL EXPERIMENT STATION
CORVALLIS, OREGON VIRGIL H. FREED

RECEIVED JULY 1, 1946

6-Bromo-1,2,3,4-tetrahydroquinaldine Hydrobromide

The bromination was carried out according to the method of Hoffmann and Königs[1] for 6-bromo-1,2,3,4-tetrahydroquinoline. To 25 g. of 1,2,3,4-tetrahydroquinaldine (0.17 mole) in 250 ml. of chloroform, 27.2 g. (0.17 mole) of bromine was added over a period of one-half hour with vigorous stirring. The temperature was kept below 40°. The chloroform was removed from the reaction mixture by distillation, and the colorless portion of the solid residue was dissolved in the minimum quantity of hot, dilute hydrobromic acid. Filtration removed the dark green, insoluble oil. When the filtrate was cooled, colorless needles of 6-bromo-1,2,3,4-tetrahydroquinaldine hydrobromide separated. The product was recrystallized twice from dilute hydrobromic acid and once from water; yield, 35 g. (67%); m. p. 200–201°.

Anal. Calcd. for $C_{10}H_{13}Br_2N$: C, 39.11; H, 4.28. Found: C, 39.20; H, 4.38.

(1) Hoffmann and Königs, *Ber.*, **16**, 727 (1883).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS NELSON J. LEONARD
URBANA, ILLINOIS MARIAN PERKINS FOX

RECEIVED JULY 20, 1946

Some New Compounds as Possible Insect Repellents

A number of new compounds were synthesized for testing as insect repellents. These compounds are listed below and brief descriptions of their preparation are given.

