

It seems therefore that except for Hg, the group II organometal halides exist as $R_2M \cdot MX_2$ complexes rather than as RMX . The reason for this is not immediately obvious.

Further work in the Zn and Ba systems is now being conducted.

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ment, and Dr. Byron Branson of the Robert A. Taft Sanitary Engineering Center of the U. S. Public Health Service for the use of counting equipment, and to acknowledge the financial support in the form of a Frederick G. Cottrell Grant from the Research Corporation. He also wishes to express his gratitude for stimulating conversations with Dr. George S. Handler, Tufts University. CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

The Electrochemical Degradation of Quaternary Ammonium Salts. II. The Mechanism of the Coupling Reaction

BY SIDNEY D. ROSS, MANUEL FINKELSTEIN AND RAYMOND C. PETERSEN

RECEIVED JULY 2, 1959

The cathodic decomposition in *N,N*-dimethylacetamide or dimethylformamide of quaternary ammonium nitrates containing benzyl, fluorenyl, cinnamyl, *p*-methoxybenzyl or α -phenylethyl groups yields the coupling products of these radicals. The reaction involves the generation and dimerization of free radicals, formed in a one-electron transfer at the cathode. This is indicated by the fact that *d*- α -phenylethyltrimethylammonium nitrate gives only inactive products.

In a previous report from this Laboratory,¹ it was shown that the electrolysis of aqueous solutions of selected quaternary ammonium salts resulted in the cleavage of one of the alkyl groups attached to nitrogen to form a hydrocarbon and a tertiary amine. For one salt, benzyldimethylanilinium trifluoroacetate, the electrolyses were carried out in both water and dimethylacetamide. In water the products were toluene and dimethylaniline but, in the latter solvent, the same amine and bibenzyl were obtained. It is our present purpose to show that coupling products are generally obtained when the reaction is effected in an appropriate non-aqueous solvent of high dielectric constant and, further, to cite evidence which indicates that these reactions involve the formation and subsequent reactions of free radical intermediates at the electrode.

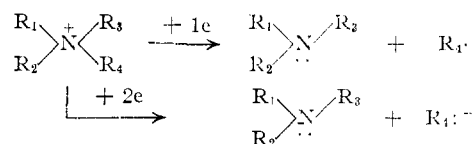
The results of six preparative experiments are summarized in Table I. The solvent in these experiments was either dimethylacetamide or dimethylformamide. No effort was made to ensure the complete decomposition of the quaternary ammonium ions in these electrolyses, and conditions for maximizing the yields were not explored. These results, therefore, have only qualitative significance and do not permit any clear decision as to the possible preparative value of this reaction.

TABLE I
CATHODIC COUPLING REACTIONS

Quaternary ammonium nitrate	Product	Yield, %
Benzyltriethylammonium	Bibenzyl	31.9
Benzyltrimethylanilinium	Bibenzyl	35.0
<i>p</i> -Methoxybenzyltrimethylammonium	4,4'-Dimethoxybibenzyl	15.0
Cinnamyltrimethylanilinium	Dicinnamyl	6.0
Fluorenyltrimethylammonium	Difluorenyl	26.1
α -Phenylethyltrimethylammonium	2,3-Diphenylbutane	30.0

(1) M. Finkelstein, R. C. Petersen and S. D. Ross, *THIS JOURNAL*, **81**, 2361 (1959).

The problem of mechanism for these reactions resolves itself into the question of whether the cathodic reaction involves a one-electron change and the formation of radical intermediates or, alternatively, a two-electron transfer and carbanion intermediates. The two possibilities may be formulated as



The coupling product could result either from dimerization of the radicals or a nucleophilic displacement reaction by the carbanion on the quaternary ammonium ion.²

