[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKYLN, AND THE U. S. VITAMIN CORPORATION]

Monomer Synthesis.[1] Triazines. A Novel Method for the Reduction of Halomethyl Groups in the Triazine Series

BY SEYMOUR L. SHAPIRO[2] AND C. G. OVERBERGER

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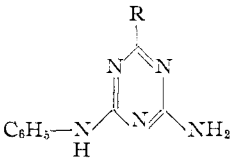
The reaction of phenylbiguanide with ethyl α-chloroacetate, methyl dichloroacetate, ethyl trichloroacetate, ethyl α-bromopropionate and ethyl β-bromopropionate to give derivatives of I, R = CH_2Cl, $CHCl_2$, CCl_3, OH and $CHBr{-}CH_3$, is described. The replacement of the chlorine or bromine in the halomethyl substituted triazines with hydrogen by reaction with iodide ion in acidic acetone is the first example of this interesting reaction in a nitrogen heterocyclic system. Evidence as to the course of the reaction between phenylbiguanide and ethyl trichloroacetate to give I, R = OH, as the major product is presented.

One of our proposed routes to a vinyltriazine led us to investigate the synthesis of compounds of Type I, R = CH_2Cl and $CHCl_2$. Thurston[3] has reported the reaction of the parent biguanide with haloesters to give haloalkyl guanamines in low boiling alcohols with or without alkoxide catalysts.

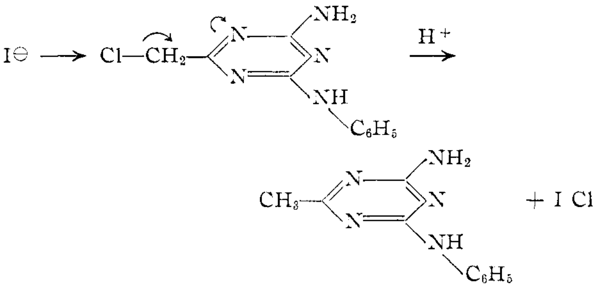


I

No examples of any simple halo substituted esters of the type studied here were reported. Recently[4] the alkoxide-catalyzed reaction of ethyl α-chloroacetate with biguanide has been reported to give 6-chloromethyl-2,4-diamino-*s*-triazine in 45% yield.

Slotta and Tschesche[5] also studied the reaction of ethyl α-chloroacetate with biguanide and reported a different reaction path to give a bicyclic derivative isolated as the hydrochloride salt, although their proposed structure is open to question as no evidence was offered.

This paper describes the reaction of phenylbiguanide with ethyl α-chloroacetate, methyl dichloroacetate, ethyl trichloroacetate, ethyl α-bromopropionate and ethyl β-bromopropionate. When phenylbiguanide is allowed to react with ethyl α-chloroacetate with a sodium methoxide catalyst in anhydrous methanol a 54% yield of I, R = CH_2Cl, was obtained. Hydrogenation of I, R = CH_2Cl, over palladium-on-calcium carbonate in ethanol, resulted in absorption of the theoretical amount of hydrogen to give I, R = CH_3, in 89.1% yield, identical with a known sample of I, R = CH_3, prepared from ethyl acetate and phenylbiguanide. Evidence as to the structures of I, R = CH_2Cl, was also obtained by the use of a reaction recently developed by Blatt,[6] namely, the reaction of picryl chloride with an acidic acetone solution of sodium iodide to give trinitrotoluene. When I, R = CH_2Cl, was treated in a similar fashion and the reaction quenched after 10 minutes, a 54.6% yield of I, R = CH_3, was obtained. This reaction can best be explained as a nucleophilic attack of iodide ion on chlorine, the process aided by the electron withdrawing properties of the nitrogen atoms which provide a seat for the charge. The reaction may also proceed by displacement on carbon of the chlorine to give the iodo compound followed by displacement of iodide ion on the iodine of the iodomethyl group.



This is the first example of this interesting type of reaction in a nitrogen heterocyclic system.

Compound I, R = CH_3, also was prepared by the reaction of phenylbiguanide and isopropenyl acetate in a methanol solution in 38.7% yield. The interesting feature of this reaction is that it proceeds smoothly without alkaline catalysis at room temperature.