TABLE I

Mol. formula	Orlando code no.	Compound	Method	Yield, %	B. p., °C.	Pressure, mm.	$n^{20}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen chlorine or sulfur Calcd.	Nitrogen chlorine or sulfur Found
$C_7H_{14}O_3$	7466	Ethylene glycol mono(*n*)valerate	A	37	110–111	11	1.4291[c]	57.5[a]	57.8	9.7	10.0		
$C_8H_{13}O_3Cl$	7434	Tetrahydrofurfuryl β-chloropropionate	C	86	89– 90	1	1.4631[c]	50.0[b]	50.4	6.8	6.8	18.4	18.8
$C_8H_{13}O_4N$	7372	2-Vinyl-5-ethyl-5-nitro-*m*-dioxane	J	26	107–110	0.5	1.4695[c]	51.3[b]	51.2	7.0	6.7	7.5	7.1
$C_8H_{14}O_6S$	7260	bis-β,β-Acetoxyethyl sulfone	N	75	172–175	0.5	1.4692	40.3[b]	39.9	5.9	6.0	13.5	14.5
$C_8H_{15}O_4N$	7431	2,2-Dimethyl-5-ethyl-5-nitro-*m*-dioxane	J	82	...	..	54-56°[e]	50.8[b]	51.1	8.0	8.2	7.4	7.5
$C_8H_{15}O_4N$	7228	2-Isopropyl-5-methyl-5-nitro-*m*-dioxane	J	73	98–103	0.5	46[d]	50.8[b]	50.9	8.0	8.0	7.4	7.2
$C_8H_{15}O_4N$	7398	2,5-Dimethyl-2-ethyl-5-nitro-*m*-dioxane	J	68	77– 78	0.5	1.4548[c]	50.8[b]	50.9	8.0	8.0	7.4	7.5
$C_8H_{16}O_3$	7414	4-Hydroxymethyl-2-propyl-1,3-dioxolane	J	77	102–103	10	1.4394[c]	60.0[b]	60.2	10.1	10.1		
$C_9H_{12}O_4$	7230	Diallyl malonate	C	75	112	9	1.4478	58.7[b]	58.8	6.6	6.6		
$C_9H_{15}O_2N$	7187	Cyclohexyl cyanoacetate	C	51	103–108	0.5	1.4620	64.7[b]	64.9	7.8	7.8	8.4	8.3
$C_9H_{17}O_3Cl$	7440	2-Butoxyethyl-α-chloropropionate	C	93	104–106	7	1.4340[c]	51.8[b]	52.0	8.2	8.3		
$C_9H_{17}O_4N$	7418	5-Methyl-2,5-diethyl-5-nitro-*m*-dioxane	J	91	87– 90	0.5	1.4549[c]	53.2[b]	53.3	8.4	8.5	6.9	6.7
$C_{10}H_9O_2N$	7222	Benzyl cyanoacetate	C	61	134–136	0.5	1.5191	68.6[b]	68.2	5.2	5.2	8.0	8.0
$C_{10}H_{14}O$	7310	1-*o*-Tolyl-2-propanol	V	55	106–111	9	1.5226[c]	80.0[b]	80.4	9.4	9.5		
$C_{10}H_{16}O_3$	7166	Methyl α-methylepoxycyclohexylideneacetate	Q	92	104–106	6	1.4615	65.2[b]	65.2	8.8	8.5		
$C_{11}H_{13}O_2N$	7209	N-Allyl 1,2,3,6-tetrahydrophthalimide	AA	88	127–129	3.0	1.5225	69.1[b]	68.8	6.9	6.9	7.3	6.8
$C_{11}H_{14}O$	7361	Allyl *o*-methylbenzyl ether	M	67	96– 98	9	1.4091[c]	81.4[a]	81.2	8.7	9.3		
$C_{11}H_{14}O$	7243	α-Methylol isobutyrophenone	W	20	110–117	1	1.5320	74.1[b]	74.0	7.9	8.4		
$C_{11}H_{14}O_2$	7349	Allyl β-phenoxyethyl ether	M	71	120–122	10	1.5110[c]	74.1[b]	73.9	7.9	7.9		
$C_{11}H_{14}O_2$	7405	Allyl *p*-methoxybenzyl ether	M	79	82– 85	0.5	1.5180[c]	74.1	73.6	7.9	8.3		
$C_{11}H_{14}O_2$	13042	β-Allyloxy-α-phenylethanol	K	31	114–116	.5	1.5189[c]	74.1[a]	74.2	7.9	8.1		
