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New Organic Compounds for Use in Insect Control

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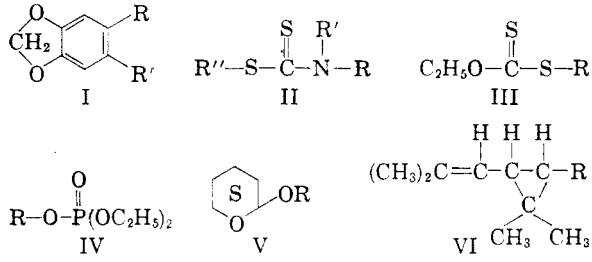
The preparation and physical constants of some new 3,4-methylenedioxyphenyl compounds, dithiocarbanilates, ethyl xanthates, diethyl phosphates, 2-substituted tetrahydropyrans, and chrysanthemumyl and chrysanthemumoyl derivatives for use in insect control are described.

In addition to the use of insecticides, other approaches that may help in the control of insect pests are explored in this Division. For example, insect attractants,[1,2] repellents,[2] and insecticide potentiating materials (synergists)[3] are being investigated. As part of these studies a variety of new compounds (sixty-six in all), including 3,4-methylenedioxyphenyl derivatives (I), dithiocarbanilates (II), ethyl xanthates (III), diethyl phosphates (IV), 2-substituted tetrahydropyrans (V), and chrysanthemumyl and chrysanthemumoyl derivatives (VI) were synthesized. Their preparation and physical constants are reported here.



Although 3,4-methylenedioxybenzyl esters (I R = H, halogen or alkyl, R′ = CH_2OCR'', with O) have been extensively investigated, compounds with α-substituted side chains (I R = halogen or alkyl, R′ = $CHR'''OCR''$, with O) have not. Two such compounds, 6-chloro-α-ethylpiperonyl chrysanthemumate and the α-methyl analog, were synthesized because of their similarity to the insecticide barthrin (6-chloropiperonyl chrysanthemumate).[4] The obvious preparative route to the intermediate α-alkyl-6-chloropiperonyl alcohol needed for the synthesis of the α-alkyl esters is *via* the reaction of 6-chloropiperonal with the appropriate Grignard reagent. This starting material, 6-chloropiperonal, was prepared initially by treating piperonal with chlorine gas,[5] but instead of the reported yield of 60%, less than 35% of the pure product was obtained consistently. In a simpler procedure the 6-chloropiperonal was obtained in 50% yield by allowing a mixture of piperonal, benzoyl peroxide, glacial acetic acid, and sulfuryl chloride to stand at room temperature for ten days.

For small-scale preparations of the α-alkyl-6-halopiperonyl alcohol intermediates, the appropriate Grignard reagent was added to a suspension of 6-chloropiperonal in a large volume of ether. Attempts to prepare the pure intermediate alcohols on a large scale by this procedure were unsuccessful because of the insolubility of 6-chloropiperonal in ether.

The chlorination of 3,4-methylenedioxyphenyl acetate (sesamyl acetate) with sulfuryl chloride proceeded in good yield without the benzoyl peroxide catalyst. This result was not anticipated, since it is reported that phenyl acetate does not react with sulfuryl chloride under mild conditions in the absence of catalyst.[6]

The investigation resulted also in a synthesis in pure form and in reasonable yield of new compounds of the type I in which R = halogen and R′ = OC_2H_4R''. In the sequence of reactions hydroxyethylation of sesamol[3,7] with ethylene carbonate was followed by acetylation of the free hydroxyl group, chlorination with sulfuryl chloride, and finally deacetylation which produced I (R = Cl, R′ = OC_2H_4OH) in good yield. Treatment of the alcohol with phosphorus tribromide gave β-bromo-2-chloro-4,5-methylenedioxyphenetole (Table I, No. 13) in 83% yield. Of interest was the finding that sesamol and 6-chlorosesamol were

(1) S. I. Gertler, L. F. Steiner, W. C. Mitchell, and W. F. Barthel, *J. Agr. Food Chem.*, **6**, 592 (1958).