The reaction of phenylbiguanide with methyl dichloroacetate under similar conditions gave I, R = $CHCl_2$, in 60.5% yield. Hydrogenation of I, R = $CHCl_2$, over palladium-on-calcium carbonate in ethanol gave I, R = CH_3, in 90% yield (100% of theoretical hydrogen absorption). I, R = $CHCl_2$, is very unreactive. The reaction with iodide ion in acetone failed and only starting material was recovered. The compound is completely stable in water and is recovered unchanged on heating with potassium acetate in acetic acid. These facts are consistent with, and are best explained by, steric hindrance to S_N2 displacement by iodide ion on either chlorine or carbon. Ostrogovitch[7] has reported that 2-dichloromethyl-4,6-diamino-*s*-triazine and the corresponding tribromo compound are stable in hot water.

I, R = $CHCl_2$, gave an immediate precipitate

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[1] This is the seventh in a series of articles concerned with the synthesis of vinyl monomers. For the preceding paper see C. G. Overberger and S. L. Shapiro, THIS JOURNAL, **76**, 93 (1954).

[2] A portion of a thesis by Seymour L. Shapiro, submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] J. T. Thurston, U. S. Patent 2,463,471, March 1, 1949.

[4] V. Ettel and J. Nosek, *Chem. Listy*, **46**, 289 (1952).

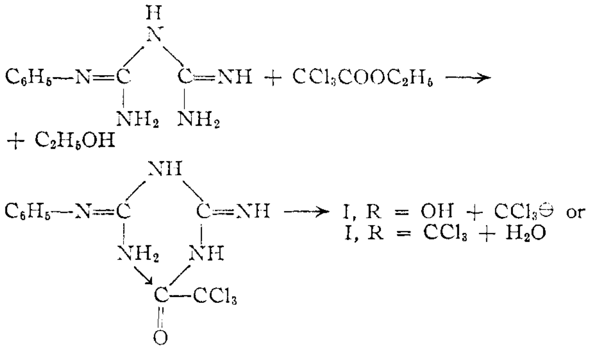
[5] K. H. Slotta and R. Tschesche, *Ber.*, **62B**, 1390 (1929).

[6] A. H. Blatt and E. W. Tristram, THIS JOURNAL, **74**, 6273 (1952). This is probably a normal case of positive halogen. The reaction is similar to the usual sodium iodide test in acetone when complete reduction instead of the formation of an iodide occurs (Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd Edition, 1948, p. 140).

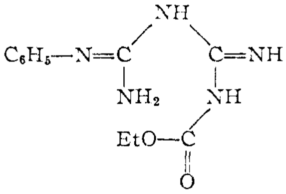
[7] A. Ostrogovitch, *Bull. soc. sci. Bucharest*, **14**, 49 (1905).

when treated with aqueous silver nitrate. When treated with alcoholic hydrogen chloride, phenylbiguanide hydrochloride was obtained. The reactivity of this triazine ring, specifically the ease of cleavage, is analogous to the preparation of difluoroacetic and trifluoroacetic acids by hydrolysis (ring opening) of the tristrifluoromethyl[8a] and trisdifluoromethyltriazines.[8b]

Reaction of phenylbiguanide with ethyl trichloroacetate gave I, R = CCl_3, only in small yield (1.3%). The major product was I, R = OH, (2-amino-4-anilino-6-hydroxy-*s*-triazine) in 83.6% yield previously reported by Smolka and Friedreich[9] as a product obtained in small yield from urea and phenylbiguanide. I, R = OH, was isolated as the main product both with sodium methoxide in methanol and without catalyst in chloroform. The reaction may be written as



The facile elimination of the trichloromethyl anion favors the formation of I, R = OH, and provides the driving force for triazine formation. It is also possible that the reaction initially involves the formation of II with the elimination of the trichloromethyl anion as reported by Blicke[10] who formylated amines with chloral in chloroform solution. This route seems less likely since cyclohexylamine on reaction with ethyl trichloroacetate in chloroform gave the amide $C_6H_{11}NHCOCCl_3$ (III) N-cyclohexyltrichloracetamide instead of the cyclohexylurethan. The displacement of a trichloromethyl group from I, R = CCl_3, seems unlikely in view of its stability in hot aqueous alcohol. Ostrogovitch[7] reported that hot acid solution was necessary to convert 2-tribromomethyl-2,4-diamino-*s*-triazine to ammeline and bromoform. I, R = OH, is soluble in alkali, forms a hydrochloride and gives a monoacetate on treatment with acetic anhydride.



