cal amount of water as could be obtained was collected in a Dean-Stark trap. The solvent was removed using a Buchler flash evaporator, and the product was recrystallized once from benzene. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer in a potassium bromide matrix. Typical characteristic absorption bands for all compounds were observed, for example: C=N, 1595 to 1630 cm.$^{-1}$ region; phenyl, 1484 to 1600, 800 to 880 cm.$^{-1}$ para substitution, 690 to 780 cm.$^{-1}$ meta substitution; C≡N, 2220 to 2222 cm.$^{-1}$; thiophene, 3067 cm.$^{-1}$; substituted furan, 1130, 1070, 1020, 930 cm.$^{-1}$; NO_2, 1325 and 1587 cm.$^{-1}$; C=O, 1567 to 1615 cm.$^{-1}$; C—O, 1362 to 1290 cm.$^{-1}$ Melting points were taken on a Hershberg melting point apparatus and are uncorrected.

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Some New Carbamates and Carbanilates

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The physical constants and elemental analyses are given for 18 carbamates and 15 carbanilates tested as synergists for three insecticides against resistant houseflies, *Musca domestica* L. Most of these compounds have not been reported previously. However, discrepancies in the physical constants of four compounds reported previously are noted.

EXTENSIVE investigation has been conducted on the chemistry, biology, and more recently, on the synergism of carbamates and carbanilates (*1-3,5,8,9,12,15,16,18*).

A study was undertaken (*13*) to evaluate noninsecticidal carbamates and carbanilates as synergists for strains of houseflies resistant to the following insecticides: Isolan (1-isopropyl-3-methylpyrazol-5-yl dimethylcarbamate), carbaryl (1-naphthyl methylcarbamate), and malathion {*S*-[1,2-bis(ethoxycarbonyl)ethyl] *O,O*-dimethyl phosphorodithioate}.

This report gives the physical constants and elemental analyses of 17 new carbamates and 12 new carbanilates made for the above study (*13*) (Table I). The physical constants for one carbamate and three carbanilates which do not agree with those reported are also included.

A typical preparation was performed as follows: Fifteen milliliters (15.4 grams, 0.114 mole) of *n*-butylchloroformate (Eastman, white label) were added to a mixture of 20 grams (0.118 mole) of diphenylamine, 100 ml. of anhydrous benzene, and 10 grams (0.094 mole) of anhydrous sodium carbonate with swirling and cooling (ice-water bath) (*4,10,11*). The reaction mixture was kept in the ice-water bath for a few hours with occasional swirling and then allowed to warm to room temperature, usually overnight. Two hundred and fifty milliliters of water were added to the mixture, and it was shaken until the sodium carbonate dissolved. The two layers were separated. The organic layer was extracted with 100 ml. of 5% aqueous hydrochloric acid and then with 100 ml. of water. After it was dried over anhydrous magnesium sulfate and filtered, the solvent was removed on a rotary evaporator. The residue crystallized at room temperature. The crude carbamate was recrystallized from 95% ethanol. Physical data of this compound (No. 16) are given in Table I.

Compounds 10 through 18 and 29 through 33 were synthesized from the appropriate diamine and chloroformate (all are commercially available) by following the general procedure described, except that the crude products were purified by either distillation or recrystallization.

The remaining esters were made from the appropriate isocyanate and alcohol, mercaptan, phenol, or thiophenol, by using standard procedures (*10,14*).

Whitehead and Traverso (*17*) supposedly obtained butyl *N,N*-diphenylcarbamate (compound 16) by alcoholysis (butanol) of 1,1,3-triphenylurea. They reported a boiling point of 158° C. at 8 mm. and a melting point of 61.5–62° C. for this carbamate. They incorrectly calculated 7.30% for nitrogen in this compound, $C_{17}H_{19}NO_2$, and found 7.32%. The correct value is 5.20.

The possible products from the butanolysis of 1,1,3-triphenylurea may be a mixture of butyl *N,N*-diphenylcarbamate and aniline and/or butyl carbanilate and diphenylamine. The melting point of butyl carbanilate prepared in the authors' laboratory was 61-63° C. [lit. 61° C., (*6*)]. The theoretical content of nitrogen in this compound, $C_{11}H_{15}NO_2$, is 7.25%.

In the authors' hands, alcoholysis of 1,1,3-triphenylurea with *n*-butyl alcohol following the general procedure of Whitehead and Traverso (*17*), gave a crude product with a melting point of 35° to 50° C. after recrystallization from petroleum ether. A portion of this crude product was dissolved in ether and extracted with concentrated hydrochloric acid. The ether solution was washed well with water, dried ($MgSO_4$), and filtered; removal of the solvent gave a crude product melting at about 33° to 40° C. This material was recrystallized from petroleum ether to give a crystalline solid, m.p. 62.5–63° C. The melting point of this material on admixture with butyl carbanilate was 62–63° C. The infrared spectrum of the crystalline solid was identical with that of butyl carbanilate.

