in acid solution in the form of a positive ion, III, similar to that found in the case of pyridine.

Experimental

The Sulfonation of Pyridine-N-oxide.—A mixture of 20 g. of fuming sulfuric acid (20%), 2 g. of pyridine-N-oxide[13] and 0.2 g. of mercuric sulfate was heated at 220–240° for 22 hours. The reaction mixture was poured into 20 ml. of water and neutralized with a hot saturated solution of barium hydroxide and finally with powdered barium carbonate. The mixture was cooled and filtered through Celite and the filtrate was treated with Norit and evaporated to a volume of 50 ml. The Norit was removed and the filtrate was evaporated to dryness leaving a solid residue. The residue was stirred with 10 ml. of ethanol, cooled overnight and filtered giving 3.5 g. of a white crystalline solid. The salt was dissolved in a minimum of water, the barium was precipitated with an equivalent amount of sulfuric acid and the mixture was filtered. Evaporation of the filtrate left 1.9 g. (51%) of solid which on recrystallization from methanol melted at 237–238°. The ammonium salt melted 261–263°.

Anal. Calcd. for $C_5H_5NO_4S$: C, 34.28; H, 2.88; equiv. wt., 175. Found: C, 34.35, 34.48; H, 2.90, 3.02; equiv. wt., 176.

A mixture of 12 g. of fuming sulfuric acid (20%) and 2 g. of pyridine-N-oxide was heated at 220–240° for 24 hours in the absence of mercuric sulfate. Upon working up the mixture as described above, an oil was obtained from the neutral solution which gave a picrate, m.p. 178–181°, which represented a 90% recovery of the pyridine-$\underset{+}{\text{N}}$-oxide.

A mixture of 40 g. of fuming sulfuric acid (20%), 10 g. of pyridine-N-oxide and 0.3 g. of mercuric sulfate was heated at 150–170° for 18 hours. After working up the mixture as described, an oil, 7.3 g., was obtained which gave the picrate of pyridine-N-oxide, m.p. 178–180°.

The Reduction of 3-Pyridine-N-oxidesulfonic Acid.—A solution of 3.5 g. of 3-pyridine-N-oxidesulfonic acid, prepared by the sulfonation of pyridine-N-oxide, in 200 ml. of 95% ethanol was treated with hydrogen at 60–70° in the presence of Raney nickel at three atmospheres pressure. The theoretical pressure drop was observed after one hour. The hot mixture was filtered and the filtrate was evaporated to dryness leaving 2.2 g. of pale green solid. The residue was dissolved in water and the solution was made basic with a saturated solution of barium hydroxide. The mixture was filtered and the barium was precipitated from the filtrate with an equivalent quantity of sulfuric acid. The mixture was filtered and the filtrate was evaporated to a volume of 5 ml. and cooled. The crystals which separated were removed, m.p. 338–339°; mixture melting point with a sample of 3-pyridinesulfonic acid, m.p. 330–334°, prepared by the sulfonation of pyridine[10] was 332–336°.

Anal. Calcd. for $C_5H_5NO_3S$: equiv. wt., 159. Found: equiv. wt., 160.

The ammonium salt was prepared from the reduction product, m.p. 217–233° dec. An authentic sample of ammonium 3-pyridinesulfonate melted at 217–233° dec. either alone or when mixed with the above sample.

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(13) H. S. Mosher, L. Turner and A. Carlsmith, *Org. Syntheses*, **33**, 79 (1953).

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2,2,2-Trifluoroethylnitroguanidine[1]

BY VIRGIL MILANI, SOL SKOLNIK AND ROBERT EVANS

RECEIVED DECEMBER 18, 1954

2,2,2-Trifluoroethylnitroguanidine has been obtained by the amination of N-nitro-S-methylpseudothiourea[2] with 2,2,2-trifluoroethylamine. This compound was used as an intermediate in the preparation of the picrate and nitrate salts of 2,2,2-trifluoroethylguanidine.

Experimental[3]

2,2,2-Trifluoroethylnitroguanidine.—To 10.1 g. (0.0747 mole) of N-nitro-S-methylpseudothiourea was added 15.0 g. (0.151 mole) of 2,2,2-trifluoroethylamine diluted with 1.0 g. of water. The mixture was heated at the reflux temperature for six hours, 2.2 g. (0.022 mole) of the amine added and then refluxed for an additional seven hours. The water and excess amine were removed under a vacuum and the residual crystalline material recrystallized from 90 ml. of hot water adjusted to a *p*H of 6 with sulfuric acid. The product was recovered in 94% yield based on the N-nitro-S-methylpseudothiourea and melted at 147–148°.