(2) S. A. Hall, N. Green, and M. Beroza, *J. Agr. Food Chem.*, **5**, 663 (1957).

(3) M. Beroza and W. F. Barthel, *J. Agr. Food Chem.*, **5**, 855 (1957); M. Beroza, *J. Agr. Food Chem.*, **4**, 49 (1956).

(4) W. F. Barthel, B. H. Alexander, J. B. Gahan, and P. G. Piquett, U. S. Patent **2,886,485**, May 12, 1959; W. F. Barthel and B. H. Alexander, *J. Org. Chem.*, **23**, 1012 (1958); W. A. Gersdorff and P. G. Piquett, *J. Econ. Entomol.*, **52**, 85 (1959).

(5) A. Parys, *Rec. Trav. Chim.*, **49**, 17 (1930).

(6) A. Peratoner, *Gazz. Chim. Ital.*, **28**, I, 197 (1898); H. C. Brown, *Ind. Eng. Chem.*, **36**, 785 (1944).

(7) J. Boeseken, W. D. Cohen, C. J. Kip, *Rec. Trav. Chim.*, **55**, 815 (1936); B. H. Alexander, T. A. Oda, R. T. Brown, and S. I. Gertler, *J. Org. Chem.*, **23**, 1969 (1958); S. I. Gertler, B. H. Alexander, and M. Beroza, *J. Org. Chem.*, **24**, 327 (1959); B. H. Alexander, S. I. Gertler, R. T. Brown, T. A. Oda, and M. Beroza, *J. Org. Chem.*, **24**, 1504 (1959).

readily hydroxyethylated with ethylene carbonate, whereas attempts to hydroxyethylate 2-(2-methylallyl)-4,5-methylenedioxyphenol or the methyl ester of 3-hydroxy-2-naphthoic acid in the same manner were unsuccessful. Molecular models indicated that steric hindrance might be responsible for the lack of reactivity.

The methyl carbanilates (Table IV, Nos. 65 and 66) were made by the procedure of Losanitsch[8] from the intermediate ammonium butyldithiocarbanilate and ammonium *p*-chlorodithiocarbanilate, which are yellow to off-white solids. The ammonium salts are new compounds similar to those described by Miller,[9] which are unstable at room temperature and decompose, liberating ammonium thiocyanate, hydrogen sulfide, and free sulfur; consequently no attempt was made to analyze them for the elements. However, the esters prepared from the salts are stable and gave good elemental analyses.

Kenner and Williams[10] describe the synthesis of diethyl phosphates from phenols and diethyl phosphite. We have found their procedure applicable to other hydroxy compounds.

The preparation of other compounds is described in the experimental section and the physical constants are given in the Tables.

The yields obtained in this study can probably be improved since purity of compounds rather than yield was emphasized.

EXPERIMENTAL

3,4-Methylenedioxyphenyl compounds (Table I). All compounds except Numbers 3–7, 12, 13, and 15 were prepared by the general procedures reported previously from this laboratory.[4,7]

2-(3,4-Methylenedioxyphenoxy)ethanol (No. 3). This compound was prepared from sesamol[7] and ethylene carbonate by the procedure of Carlson and Cretcher.[11]

2-(3,4-Methylenedioxyphenoxy)ethyl acetate (No. 4). Acetyl chloride (0.61 mole) was added dropwise to a stirred solution of 2-(3,4-methylenedioxyphenoxy)ethanol (0.61 mole), pyridine (0.61 mole) and benzene (500 ml.) at 25°. After standing overnight at room temperature, the mixture was transferred to a separatory funnel, where it was washed successively with water, 5% aqueous hydrochloric acid, water, saturated sodium bicarbonate, and saturated sodium chloride. The benzene layer was dried, and after removal of the benzene the residue was distilled. The first fraction boiled at 163–168°/23 mm. and was obtained in 33% yield; n_D^{25} 1.5269. The second fraction, which contained the desired product (No. 4) boiled at 122–135°/1 mm. and solidified in the receiving flask. The solid melted at 56–58° after recrystallization from aqueous ethanol. A mixed melting point with the starting material, 2-(3,4-methylenedioxyphenoxy)ethanol, which melted at 57–58°, was depressed to 38–48°.