Some qualitative evidence which favors the free-radical mechanism has been presented,¹ but definitive proof is lacking. An experiment with an optically active quaternary ammonium salt would permit a clear choice between the alternatives provided that the cleavage occurred at the asymmetric carbon atom and the coupled product was not formed in only the *meso* form. α -Phenylethyltrimethylammonium nitrate proved suitable for this purpose. It could be obtained optically active and gave both *meso*- and *dl*-2,3-diphenylbutane on electrolysis. In the electrochemical decomposition of active α -phenylethyltrimethylammonium nitrate, that portion of the hydrocarbon product which was not *meso* would be expected to be totally inactive, if free radicals are the intermediates. Since the radicals, if formed, are formed singly rather than in pairs, this is a more straightforward case than the decomposition of a diacyl peroxide where

(2) Mechanisms involving hydrogen abstraction from the quaternary ammonium ion by the carbanion, $R_4 \cdot^-$, have not been considered, since the hydrocarbon R_4H was not found in the products under the present experimental conditions. Hydrogen abstraction is, in fact, a more probable reaction for these species than is displacement, and this may be considered as evidence against the carbanion mechanism.

a cyclic decomposition mechanism or cage effects can result in the formation of some optically active coupled product. In fact, some active 2,3-diphenylbutane was obtained by Greene from the reaction of active hydratropoyl chloride with sodium peroxide.³ The ionic mechanism, in contrast, demands that some optically active 2,3-diphenylbutane be formed. This is true whether or not the carbanion formed at the electrode retains its configuration, since the final product is formed by a displacement reaction on the asymmetric carbon atom of the quaternary ammonium ion. This reaction would proceed with inversion rather than racemization of this latter carbon atom.

d- α -Phenylethylamine ($[\alpha]^{25D} +31.3^\circ$) was converted to *d*- α -phenylethyltrimethylammonium iodide ($[\alpha]^{25D} +12.1^\circ$), and the iodide was transformed to the nitrate ($[\alpha]^{25D} +22.6^\circ$). Electrolysis of the nitrate in dimethylformamide resulted in a 30% yield of a mixture of *meso*- and *dl*-2,3-diphenylbutane. The bulk of the *meso*-hydrocarbon was separated from the mixture by crystallization from methanol. The remaining product, a liquid at room temperature, was shown both by vapor phase chromatography and infrared analysis to consist of trace amounts of acetophenone, less than 15% of the *meso* isomer and the remainder, *dl*-2,3-diphenylbutane. This latter fraction was completely devoid of optical activity.⁴

Two experiments attest to the optical stability of α -phenylethyltrimethylammonium nitrate under the experimental conditions. The *d*-salt (15% solution in dimethylformamide) had $[\alpha]^{25D}$ equal to $+18.0^\circ$ initially and $[\alpha]^{25D}$ equal to $+17.7^\circ$ after standing in solution at room temperature for 50 hr. Since the electrolysis was carried out in an ice-water-bath for 17.8 hr., it is concluded that there is no appreciable racemization in the absence of an electric field. In a second experiment, the *l*-salt ($[\alpha]^{25D} - 18.4^\circ$) was electrolyzed partially, and the undecomposed salt was recovered. Although the salt was not obtained completely pure and could not be crystallized, its activity was only slightly lower ($[\alpha]^{25D} -16.9^\circ$). The hydrocarbon product was isolated and proved to be identical in composition to that obtained in the more complete electrolysis.

This result is in accord with the free-radical mechanism. A one-electron transfer at the cathode results ultimately in the formation of α -phenylethyl radicals which then dimerize to give the observed final products. Since the radicals involved would not be expected to maintain a tetrahedral configuration, the diphenylbutane obtained would show no optical activity. Equally important, this optical result is inconsistent with a carbanion mechanism. This experiment, therefore, permits a choice between the two classes of mechanisms.

It seemed of interest to compare the composition of the 2,3-diphenylbutane product obtained by a

(3) F. D. Greene, *THIS JOURNAL*, **77**, 4869 (1955).