Anal. Calcd. for $C_3H_5O_2N_4F_3$: N, 30.1; F, 30.62; NO_2-N, 7.52. Found: N, 29.75; F, 30.51; NO_2-N, 7.45.

2,2,2-Trifluoroethylguanidine Picrate.—A mixture of 2.5 g. (0.0134 mole) of 2,2,2-trifluoroethylnitroguanidine, 0.125 g. of palladium black and 62 ml. of 15% acetic acid was placed in a modified Skita[4] hydrogenation apparatus and subjected to hydrogenolysis[5] overnight at slightly above atmospheric pressure and room temperature. The palladium black was removed and the filtrate treated with 3.07 g. (0.0134 mole) of picric acid in 25 ml. of hot absolute ethanol. The solution was allowed to crystallize overnight at room temperature. The yellow needle-like crystals began decomposing at 183° and were completely liquid at 193°.

Anal. Calcd. for $C_9H_9O_7N_6F_3$: N, 22.70; F, 15.40. Found: N, 22.7; F, 15.32.

2,2,2-Trifluoroethylguanidine Nitrate.—The picrate of 2,2,2-trifluoroethylguanidine (2.0 g., 0.0054 mole) was treated with 10 ml. of 20% nitric acid, the precipitated picric acid removed, and the filtrate extracted with ether until colorless. The remaining aqueous solution was evaporated to dryness, the residue dissolved in ethanol, and ether added until the crystalline precipitate of 2,2,2-trifluoroethylguanidine nitrate appeared. The nitrate salt melted at 134–136°.

Anal. Calcd. for $C_3H_7O_3N_4F_3$: N, 27.45; F, 27.94. Found: N, 27.40; F, 27.85.

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(1) Publication approved by the Bureau of Ordnance, Navy Department. The conclusions and opinions are those of the authors and are not to be construed as representing an official statement of the Navy Department.

(2) L. Fishbein and J. A. Gallaghan, THIS JOURNAL, **76**, 1877 (1954).

(3) All melting points were measured on a Kofler micro hot-stage.

(4) A. Skita and W. A. Meyer, *Ber.*, **45**, 3589 (1912).

(5) Procedure of Dr. J. A. Gallaghan of this Laboratory.

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Substituent Effects on the Reactions of Benzoate Ions with 2,4-Dinitrochlorobenzene and Methyl Iodide

BY LAWRENCE R. PARKS, GEORGE S. HAMMOND AND M. FREDERICK HAWTHORNE

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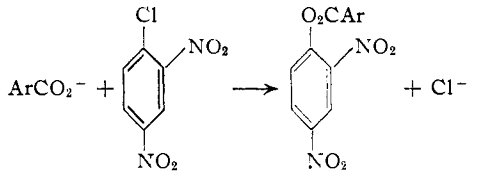
In a continuation of our studies designed to cast light upon the transition state configurations[1] involved in aromatic nucleophilic displacements we have investigated the effects of substituents on the nucleophilic reactivity of benzoate ions in reaction 1.



(1)

As is indicated by the data in Table I, the rates of reaction of benzoate, *p*-methoxybenzoate and *p*-

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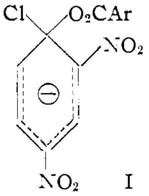
(1) For general discussion and references see G. S. Hammond and L. R. Parks, THIS JOURNAL, **77**, 340 (1955).

nitrobenzoate were grouped very closely together. Application of the Hammett equation

$$\log \frac{k}{k_0} = \rho\sigma \qquad (2)$$

to the data gives a value of -0.2 for the ρ-constant. This should be compared with an estimated value of ρ of about 1.5 for the ionization of benzoic acids in the same medium.[2] From the insensitivity to substituent effects we infer that the transition state in reaction 1 has not approached configuration I at all closely since in such a structure the


I

negative charge would be moved much farther from the polar substituent than it is in the carboxylate ion. In other words, bond formation has made only limited progress in the transition state.

