lized as large, dark-orange needles, m.p. 190–191°. *Anal.* Calcd. for $C_{26}H_{24}N_4O_6$: C, 63.02; H, 5.08. Found: C, 63.02; H, 5.01.

***trans*-3,4-Bis-(*p*-methoxyphenyl)-cyclopentanone.**—Methyl *dl*-β,γ-bis-(*p*-methoxyphenyl)-adipate, m.p. 64–65°, 0.5 g. was subjected to ring closure as described above. The product, purified through Girard reagent and recrystallized from ligroin, was obtained in 66% yield; m.p. 110–111°. *Anal.* Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.85; H, 6.58.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE GEORGE P. MUELLER
KNOXVILLE, TENNESSEE FLEUR C. BATEMAN

RECEIVED APRIL 5, 1952

p-Fluorophenacyl Bromide Salts[1]

In order to obtain a variety of quaternary salts of heterocyclic nitrogen compounds all having the same quaternizing group attached to the nitrogen, so that correlations between structure and biological activity might be studied more conveniently, the salts listed in Table I were prepared for comparison with those previously reported.[2] The methods of preparation were in general the same as those described in the previous publications, care being taken to avoid altering any reactive substituent groups present on the rings. The solid heterocyclic bases which were insoluble in chloroform were treated with *p*-fluorophenacyl bromide in acetone or alcohol. The quinolinium and isoquinolinium salts were only slightly soluble in water, while the pyridinium and pyrazinium compounds were more soluble.

TABLE I

p-FLUOROPHENACYL BROMIDE SALTS

Salt from	Empirical formula	M.p.,[a] °C.	Ionic halogen, % Calcd.	Found
A. Substituted pyridines				
γ-Picoline	$C_{14}H_{13}BrFNO$	165–168	25.77	25.62, 25.64
2,6-Lutidine	$C_{15}H_{15}BrFNO$	248	24.65	24.30, 24.40
4-*n*-Amylpyridine	$C_{18}H_{21}BrFNO$	181	21.81	21.79, 21.80
2-*n*-Hexylpyridine	$C_{19}H_{23}BrFNO$	180	20.96	20.82, 20.78
2-Propanolpyridine	$C_{16}H_{15}BrFNO_2$	163	22.50	22.27, 22.41
3-Hydroxypyridine	$C_{13}H_{11}BrFNO_2$	223	25.61	25.36, 25.39
3-Aminopyridine	$C_{13}H_{12}BrFN_2O$	200–202	25.68	25.60, 25.70
3-Acetaminopyridine	$C_{15}H_{14}BrFN_2O_2$	177–179	22.63	22.88, 22.79
3-Acetylpyridine	$C_{15}H_{13}BrFNO_2$	172–173	23.62	23.51, 23.82
3-Cyanopyridine	$C_{14}H_{10}BrFN_2O$	212	24.88	24.87, 24.98
Ethyl nicotinate	$C_{16}H_{15}BrFNO_3$	90	21.70	21.31, 21.36
Nicotinamide	$C_{14}H_{12}BrFN_2O_2$	226–228	23.56	23.23, 23.42
B. Quinoline and isoquinolines				
Quinoline	$C_{17}H_{13}BrFNO$[b]	235	23.08	23.06, 23.54
Isoquinoline	$C_{17}H_{13}BrFNO$	202	23.08	23.04, 23.01
3-Methylisoquinoline	$C_{18}H_{15}BrFNO$	135–136	22.19	22.15, 21.98
C. Chloropyrazine				
2-Chloropyrazine[c]	$C_{12}H_9BrClFN_2O$	183		[d]

[a] In nearly all cases the compounds melted with decomposition. [b] The corresponding iodide, $C_{17}H_{13}FINO$, m. p. 190–191°, calcd. I, 32.28; found I, 31.91, 32.45. [c] The product may be either the 3-chloropyrazinium salt or the 2-chloropyrazinium salt, but the former seems more likely since 3-bromopyridine reacts more readily than 2-bromopyridine. [d] Calcd.: C, 43.46; H, 2.74. Found: C, 43.57; H, 2.87.

Samples of these compounds have been submitted to the National Cancer Institute or the Midwest Research Institute for screening against tumors and data showing the variations in biological activity are to be published elsewhere.