(4) 2,3-Diphenylbutane has been resolved (H. H. Richardson, E. J. Underhill, A. C. Brook and G. F. Wright, *ibid.*, **69**, 937 (1947)). The specific rotation of the *dd*-isomer was -94.9° while that of the *ll*-2,3-diphenylbutane was $+99.8^\circ$. Since these specific rotations are high, even small amounts of active product in our experiment would be detectable, and the optical course of the electrochemical reaction is unequivocal.

known free-radical process. The decomposition of 1-azo-bis-1-phenylethane was chosen for this purpose,⁵ and the reaction was studied both in dimethylformamide and in the absence of a solvent. The results are summarized in Table II. The most precise analytical result is for the decomposition of the azo compound in the absence of solvent, and it is possible that the other two results are identical with it, within the limits of experiment accuracy. At any rate, there are no large differences in the product compositions.

TABLE II

Reaction	% <i>meso</i>	% <i>dl</i>
Electrolysis of quaternary ammonium compd.	46	54
Decompn. of azo compd., no solvent	41.5	58.5
Decompn. of azo compd. in dimethylformamide	50	50

Finally, an effort was made to prepare 2,3-diphenylbutane by an ionic reaction. The Grignard reagent prepared from α -phenylethyl bromide was allowed to react with *dl*- α -phenylethyltrimethylammonium iodide. This resulted in a 32% yield of a mixture of roughly equal parts of *meso*- and *dl*-2,3-diphenylbutane. However, a similar yield of the diphenylbutane resulted when the same Grignard reagent was treated with benzyltriethylammonium chloride. In this latter case, the product of a displacement reaction on the quaternary ammonium ion would have been 1,2-diphenylpropane. We conclude, therefore, that in both of the above reactions, the diphenylbutane was formed during the preparation of the Grignard reagent.

Experimental

All melting points and boiling points are uncorrected.

Solvents.—Dimethylformamide (DMF) was dried and purified according to Method I of Thomas and Rochow.⁶ A middle fraction, b.p. 34° at 8 mm., was used.

N,N-Dimethylacetamide (DMA), Eastman Kodak Co. white label, was shown by vapor phase chromatography (v.p.c.) to contain only a very small amount of water as an impurity.

Electrolysis Procedure.—The electrolysis cell consisted of a 150-ml. tall-form beaker containing a solution of the organic salt. An ice-water-bath surrounded the cell, and the cell contents were mixed with a magnetic stirrer. The cathode was a cylindrical piece of aluminum foil, 5 cm. high and 7.6 cm. in circumference, immersed in the solution. A gold wire anode dipped into the solution inside the cathode. Current was supplied by a voltage regulated d.c. power supply. The applied voltages varied from 60 to 200 volts. An ammeter was connected in series. Unless otherwise stated, the amperage indicated for the individual electrolyses did not vary more than 10% during an experiment.

Quaternary Ammonium Halides.—These various salts were prepared as described in the previous paper¹: benzyltriethylammonium chloride, benzyldimethylanilinium bromide, fluorenyltrimethylammonium bromide.

α -Phenylethyltrimethylammonium iodide was prepared according to Norcross and Openshaw.⁷

Cinnamyl dimethylanilinium bromide was prepared by the reaction of cinnamyl bromide with dimethylaniline.

Anal. Calcd. for $C_{17}H_{20}NBr$: Br, 25.11. Found: Br, 25.16.

Quaternary Ammonium Nitrates.—The conversion of the quaternary ammonium halides to the hydroxides has been described.¹ Aqueous solutions of the quaternary ammonium hydroxides were neutralized to phenolphthalein with 1:4 nitric acid, and the water was removed *in vacuo*.

(5) S. G. Cohen, S. J. Groszoz and D. B. Sparrow, *ibid.*, **72**, 3497 (1950).

(6) A. B. Thomas and E. G. Rochow, *ibid.*, **79**, 1843 (1957).

(7) G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1174 (1949).

The solids obtained were crystallized from isopropyl alcohol-ether.

Alternatively, an aqueous solution of the quaternary ammonium halide was treated with the theoretical amount of silver nitrate solution. The silver halide was filtered, and the salt was obtained by concentration *in vacuo*.

The quaternary ammonium nitrates prepared and their melting points are: benzyltriethylammonium, 108–110°; benzyltrimethylammonium, 156–157°; fluorenyltrimethylammonium, 171–175°; cinnamyltrimethylammonium, 107–108°; α -phenylethyltrimethylammonium, 69–72°.