$C_{11}H_{14}O_3$	7496	1,2-Propylene glycol, monophenylacetate	B	65	117–118	.5	1.5099[c]	68.0[a]	68.4	7.3	7.4		
$C_{11}H_{14}O_4$	13034	Diethylene glycol, monobenzoate	T	62	127–130	.5	1.5200[c]	62.8[a]	62.9	6.7	6.8		
$C_{11}H_{15}O_2N$	7395	N-Isopropyl 1,2,3,6-tetrahydrophthalimide	AA	80	99–100	.5	58°[d]	68.4[b]	68.0	7.8	7.6	7.3	6.8
$C_{11}H_{15}O_2N$	7410	N-Allyl hexahydrophthalimide	AA	81	109–113	2	1.5078[c]	68.4[b]	68.4	7.8	8.0	7.3	7.2
$C_{11}H_{18}O_3$	7241	Methyl α-methylepoxy-4-methylcyclohexylidene acetate	Q	60	101–105	4	1.4594	66.6[b]	66.8	9.9	9.0		
$C_{12}H_{12}O_3$	7161	3-Butyn-1-yl anisate	T	54	123-124	0.5	1.5396	70.6[b]	70.7	5.9	5.9		
$C_{12}C_{14}O_3$	7219	Methyl α,β-dimethyl β-phenylglycidate	Q	35	97–106	.5	42[d]	69.9[a]	70.0	6.8	7.0		
$C_{12}H_{13}O_2N$	7447	N-Allyl 3-methyl-1,2,3,6-tetrahydropthalimide	AA	87	112–113	.5	1.5190[c]	70.2[b]	69.9	7.4	7.4	6.8	6.4
$C_{12}C_{15}O_2N$	7436	N-Isopropyl-3,6-endomethylene 1,2,3,6-tetrahydrophthalimide	AA	89	118–120	1	88.89[e]	70.2[b]	70.5	7.4	7.5	6.8	6.6
$C_{12}H_{16}O$	7354	Allyl β-(*o*-tolyl)-ethyl ether	M	72	113–115	11	1.5189[c]	81.8[b]	71.5	9.2	9.2		
$C_{12}H_{16}O_3$	13003	*p*-Tolyl isobutyl carbonate	I	92	90– 92	0.5	1.4790[c]	69.2[a]	69.6	7.8	8.2		
$C_{12}H_{17}O_2N$	7145	N-*n*-Butyl-1,2,3,6-tetrahydrophthalimide	AA	97	129–131	3	1.5003	69.5[b]	69.7	8.3	8.0	6.8	6.6
$C_{12}H_{17}O_2N$	7396	N-Isobutyl-1,2,3,6-tetrahydrophthalimide	AA	89	117–119	2	1.5010[c]	69.5[b]	69.7	8.3	8.1	6.8	6.6
$C_{12}H_{17}O_2N$	7184	Allyl cyclohexylcyanoacetate	G	65	116–119	0.5	1.4662	69.5[b]	69.2	8.3	8.3	6.8	7.3
$C_{12}H_{19}O_2N$	7175	Isopropyl cyclohexylcyanoacetate	G	58	101–104	.5	1.4557	68.9[b]	69.1	9.2	9.1	6.7	6.6
$C_{12}H_{19}O_2N$	7170	Propyl cyclohexylcyanoacetate	G	81	104–106	.5	1.4591	68.9[b]	69.3	9.2	8.8	6.7	6.6
$C_{12}H_{19}O_2N$	7223	Ethyl 4-methylcyclohexylcyanoacetate	G	58	110–111	.5	1.4610	68.9[b]	69.3	9.2	9.1	6.7	6.9
$C_{12}H_{19}O_2N$	7464	2-Methylcyclohexyl α-cyanobutyrate	C	63	98–100	.5	1.4524[c]	68.9[b]	68.7	9.2	9.3	6.7	6.8
$C_{12}H_{19}O_2N$	7468	4-Methylcyclohexyl α-cyanobutyrate	C	80	97–101	.5	1.4510[c]	68.9[a]	68.4	9.2	9.2	6.7	6.7
$C_{12}H_{19}O_2N$	7409	N-*n*-Butyl hexahydrophthalimide	AA	87	115–118	2	1.4907[c]	68.9[b]	69.0	9.2	8.8	6.7	6.5
$C_{12}H_{20}O$	7275	2,2-Diallylcyclohexanol	L	60	107–111	6	1.4860	79.9[b]	80.0	11.2	10.9		
$C_{12}H_{20}O_3$	7202	Propyl α-methylepoxycyclohexylideneacetate	R	59	109–113	0.5	1.4757	67.9[b]	67.6	9.5	9.5		