II

Reaction of phenylbiguanide with ethyl α-bromopropionate gave I, R = $-CHBrCH_3$, in 18.7% yield. Phenylbiguanide hydrobromide was formed also, identified by comparison with a known sample, probably formed on dehydrohalogenation of I, R = $-CHBrCH_3$. It was demonstrated that treatment of I, R = $CHBrCH_3$, with phenylbiguanide yielded phenylbiguanide hydrobromide and a polymeric residue. Reaction with iodide ion as described previously gave I, R = $-CH_2CH_3$, in 88.7% yield (2-ethyl-4-amino-6-anilino-*s*-triazine) identical with a known sample prepared from ethyl propionate and phenylbiguanide.[11]

When phenylbiguanide reacts with ethyl β-bromopropionate in methanol solution with sodium methoxide, dehydrohalogenation occurs to give phenylbiguanide hydrobromide and ethyl acrylate. I, R = $-CH_2CH_2OCH_3$, is then formed by a reaction of phenylbiguanide with ethyl acrylate in the presence of the sodium methoxide.[12]

Experimental[13]

2-Chloromethyl-4-amino-6-anilino-*s*-triazine (I, R = CH_2Cl).—A solution of sodium methoxide, 6.9 g. (0.3 g. atom) of sodium in 250 ml. of anhydrous methanol was prepared, cooled and maintained at −40°, while 36.8 g. (0.3 mole) of ethyl α-chloroacetate was added slowly with stirring. Finely powdered phenylbiguanide, 53 g. (0.3 mole), was then added with stirring. One hour after the reaction mixture was allowed to reach room temperature, 25 ml. of concentrated hydrochloric acid in 75 ml. of methanol was added, with cooling, to the white paste which had formed. The reaction mixture was allowed to stand overnight and the white precipitate removed by filtration. The methanol filtrate was diluted with 2 volumes of water and on standing gave 9.5 g. of product, m.p. 144–146°. The initial precipitate was treated with 500 ml. of acetone, any solid removed by filtration and the filtrate diluted with 500 ml. of water, which on standing gave 16.5 g. of product, m.p. 145–146°; total yield based on phenylbiguanide reacted (54%). The acetone-insoluble portion was suspended in 500 ml. of water, the *p*H adjusted to 6.0 with hydrochloric acid and the solution concentrated to 120 ml. On cooling, 20.0 g. (31.2%) of phenylbiguanide hydrochloride was obtained, m.p. 245–246° I, R = CH_2Cl, was recrystallized from a methanol–water solution, m.p. 144–145° (browning before melting).

Anal.[14] Calcd. for $C_{10}H_{10}ClN_5$: C, 50.96; H, 4.28; Cl, 15.0. Found: C, 51.10; H, 4.57; Cl, 14.8.

2-Methyl-4-amino-6-anilino-*s*-triazine (I, R = CH_3).—The compound was prepared from ethyl acetate and phenylbiguanide according to the procedure described by Oldham, m.p. 178–180° (178°).[11]

I, R = CH_3, from Isopropenyl Acetate and Phenylbiguanide.—A solution of 17.7 g. (0.1 mole) of phenylbiguanide in 40 ml. of methanol was treated with 20.0 g. (0.2 mole of isopropenyl acetate. After a short induction period when the reaction apparently became cooler, a vigorous exothermic reaction ensued. After standing 24 hours, the reaction mixture was poured into 200 ml. of water and a solid crystallized over a 24-hour period. The pure product was collected and dried, 7.7 g. (38.7%), m.p. 177–178°, mixed m.p. with I, R = CH_3, 179–181°.

