The compounds and their physical properties are found in Table I. It may be seen that high yields of condensation products are obtained in all cases. It is of interest to note that while the copper salts of the β-diketones containing the perfluoromethyl group melted with decomposition, several of the homologous perfluoro-*n*-propyl derivatives gave copper chelates which melted without apparent decomposition.

Work is now in progress in our laboratory to extend this work to the acylation of a variety of ketones containing alpha methylene and methinyl groups.

Experimental[9]

Starting Materials (a) Ethyl Trifluoroacetate.—This ester was purchased from the Dow Chemical Company, Pittsburg, California.

(b) **Ethyl Perfluoro-*n*-butyrate.**—This ester, b.p. 93–94°, was prepared in 75–85% yield by the reaction of perfluorobutyric acid with absolute ethanol in the presence of concentrated sulfuric acid following the method developed by the Minnesota Mining and Manufacturing Company.[10]

(c) **Heterocyclic Ketones.**—The necessary thiophene and furan ketones were prepared by methods developed in this Laboratory.[5,6,7,8]

Methods for Preparing Fluorinated β Diketones. Procedure I.—The apparatus used in these condensations consisted of a 1000-ml. three-neck, round-bottom flask equipped with ground-glass joints, a mercury-sealed stirrer, an addition funnel and a reflux condenser (protected from atmospheric moisture by a drying tube filled with Drierite). To 0.315 mole (18 g.) of commercial 95% sodium methoxide,[11] suspended in 300 ml. of anhydrous ether, was added 0.3 mole (36.2 g.) of ethyl trifluoroacetate over a period of 30 minutes. To the rapidly stirred mixture, 0.3 mole of the appropriate ketone, dissolved in 50 ml. of anhydrous ether, was added over a fifteen minute period. Stirring was continued for two hours longer and then the mixture was allowed to stand for twelve hours at room temperature. Then, 0.36 mole (20.6 ml.) of glacial acetic acid, dissolved in 100 ml. of water, was added. This was followed by the addition of 0.22 mole (21.4 g.) of anhydrous magnesium acetate, dissolved in 125 ml. of water. The reflux condenser was replaced by a condenser set up for downward distillation and the ether removed by distillation on a steam bath. The magnesium chelate, which precipitated, was filtered and washed with 100 ml. of water. The chelate was placed in a 2 liter round-bottom flask, covered with 500 ml. of water and the mixture steam-distilled to remove any unreacted ketone. After the ketone had been removed, as indicated by the fact that the distillate no longer consisted of two phases, 0.3 mole (16.6 ml.) of concentrated sulfuric acid, dissolved in 30 ml. of water, was added to the flask and steam distillation continued until the distillate no longer gave a positive color test with alcoholic iron(III) chloride solution. The distillate was extracted with ether, the extracts dried over Drierite, the solvent distilled and the residue fractionated in vacuum to give the β-diketone.

Procedure Ia.—This procedure is identical with Procedure I except that the diketone was chelated by means of copper(II) acetate.

Procedure II.—This method is similar to Procedure I except that after the acetic acid is added, the mixture is extracted with ether until the extracts no longer give a positive test with iron(III) chloride. The extracts are dried over Drierite, the solvent distilled and the residue fractionated in vacuum.

Procedure III.—This method is identical with Procedure I except that after the magnesium chelate is filtered, it is placed in a 2-liter separatory funnel, 500 ml. of 15% sulfuric acid is added and the mixture shaken and extracted with ether. The extracts are then treated as described in Procedure II.

Procedure IIIa.—This method is identical with Procedure III except that copper(II) acetate is used in place of magnesium acetate.

Procedure IV.—This method is identical with Procedure I except that after the diketone had been steam distilled, it was filtered and recrystallized.

Procedure IVa.—This method is identical with Procedure IV except that copper(II) acetate is used in place of magnesium acetate.

Acknowledgment.—The authors gratefully acknowledge the financial support of the United States Atomic Energy Commission during the course of this investigation.

PITTSBURGH, PENNA. RECEIVED APRIL 5, 1951

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[9] All analyses were performed by Mr. George Stragand of the Microanalytical Laboratory of the University of Pittsburgh.

[10] Private communication from Mr. J. M. Rogers, Minnesota Mining and Manufacturing Co., Saint Paul, Minnesota.