Table I. Data on Carbamates

No.	Compound	B.P., °C. (Mm.)[a]	n_D^{25} or M.P., °C.[b]	Molecular Formula
	Esters of Substituted Carbamic Acids			
1	Methyl-, propyl	84.5–85(14)	1.4234	$C_5H_{11}NO_2$
2	Propyl-, propyl	103(13)	1.4292	$C_7H_{15}NO_2$
3	Propyl-, butyl	115.5–115.8(14)	1.4327	$C_8H_{17}NO_2$
4	Propylthio-, *S*-phenyl		75.5–77	$C_{10}H_{13}NOS$
5	Isopropyl-, butyl[d]	106–106.8(14)	1.4300	$C_8H_{17}NO_2$
6	Isopropylthio-, *S*-phenyl		98–102	$C_{10}H_{13}NOS$
7	Pentylthio-, *S*-butyl[d]	172–175(16)	1.4822	$C_{10}H_{21}NOS$
8	Pentylthio-, *S*-phenyl[d, e]		35–37	$C_{12}H_{17}NOS$
9	Cyclohexyl-, butyl[d]		53–54	$C_{11}H_{21}NO_2$
10	Diisobutyl-, phenyl[d]	94–102(0.05)	1.4899	$C_{15}H_{23}NO_2$
11	Diisobutylthio-, *S*-phenyl[d, e]	127–129(0.11)	1.5318	$C_{15}H_{23}NOS$
12	Di-*sec*-butyl-, phenyl[d, e]	112.5–114.5(0.13)	1.4988	$C_{15}H_{23}NO_2$
13	Di-*sec*-butylthio-, *S*-phenyl[d]	133–135(0.12)	1.5405	$C_{15}H_{23}NOS$
14	*N,N*-(2,5-ethanohexamethylene)-, phenyl[d, e, f]		72.5–74	$C_{15}H_{19}NO_2$
15	Diphenyl-, 3-chloropropyl[d]		57–59	$C_{10}H_{16}ClNO_2$
16	Diphenyl-, butyl[d, e]		55.5–56.5[g]	$C_{17}H_{19}NO_2$
17	Diphenyl-, pentyl[d]		45–46	$C_{18}H_{21}NO_2$
18	Diphenyl-, *p*-nitrobenzyl[d]		141.5–143.5	$C_{20}H_{16}N_2O_4$
	Esters of Substituted Carbanilic Acids			
19	2-(1-aziridinyl) ethyl[d, e]		92–94.5	$C_{11}H_{14}N_2O_2$
20	*m*-Chlorophenyl		124–125	$C_{13}H_{10}ClNO_2$
21	2-Chloro-4-*tert*-butylphenyl		126–132	$C_{17}H_{18}ClNO_2$
22	*o*-Tolyl[d]		132–134[h]	$C_{14}H_{13}NO_2$
23	2,6-Xylyl[d]		148–150.5[i]	$C_{15}H_{15}NO_2$
24	2,5-Dichlorothio-, *S*-isopropyl[d, e]		79–82.5[j]	$C_{10}H_{11}Cl_2NOS$
25	2,5-Dichloro-butyl[d]	122–126(0.06)	1.5400	$C_{11}H_{13}Cl_2NO_2$
26	*o*-Methylthio-, *S*-phenyl		136–138	$C_{14}H_{13}NOS$
27	*m*-Methylthio-, *S*-phenyl		80–82	$C_{14}H_{13}NOS$
28	*p*-Methylthio-, *S*-phenyl		122–125	$C_{14}H_{13}NOS$
29	*N*-Ethyl-, phenyl[d]	135–140(0.13)	1.5620	$C_{15}H_{15}NO_2$
30	*N*-Propyl-, phenyl[d]	142–147(0.095)	1.5556	$C_{16}H_{17}NO_2$
31	*N*-Isopropyl-, phenyl[d]		98.5–101	$C_{16}H_{17}NO_2$
32	*N*-Butyl-, phenyl[d]	147–152.5(0.12)	1.5486	$C_{17}H_{19}NO_2$
33	*N*-Isopentyl-, phenyl[d]	156–159(0.18)	1.5415	$C_{18}H_{21}NO_2$

[a] Boiling points uncorrected. [b] Melting points taken on a Thomas-Hoover capillary melting point apparatus and are corrected. [c] Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Spectral data have been deposited with ADI. [d] Infrared spectrum is compatible with the assigned structure. [e] Nuclear magnetic resonance spectrum is compatible with

and Carbanilates

Elemental Analysis[c]							
C		H		N		S	
Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
				11.96	11.85		
				9.65	9.65		
				8.80	8.72		
				7.18	7.21		
				8.80	9.51		
				7.18	7.20		
59.06	58.93	10.41	10.47	6.89	7.09	15.77	15.74
64.53	64.75	7.67	7.56	6.27	6.24	14.36	14.13
				7.03	7.34		
72.25	72.69	9.30	9.48	5.62	5.89		
67.88	67.90	8.74	8.76	5.28	5.54	12.08	12.15
72.25	72.28	9.30	8.94	5.62	5.44		
67.88	67.78	8.74	8.65	5.28	5.40	12.08	12.15
73.44	73.39	7.81	7.70	5.71	5.93		
				4.83	4.84		
75.81	75.93	7.11	7.18	5.20	5.23		
				4.94	4.89		
				8.04	7.90		
64.06	64.26	6.84	6.80	13.58	13.83		
				5.66	5.68		
				4.61	4.94		
73.99	74.32	5.77	6.15	6.16	6.02		
74.66	74.45	6.27	6.07	5.81	6.10		
45.46	45.91	4.20	4.17	5.30	5.74		
				5.34	5.42		
				5.76	5.71		
				5.76	5.79		
				5.76	5.76		
				5.81	5.91		
				5.49	5.64		
				5.49	5.46		
				5.20	5.16		
				4.94	4.69		

the assigned structure. [f] Phenyl ester of 3-azabicyclo[3.2.2]nonane-3-carboxylic acid. [g] M.p., 61.5–62° C. (*17*), see text. [h] M.p., 141° C., 143° C. (*6*). [i] M.p., 133° C. (*6*). [j] M.p., 88–88.5° C. (*7*).

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