TABLE I (*Concluded*)

Mol. formula	Orlando code no.	Compound	Method	Yield, %	B. p., °C.	Pressure, mm.	$n^{20}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen chlorine or sulfur Calcd.	Nitrogen chlorine or sulfur Found
$C_{12}H_{20}O_5$	13022	Ethyl 2-acetoxy-1-hydroxycyclohexylacetate	F	70	152–157	9	1.4638	59.0[a]	58.8	8.3	8.4		
$C_{13}H_{13}O_3Cl$	7172	Allyl β-*p*-chlorobenzoylpropionate	C	77	137–139	2	43–44[c]	61.8[b]	62.2	5.2	5.3	14.0	14.4
$C_{13}H_{14}O_3$	7167	Allyl β-benzoylpropionate	C	53	117–119	0.1	1.5243	71.5[b]	72.0	6.5	6.7		
$C_{13}H_{16}O_3S$	7263	2-*p*-Toluenesulfonyl cyclohexanone	O	32	...	..	80–82°[e]	61.9[b]	62.2	6.4	6.6	12.7	13.2[f]
$C_{13}H_{17}O_2N$	7411	N,*n*-Butyl-3,6-endomethylene-1,2,3,6-tetrahydrophthalimide	AA	93	128–129	1	1.5090	71.2[b]	71.7	7.8	8.1	6.4	6.4
$C_{13}H_{17}O_2N$	7408	N-Isobutyl-3,6-endomethylene 1,2,3,6-tetrahydrophthalimide	AA	87	107–110	1	89–90°[e]	71.2[b]	71.6	7.8	7.9	6.4	6.5
$C_{13}H_{19}O_2N$	7446	N-*n*-Butyl-3-methyl-1,2,3,6-tetrahydrophthalimide	AA	87	119–121	0.5	1.4970[c]	70.6[b]	70.5	8.7	8.7	6.3	5.9
$C_{13}H_{20}O_2$	7182	3-Methyl-1-pentyn-3-yl hexahydrobenzoate	U	43	113–116	8	1.4638	75.0[b]	75.4	9.7	9.6		
$C_{13}H_{20}O_3N$	7486	*o*-Carbomethoxy N,N-diethyl 1,2,3,6-tetrahydrobenzamide	Y	70	110–112	0.1	1.4879[c]	65.2[b]	65.4	8.9	8.7	5.9	6.1
$C_{13}H_{21}O_3N$	7226	2-Ethoxylethyl cyclohexylcyanoacetate	G	49	122–124	.5	1.4611	65.2	65.3	8.9	8.8		
$C_{13}H_{24}O_3$	7442	2-Ethylhexyl β,β-dimethylglycidate	Q	46	93– 95	.5	1.4361[c]	68.4[b]	68.7	10.6	10.5		
$C_{14}H_{18}O_3$	7171	Allyl β-*p*-toluylpropionate	C	83	153	1.5	1.5250	72.4[b]	72.5	6.9	6.9		
$C_{14}H_{18}O_4$	7191	Allyl β-anisoylpropionate	C	84	...	..	51–52°[e]	67.7[b]	68.1	6.5	6.6		
$C_{14}H_{18}O_3$	7415	Propyl α-ethyl-β-phenylglycidate	Q	67	105–108	0.5	1.5087[c]	72.4[a]	72.0	6.9	7.3		
$C_{14}H_{18}O_3$	7133	Isopropyl β-methyl-β-(*p*-tolyl)glycidate	Q	47	102–104	.1	1.4986	71.8[b]	71.8	7.7	7.8		
$C_{14}H_{18}O_3$	7188	Isopropyl β-ethyl-β-phenylglycidate	Q	58	107–109	.5	1.4962	71.8[b]	71.7	7.7	7.6		
$C_{14}H_{22}O_4$	7151	1,1-Dimethylol-2,4-dimethylcyclohex-4-ene, diacetate	E	56	129–131	.5	1.4693	66.1[b]	66.5	8.7	8.9		
$C_{14}H_{23}O_4N$	7216	2-(2,4-Dimethylcyclohex-4-en-1-yl)-5-ethyl-5-nitro-*m*-dioxane	J	70	137–139	.5	1.4903	62.4[b]	62.6	8.6	8.6	5.2	5.5
$C_{14}H_{27}O_4NS$	7337	Morpholide of *n*-octyl carboxymethyl sulfone	P	50			82–84°[e]	55.1[b]	55.2	8.9	8.9	10.5	10.9
$C_{14}H_{28}O_4S$	7331	N-Decyl carboethoxymethyl sulfone	X	50	174–176	1	1.4640[c]	57.5[b]	57.2	9.7	9.9	11.0	11.4
$C_{15}H_{15}O_2N$	7190	N-Benzyl-1,2,3,6-tetrahydrophthalimide	AA	88	175–178	0.5	....	74.7[b]	75.0	6.3	6.2	5.8	5.8
$C_{15}H_{18}O_3$	7247	Propyl δ-benzallevulinate	S	16	154–160	.5	....	73.2[b]	73.0	7.4	7.1		
$C_{15}H_{18}O_3$	7132	Allyl δ-benzoylvalerate	C	95	194–195	7	1.5169	73.2[b]	73.5	7.4	7.3		
$C_{15}H_{20}O_3$	7134	Isopropyl δ-benzoylvalerate	C	72	161–162	3	33°[d]	72.6[b]	72.6	8.1	8.0		
$C_{15}H_{24}O_2$	7155	2,3-Dimethyl-1,2,3,6-tetrahydrobenzaldehyde, allyl acetal	J	45	128–132	13	1.4730	76.2[b]	76.3	10.2	9.9		
$C_{15}H_{24}O_2$	7148	3-Octyn-1-yl hexahydrobenzoate	R	49	113–116	0.5	1 .4738	76.2[b]	76.7	10.2	9.9		
$C_{15}H_{24}O_2$	7189	3,5-Dimethyl-1-hexyn-3-yl hexahydrobenzoate	U	58	88– 89	.5	1.4627	76.2[b]	76.4	10.2	10.0		
$C_{15}H_{29}ON$	7146	N,N-Diethyl undecylenamide	Z	95	127–130	1	1.4618	75.3[b]	75.3	12.2	11.9	5.9	5.9
$C_{15}H_{16}O_4$	7229	Diallyl benzalmalonate	D	87	144–147	.5	1.5489	70.6[b]	70.8	5.9	6.4		
$C_{16}H_{19}O_2N$	7240	Benzyl cyclohexylcyanoacetate	G	56	162–168	.5	1.5178	75.0[b]	74.7	7.1	7.3	5.5	5.6
$C_{16}H_{20}O_4$	7239	Di-isopropyl benzalmalonate	D	90	127–130	.5	1.5197	69.5[b]	69.6	7.3	7.2		
$C_{17}H_{20}O_6$	7181	Mono-2-benzyloxyethyl 1,2,3,6-tetrahydrophthalate	H	41	205–215	.5	1.5230	67.1[b]	66.6	6.6	6.8		
$C_{18}H_{18}O_3$	7168	Phenethyl β-methyl-β-phenylglycidate	R	58	167–172	.5	1.5621	76.6[b]	76.4	6.5	6.5		

