n-hexane. The yield of purified dodecyltetramethylenephosphine oxide was 1.0 gram, m.p. 62° C.

Anal. Calcd. for $C_{16}H_{33}OP$ (272.4): C, 70.50; H, 12.21; P, 11.37%. Found: C, 70.77; H, 11.98; P, 11.40%.

Dodecylpentamethylenephosphine Oxide. The starting product, pentamethylenephenylphosphine, is known (*3*). Here, again, the reaction product was not distilled, but decomposed with ammonium chloride solution. From 8 grams of magnesium, 38 grams of 1,5-dibromopentane, and 20 grams of dichlorophenylphosphine, the yield of pentamethylenephenylphosphine was 5.24 grams, b.p. 140° C./13 mm. (oil bath temp., 240° C.).

To 5.24 grams of the cyclic phosphine there were added 7.32 grams of dodecyl bromide, and the homogeneous mixture was heated for 3 hours at 100°-10° C., in an atmosphere of nitrogen. The product (which could not be brought to crystallization) was dissolved in 70 ml. of distilled water and treated with a solution of 27 grams of sodium hydroxide in 70 ml. of water. The mixture was heated for one hour at 90° C., with rapid stirring. The oil was extracted with 200 ml. of ether, and the extract washed with 20 ml. of water and dried over anhydrous sodium sulfate. The yield of crude dodecylpentamethylenephosphine oxide amounted to 7.0 grams. This was recrystallized from 100 ml. of *n*-hexane, giving 4.5 grams of pure phosphine oxide, m.p. 78° C.

Anal. Calcd. for $C_{17}H_{35}OP$ (286.4): C, 71.28; H, 12.32; P, 10.81. Found: C, 71.54; H, 12.26; P, 10.57.

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Synthesis of Some Chloro- and Iodoacetanilides

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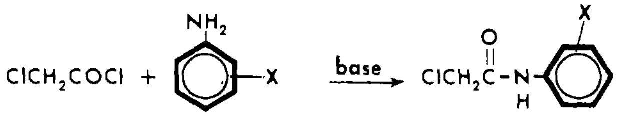
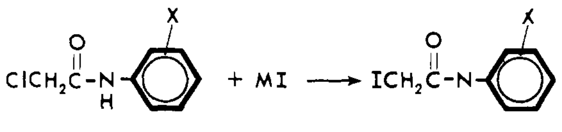
Sixteen acetanilides were prepared and characterized. These included principally chloro- and iodoacetanilides having halogen or alkoxy substituents on the aromatic ring.

A WELL known method to characterize carboxylic acids (*1*) is the preparation of anilides, haloanilides, or toluides by reaction of the acid halide with the corresponding aromatic amine. The derivatives obtained are usually solids which are easily purified and serve as a quick and accurate identification of the carboxylic acid. Recently, the authors prepared in their laboratory several chloro- and iodoacetanilides in which the aromatic ring was substituted with chlorine, bromine, or iodine or with methoxyl or ethoxyl groups. In addition, they prepared 2′-chloro-5′-trifluoromethyl-2-(2,4-dichlorophenoxy)acetanilide, *p*-chloroacetoxy-2-chloroacetanilide, and *p*-iodoacetoxy-2-iodoacetanilide. The chloroacetanilides were prepared from the corresponding aniline derivative and chloro- or dichloroacetyl chloride. The iodo analogs were then prepared from these materials by reaction with potassium or sodium iodide in acetone.



(1)



(2)

where X is Cl, Br, I, OMe, OEt, and M is Na or K

All compounds exhibited characteristic NH stretching vibrations at 2.99 to 3.11 microns (unbonded) and in some cases bonded NH stretching at 2.95 microns. Aliphatic C—H stretch occurred at 3.30 to 3.56 microns with a few as low as 3.21 microns while aromatic C—H stretch was seen at 3.20 to 3.25 microns with a few as high as

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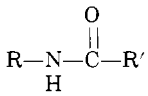
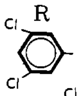
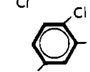
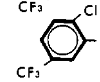
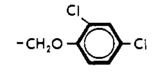
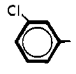
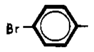
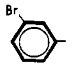
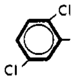
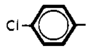
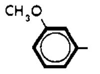
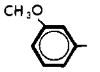
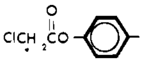
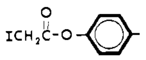
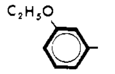
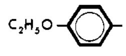
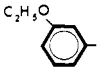
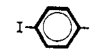
Table I. Characterization of Acetanilides