Reaction of I, R = CH_2Cl with Iodide Ion.—A solution of 235 mg. (0.001 mole) of I, R = CH_2Cl, in 1.2 ml. of acetone was added to 1.5 g. of sodium iodide dissolved in 5 ml. of acetone and 0.5 ml. of acetic acid.[6] The reaction mixture turned dark brown almost instantly, and after 10 minutes it was added to a solution of 125 mg. of sodium bisulfite in 8 ml. of water. On standing, 200 mg. of light yellow crystals separated, m.p. 234–238°. These are water soluble and are believed to be the hydriodic acid salt of I, R = CH_3. The crystals were dissolved in water, the solution decolorized with Norite and filtered. The filtrate was adjusted to a

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[8] (a) T. R. Norton, THIS JOURNAL, **72**, 3527 (1950); (b) D. D. Coffman, U. S. Patent 2,442,995, June 8, 1948; *C. A.*, **42**, 6842 (1948).

[9] A. Smolka and A. Friedreich, *Monatsh.*, **11**, 1 (1890).

[10] F. A. Blicke and C. Lu, THIS JOURNAL, **74**, 3933 (1952).

[11] W. N. Oldham, U. S. Patents (a) 2,344,784, Mar. 21, 1944 (b) 2,309,663, Feb. 2, 1943.

[12] This reaction will be reported in a forthcoming paper, C. G. Overberger and S. L. Shapiro, THIS JOURNAL, **76**, Jan. (1954).

[13] All melting points are uncorrected.

[14] Analysis by Drs. Weiler and Strauss, Oxford, England.

*p*H of 9.0 with sodium hydroxide and, on standing, 110 mg. of white crystals of I, R = CH_3, separated, m.p. 177–179° (54.6%), mixed m.p. with a known sample, m.p. 178–180°, mixed m.p. 178–180°.

Hydrogenation of I, R = CH_2Cl.—Hydrogenation of 5.28 g. (0.0224 mole) of I, R = CH_2Cl, was carried out in 200 ml. of absolute ethanol with 0.2 g. of palladium-on-calcium carbonate. The theoretical amount of hydrogen was absorbed in 1.5 hours. The reaction mixture was filtered and the filtrate concentrated to dryness on the water-pump to give 4.87 g. of a light yellow powder, m.p. 240–250° dec., which was water soluble and gave a positive chloride ion test (probably the hydrochloride of I, R = CH_3). One gram was dissolved in 35 ml. of warm water, Norite added, and the filtrate was made alkaline by the addition of 1 *N* sodium hydroxide. The white precipitate of I, R = CH_3, was obtained, 0.82 g. (89.1%), m.p. 174–175°, mixed m.p. with authentic I, R = CH_3, m.p. 178–179°, mixed m.p. 176–178°.

2-Dichloromethyl-4-amino-6-anilino-*s*-triazine (I, R = $CHCl_2$).—To a solution of sodium methoxide containing 3.0 g. (0.13 g. atom) of sodium in 120 ml. of anhydrous methanol was added 20 g. (0.113 mole) of phenylbiguanide. The reaction mixture was cooled to 0° and upon addition of 14.3 g. (0.113 mole) of methyl dichloroacetate, with added cooling to −20°, complete solution was effected. The reaction mixture was stored at 10° for 72 hours and then 6 hours at 20°, neutralized with a solution of 10 ml. of concentrated hydrochloric acid, diluted to 40 ml. with methanol and allowed to evaporate to dryness. The white residue was treated with 150 ml. of water and the solid removed by filtration. The water-insoluble material was dissolved in 1.3 l. of ethanol, decolorized with Norite, filtered, and the filtrate diluted with 3 l. of water. Long white crystals of I, R = $CHCl_2$, 14 g. (60.5%), m.p. 154–155°, were obtained, yield based on phenylbiguanide reacted.

Anal. Calcd. for $C_{10}H_9Cl_2N_5$: C, 44.46; H, 3.32; N, 25.9. Found: C, 44.39; H, 3.63; N, 25.8.

Concentration of the filtrate gave 5.0 g. of phenylbiguanide hydrochloride, m.p. 245–246°.

Reaction of I, R = $CHCl_2$, with iodide ion according to the previously described procedure gave 90.5% yield of recovered starting material after 10 days at room temperature; prolonged refluxing of I, R = $CHCl_2$, in an alcohol–water solution gave 95% recovery of starting material. Reaction with potassium acetate in acetic acid gave a 65% yield of recovered material. Reaction with ethanolic silver nitrate on warming, gave a dense white precipitate, the analysis of which indicated an organic silver complex.