The aforementioned first fraction was identified as sesamyl acetate by comparing it with the sesamyl acetate previously reported by Beroza;[3] its isolation from the reaction mixture in 33% yield indicates that 2-(3,4-methylenedioxyphenoxy)-ethanol was partly cleaved, probably because of the hydrogen chloride liberated during the formation of the ester from the acid chloride.

2-(2-Chloro-4,5-methylenedioxyphenoxy)ethyl acetate (No. 15). Sulfuryl chloride (0.5 mole) was added dropwise to a stirred solution of 2-(3,4-methylenedioxyphenoxy)ethyl acetate (0.4 mole) in glacial acetic acid (200 ml.) while maintaining a temperature below 50°. After addition of the sulfuryl chloride, the mixture was stirred at room temperature for 0.5 hr., then poured into ice and water with stirring. Crystallization occurred on standing. The crystals were filtered off, washed with water, dried, and recrystallized from ethanol.

β-Bromo-2-chloro-4,5-methylenedioxyphenetole (No. 13). A mixture of 2-(2-chloro-4,5-methylenedioxyphenoxy)ethyl acetate (0.2 mole) and 2*N* sodium methylate (110 ml.) was allowed to stand at 25° overnight, and then poured into ice and water with stirring, whereupon crystallization occurred. The crystals were washed with water, dried, and recrystallized from ethanol, giving practically pure 2-(2-chloro-4,5-methylenedioxyphenoxy)ethanol, which melted at 82–83°. Treatment of this compound (0.6 mole) with phosphorus tribromide (0.19 mole)[12] at 75–80°, with stirring for 2 hr. produced a residue which when poured into ice and water gave the crystalline β-bromo-2-chloro-4,5-methylenedioxyphenetole.

2-Bromo-4,5-methylenedioxy-α-toluenethiol (No. 6). 6-Bromopiperonyl bromide[4] was treated with thiourea according to the procedures described by Urquhart and co-workers.[13]

6-Bromopiperonyl thioacetate (No. 7). Prepared from 2-bromo-4,5-methylenedioxy-α-toluenethiol, benzene, acetyl chloride, and pyridine in the usual way.

2-Chloro-4,5-methylenedioxyphenyl acetate (No. 12). Sulfuryl chloride (0.26 mole) was added dropwise to a stirred solution of sesamyl acetate[3] (0.25 mole) and glacial acetic acid (90 ml.) at 25°. The solution turned blue initially, but later became yellow as the temperature rose to 40°. After stirring for 0.25 hr. at 35–40° to remove sulfur dioxide and hydrogen chloride, the solution was poured into ice and water, where precipitation of the crystalline product occurred.

6-Chloropiperonal. A solution of piperonal (0.25 mole), glacial acetic acid (200 ml.), benzoyl peroxide (10 g.), and sulfuryl chloride (0.75 mole) was allowed to stand at room temperature for 10 days. It was then poured into a well stirred ice and water mixture, where crystallization occurred. The crystals, after being washed with cold water and dried, were recrystallized from aqueous ethanol and obtained in 50% yield; a mixed melting point with an authentic sample melting at 114–115° was not depressed.[14]

Ethers of tetrahydropyran (Table II). The ethers were prepared in diethyl ether from the alcohol, 2,3-dihydropyran, and a catalytic amount of concentrated hydrochloric acid, according to procedure described by Ott.[15]

Xanthates (Table II). The compounds were made in the usual way from the alkyl or aryl halide, potassium xanthogenate, and ethanol.[16]

Diethyl phosphates (Table II). The phosphates were made from the phenol or alcohol and diethyl hydrogen phosphite, according to a minor modification of the procedure of Kenner and Williams.[10] It seemed preferable to stir rather than

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(9) L. P. Miller, *Contrib, Boyce Thompson Inst.*, **5**, 31 (1933).