$$R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-R'$$

Compound	R	R′	Yield, %	M.P., ° C.	Amide Carbonyl Absorption, Microns	Analysis	
						Calcd.	Found
2,2,3′,5′-Tetrachloroacetanilide		—$CHCl_2$	58	138-9	5.95	C, 35.2 H, 1.8; N, 5.1	C,35.3 H, 2.0 N, 5.2
2′-Chloro-5′-trifluoromethyl-2-iodoacetanilide		—CH_2I	73	138	6.01	C, 29.7 H, 1.6 I , 34.9	C, 29.6 H, 1.6 I , 34.7
2′-Chloro-5′-trifluoromethyl-2-(2,4-dichlorophenoxy)acetanilide			45	200-1	5.89	C, 45.2 H, 2.3 N, 3.5	C, 45.1 H, 2.3 N, 3.4
3′-Chloro-2-iodoacetanilide		—CH_2I	49	89-9.5	6.09	C, 32.5 H, 2.4 I , 43.0	C, 32.3 H, 2.4 I , 43.0
4′-Bromo-2-iodoacetanilide		—CH_2I	71	179-80	5.92	C, 28.2 H, 2.1 I , 37.3	C, 28.0 H, 2.1 I , 37.6
3′-Bromo-2-iodoacetanilide		—CH_2I	63	99-9.5	6.06	C, 28.2 H, 2.1 I , 37.3	C, 28.0 H, 2.2 I , 37.1
2′,5′-Dichloro-2-iodoacetanilide		—CH_2I	68	177-8	6.05	C, 29.2 H, 1.8 N, 4.3	C, 29.2 H, 1.9 N, 4.3
4′-Chloro-2-iodoacetanilide		—CH_2I	30	180-80.5	5.88	C, 32.6 H, 2.4 N, 4.7	C, 32.6 H, 2.3 N, 4.7
N-(Chloroacetyl)-*m*-anisidide		—CH_2Cl	45	93-4	5.98	C, 54.2 H, 5.0 N, 7.0	C, 53.9 H, 5.0 N, 6.9
N-(Iodoacetyl)-*m*-anisidide		—CH_2I	42	94.5-6	6.07	C, 37.2 H, 3.5 N, 4.8	C, 37.3 H, 3.7 N, 4.2
p-Chloroacetoxy-2-chloroacetanilide		—CH_2Cl	14	168-9	6.00	C, 45.8 H, 3.5 Cl, 27.0 N, 5.6	C, 45.7 H, 4.0 Cl, 26.9 N, 5.2
p-Iodoacetoxy-2-iodoacetanilide		—CH_2I	20	166-8	6.01	C, 27.0 H, 2.0 N, 3.1	C, 27.0 H, 2.0 N, 3.5
N-(Chloroacetyl)-*m*-phenetidide		—CH_2Cl	70	124-6	5.93	C, 56.2 H, 5.7 N, 6.6	C, 56.0 H, 5.7 N, 6.5
N-(Iodoacetyl)-*p*-phenetidide		—CH_2I	46	138.5-41	6.08	C, 39.4 H, 4.0 N, 4.6	C, 39.3 H, 4.2 N, 4.3
N-(Iodoacetyl)-*m*-phenetidide		—CH_2I	75	108-10	6.04	C, 39.4 H, 4.0 N, 4.6	C, 39.0 H, 4.0 N, 4.6
4′-Iodo-2,2-dichloroacetanilide		—$CHCl_2$	15	155-58	5.99	C, 29.1 H, 1.8 N, 4.2	C, 28.8 H, 1.8 N, 4.2

3.30 microns. Amide carbonyl absorption occurred at 5.95 to 6.10 microns. One compound, 4′-chloro-2-iodoacetanilide, showed this absorption at 5.88 microns. Secondary amide absorption was seen at 6.41 to 6.60 microns and $C=C$ in plane vibration occurred at 6.18 to 6.33 and 6.61 to 6.89 microns. Aromatic substitution patterns were determined in the region 11.29 to 14.60 microns and were consistent in all cases with the described structures. The frequency of amide carbonyl absorption for each compound is given in Table I.

EXPERIMENTAL

All starting materials were obtained from Matheson, Coleman and Bell or Distillation Products Industries as reagent or practical grade and were used without further purification. Melting points were taken on a Thomas Hoover melting point apparatus or in a Thiele tube equipped with stirring motor and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. Compounds were either examined in a KBr matrix or as a cast film from chloroform.

Two general procedures were used to prepare the chloroacetanilides. Both procedures are thoroughly documented in the literature and differed only in the choice of base (organic or inorganic) used in a given reaction. To convert the chloroacetanilide to the iodo derivative, the compound was refluxed with potassium or sodium iodide in acetone. Table I lists the compounds prepared together with their melting points, yields, and elemental analyses.