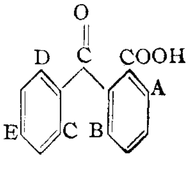
[11] Purchased from the Mathieson Chemical Corporation, Niagara Falls, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Normal and Pseudo Esters of 2-Benzoylbenzoic Acid Types. III

BY MELVIN S. NEWMAN AND CHESTER W. MUTH[1]

A study of the Fischer–Speier esterification of all of the substituted 2-benzoylbenzoic acids of formula shown, with or without methyl groups at positions A, B, C and D has been completed. Generalizations concerning the effect of structure on the formation of normal and pseudo methyl esters are made.



The impetus for the work herein reported arose from the observation that 2-benzoyl-1-naphthoic acid[2] formed the pseudo methyl ester on esterification by the Fischer–Speier method whereas 2-benzoylbenzoic acid had been shown to form entirely the normal ester under similar conditions.[3] In order to learn more about the structural features responsible for the formation of normal and pseudo esters, we undertook to study the esterification of the twelve possible 2-benzoylbenzoic acids with or without methyl groups at the lettered positions, A, B, C and D. In certain cases, a methyl group at E was also included because of greater ease of preparation.[4] In this paper, we summarize our findings to date in Table I which includes data from previous publications,[4,5] together with new

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[1] Taken from Ph.D. thesis of C. W. M., 1949. Present address: Department of Chemistry, West Virginia University, Morgantown, W. Va.

[2] L. F. Fieser and M. S. Newman, THIS JOURNAL, **58**, 2376 (1936).

[3] H. Blaskuda, *Ber.*, **7**, 987 (1894); A. Haller and A. Guyot, *Bull. soc. chim.*, [3] **25**, 49 (1901); H. Meyer, *Monatsh.*, **25**, 475 (1904).

[4] M. S. Newman and B. T. Lord, THIS JOURNAL, **66**, 731 (1944).

[5] M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1537 (1941).

data on acids II,[4] VI,[6] VII,[6] IX,[5] X[6] and XI.[6]

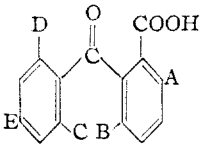
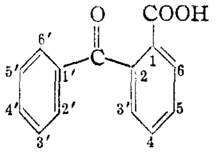


TABLE I

FISCHER–SPEIER ESTERIFICATION OF SUBSTITUTED 2-BENZOYLBENZOIC ACIDS



	Acid	Yield, %[a]	Type of ester Normal	Pseudo	Keto acid, % by U.V. analysis
		91	All[b]		100
II	6-Methyl	87[c]	65[d]	35[d,f]	35
III	3-Methyl	85	All[b]		80
IV	2′,4′-Dimethyl	90	All		97
V	3,6-Dimethyl	90		85	14
VI	2′,4′,6-Trimethyl	94	All[b]		88
VII	2′,3,4′-Trimethyl	96	All[b]		102
VIII	2′,4′,6′-Trimethyl	94	All[b]		[h]
IX	2′,3,4′,6-Tetramethyl	88[c,e]	68[d]	32[d]	22
X	2′,4′,6,6′-Tetramethyl	4[f,g]	All[b]		[h]
XI	2′,3,4′,6′-Tetramethyl	87	All[b]		[h]
XII	2′,3,4′,6,6′-Pentamethyl	78	All[b]		[h]

[a] Yields represent ester mixture obtained after refluxing for periods of 15 to 48 hours in methanol containing hydrogen chloride and recrystallization of solid ester. [b] The crude ester originally obtained was almost pure without recrystallization. [c] Represents vacuum distilled ester. [d] Composition determined by infrared absorption spectrum analysis. [e] This value supersedes that reported in reference 4. [f] This value supersedes that reported in reference 5. [g] Esterification for nine days. The yield of crude unrecrystallized ester was 9%. [h] Since we have as yet been unable to secure pure pseudo ester of these acids, no ultraviolet analysis of the free acid in methanol has been attempted.

The following points are of interest in connection with the acid-catalyzed esterification of 2-benzoylbenzoic acid types with methanol. (1) Pseudo esters are formed only from acids which have a methyl group at A. (2) If an acid has a methyl group at A and also one at C, or at C and D, no pseudo ester is formed. (3) In acids which have a methyl group at A, the addition of a methyl group at B gives rise to surprising effects. These effects are illustrated by considering the following pairs of acids: II and V, VI and IX, and X and XII.

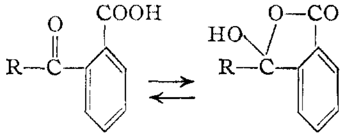
II and V.—It is to be noted that II yields a mixture of methyl esters in which the amount of pseudo ester is about 35%. Yet in V, where a methyl group is added at position B, the amount of pseudo ester rises to about 85%.