TABLE I

RATE CONSTANTS FOR REACTION OF 2,4-DINITROCHLOROBENZENE AND METHYL IODIDE WITH POTASSIUM SALTS OF *p*-METHOXY-, *p*-NITRO- AND UNSUBSTITUTED BENZOIC ACID IN 60% DIOXANE SOLUTION

Halo cmpd.	Potassium benzoate	Temp., °C.	$k \times 10^{-6}$, l. mole^{-1} sec.$^{-1}$	ρ
Dinitro-	*p*-Methoxy-	93	47.6	
chloro-	Unsubstd.	93	41.7	
benzene	*p*-Nitro-	93	22.8	−0.20
Methyl	*p*-Methoxy-	25.5	14.7	
iodide	Unsubstd.	25.5	14.5	
Methyl iodide	*p*-Nitro-	25.5	9.47	−0.12

For purposes of comparison the rates of a typical displacement at a saturated carbon atom, reaction 3, were measured in the same solvent.

$$ArCO_2^- + CH_3I \longrightarrow ArCO_2CH_3 + I^- \qquad (3)$$

The ρ-constant for this reaction was found to be -0.120 which indicates that bond making is less complete in the aliphatic displacement than in the aromatic case. This is the comparison which would have been anticipated.

Since bond-breaking in displacements on aryl halides probably makes little progress until bond-making has been nearly completed[1] it would not be expected that displacement by benzoate would be aided by electrophilic catalysis. We attempted to study the rate of reaction of the same aryl halide with silver benzoate in acetonitrile as the solvent. The displacement reaction, if it occurred at all, was very slow and only tars were produced. The qualitative observation is at least consistent with our hypothesis.

This work, in conjunction with that previously reported, shows that the transition states in activated aromatic nucleophilic displacements vary a great deal in their location along the reaction coördinates for the various reactions. Benzoate ions should not represent an extreme example and bond-making should be even less important with more highly basic nucleophiles such as hydroxide, alkoxide or amide ions. It is interesting to note that the rates of displacements by substituted anilines on 2,4-dinitrochloronaphthalene and 2,4-dinitrochlorobenzene have very large ρ-constants,[4] a fact which is consistent with our view that the transition states in displacements by amines are located much farther along the reaction coördinate than is the case with strong negatively charged nucleophiles.

Experimental

Silver benzoate was prepared by treating 40 g. of benzoic acid in 300 ml. of water containing 11.7 g. of ammonium hydroxide with 56.7 g. of silver nitrate. The product was obtained as a heavy white crystalline material which was filtered, washed with water and methanol and dried in an oven at 70°. The product weighed 39 g. (53%) and did not darken with age. The use of ammonium hydroxide seemed very superior to the more commonly used sodium hydroxide which gives products that darken badly. Further purification was accomplished by recrystallization from acetonitrile as solvent. The process is tedious because of the limited solubility of the silver salt in acetonitrile.

Potassium salts of *p*-methoxybenzoic, *p*-nitrobenzoic acid and benzoic acids were prepared by adding slightly less than a stoichiometric amount of potassium hydroxide to a well-stirred slurry of benzoic acid in water. The water was then evaporated and the white solid was recrystallized several times from ethanol and dried in an oven at 70°.

2,4-Dinitrochlorobenzene was prepared by dinitration of chlorobenzene and purified by recrystallization from 80% ethanol, m.p. 51–52°.

Methyl iodide (Matheson, Coleman and Bell, Inc.) was purified by fractional distillation, b.p. 42–43°.

Reaction of Silver Benzoate with 1-Chloro-2,4-dinitrobenzene in Acetonitrile.—The insolubility of silver benzoate in acetonitrile limited the concentration to less than 0.005 *M*. Five ml. of 0.005 *M* silver benzoate was added to 5 ml. of 0.005 *M* 2,4-dinitrochlorobenzene in acetonitrile in a tightly stoppered tube. The contents were frozen in a Dry Ice-bath, evacuated and sealed off. The sealed ampules were placed in an oil-bath at 77°. The desired displacement reaction did not proceed cleanly and the reaction mixture became filled with a heavy, black, tarry deposit. Analysis of the mixture for halide ion gave very erratic results. It was decided to use potassium benzoate as an ion source rather than silver benzoate.