(10) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).

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(14) K. Weisze, *Ber.*, **43**, 2605 (1910).

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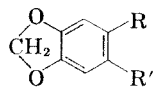
TABLE I

3,4-Methylenedioxyphenyl Compounds



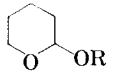
No.	R	R′	Yield, %	B.P., °C./Mm.	n_D^{25} or M.P.	Molecular Formula	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1	H	$-O_2C-(CH_2)_6CH_3$	75	156–160/0.7	1.4967	$C_{15}H_{20}O_4$	68.16	68.89	7.63	7.77
2	H	$-O_2C-CH_2C_6H_5$	78	152–162/0.15	1.5712	$C_{15}H_{12}O_4$	70.30	70.08	4.72	4.66
3	H	$-OC_2H_4OH$	59	—	57–58 (toluene)	$C_9H_{10}O_4$	59.33	59.82	5.53	5.23
4	H	$-OC_2H_4O_2C-CH_3$	38[a]	—	56–58 (alcohol and water)	$C_{11}H_{12}O_5$	58.92	58.82	5.40	5.64
5	H	$-O_2C-CH_3$	33[a]	163/24	—	$C_9H_8O_4$	60.00	59.79	4.47	4.48
6	Br	$-CH_2SH$	99	112–128/0.2	70–71[b] (alcohol)	$C_8H_7BrO_2S$	38.88	37.81	2.86	3.14
7	Br	$-CH_2S(=O)-CH_3$	47	—	108–109 (benzene and petroleum ether)	$C_{10}H_9BrO_3S$	41.54	41.42	3.11	3.15
8	Br	$-CH_2OCH_2-CH(C(CH_3)_2)-CH=CH-CH=C(CH_3)_2$	55	165–173/0.5	1.5410	$C_{18}H_{23}BrO_3$	58.86	59.16	6.31	6.50
9	Br	$-CH_2OC_2H_4OC_4H_9$	61	148–157/0.5	1.5260	$C_{14}H_{19}BrO_4$	50.77	51.00	5.78	5.73
10	Br	$-CH_2OCH(CH_3)CH_2OCH_3$	52	124–131/0.3	1.5410	$C_{12}H_{15}BrO_4$	47.54	47.42	4.99	4.89
11	Br	$-CH_2OC_2H_4OC_2H_4OC_4H_9$	59	161–173/0.2	1.5221	$C_{16}H_{23}BrO_5$	51.27	51.08	6.18	6.32
12	Cl	$-O_2C-CH_3$	64	—	86–87 (alcohol)	$C_9H_7ClO_4$	50.37	50.52	3.29	3.49
13	Cl	$-OC_2H_4Br$	83	—	73–74 (propanol)	$C_9H_8BrClO_3$	38.67	38.49	2.88	2.80
14	Cl	$-OC_2H_4OC(=O)-CH(C(CH_3)_2)-CH=CH-C(CH_3)=CH_2$	58	197–198/1.0	1.5335	$C_{19}H_{23}ClO_5$	62.21	62.23	6.32	6.12
15	Cl	$-OC_2H_4OC(=O)-CH_3$	77	—	64–65 (alcohol)	$C_{11}H_{11}ClO_5$	51.07	50.73	4.29	4.24
16	Cl	$-CH(C_2H_5)OC(=O)-CH(C(CH_3)_2)-CH=CH-C(CH_3)=CH_2$	73[c]	160–177/0.3	1.5281	$C_{20}H_{25}ClO_4$	65.83	65.93	6.91	6.99
17	Cl	$-CH_2OC_2H_4OCH_3$	65	172–189/26	1.5307	$C_{11}H_{13}ClO_4$	54.00	53.76	5.35	5.46
18	Cl	$-CH_2OCH_2-CH(C(CH_3)_2)-CH=CH-C(CH_3)=CH_2$	50	146–149/0.2	1.5296	$C_{18}H_{23}ClO_3$	66.97	66.78	7.18	7.36