[a] S. R. Olsen. [b] Arlington Laboratories. [c] $n^{25}D$. [d] Set point. [e] Melting point. [f] Sulfur.

The compounds described in this paper were prepared under a contract between the Office of Scientific Research and Development and The Ohio State University Research Foundation.

Methods

A. An aqueous solution of sodium valerate and an excess of ethylene chlorohydrin were refluxed in the presence of a small amount of sodium iodide for six hours.

B. The half ester of the glycol was the main reaction product when esterification was carried out as described in Method C using a large excess of glycol.

C. Esterification was accomplished by refluxing the theoretical quantities of alcohol and acid with a catalytic amount of *p*-toluenesulfonic acid in the presence of a hydrocarbon solvent of such boiling point as to permit the water formed during the reaction to be removed.

D. Benzaldehyde was condensed with diallyl and di-

isopropyl malonates in the presence of a morpholine–acetic acid catalyst in a benzene solution. The water formed during the reaction was removed by distillation from the solution.

E. A mixture of crotonaldehyde and 80% isoprene was heated to 170° in a metal bomb. The initial reaction carried the temperature to about 230°. When the temperature began to drop the bomb was cooled, opened and the product distilled under reduced pressure using a helices-packed column with a total condensation partial take-off head. 2,4-Dimethyl-1,2,3,6-tetrahydrobenzaldehyde, b. p. 70–71° (10 mm.), was formed in a 44% yield. An alcoholic solution of 2,4-dimethyl-1,2,3,6-tetrahydrobenzaldehyde and formaldehyde was refluxed four to five hours following the addition of 50% potassium hydroxide solution. 1,1-Dimethylol-2,4-dimethylcyclohexene-4, b. p. 123–124° (1 mm.), was formed in 83% yield. The diacetate of 1,1-dimethylol-2,4-dimethylcyclohexene-4 was prepared by refluxing the diol with acetic anhydride and distilling the acetic acid formed.

F. 2-Acetoxycyclohexanone, b. p. 109–115° (12 mm.), was prepared in 54% yield by refluxing 2-chlorocyclohexanone and anhydrous sodium acetate in acetic acid for eight hours. The Reformatsky reaction was carried out by adding zinc foil to a dry solution of 2-acetoxycyclohexanone and ethyl bromoacetate in benzene.

G. The ketone was refluxed with a 10% excess of the given 2-cyano ester in the presence of an ammonium acetate–acetic acid catalyst.[2] The water formed during the reaction was removed by distillation from benzene solution. The resulting cyclohexylidenecyano ester was hydrogenated in ethyl alcohol over platinum oxide at low pressure.

H. 1,2,3,6-Tetrahydrophthalic anhydride was added to sodium benzyloxyethylate in benzene and the mixture refluxed three hours. Acidification of the alkali-soluble fraction yielded the half ester.

I. Isobutyl chlorocarbonate was added to a cold ether solution of *p*-cresol in the presence of pyridine.

J. The ketone or aldehyde and alcohol were refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid and of a hydrocarbon solvent of such nature that the water could be removed by distilling the water–hydrocarbon mixture.

K. Styrene oxide and allyl alcohol were warmed together five hours in the presence of a catalytic amount of phosphoric acid.

L. 2,2-Diallylcyclohexanone was reduced by the Meerwein–Ponndorf method.

M. The sodium alcoholate was prepared by adding the given alcohol to a suspension of sodamide in ether–benzene. Allyl bromide was then added and the mixture refluxed twelve hours.

N. bis-β-Hydroxyethyl sulfide was esterified by means of acetic anhydride and then oxidized with 30% hydrogen peroxide in acetic acid–acetic anhydride at 80°. The crude oxidation mixture of di-(2-acetoxyethyl) sulfone was distilled *in vacuo* to yield the pure product.

