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
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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.

PURDUE UNIVERSITY G. BRYANT BACHMAN
LAFAYETTE, INDIANA GEORGE M. PICHA
RECEIVED JUNE 8, 1946

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(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).

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.

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(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
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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.

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

NOYES CHEMICAL LABORATORY
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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.