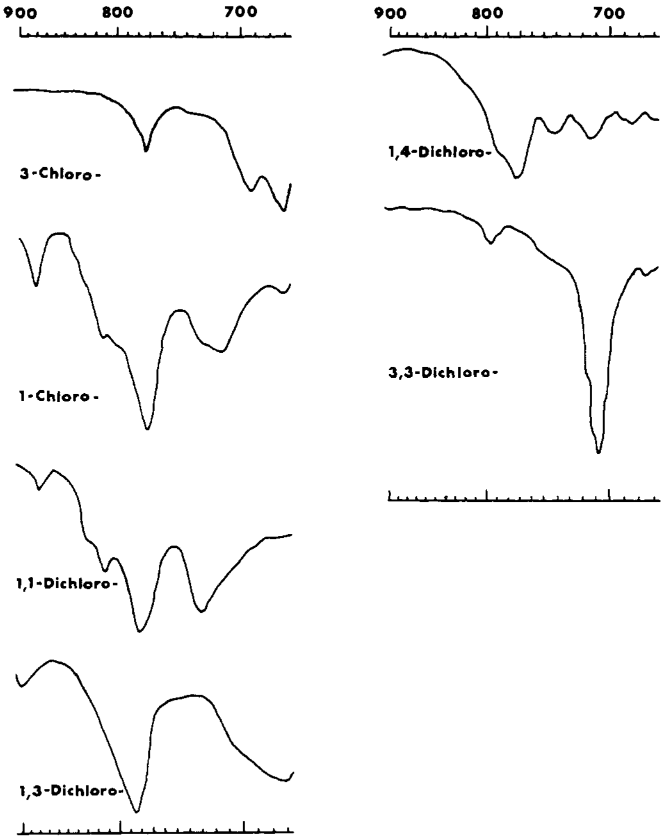

Figure 1. Infrared spectra (liquid film) of mono- and dichlorobutanones
Perkin-Elmer Model 137 spectrophotometer

EXPERIMENTAL

Chlorinations were carried out by the methods and variations listed below. In working up the reaction products, the water-insoluble part was washed with water and sodium carbonate solution until neutral to Congo red, dried (MgSO$_4$), and distilled once at atmospheric pressure without fractionation. The mono- and dichlorobutanones were separated by vapor-phase chromatography using an F. and M. Model 500 programmed temperature gas chromatograph and a 6-foot Carbowax column, temperature-programmed when advantageous. The yield of each product was estimated by measuring the area under the VPC signal.

Chlorinations in Aqueous Solution. The method of Kling (*9*) was used with the following variations: (A) The reaction temperature was not allowed to exceed 40° C., and (B) the maximum reaction temperature was 60° C.

Chlorinations with Sulfuryl Chloride. These were based on earlier methods employed for the chlorination of 2-pentanone (*1, 3, 14*). The following variations were introduced: (C) sulfuryl chloride (2 equiv.) added to butanone (1 equiv.) at 0° to 5° C.; (D) sulfuryl chloride (1 equiv.) added to butanone (10 equiv.) at reflux temperature; (E) sulfuryl chloride (1 equiv.) added to butanone (1 equiv.) in *n*-pentane solvent (5 volume dilution) at 25° C.; (F) as for E, but at 0° C. For our purposes, method D or F was convenient for the preparation of pure 3-chlorobutanone in 75 to 80% yields, using a preparative gas chromatograph. The percentage distribution of products by the various methods, and spectral characteristics of the six different products obtained, are summarized in Table I.

ACKNOWLEDGMENT

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Synthesis and Characterization of Several Schiff Bases

D. V. LOPIEKES
Monsanto Research Corp., Boston Laboratory, Everett, Mass. 02149

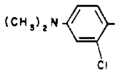
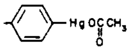
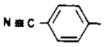
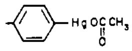
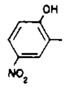
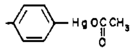
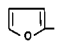
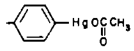
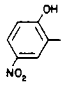
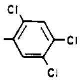
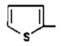
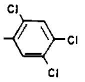
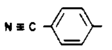
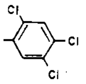
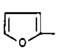
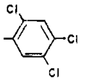
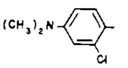
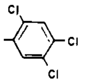
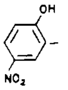
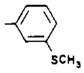
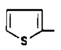
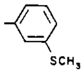
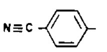
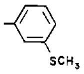
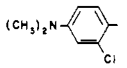
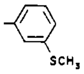
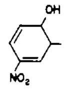
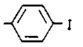
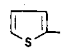
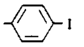
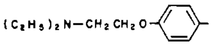
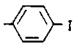
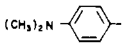
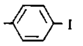
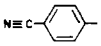
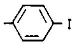
The reaction of a substituted aniline with an aldehyde has been used to prepare several new compounds. Yields, melting points, and elemental analyses are given.