TABLE I *Continued*

No.	R	R′	Yield, %	B.P., °C./Mm.	n_D^{25} or M.P.	Molecular Formula	Analyses			
							Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
19	Cl	—CO_2CH_2CH(C(CH_3)$_2$)—CH—CH=C(CH_3)—CH_3	33	—	70–71 (alcohol)	$C_{18}H_{21}ClO_4$	64.18	64.37	6.28	6.26
20	Br	—CH(O—)—OCH_2CH_2—	83	—	72–73 (alcohol)	$C_{10}H_9BrO_4$	43.97	43.94	3.30	3.42
21	Br	—CH(O—)—$OCH(CH_3)CH_2$—	87	130–131/0.3	1.5638	$C_{11}H_{11}BrO_4$	45.99	46.56	3.83	3.99
22	Br	—CH(O—)—$OCH(CH_3)CH_2CH_2$—	47	—	112–113 (alcohol)	$C_{12}H_{13}BrO_4$	47.85	48.14	4.32	4.56
23	Br	—CH(O—$CH_2CH(C_2H_5)$—)—$OCH(C_3H_7)$—	48	—	67–68 (alcohol)	$C_{16}H_{21}BrO_4$	53.79	54.52	5.88	6.03
24	Br	—CH(O—)—$OCH_2C(CH_3)_2CH_2$—	96	—	114–115 (alcohol)	$C_{13}H_{15}BrO_4$	49.53	49.07	4.76	4.69
25	Br	—CH(O—)—$OC_2H_4CH_2$—	84	—	93–95 (alcohol)	$C_{11}H_{11}BrO_4$	46.01	45.85	3.76	3.71
26	Cl	—CH(O—)—$OCH(CH_3)CH_2$—	85	111–112/0.1	1.5442	$C_{11}H_{11}ClO_4$	54.43	54.61	4.53	4.73
27	Cl	—CH(O—)—$OCH(CH_3)CH_2CH_2$—	79	—	115–116 (alcohol)	$C_{12}H_{13}ClO_4$	56.14	55.82	5.07	5.21

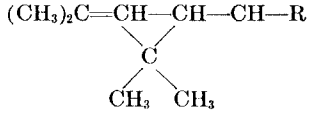
[a] See preparation of this compound in Experimental section. [b] This product contains an impurity that we could not remove. [c] The α-methyl analog was also prepared, but we were unable to purify the product; the boiling range was 168–183°/0.8 mm., $n_D^{25°}$ 1.5304.

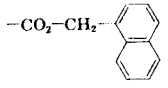
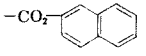
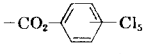
TABLE II