VI and IX.—Note that VI yields all normal methyl ester, whereas IX yields about 32% of pseudo ester. Here again, the substitution of a methyl group at position B causes an unexpected result.

X and XII.—Compound X esterifies with great difficulty, only about 9% being esterified after refluxing for nine days with methanolic hydrogen chloride, whereas XII esterifies normally in several hours. It is difficult to understand why an extra methyl group at B should allow for esterification of XII when X esterifies with such difficulty. Although all of these effects are probably steric in origin, an examination of molecular models gives no obvious clue to the reason for this behavior.

With regard to esterification by the methods we have used in this and previous publications,[4,5] the following points are of interest. (1) Diazomethane always yields the pure normal methyl ester. (2) When the acid chloride is treated with methanol and pyridine, the ester is always the pseudo form, except as noted below in (3). (3) Acids having methyl groups at C and D yield mainly normal ester under all conditions of esterification that we have used. Some evidence of the formation of small amounts of pseudo esters has been obtained but more work is required to establish this point.

The ultraviolet absorption spectra of all of the acids, normal methyl esters and pseudo methyl esters prepared in this and previous work[4,5] have been taken in methanol. The normal esters have a maximum near 250 mμ whereas this band is almost entirely lacking in the pseudo esters. By comparing the intensity of absorption at the appropriate wave length near 250 mμ in the free acid to that of the normal and pseudo esters, it is possible to estimate the position of the keto acid–hydroxylacetone equilibrium.[7]



The last column in Table I records the per cent. of acid in the ketoacid form as determined by analysis of the ultraviolet absorption curves. It is interesting to note that the per cent. of acid in the keto acid form thus determined parallels fairly closely the amount of normal methyl ester formed under the acid-catalyzed esterification conditions of our experiments.

Where the parallelism fails appreciably (> 15%) there is more normal ester formed than expected, *e.g.*, compounds II, III and IX.

Experimental[8]

Preparation of Methyl Esters.—The methyl esters were prepared and isolated essentially as described in detail in previous work.[5] Their properties and analyses are recorded in Table II. The esters in column A were made by Fischer–Speier esterification for periods which varied from 12 to 48 hours (in one case, X, esterification was only 9% complete after nine days), in column B by diazomethane treatment, and in C by treatment of the acid chloride with methanol in pyridine.

Infrared Absorption Spectra.[9]—Analysis of the mixture of isomeric methyl esters formed from two of the ketoacids, II and IX, was accomplished with the aid of infrared absorption spectra. By plotting the extinction at 6.00, 7.95, 10.63 and 13.15 μ against per cent. composition of synthetic mixtures of normal and pseudo esters of II (using a Beck-

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(6) The preparation and proof of structure of these acids has been described, M. S. Newman and C. W. Muth, *ibid.*, **72**, 5191 (1950).

(7) We are indebted to Dr. H. Hemmendinger of the Central Research Laboratory, General Aniline and Film Corp., Easton, Pa., for these measurements and their interpretation.

(8) All melting points corrected.

(9) The authors wish to express their thanks to Mrs. Arlene Brooks for the infrared spectral determinations.

TABLE II

PROPERTIES, YIELDS AND ANALYSIS OF METHYL ESTERS

Acid	A (Fischer) Yield,[a] %	M.p., °C.	B (Normal) Yield,[a] %	M.p., °C.	C (Pseudo) Yield,[a] %	M.p., °C.	Formula	Calcd. C	Calcd. H	Found[c] C	Found[c] H
VI	94	42.4–45.2	64	43.5–46.0	81	56–58	$C_{18}H_{18}O_3$	76.6	6.4	76.7	6.4n
										76.4	6.5n
										76.4	6.6p
VII	96	58.5–61.0	86	60.0–61.5	36	95.5–98.5	$C_{18}H_{18}O_3$	76.6	6.4	76.2	6.3n
										76.5	6.5p
X	4	111.8–113.6	94	112–113.6	46[b]	111–113	$C_{19}H_{20}O_3$	77.0	6.8	77.0	6.5n
										76.9	6.4n
XI	87	113–115	86	113–114.8	25[b]	113–115.2	$C_{19}H_{20}O_3$	77.0	6.8	77.1	6.7n
										77.3	6.5n