Fluorenyltrimethylammonium nitrate was analyzed by the Kjeldahl method.

Anal. Calcd. for $C_{16}H_{18}N_2O_3$: N, 9.78. Found: N, 9.60.

Optically Active α -Phenylethyltrimethylammonium Nitrate.— α -Phenylethylamine was resolved by the procedure of Ingersoll.⁹ The *d*-isomer, $[\alpha]^{25}_D +31.3^\circ$ (*l*, 1 dm., 7.5% in ethanol), was converted to α -phenylethyltrimethylammonium iodide, $[\alpha]^{25}_D +12.1^\circ$ (*l*, 1 dm., 5% in water), by the method of Norcross and Openshaw.⁷ The usual procedure was used to prepare the nitrate, $[\alpha]^{25}_D +22.6^\circ$ (*l*, 1 dm., 7% in DMF). The *l*-isomer was converted by the same sequence to the quaternary ammonium nitrate, $[\alpha]^{25}_D -18.4^\circ$ (*l*, 1 dm., 15% in DMF).

***p*-Methoxybenzyltrimethylammonium Trifluoroacetate.**—A solution of *p*-methoxybenzyltrimethylamine¹⁰ (18 g., 0.109 mole) in acetone was treated with an excess of methyl iodide in acetone. A vigorous reaction occurred, and the mixture was let stand. On addition of ether to complete precipitation, *p*-methoxybenzyltrimethylammonium iodide (30 g., 88%) was obtained.

Anal. Calcd. for $C_{11}H_{18}ONI$: I, 41.32. Found: I, 41.90.

An aqueous solution of the salt (15 g.) was stirred magnetically with an excess of silver oxide. The clear solution, obtained by filtration, was neutralized with trifluoroacetic acid. The water was removed *in vacuo*, and the residual white, crystalline solid (9 g., 63%) was used directly in the electrolysis.

Bifluorenyl.—Authentic bi-9-fluorenyl was prepared by the Clemmensen reduction of fluorenone according to Harris, White and McNeil.¹¹ Chromatography on alumina and two crystallizations from benzene-ethanol gave white needles, m.p. 236–238°.

***meso*- and *dl*-2,3-Diphenylbutane.**—The procedure of Conant and Blatt was modified.¹² A solution of α -bromoethylbenzene (80.5 g., 0.435 mole) in ether (200 ml.) was added slowly to magnesium (10.6 g., 0.435 g. at.) in a 1-liter, 3-necked flask equipped with a mechanical stirrer and reflux condenser. A vigorous reaction ensued, and the mixture was refluxed with stirring for 2.5 hr. after the addition of the halide was completed. Anhydrous cupric chloride (53 g., 0.394 mole; dried at 110° for 24 hr.) was added in portions with stirring, after which the mixture was refluxed for an additional 45 minutes. Ice and dilute hydrochloric acid were added cautiously with stirring and external cooling until no further heat was evolved. The mixture was extracted three times with ether, and the ether extracts were washed with water, saturated sodium bicarbonate solution and finally water again. The solution was dried over magnesium sulfate; the ether was distilled and the residue was taken up in hot hexane. Methanol was added, and the hexane was boiled away. On cooling, 15.3 g. of the *meso*-compound was obtained, m.p. 122–124° after recrystallization from methanol. The mother liquors were concentrated, yielding an additional 1.4 g. of the *meso* isomer (total yield 36.6%). Distillation of the mother liquor gave 14.9 g. (32.7%) of the *dl*-isomer; b.p. 78–83° at 0.1 mm., n^{25}_D 1.5548, n^{25}_D 1.5533 after redistillation.