Hydrogenation of I, R = $CHCl_2$.—Two grams of I, R = $CHCl_2$ (0.0074 mole) in 90 ml. of ethanol absorbed the theoretical amount of hydrogen over 1 g. of palladium-on-calcium carbonate in 50 minutes at room temperature to give on removal of the alcohol, the hydrochloride. This solid was dissolved in dilute acid, the solution treated with Norite, and the filtrate made alkaline with sodium hydroxide to give a white solid, 1.33 g. (90%), m.p. 178–179° of I, R = CH_3, mixed m.p. 179–181°.

Acid Hydrolysis of I, R = $CHCl_2$.—The procedure was similar to that described by Norton[8a] who hydrolyzed tris-trifluoromethyl-*s*-triazine to ethyl trifluoroacetate. To 20 ml. of a solution prepared from 32 ml. of 95% ethanol, 44 ml. of concentrated hydrochloric acid and 35 ml. of water was added 1.5 g. (0.0056 mole) of I, R = $CHCl_2$, and the solution was refluxed for 45 minutes. The reaction mixture was evaporated to dryness on a steam-bath and treated with 25 ml. of warm water. Norite was added, the solution filtered and the *p*H adjusted to 6.5. A precipitate, 250 mg. (21%), m.p. 240–243°, of phenylbiguanide hydrochloride was obtained. Recrystallization from water gave white crystals, m.p. 244–246°, mixed m.p. with an authentic sample, 244–246°, mixed m.p. 244–246°.

2-Amino-4-anilino-6-hydroxy-*s*-triazine (I, R = OH).—Finely powdered phenylbiguanide (60 mesh sieve), 17.7 g. (0.1 mole) was suspended in 100 ml. of chloroform and 19.2 g. (0.1 mole) of ethyl trichloroacetate was added with stirring. No reaction appeared to take place and the reaction mixture was refluxed for five hours with considerable thickening in consistency being observed after the first hour. The solid was removed by filtration, a white powder melting above 300°, 17.0 g. (83.6%). The solid was washed successively with hot water, ethanol and dioxane.

Anal. Calcd. for $C_9H_9N_5O$: C, 53.19; H, 4.46; N, 34.5. Found: C, 53.50; H, 4.88; N, 34.6.

The product is very insoluble in all common solvents. The chloroform filtrate was evaporated to dryness to give a yellow solid which was recrystallized several times from a methanol–water mixture, 0.4 g. (1.3%), m.p. 170–172° (I, R = CCl_3).

Anal. Calcd. for $C_{10}H_8Cl_3N_5$: C, 39.43; H, 2.65. Found: C, 39.50; H, 2.81.

I, R = OH, was also isolated in 69.8% yield if sodium methoxide was used as described in the preparation of I, R = $CHCl_2$.

The acetate of I, R = OH, was prepared from acetic anhydride to which catalytic amounts of sulfuric acid had been added. The product was recrystallized 4 times from acetonitrile and melted with browning at 235° and decomposition at 243°. The position of the acetyl group was not established.

Anal. Calcd. for $C_{11}H_{11}N_5O_2$: C, 53.87; H, 4.52. Found: C, 53.81; H, 4.67.

The hydrochloride of I, R = OH, was prepared by heating 3.0 g. in 150 ml. of 3 *N* hydrochloric acid. Long needles precipitated on cooling, 1.8 g. (43.6%), m.p. 127–130°, which gave a correct analysis for the dihydrate of the hydrochloride.

Anal. Calcd. for $C_9H_9N_5OHCl \cdot 2H_2O$: C, 39.21; H, 5.12. Found: C, 39.50; H, 5.20.

N-Cyclohexyltrichloroacetamide.—Cyclohexylamine, 9.9 g. (0.1 mole), and 19.2 g. (0.1 mole) of ethyl trichloroacetate were dissolved in 100 ml. of chloroform and the solution refluxed for 3 hours. Removal of the chloroform gave 21.0 g. (86%). Recrystallization from a methanol–water solution gave a m.p. 97–99°.

Anal. Calcd. for $C_8H_{12}Cl_3NO$: C, 39.29; H, 4.95. Found: C, 39.36; H, 5.15.