XANTHATES ($C_2H_5OC(=S)—SR$), DIETHYL PHOSPHATES ($R—OP(=O)—(OC_2H_5)_2$), AND TETRAHYDROPYRAN DERIVATIVES 

No.	R	Yield, %	B.P./Mm.	n_D^{25}	Molecular Formula	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Other Calcd.	Other Found
				Xanthates							
28	i-C_3H_7	77	86–90/14	1.5231	$C_6H_{12}OS_2$	43.86	44.16	7.37	7.18	—	—
29	—$CH_2C{\equiv}CH$	44	112–119/15	1.5409	$C_6H_8OS_2$	44.97	44.87	5.03	5.56	—	—
30	—CH(—CH_2—CH_2)—CH_2—CH_2	76	123–136/17	1.5497	$C_8H_{14}OS_2$	50.48	50.52	7.41	7.36	—	—
31	—$C_2H_4C_6H_5$	77	116–117/0.6	1.5869	$C_{11}H_{14}OS_2$	58.37	58.73	6.23	6.42	—	
				Diethyl phosphates							
32	3,4-CH_2O_2—C_6H_3—	70	133–142/0.15	1.4926	$C_{11}H_{15}O_6P$	—	—	—	—	(P) 11.30	11.52
33	2-Br-4,5-CH_2O_2—C_6H_2—	58	170–172/0.5	1.5228	$C_{11}H_{14}BrO_6P$	—	—	—	—	(Br) 22.63	22.61
34	3-CH_3—C_6H_4—CH_2—	37	123–125/0.4	1.4816	$C_{12}H_{19}O_4P$	55.81	55.38	7.42	7.36	—	—
35	3,4-$(CH_3)_2$—C_6H_3—CH_2—	41	133–135/0.4	1.4865	$C_{13}H_{21}O_4P$	57.34	56.42	7.78	7.50	—	—
36	2,4-$(CH_3)_2$—C_6H_3—CH_2—	30	128–130/0.3	1.4849	$C_{13}H_{21}O_4P$	57.34	56.57	7.78	7.52	—	—
37	—$CH_2C{\equiv}CH$	55	136–141/25	1.4274	$C_7H_{13}O_4P$	43.75	43.44	6.82	6.71	—	—
38	—$CH_2C(CH_3){=}CH_2$	51	127–133/21	1.4239	$C_8H_{17}O_4P$	46.15	46.28	8.23	8.53	—	—
				Tetrahydropyrans							
39	—$C_2H_4OC_2H_4OC_4H_9$	71	162–176/18	1.4447	$C_{13}H_{26}O_4$	63.38	63.35	10.64	10.56	—	—
40	—CH_2—CH—CH—CH—C(—CH_3)(—CH_3)—CH_3	62	140–147/17	1.4719	$C_{15}H_{26}O_2$	75.58	75.45	11.00	10.94	—	—
41	—CH_2—C_6H_2—2Br—4,5-CH_2O_2	48	147–149/0.2	1.5565	$C_{13}H_{15}BrO_4$	49.54	48.65	4.80	4.73	—	—
42	—$C_2H_4OC_2H_4OCH_3$	48	131–146/20	1.4458	$C_{10}H_{20}O_4$	58.80	59.06	9.87	9.82	—	—

TABLE III. CHRYSANTHEMUMYL AND CHRYSANTHEMUMOYL DERIVATIVES



No.	R	Yield, %	B.P./Mm.	$n_D^{25°}$	Molecular Formula	Analyses			
						Carbon		Hydrogen	
						Calcd.	Found	Calcd.	Found
43	$-CH_2OH$	92	107–108/14	1.4707	$C_{10}H_{18}O$[a]	77.92	76.92	11.76	11.74
44	$-CH_2O_2C-CH_3$	81	112–113/14	1.4557	$C_{12}H_{20}O_2$	73.47	73.55	10.20	10.18
45	$-CH_2O_2C-C_2H_5$	62	121–122/13	1.4548	$C_{13}H_{22}O_2$	74.29	74.49	10.48	10.62
46	$-CH_2O_2C-C_6H_4o-CH_3$	87	123–124/0.3	1.5152	$C_{18}H_{24}O_2$	79.41	79.14	8.82	8.55
47	$-CH_2O_2C-C_6H_4p-OCH_3$	83	146–148/0.3	1.5253	$C_{18}H_{24}O_3$	75.00	74.85	8.33	8.34
48	$-CO_2CH_2CH=CH_2$	94	119–120/12	1.4693	$C_{13}H_{20}O_2$	74.95	74.55	9.67	9.45
49	$-CO_2CH_2CH(CH_3)_2$	91	124–125/12	1.4569	$C_{14}H_{24}O_2$	74.75	74.24	10.78	10.94
50	$-CO_2CH(CH_3)C_2H_5$	89	121–122/12	1.4554	$C_{14}H_{24}O_2$	74.75	74.48	10.78	10.70
51	$-CO_2C_2H_4Br$	80	87–88/0.3	1.4908	$C_{12}H_{19}BrO_2$[b]	52.37	53.46	6.95	7.12
52	$-CO_2CH(CH_3)_2$	84	110–111/12	1.4538	$C_{13}H_{22}O_2$	74.23	73.56	10.54	10.25
53	$-CO_2C_4H_9$	89	132/12	1.4594	$C_{14}H_{24}O_2$	74.75	74.85	10.78	11.02
54		38	167–170/0.2	1.5694	$C_{21}H_{24}O_2$	81.78	81.52	7.84	7.54
55		53		82–83 (alcohol)	$C_{20}H_{22}O_2$[c]	81.60	81.22	7.53	7.37
56		53	169–171/0.2	1.5600	$C_{16}H_{15}Cl_5O_2$	46.13	45.89	3.63	3.64
57	$-CO_2C_2H_4SC_2H_5$	76	110–127/0.8	1.4890	$C_{14}H_{24}O_2S$[a]	65.58	65.71	9.43	9.29