1-Azo-bis-1-phenylethane.—Acetophenone azine was prepared and reduced to the hydrazine, which was isolated as the hydrochloride, as described by Cohen, Groszos and

Sparrow.⁵ We found it more convenient to effect the oxidation of the hydrazine to the azo compound using mercuric oxide rather than hydrogen peroxide. In a typical preparation the hydrazine hydrochloride (0.05 mole) was partitioned between 10% sodium hydroxide (100 ml.) and ether (100 ml.). The aqueous layer was extracted again with ether (100 ml.). The ether extracts were combined and dried over magnesium sulfate. The solution was separated from the drying agent and stirred at room temperature for 7 hours with mercuric oxide (0.10 mole). The solids were filtered, the solvent was removed and the crude product was crystallized from methanol. The yields of 1-azo-bis-1-phenylethane, m.p. 72–74°, varied between 45 and 60%.

Decomposition of 1-Azo-bis-1-phenylethane in DMF.—A solution of the azo compound (4.76 g., 0.02 mole) in DMF (100 ml.) was heated at 110° for 23 hr. The reaction mixture was poured into salt water (1 liter) and extracted three times with ether. The ether extracts were washed twice with water and dried over magnesium sulfate. The ether was distilled through a Vigreux column, and the residue was dissolved in a minimum of hot methanol. Cooling gave 1.56 g. of *meso*-2,3-diphenylbutane, m.p. 120–122°. The methanol was removed from the mother liquor, and the residue was distilled *in vacuo* through a short-path still, yielding 2.15 g. of a yellowish liquid, n^{25}_D 1.5566. The liquid was shown by v.p.c. to be largely 2,3-diphenylbutane (approximately 6 parts *dl*- to 1 part *meso*-isomer) contaminated with a small amount of acetophenone. This was confirmed by infrared spectroscopy. The total product composition was roughly 50% *meso*- and 50% *dl*-2,3-diphenylbutane.

Decomposition of 1-Azo-bis-1-phenylethane without Solvent.—The azo compound (2 g., 0.0084 mole) was sealed *in vacuo* in a 300-ml. flask. After heating at 105–110° for 18 hr., analysis of the flask contents by infrared showed 41.5% *meso*- and 58.5% *dl*-2,3-diphenylbutane.

Analysis of 2,3-Diphenylbutane Mixtures.—The analytical methods used to determine the composition of mixtures containing *meso*- and *dl*-2,3-diphenylbutane warrant some comment. When the two isomers are free from any third component, analysis by infrared spectroscopy is the preferred method. The spectra were taken on 0.25 *M* solutions in carbon disulfide using a Baird spectrophotometer, and the bands at 9.5 and 12.5 μ , present in the *meso*-isomer but absent in the *dl*-isomer, were used to determine the percentage composition. Since there is no suitable absorption band uniquely characteristic of the *dl*-modification, this method becomes unsatisfactory when a third component is present. In this circumstance, vapor phase chromatography becomes the preferred procedure. A Perkin-Elmer model 154B vapor fractometer with a K column operated at 220° and 20 lb. helium pressure was used. The retention times were in the neighborhood of 20 minutes for both isomers, with the *dl*-2,3-diphenylbutane appearing approximately 1.5 minutes earlier than the *meso*.

Electrolyses. Benzyltriethylammonium Nitrate.—A solution of the salt (12.7 g., 0.05 mole) in DMA (100 ml.) was electrolyzed for 16.5 hr. at 0.2 amp. The cell contents were poured into salt water (1000 ml.) and extracted with ether. The extract was washed with water, 1:1 hydrochloric acid and again with water. The solution was dried over magnesium sulfate, and the ether distilled through a Vigreux column. The residual solid, 1.45 g. (31.9%), melted at 48.5–50.5°. Crystallization from methanol gave white crystals, m.p. 51–52°; mixed m.p. with authentic bibenzyl,¹³ 51.5–53°.

Benzyltrimethylammonium Nitrate.—A solution of the salt (13.7 g., 0.05 mole) in DMF (100 ml.) was electrolyzed for 16 hr. at 0.2 amp. The cell contents were poured into salt water (1000 ml.), and the solution was extracted four times with 250-ml. portions of ether. The ether extract was washed twice with water, three times with 100-ml. portions of 1:1 hydrochloric acid and again with water. The ether solution was dried over magnesium sulfate, and the ether was distilled through a Vigreux column, leaving 1.60 g. (35%) of an off-white solid. Crystallization from methanol gave white crystals, m.p. 51–53°; mixed m.p. with authentic bibenzyl, 52–54°.