2-α-Bromoethyl-4-amino-6-anilino-*s*-triazine (I, R = $CHBrCH_3$).—A solution of sodium methoxide containing 2.3 g. (0.1 g. atom) of sodium in 65 ml. of anhydrous methanol was prepared, cooled and maintained at −40° while 18.1 g. (0.1 mole) of ethyl α-bromopropionate was added slowly with stirring. Finely powdered phenylbiguanide, 17.7 g. (0.1 mole), was added and the solution stirred and maintained at −40° for 15 minutes. The reaction mixture was allowed to attain room temperature and continue to stand for two hours. The reaction mixture was poured onto 200 g. of cracked ice and the white precipitate removed by filtration. The filtrate on standing gave a precipitate of 6.7 g. (25.9%) of phenylbiguanide hydrobromide, m.p. 241–242°, mixed with a known sample, m.p. 241–243°, mixed m.p. 240–242°.

Anal. Calcd. for $C_8H_{12}BrN_5$: C, 37.22; H, 4.68. Found: C, 37.36; H, 4.59.

The white precipitate which softened to an oil in the air was dissolved in 100 ml. of benzene, dried over Drierite and treated with Norite.[12] On standing for 29 hours, there was obtained 5.5 g. (18.7%) of I, R = $-CHBr-CH_3$, m.p. 132–135°, recrystallized from a methanol–water solution, m.p. 135–136°.

Anal. Calcd. for $C_{11}H_{12}N_5Br$: C, 44.91; H, 4.11; N, 23.8. Found: C, 44.81; H, 3.86; N, 24.2.

Reaction of I, R = $CHBrCH_3$, with Iodide Ion.—Four hundred eighty-five mg. (0.00164 mole) of I, R = $CHBrCH_3$, was dissolved in 1.7 ml. of acetone and added to 5 ml. of the sodium iodide solution previously described. The reaction mixture became dark brown rapidly and after 1 hour a precipitate appeared. The reaction mixture was allowed to stand overnight and poured into a solution of 250 mg. of sodium bisulfite in 16 ml. of water, the precipitate being dissolved. The reaction mixture on standing several days gave 510 mg. of water-soluble crystals, probably the hydriodic acid salt of I, R = $-CH_2CH_3$. The crystals were dissolved in hot water, the solution decolorized with Norite and after filtration adjusted to a *p*H of 9.0 with dilute sodium hydroxide. A precipitate of I, R = $-CH_2CH_3$ separated, 310 mg. (88.7%), m.p. 159–159.5°, mixed m.p. 158.5–159.5°.

2-β-Methoxyethyl-4-amino-6-anilino-*s*-triazine (I, R = $-CH_2CH_2OCH_3$).—A solution of sodium methoxide containing 2.3 g. (0.1 g. atom) of sodium in 40 ml. of methanol was cooled to −40° while 18.1 g. (0.1 mole) of ethyl β-bromopropionate was added dropwise with stirring. A thin slurry of phenylbiguanide, 17.7 g. (0.1 mole), in 40 ml. of methanol was added slowly while the temperature was maintained at −40°. On standing overnight, white crystals separated, 7.2 g. (33.6%), m.p. 241–243°, identical with a known sample of phenylbiguanide hydrobromide, m.p. 241–243°, mixed m.p. 241–243°.

The filtrate was allowed to stand for three to five days and poured into 350 ml. of 10% trichloroacetic acid. A white precipitate separated, 11.0 g. (26.6%), m.p. 138–139°,[12] the trichloroacetic acid salt of I, R = $-CH_2CH_2-O-CH_3$. The free base, 5.9 g. (90.5%), was liberated by the addition of dilute aqueous methanolic alkali, m.p. 116–118°, mixed m.p. 114–118°.[11b,12]

Acknowledgment.—We are grateful to Dr. Louis H. Freedman of the U. S. Vitamin Corporation, Yonkers, N. Y., for his generosity in allowing one of us to use the facilities of their laboratories. We would also like to thank the American Cynamid Company for a generous supply of phenylbiguanide.