[a] Crude product prepared earlier by W. F. Barthel (unpublished data). [b] Slowly decomposes on standing. [c] Crude product prepared earlier by N. Mitlin, N. Green, W. A. Gersdorff, and M. S. Schechter, U. S. Dept. Agr., **ARA E-865**, 5 pp. (1953).

TABLE IV. OTHER COMPOUNDS

No.	Name	Yield, %	B.P./Mm.	n_D^{25} or M.P.	Molecular Formula	Analyses					
						Carbon		Hydrogen		Nitrogen	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
58	Isopentyl 1-naphthoate	72	148–151/0.4	1.5638	$C_{16}H_{18}O_2$	79.31	79.50	7.49	7.25	—	—
59	*N*-(*p*-Phenylazophenyl)-1-naphthamide	53	—	212–214 (alcohol)	$C_{23}H_{17}N_3O$	—	—	—	—	11.96	12.04
60	*N*,*N*-Dipropyl-1-naphthamide	78	146–149/0.2	1.5745	$C_{17}H_{21}NO$	79.96	80.34	8.29	8.17	—	—
61	*N*,*N*-Diethyl-1-naphthamide	77	145–148/0.3	1.5910	$C_{15}H_{17}NO$	79.28	79.06	7.52	7.33	—	—
62	*N*-(1-Naphthoyl)piperidine	47	160–185/0.3	97° (alcohol)	$C_{16}H_{17}NO$	—	—	—	—	5.85	5.99
63	α-Ethylbenzyl trichloroacetate	66	80–84/0.2	1.5134	$C_{11}H_{11}Cl_3O_2$	46.92	47.45	3.94	4.32	—	—
64	2-(Ethylthio)ethyl butyrate	80	106–110/12	1.4543	$C_8H_{16}O_2S$	54.50	55.15	9.15	8.95	—	—
65	Methyl butyldithiocarbanilate	30	—	68–70 (alcohol)	$C_{12}H_{17}NS_2$	—	—	—	—	5.85	5.68
66	Methyl *p*-chlorodithiocarbanilate	46	—	108–110 (methanol)	$C_8H_8ClNS_2$	—	—	—	—	6.43	6.47

shake the reaction mixture, and also to wash any aliphatic organic layers containing the crude unsaturated phosphate esters with a saturated salt solution rather than with dilute hydrochloric acid.

Chrysanthemumyl and chrysanthemumoyl derivatives (Table III). The chrysanthemumyl derivatives were made from chrysanthemumyl alcohol, prepared by reducing synthetic ethyl chrysanthemumate with lithium aluminum hydride in the usual way. The double bond was not affected by this reduction. The esters of the alcohol were made *via* the acid chloride route with pyridine as an acid acceptor. Similarly the esters of synthetic chrysanthemumic acid were made from chrysanthemumoyl chloride.[17]

Preparation of other compounds (Table IV). The esters and amides were obtained in the usual manner from a mixture of the alcohol, phenol, or amine with the proper acid chloride, pyridine, and benzene. The methyl and ammonium dithiocarbanilates were made by the general procedure of Miller[9] and Losanitsch.[8]

BELTSVILLE, MD.

(17) Y. L. Chen and W. F. Barthel, *J. Am. Chem. Soc.*, **75**, 4287 (1953).