Cinnamyltrimethylammonium Nitrate.—A solution of the salt (7 g., 0.0233 mole) in DMF (100 ml.) was electrolyzed for 11.8 hr. at 0.2 amp. The cell contents were worked up in

(8) S. D. Ross and M. Finkelstein, *This Journal*, **79**, 6547 (1957).

(9) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 506.

(10) E. L. Eliel, T. N. Ferdinand and Sr. M. C. Herrman, *J. Org. Chem.*, **19**, 1693 (1954).

(11) A. S. Harris, E. N. White and D. McNeil, *J. Chem. Soc.*, 4216 (1955).

(12) J. B. Conant and A. H. Blatt, *This Journal*, **50**, 551 (1928).

(13) Y. I. Miukhaenko and N. P. Protasava, *J. Russ. Phys. Chem. Soc.*, **53**, I, 347 (1921); *C. A.*, **18**, 2338 (1924).

the usual manner except that benzene was used for the extractions. The product was obtained as white crystals, m.p. 69–71°, yield, 165 mg. (6%). Crystallization from methanol gave white plates, m.p. 76°. The melting point reported for bicinnamyl is 81–82°.¹⁴ The trinitrobenzene complex formed orange needles, m.p. 143–144°, reported¹⁴ m.p. 145°.

***p*-Methoxybenzyltrimethylammonium Trifluoroacetate.**—A solution of the salt (9 g., 0.03 mole) in DMA (100 ml.) was electrolyzed at an average current of 0.11 amp. (The initial current of 0.17 amp. fell to 0.05 amp. during the course of the electrolysis.) The cell contents were poured into water and filtered. An off-white solid, 526 mg. (15%), was obtained. After crystallization from ethanol the m.p. was 124°; m.p. reported¹⁵ for *p,p'*-dimethoxybibenzyl, 125°.

Fluorenyltrimethylammonium Nitrate.—A solution of the salt (14.3 g., 0.05 mole) in DMF (100 ml.) was electrolyzed for 10 hr. at a current of 0.2 amp. The cell contents were poured into water and filtered with suction. The resultant dark solid was digested with benzene, and the benzene was removed *in vacuo*. The residue was digested four times with hexane, and the hexane was evaporated to give an orange-white solid, 2.15 g. (26.1%). Two crystallizations from benzene-ethanol gave material with m.p. 233–236°; mixed m.p. with authentic bifluorenyl, 235–237°.

***d*- α -Phenylethyltrimethylammonium Nitrate.**—A solution of the dextrorotatory salt (7.0 g.) in DMF (100 ml.) was electrolyzed for 17.8 hr. at 0.4 amp. The initial voltage was 65 v., and the final voltage necessary to maintain the current constant was 100 v. The cell contents were poured into salt water (1000 ml.). The solution was extracted four times with ether, and the ether extracts were washed successively with water, 1:1 hydrochloric acid, water, saturated sodium bicarbonate solution and water. After drying over magnesium sulfate, the ether was distilled through a Vigreux column, and the residue was taken up in a small amount of hot methanol. On cooling, a white solid (355 mg.) was obtained, m.p. 121–122°; mixed m.p. with authentic *meso*-2,3-diphenylbutane, 122–123°. The methanol was distilled from the mother liquor, and the residue was distilled *in*

vacuo through a short-path still to yield 624 mg. of product, n_D^{20} 1.5512. The total yield of 2,3-diphenylbutanes was 30%.

The above liquid product was completely devoid of optical activity. It was analyzed by v.p.c. and shown to consist almost entirely of mixed 2,3-diphenylbutanes, containing a maximum of 15% of the *meso*-isomer. A very small amount of acetophenone also was present. These analytical results were confirmed by infrared spectroscopy. Repeat experiments gave the same optical results, and the same percentages of *meso*- and *dl*-products were obtained with the *dl*-salt.