COMPOUNDS of the structure R—CH=N—R′ have been prepared by reacting *p*-(acetoxymercuri) aniline, 2,4,5-trichloroaniline, 3-methylthioaniline, and *p*-iodoaniline with various aldehydes in benzene as described by a published procedure (*1*). Table I summarizes the yield, melting point, and elemental analysis of the compounds prepared. The infrared spectra were consistent in each instance with the desired structure. All starting materials were used as obtained from commercial sources.

EXPERIMENTAL

A benzene solution of aldehyde (0.2 mole) and substituted aniline (0.2 mole) were refluxed until as close to the theoreti-

Table I. Physical Properties and Analytical Data for R—CH=N—R′

R	R′	Yield, %	M.P., °C.	Empirical Formula	Analysis					
					Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
		80	188-190	$C_{17}H_{17}ClHgN_2O_2$	39.5[a]	39.5	3.5	3.5	5.4	5.4
		85	202-204	$C_{16}H_{16}HgN_2O_2$	41.3	41.1	2.6	2.8	6.0	5.8
		90	330(dec.)	$C_{15}H_{21}HgN_2O_5$	35.9	35.9	2.4	2.7	5.6	5.4
		67	172-174	$C_{13}H_{11}HgNO_3$	36.3	36.0	2.6	2.6	3.2	3.4
		54	272-273	$C_{13}H_7Cl_3N_2O_3$	45.2[b]	44.9	2.0	2.0	...	...
		90	72-74	$C_{11}H_6Cl_3NS$	45.5[c]	45.2	2.1	2.0	4.8	4.8
		59	174-177	$C_{14}H_7Cl_3N_2$	54.3	54.4	2.3	2.3	9.1	9.0
		78	87-90	$C_{11}H_6Cl_3NO$	48.2	47.9	2.2	2.3	5.1	5.1
		53	170-172	$C_{15}H_{12}Cl_4N_2$	49.7	50.1	3.3	3.4	7.9	8.0
		78	148-150	$C_{14}H_{12}N_2O_3S$	58.3	58.1	4.2	4.1	9.7	9.5
		79	[d]	$C_{12}H_{11}NS_2$	61.8	62.0	4.7	4.9	6.0	6.1
		97	99-101	$C_{15}H_{12}N_2S$	71.4	70.9	4.8	4.6	11.1	10.9
		94	103-106	$C_{16}H_{17}ClN_2S$	63.1[e]	63.2	5.6	5.8	9.2	9.4
		89	214-216	$C_{13}H_9IN_2O_2$	44.3[f]	44.1	2.5	2.4	...	...
		71	101-103	$C_{11}H_8INS$	42.2[g]	42.2	2.6	2.6	...	...
		95	49-51	$C_{19}H_{23}INO$	54.1	53.9	5.5	5.3	6.6	6.5
		91	122-124	$C_{15}H_{14}ClIN_2$	46.8[h]	47.0	3.8	3.7	...	...
		68	164-166	$C_{14}H_9IN_2$	50.6	50.8	2.7	2.6	8.4	8.3

[a] Calcd. for Cl, 6.8; found: Cl, 6.8. [b] Calcd. for Cl, 30.8; found: Cl, 30.6. [c] Calcd. for Cl, 36.5; found: Cl, 36.4. [d] Liquid, b.p. 149° C./0.10 mm. [e] Calcd. for Cl, 11.6; found: Cl, 11.4. [f] Calcd. for I, 36.1; found: I, 35.8. [g] Calcd. for I, 40.5; found: I, 40.4. [h] Calcd. for: Cl, 9.1; I, 33.0; found: Cl, 8.6; I, 32.6.

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; $C\equiv N$, 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.

ACKNOWLEDGMENT

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Some New Carbamates and Carbanilates

T. M. VALEGA and J. C. INGANGI
Entomology Research Division, Agriculture Research Service, U. S. Department of Agriculture, Beltsville, Md. 20705

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.