We wish to express our thanks to Dr. M. J. Shear and Dr. J. L. Hartwell of the National Cancer Institute and Dr. L. H. Goodson and Dr. W. M. Hoehn of the Midwest Research Institute for their interest in this project, to Dr. J. H. Clark of the American Cyanamid Company for the 2-chloropyrazine used, and to Miss Marguerite Close for carrying out several of the Volhard halogen determinations and to the Microanalytical Laboratory of the National Institute of Health for the carbon and hydrogen analyses.

(1) This research was supported in part by a research grant from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) C. T. Bahner, W. K. Easley, M. D. Pickens, H. D. Lyons, L. L. Norton, B. G. Walden and G. E. Biggerstaff, THIS JOURNAL, 73, 3499 (1951); C. T. Bahner and L. L. Norton, *ibid.*, 72, 2881 (1950).

CARL TABB BAHNER
CARSON-NEWMAN COLLEGE WILLIAM KENNETH EASLEY
JEFFERSON CITY, TENNESSEE BETTY GAY WALDEN
HAROLD D. LYONS
GEORGE E. BIGGERSTAFF

RECEIVED MARCH 24, 1952

Methyl Esters of Substituted Benzoic Acids[1]

Methyl *p*-phenoxybenzoate.—*p*-Phenoxybenzoic acid was prepared by carbonation of the Grignard reagent made in the usual way from 25 g. of *p*-bromodiphenyl ether. Pouring the Grignard solution onto crushed dry ice gave only very small amounts of the desired acid, but carbonation by the method of Hussey[2] yielded 7.5 g. (35%) of *p*-phenoxybenzoic acid, m.p. 158–160°. The methyl ester was prepared by boiling 5.15 g. of the acid with 70 ml. of methyl alcohol and 7 ml. of sulfuric acid for two hours, distilling off most of the methanol and washing the solid product with a solution of sodium bicarbonate and then with water. Recrystallization from methanol–water mixture yielded 4.0 g. (65%) of colorless crystalline methyl *p*-phenoxybenzoate, m.p. 59.5–60°. The ester is biaxial, crystallizing in the orthorhombic system, optically positive with 2V = 85°; α, 1.515; β, 1.573; γ, 1.667 (calculated), exhibiting prismatic habit and irregular cleavage.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.90; H, 5.34.

Methyl *p*-Ethoxybenzoate.—A similar esterification with *p*-ethoxybenzoic acid gave the methyl ester in 75% yield. Recrystallization was effected from methanol–water and from ligroin. This ester forms colorless crystals melting at 37.5–38° to a colorless liquid which boils at 260°. The crystals are orthorhombic, with 2V = 85–90°, showing prismatic habit and irregular fracture.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.71; H, 6.71.

Methyl anisate was found to have crystallographic properties similar to the two preceding esters. Microscopic examination showed crystals of this compound to be biaxial, orthorhombic, optically negative, with 2V = 70–75°, exhibiting irregular prismatic habit and platy cleavage.

Methyl 3,4-Dichlorobenzoate.—Although it has been mentioned in a patent,[3] no properties of this compound have been reported. It was prepared in 81% yield from the corresponding acid by a similar Fischer esterification, followed by recrystallization from methanol. The ester crystallizes in long colorless prismatic needles, also in the orthorhombic system; m.p. 46.5–47.5°; b.p. 248°.

Anal. Calcd. for $C_8H_6O_2Cl_2$: C, 46.86; H, 2.95. Found: C, 46.97; H, 3.15.

(1) All temperatures are corrected.

(2) A. S. Hussey, THIS JOURNAL, 73, 1364 (1951).

(3) R. S. Long (to American Cyanamid Co.) U. S. Patent 2,392,167 (1946).

ROBERT WEST
MALLINCKRODT CHEMICAL LABORATORY SEVERO ORNSTEIN
HARVARD UNIVERSITY DONALD MCKEE
CAMBRIDGE, MASSACHUSETTS ROBERT LAYZER

RECEIVED JULY 31, 1951

Preparation of Cerous Ammonium Acetylacetonate

To 6 ml. (0.058 mole) of refluxing acetylacetone was added 6 ml. (0.091 mole) of concentrated ammonium hydroxide and the mixture refluxed for ten minutes. A solution of 500 mg. (0.0012 mole) of cerous nitrate hexahydrate in 3 ml. water was then introduced dropwise and the resulting solution refluxed for ten minutes. The solution was allowed to