BROOKLYN, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Benzidine Rearrangement. IV. Kinetics of the Rearrangement of *o*-Hydrazotoluene[1]

BY ROBERT B. CARLIN AND RAYMOND C. ODIOSO

RECEIVED AUGUST 10, 1953

The spectrophotometric analytical method was used to study the rate of rearrangement of *o*-hydrazotoluene by hydrogen chloride in 95% ethanol. *o*-Tolidine was shown to be the sole rearrangement product under the imposed conditions. The rate is first order with respect to *o*-hydrazotoluene concentration, but, in contrast with the rearrangements of hydrazobenzene which are second order in acid concentration, the order of participation of acid concentration in the rate expression for the rearrangement of *o*-hydrazotoluene is 1.6. Chloride ion concentration is not involved in the rate expression. Activation energies for the process (18.7, 19.1 and 20.2 kcal./mole) were computed from measurements carried out under three sets of conditions, and an entropy of activation (−0.62 kcal./deg./mole) was calculated; but little significance is attributed to these quantities. There is a positive salt effect on the rate which is similar in magnitude with that observed in investigations of the rearrangements of hydrazobenzene. Increasing the proportion of water in the solvent causes a rate increase, but replacement of part of the ethanol by dioxane effects little change. Arguments are advanced to show that the observations resulting from this investigation can be reconciled with Hammond's proposed reaction sequence for the benzidine rearrangement.

Recent kinetic studies of the acid-catalyzed rearrangements of hydrazobenzene have demonstrated that the reaction rate is first order with respect to hydrazobenzene concentration[2–5] and second order with respect to acid concentration,[3–5] that there is a positive salt effect upon the rate[3,4] which satisfies the Brønsted–Bjerrum equation,[5] that the rate increases steadily with increasing dielectric constant in ethanol–water solutions,[5] that the reactions are subject to general acid catalysis[6] and that the simultaneous rearrangements to benzidine and diphenyline are identical kinetically and substantially free, under the chosen conditions, of side reactions such as disproportionation.[4] In an effort to observe the effects of substituents on the kinetics, a series of investigations of the rates of rearrangements of some substituted hydrazobenzenes has been undertaken. This paper reports the results of a study of the kinetics of the hydrogen chloride-catalyzed rearrangement of *o*-hydrazotoluene (2,2′-dimethylhydrazobenzene).

Using the analytical technique first described by Dewar,[2] Croce and Gettler[5] measured the rates, activation energy, PZ factor and related quantities for the transformation of *o*-hydrazotoluene by hydrogen chloride in 90% ethanol; however, the product or products of the transformation were not disclosed, and the salt and solvent effects and the order of the effect of acid concentration on the rate were not investigated. In the study reported here the spectrophotometric analytical method first used in kinetic measurements of the rearrangements of hydrazobenzene[4] was again employed, so that both the concentration of *o*-hydrazotoluene and that of *o*-tolidine (3,3′-dimethyl-4,4′-diaminobiphenyl), its sole transformation product, could be followed simultaneously. The order in which acid concentration appears in the rate expression was determined, and the salt effect and some observations related to medium effects were recorded.

The solvent chosen for most of the rate runs on *o*-hydrazotoluene was 95% ethanol, in order that the results could be compared justifiably with those from the preceding study of hydrazobenzene,[4] in which the same solvent was used. The ultraviolet extinction curves for *o*-hydrazotoluene and *o*-tolidine were determined in 95% ethanol solution (Fig. 1). Then *o*-hydrazotoluene was subjected to the action of hydrogen chloride in 95% ethanol under the same conditions which were to be used in the rate runs, and the extinction curve for the product solution was identical, within experimental error, with that of *o*-tolidine solutions. Therefore, *o*-tolidine was the sole product under the imposed conditions, and the absence of rearrangements to other isomers and of disproportionation was demonstrated. This observation contrasts with those of previous investigators,[7] who have reported that diphenyline formation and disproportionation accompany the main reaction when *o*-hydrazotoluene is boiled with concentrated hydrochloric acid. The apparent discrepancy undoubtedly can be attributed to the well known effect of change in reaction

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[1] From the D.Sc. Thesis by Raymond C. Odioso.

[2] M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946).

[3] G. S. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).

[4] R. B. Carlin, R. G. Nelb and R. C. Odioso, *ibid.*, **73**, 1002 (1951).

[5] L. J. Croce and J. D. Gettler, *ibid.*, **75**, 874 (1953).

[6] M. D. Cohen and G. S. Hammond, *ibid.*, **75**, 880 (1953).

[7] E. Noelting and P. Werner, *Ber.*, **23**, 3252 (1890).