O. A dilute alcoholic solution of sodium *p*-toluenesulfinate and 2-chlorocyclohexanone was refluxed three hours.

P. Methyl bromoacetate reacted with sodium *n*-octyl mercaptide in absolute ethyl alcohol solution to form *n*-octyl carbomethoxymethyl sulfide. The crude sulfide was oxidized readily at 80° in acetic acid–acetic anhydride solution by means of 30% hydrogen peroxide. Saponification of the *n*-octyl carbomethoxymethyl sulfone using 20% sodium hydroxide gave crude *n*-octyl carboxymethylsulfone in 46% over-all yield. The acid chloride of *n*-octyl carboxymethylsulfone was prepared in the usual manner using thionyl chloride. The acid chloride in benzene was added to a benzene solution of morpholine, thus yielding the desired morpholide.

Q. The Darzens–Claisen reaction was carried out by adding in small quantities 1.5 moles of 95% sodium methylate (Mathieson Alkali Works) to a stirred solution of one mole of ketone and 1.5 moles of chlorester in 400–500 cc. of dry ether. The temperature was maintained at 0–5° for five hours and at room temperature for fifteen hours.

R. An ester interchange was effected by refluxing a methyl or ethyl ester with an excess of a higher boiling alcohol and distilling off the methyl or ethyl alcohol formed. *p*-Toluenesulfonic acid was used as the catalyst.

S. Benzaldehyde and levulinic acid were condensed in the presence of sodium hydroxide.[3] The crude acid was esterified as described in Method C.

T. Esterification was accomplished by adding the acid chloride to an ice-cold solution of alcohol and pyridine in benzene.

U. Esterification as in Method T except that no attempt was made to keep the solution cold.

V. Propylene oxide was added to an ethereal solution of *o*-tolylmagnesium bromide. The ether was replaced with benzene and the reaction mixture refluxed overnight.

W. Isobutyrophenone and formalin were refluxed three hours in the presence of potassium hydroxide. A large amount of ketone was recovered.

X. Ethyl bromoacetate reacted with sodium *n*-decyl mercaptide in absolute alcohol to give *n*-decyl carboethoxymethyl sulfide. The crude sulfide was oxidized at 80° with 30% hydrogen peroxide in acetic acid–acetic anhydride solution.

Y. Equivalent amounts of 1,2,3,6-tetrahydrophthalic anhydride and diethylamine were allowed to react together. The crude product was taken up in benzene and converted to the acid chloride by the use of thionyl chloride. The acid chloride was esterified as described in Method T.

Z. Undecylenyl chloride was added to a large excess of diethylamine at 0°.

AA. The phthalimides were prepared by the strong heating of the properly substituted phthalic anhydride with an excess of primary amine, followed by vacuum distillation.

(2) Cope, THIS JOURNAL, **63**, 3452 (1941).

(3) Rapson and Shuttleworth, *J. Chem. Soc.*, 33 (1942).

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Alkyl Selenocyanates

The new selenocyanates listed in Table I have been prepared according to the method of Wheeler and Merriam.[1]

Procedure.—A solution of 0.25 mole of the alkyl bromide (Columbia Organic Chemicals Co., Inc.) and 0.3 mole of potassium selenocyanate (prepared from elemental selenium and potassium cyanide in water[2] or absolute alcohol,[3] the latter method being preferable for laboratory use) in 250 cc. of hot 95% ethanol was refluxed for six hours during which time crystals of potassium bromide separated. Most of the alcohol was then distilled off, water added, and the mixture extracted with ether–benzene. The solution was distilled after drying over anhydrous sodium sulfate.

The resulting selenocyanates are more toxic to fungi than the corresponding thiocyanates, but their disgusting odor forbids their use. In the case of the decyl compound this odor may be ascribable to the small quantity of volatile forerun obtained in the distillate. The yellow *n*-

TABLE I

Selenocyanates	B. p., °C.	mm.	Yield, %	Formula	% Nitrogen Calcd.	Found
n-Butyl	88–90	13	44	C_5H_9NSe	8.64	8.71
n-Hexyl	114	13	69	$C_7H_{13}NSe$	7.37	7.24
n-Decyl	97–98	0.2	67	$C_{11}H_{21}NSe$	5.69	5.44

(1) Wheeler and Merriam, THIS JOURNAL, **23**, 299 (1901).

(2) Schiellerup, *Ann.*, **109**, 125 (1859).

(3) Birckenbach and Kellermann, *Ber.*, **58**, 790 (1925).