[a] In all cases, the per cent. yield means the yield of crystalline product with the indicated melting point. [b] These esters were the same as those prepared with diazomethane. A large amount of lower melting material was also obtained some of which was probably pseudo ester. [c] Analyses marked n are for normal esters, analyses marked p are for pseudo esters. Microanalyses by Mrs. E. H. Klotz.

man IR-2 instrument) in the ranges of 30, 35 and 40% pseudo ester working curves were obtained. The normal ester absorbed strongly at 6.00 and 7.95 μ and the pseudo weakly whereas the reverse was true for the other two points. By determining the extinction at all four positions for the ester mixture obtained by Fischer–Speier esterification of II it was determined that the mixture contained 35.5 ± 2.5% pseudo methyl ester. In a similar way, the composition of the esters formed from IX was found to be 32 ± 2% pseudo methyl ester. In the latter case, a Baird Associates instrument was used and the extinctions at 5.70 μ (high extinction for pseudo, low for normal), 5.80 and 6.00 (high extinction for normal, low for pseudo) were used for analysis. All measurements involved 10 mg. of ester per ml. of carbon disulfide and the same cell was used throughout an analysis for one pair of isomers.

COLUMBUS 10, OHIO RECEIVED MARCH 28, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE]

Kinetics of the Brominolysis of Benzeneboronic Acid in Aqueous Acetic Acid Solution

BY HENRY G. KUIVILA AND ELIOT K. EASTERBROOK

The kinetics of the brominolysis of benzeneboronic acid in aqueous acetic acid solution have been investigated. The reaction is first order in bromine and in benzeneboronic acid. Its rate increases with the water content of the solvent. The reaction shows a positive salt effect, catalysis by bases and retardation by acids. The bearing of these observations on the mechanism is discussed.

Electrophilic substitution reactions in the aromatic series, such as nitration and halogenation, have been frequently investigated and are fairly well understood. But similar reactions in which an atom or group other than hydrogen is replaced have, for the most part, been neglected from the standpoint of detailed kinetic investigation. An obvious source of compounds of this type is the organometallic field. However, only a few types of organometallic compounds have been found to undergo electrophilic displacement reactions at measurable rates. Among these the cleavage of organomercurials with acids have received considerable attention from Kharasch and his coworkers from the standpoint of reactivity.[1] More recently Corwin and Naylor[2] have investigated the kinetics of the cleavage of diphenylmercury by acetic and formic acids and Winstein[3] has discussed investigations on the reactions of organomercuric halides with halogens.

The aromatic boronic acids constitute another group of organometallic compounds in which some electrophilic displacement reactions proceed at measurable rates. Melnikoff[4] has shown that the reaction between bromine and aromatic boronic acids in water proceeds quantitatively

$$ArB(OH)_2 + Br_2 + H_2O \longrightarrow ArBr + H_3BO_3 + HBr \quad (I)$$

This reaction was chosen as the first of a series to be subjected to kinetic study. It was hoped thereby to gain some information concerning the mechanism of the reaction in particular and of electrophilic displacement reactions in general.

Experimental

Reagents.—The acetic acid was purified by treatment with chromic acid and distillation through a column with 40 theoretical plates. The acetic acid percentages given are percentages by volume. Sodium chloroacetate and sodium dichloroacetate were prepared from the acids by the method of Bischoff and Walden.[5] Sodium perchlorate (Eimer and Amend) was recrystallized from water and dried for several days at 110°. Baker C.P. sodium acetate was used in the experiments here reported. The Reagent Grade salt from another source gave anomalous kinetics. The sodium benzoate was Mallinckrodt U.S.P. and the other reagents were C.P. or Reagent Grade and were used without further purification.

The bromine was distilled from potassium bromide, the

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[1] M. S. Kharasch, R. R. Legault and W. R. Sprowls, *J. Org. Chem.*, **3**, 409 (1938–1939), and preceding papers of the series.

[2] A. H. Corwin and M. A. Naylor, THIS JOURNAL, **69**, 1004 (1947).

[3] S. Winstein, Paper presented at the Conference on Reaction Mechanisms, Northwestern University, Evanston, Illinois, September 1, 1950.

[4] N. N. Melnikoff, *J. Gen. Chem. U. S. S. R.*, **6**, 636 (1936); *C. A.*, **30**, 5571 (1936); *ibid.*, **8**, 1766 (1938); *C. A.*, **33**, 4908 (1939).

[5] C. A. Bischoff and P. Walden, *Ann.*, **279**, 46 (1894).