Kinetics of the Reaction of Potassium Benzoate with 2,4-Dinitrochlorobenzene in 60% Dioxane Solution.—The dioxane for use as solvent was purified by the method of Beste and Hammett.[5] Solid sodium hydroxide was added to the refluxing dioxane at intervals until no red, tarry material coated the freshly added sodium hydroxide pellets. After filtering, the dioxane was refluxed with metallic sodium for several hours until no discoloration of molten, freshly added sodium was noted. The system was protected from atmospheric moisture by a calcium chloride tube filled with drierite. At the end of the reflux period, the dioxane was subjected to fractional distillation and the middle fraction boiling at 101.8° was retained. The first and last quarters were discarded. Distilled water was added to make a solution 60% (by volume) dioxane which was used as a solvent in the following reactions.

Five ml. of 0.1 *M* potassium benzoate and 5 ml. of 0.1 *M* 2,4-dinitrochlorobenzene were placed in a constricted tube and immmediately frozen in a Dry Ice-bath. The tubes were evacuated and sealed off. The sealed ampules were placed in a bath at 93°. Individual tubes were removed at intervals, opened and poured into small separatory funnels containing 10 ml. of benzene, 4 ml. of nitrobenzene, 5 ml. of 1 *N* nitric acid and a carefully measured quantity of standard aqueous silver nitrate. The separatory funnel was shaken thoroughly and the aqueous layer was collected.

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(2) The value is estimated by extrapolation from dioxane–water media containing less dioxane.[3]

(3) H. L. Goering, T. Rubin and M. S. Newman, THIS JOURNAL, **76**, 787 (1954).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1939.

(5) G. Beste and L. Hammett, THIS JOURNAL, **62**, 2481 (1940).

The silver chloride is wet by the nitrobenzene and remains at the boundary between the two layers and this avoids the necessity of filtering it off. The benzene layer was washed carefully twice with 10-ml. portions of distilled water, and the three aqueous layers containing the excess silver nitrate were combined for analysis. The excess silver nitrate was determined by titration with potassium thiocyanate. The normal Volhard technique of using ferric alum as indicator was not sensitive enough to give good results. The end-point could be found much more accurately potentiometrically with a silver electrode in the titration cell and a standard calomel electrode connected by a salt bridge filled with potassium chlorate.

A typical rate run with equal concentrations of benzoate ion and 2,4-dinitrochlorobenzene is shown in Table II.

TABLE II

RATE CONSTANTS FOR REACTION OF POTASSIUM BENZOATE WITH 2,4-DINITROCHLOROBENZENE IN 60% DIOXANE AT 93°

Time increment, min.	$k \times 10^5$, l. mole^{-1} sec.$^{-1}$
720	4.27
960	4.37
1440	4.20
1680	4.21
2760	4.30
7650	4.03
Average	4.23

A second run was made with samples containing 0.1 *M* benzoic acid (concentration of the two reactants, 0.05 *M*) in order to test the possibility that the attacking reagent was the hydroxide ion produced by hydrolysis of benzoate. The rate constant obtained (3.67×10^{-5} l. mole^{-1} sec.$^{-1}$) was close enough to that obtained with no benzoic acid added to establish the fact that benzoate is the principal attacking species. To further establish this point a run was made with the concentration of potassium benzoate twice that of the substrate. The rate constant, 4.23×10^{-5} l. mole^{-1} sec.$^{-1}$, was the same as that obtained in the first run. The concentrations used and the rate constants obtained are summarized in Table III.

TABLE III

RATE CONSTANTS FOR REACTION OF POTASSIUM BENZOATE WITH 2,4-DINITROCHLOROBENZENE WITH VARYING CONCENTRATIONS OF REACTANTS

Run	Concn. potassium benzoate, mole/liter	Concn. of dinitro-chlorobenzene, mole/liter	Concn. benzoic acid, mole/liter	$K_{93} \times 10^5$, l. mole^{-1} sec.$^{-1}$
1	0.0500	0.0500		4.23
2	.0500	.0500	0.1000	3.67
3	.0667	.0333		4.23

The reactions of potassium *p*-methoxybenzoate and *p*-nitrobenzoate with 2,4-dinitrochlorobenzene were carried out in an identical manner with that described above for the potassium salt of the unsubstituted benzoic acid. The rate constants are summarized in Table I.

Investigation of Reaction Products.—When the reaction mixture was poured into a separatory funnel containing water and benzene, the aqueous layer was colored a distinct yellow. The addition of acid followed by shaking almost completely removed the color from the aqueous layer. The behavior led us to suspect that 2,4-dinitrophenol was formed by hydrolysis of the expected ester product during the reaction.