ACKNOWLEDGMENT

Elemental analyses were performed by Carol K. Fitz, Needham Heights, Mass. and Galbraith Laboratories, Knoxville, Tenn.

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Acylbisdiazomethanes

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Adipoylbisdiazomethane and terephthaloylbisdiazomethane were used in testing the following new or modified reactions: silver acetate and water to initiate the Wolff rearrangement, 12% hydriodic acid to change the diazomethyl group to iodomethyl, iodine to convert diazomethyl to diiodomethyl, and nitric acid (without sodium nitrate) in ether solution to synthesize nitric esters.

MANY different systems have been used to initiate the rearrangement of acyldiazomethanes: $RCOCHN_2 + H_2O$ (catal.) $\rightarrow RCH_2COOH$. Originally, Wolff (*9*) used ammoniacal silver nitrate, but this and many other systems have proved to be quite erratic. Newman and Beal (*6*) reported an effective system, namely, silver benzoate and triethylamine, and they stressed the need for the triethylamine or a comparable base. This study shows that water works effectively in place of triethylamine and that silver acetate may replace silver benzoate. If used with ammonia, the new procedure (silver acetate and water) gives rise to amides, and if used with methanol, it yields methyl esters.

This rearrangement and other reactions were tested with acylbisdiazomethanes, $N_2CH—CO—R'—CO—CHN_2$, rather than the simpler acyldiazomethanes, $RCOCHN_2$. From adipoylbisdiazomethane (*8*), $(—CH_2CH_2COCHN_2)_2$, were obtained good yields of suberic acid, its amide, or its methyl ester.

Halomethyl ketones have been made from acyldiazomethanes by reaction with hydrochloric and hydrobromic acids but not with hydriodic acid: $RCOCHN_2 + HX \rightarrow RCOCH_2X + N_2$. In one reported application (*11*) of 48% hydroiodic acid there was reduction rather than iodination—e.g., benzoyldiazomethane into acetophenone. Iodomethyl ketones have been made previously by reaction of chloromethyl ketones with sodium iodide. If the concentration of hydriodic acid is about 12%, it is now established that iodination proceeds smoothly. In this manner, terephthaloylbisdiazomethane (*3, 7*) $N_2CHCO—C_6H_4—COCHN_2$, was converted into *p*-bis(iodoacetyl)benzene, $C_6H_4(COCH_2I)_2$.

Wolff (*10*) established in 1902 that iodine reacts with acyldiazomethanes: $RCOCHN_2 + I_2 \rightarrow RCOCHI_2 + N_2$, but the reaction has not been tested with acylbisdiazomethanes. In dioxane solution, iodine reacts smoothly with both adipoyl- and terephthaloylbisdiazomethane to yield, respectively, 1,1,8,8-tetraiodo-2,7-octanedione and *p*-bis(diiodoacetyl)benzene.

Fahr (*4*) synthesized 2,7-dioxo-1,8-octanediol dinitrate, $(—CH_2CH_2COCH_2ONO_2)_2$, in 41% yield from adipoylbisdiazomethane in methanol, using an aqueous mixture of nitric acid and sodium nitrate. To prepare the same compound in 62% yield, sodium nitrate was omitted, and ether was used as solvent for the mixture of adipoylbisdiazomethane and 70% nitric acid. Fahr's difficulty in combustion analysis was confirmed and both his value and ours for hydrogen were good, but both results for carbon and nitrogen were outside desired limits. Terephthaloylbis(methyl nitrate), $C_6H_4(COCH_2ONO_2)_2$, a new compound, was similarly synthesized from terephthaloylbisdiazomethane and 70% nitric acid in dioxane. Again, its analysis for nitrogen was unsatisfactory in spite of the apparent purity of the crystalline product.

EXPERIMENTAL

Reagents. Adipoylbisdiazomethane (*8*), prepared from adipoyl chloride and diazomethane, was obtained as yellow crystals, m.p. 70–72.5° C. Terephthaloylbisdiazomethane was reported by Ross (*7*) to decompose at 200° and by Dashevskaya (*3*) at 169° C. Both of their syntheses were by way of terephthaloyl chloride and diazomethane in dry ether. The decomposition point of the product made by their method was influenced by the purity of the acyl chloride since the diazo product did not lend itself to purification by crystallization. If the chloride was crystallized from hexane just before use, the decomposition point of the yellow crystals was 194°; otherwise, it was 180–4° C. Crystallization of the product from benzene lowered