Two experiments demonstrate that α -phenylethyltrimethylammonium nitrate is optically stable under the experimental conditions. The *d*-salt (15% in DMF) had $[\alpha]_D^{25}$ equal to +18.0° initially and $[\alpha]_D^{25}$ equal to +17.7° after standing in solution for 50 hr. at room temperature. In a second experiment a solution of 19.9 g. (0.088 mole) of the *l*-salt ($[\alpha]_D^{25} - 18.4^\circ$) in 130 ml. of DMF was electrolyzed for 3.9 hr. at 0.4 amp. with an applied voltage of 75 v. The observed rotation for this solution was -2.82° . If the current efficiency were 100%, 5.9 hr. would be required for total reaction. After electrolysis the light yellow solution was filtered, and the observed rotation was -2.37° . The DMF was distilled *in vacuo* and the residual oil was distributed between water and ether. The ether layer was dried over magnesium sulfate and distilled. The product, consisting of mixed 2,3-diphenylbutanes (infrared spectrum), amounted to 0.771 g. (0.00367 mole). Using the amount of product isolated as a measure of the extent of decomposition of *l*- α -phenylethyltrimethylammonium nitrate, the optical activity of the unreacted salt was calculated; $[\alpha]_D^{25} - 16.9^\circ$ (1 dm., 14% in DMF). The aqueous layer was concentrated to a tan oil which could not be induced to crystallize. It was sucked as dry as possible and its optical rotation was determined; $[\alpha]_D^{25} - 15.6^\circ$ (1 dm., 17% in DMF). Since the salt was not pure, this is a minimum value and less reliable than the previous rotation.

Acknowledgment.—We are indebted to Dr. E. Robert Coburn of Bennington College for the resolution of α -phenylethylamine and Mr. John E. Barry of these laboratories for the infrared spectra. NORTH ADAMS, MASS.

(14) J. v. Braun and Z. Kohler, *Ber.*, **51**, 79 (1918); R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 144 (1928).

(15) J. S. Buck and S. S. Jenkins, *THIS JOURNAL*, **51**, 2162 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT SANTA BARBARA]

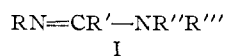
Mechanism of Hydrolysis of N,N'-Diarylformamidines in Acidic Solutions

BY ROBERT H. DEWOLFE

RECEIVED AUGUST 11, 1959

The effects of aryl substituents, temperature, solvent polarity, solvent acidity and nucleophilic catalysts on the rate of hydrolysis of symmetrically substituted N,N'-diarylformamidines have been investigated. In solutions of mineral acids, rate of hydrolysis is given by the equation $k_1 = C_{\text{H}_3\text{O}^+} a_{\text{H}_2\text{O}}/h_0$. This fact and other experimental observations indicate that diarylformamide hydrolysis in acidic solutions involves nucleophilic attack by water on hydrated amidinium ions.

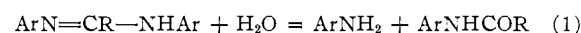
Mechanisms of hydrolysis and saponification of amides have been worked out in some detail.¹ Very little information is available concerning hydrolysis reactions of amidines, however. These compounds (I)



are nitrogen analogs of amides, and undergo many of the same reactions, such as hydrolysis, saponification and aminolysis. They differ from amides primarily in being much more basic.

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 784; (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 295; (c) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 365; (d) J. T. Edwards and S. C. R. Meacock, *J. Chem. Soc.*, 2000 (1957).

The only kinetic investigation of formamide hydrolysis yet reported is that of DeWolfe and Roberts,² who studied the hydrolysis of N,N'-diphenylformamide in acidic aqueous dioxane. This reaction (equation 1, Ar = C₆H₅, R = H) yields aniline and formamide



The formamide hydrolyzes, more slowly, to aniline and formic acid. Hydrolysis of this amidine was found to be general acid-catalyzed in buffer solutions. In dilute hydrochloric acid solutions, the rate of hydrolysis was nearly independent of hydrogen ion concentration and ionic strength. The reaction was found to obey the rate equation

(2) R. H. DeWolfe and R. M. Roberts, *THIS JOURNAL*, **76**, 2942 (1953).