A sample of 2,4-dinitrophenyl benzoate was prepared by heating stoichiometric amounts of 2,4-dinitrophenol and benzoyl chloride in an oil-bath at 180° for two hours. The product was recrystallized from benzene to give a pale yellow crystalline material, m.p. 132–133°. Solutions of this ester in 60% dioxane were heated with potassium benzoate at 93° for 12 hours. The solutions became a darker yellow with heating and when poured into a separatory funnel containing benzene and water the same color changes described above were noted. Evaporation of the aqueous layer (not acidified) yielded a considerable amount of the potassium salt of 2,4-dinitrophenol. These results indicate that the replacement of halogen from activated aromatic positions would not be a good method of preparing the corresponding phenyl esters.

The Displacement of Iodide from Methyl Iodide by Benzoate Ions.—The reaction conditions and method of analysis were identical with those in the preceding section. It was unnecessary to use nitrobenzene to wet the silver halide since silver iodide does not interfere with Volhard determinations.[6] The reaction was run at 93° in sealed ampules and proceeded to completion in a few hours. A sample without the benzoate attacking agent showed a considerable amount of displaced iodide after a few hours of heating at 93°. This was attributed to hydrolysis at the high temperature. The reaction then was run at a lower temperature of 25.5° where hydrolysis is much slower but still not negligible. Corrections for the amount of hydrolysis were applied by running blanks.[7] The rate constants obtained are listed in Table I.

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(6) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 185.

(7) It has been pointed out by a referee that the blank does not necessarily correct the bimolecular displacement by hydroxide ion produced by the hydrolysis of the benzoate ions. One could seek an explicit demonstration that this side reaction is unimportant by applying the same test as was reported above in the case of displacements on the activated aryl halides. This was not deemed necessary in the case of the methyl iodide reaction since the relative importance of reaction by the benzoate ions and hydroxide can be estimated readily by the method of Swain and Scott.[8] The *n* value for hydroxide is 4.2 and that for benzoate ions cannot be a great deal less than 2.7, the value for acetate. The *s*-value for methyl iodide is 1.15[9] so the value of log ($k_{OH^-}/k_{RCO_2^-}$) must be of the order of 1.7 to 2.0. In water the hydrolysis of benzoate (K_i for benzoic acid is 6.8×10^{-5}) in a 0.1 *N* solution would produce hydroxide ion at a concentration of less than 10^{-6} *M*. This means that $k_{RCO_2^-}[RCO_2^-]$ would exceed $k_{OH^-}[OH^-]$ by about two orders of magnitude. In the dioxane–water mixture the hydrolysis would be still less extensive and the rate difference would become still larger.

(8) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(9) M. F. Hawthorne, G. S. Hammond and B. M. Graybill, *ibid.*, **77**, 486 (1955).

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The Synthesis of α-Methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$ butenolide and its Reduction with Lithium Aluminum Hydride

BY FAUSTO RAMIREZ AND MORDECAI B. RUBIN[1]

RECEIVED DECEMBER 15, 1954

During an investigation[2] into the possibility of effecting partial reduction of γ-aryl-$\Delta^{\alpha,\beta}$- and γ-aryl-$\Delta^{\beta,\gamma}$-butenolides with lithium aluminum hydride, α-methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$-butenolide (I) was prepared from α-methyl-β-(2-naphthoyl)-propionic acid (III). The $\Delta^{\alpha,\beta}$-butenolide I resulted from the keto-acid III upon treatment with a few drops of sulfuric acid in an acetic acid–acetic anhydride mixture. The isomeric $\Delta^{\beta,\gamma}$-butenolide could not be obtained under conditions which yielded the $\Delta^{\beta,\gamma}$-butenolide from β-benzoyl-α-methylpropionic acid.[2] The similarity between the course of reduction of α-methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$-butenolide (I) and α-methyl-γ-phenyl-$\Delta^{\alpha,\beta}$-butenolide[2] with lithium aluminum hydride is indicated by the considerable similarity of the infrared spectra obtained from the crude reaction products in each case. No partial reduction to γ-hydroxy-α,β-unsaturated aldehyde was achieved.

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(1) Union Carbide and Carbon Fellow, 1952–1953. From part of the Ph.D. Thesis of M.B. Rubin.

(2) F. Ramirez and M. B. Rubin, THIS JOURNAL, **77**, in press (1955).