

solution was made strongly alkaline and the organic base which separated was extracted with ether. Evaporation of the ether gave 3.92 g. of gummy white solid (57.6% yield calculated as *N,N*-dimethyl-2,2,2-triphenylethylamine). Recrystallization of this product from ethyl alcohol gave 2.79 g. of light tan crystals which melted sharply at 112° and gave no melting point depression when admixed with *N,N*-dimethyl-2,2,2-triphenylethylamine prepared as indicated previously under the preparation of 2,2,2-triphenylethyltrimethylammonium iodide. Moreover, the two samples of amine had identical infrared absorption spectra in carbon disulfide solution.

The ether phase from which the amine had been precipitated was washed with aqueous sodium hydroxide and then water, and dried over anhydrous magnesium sulfate. Evaporation of the ether *in vacuo* gave 2.26 g. of viscous brown neutral products. Analysis of this product by vapor phase chromatography gave 1.1 mmoles (4.8%) of 1,1,2-triphenylethane, 5.0 mmoles (22%) of 1,1,1-triphenylethane, 2.7 mmoles (12%) of triphenylethylene, and no detectable diphenylmethane.

Pyrolysis of 2,2,2-Triphenylethyltrimethylammonium Iodide in Boiling Dioxane.—In a 200-ml. Claisen flask equipped with dropping funnel and condenser set for distillation was placed 1.05 g. (2.36 mmoles) of 2,2,2-triphenylethyltrimethylammonium iodide and 100 ml. of anhydrous dioxane. The mixture was heated to the boiling point with stirring provided by a glass-enclosed magnetic stirring bar. The quaternary salt remained essentially undissolved in the dioxane. The solvent was slowly distilled from the flask while additional solvent, to replenish that removed, was added through the dropping funnel. In this manner some 300 ml. of dioxane was distilled in 2 hr. To the dioxane distillate was added 110 ml. of 95% ethanol containing 0.84 g. of silver nitrate. After standing for 2 hr. the solution contained a yellow precipitate. Water (1.2 l.) was added and the solution was allowed to stand several days before filtration. The yellow precipitate was washed with dilute nitric acid and then water and after drying amounted to about 1 mg. of silver iodide.

The remaining solution and precipitate of 2,2,2-triphenylethyltrimethylammonium iodide was rinsed into a 1-l. flask with 500 ml. of anhydrous dioxane and the flask was attached to a fractionating column, 62 cm. long by 15 mm. diameter, packed with glass helices. The column was operated under slow take-off at about maximum reflux such that over a period of 16 hr. some 350 ml. of distillate was collected. The distillate was treated with alcoholic silver nitrate as previously described and yielded 0.491 mg. (89% yield) of silver iodide precipitate. During the fractional distillation nearly all of the solid quaternary salt in the distillation pot disappeared. The solution remaining in the pot was filtered to remove a small quantity of solid, the dioxane was removed *in vacuo* on a steam bath, and the residue was taken up in 15 ml. of 95% ethanol. The solution upon chilling deposited 0.44 g. (62% yield calculated as *N,N*-dimethyl-2,2,2-triphenylethylamine) of light brown crystals, m.p. 107–109.5°. Treatment with Nuchar C in ethanol, followed by recrystallization from ethanol and then acetone, gave 0.30 g. of pale cream cubic crystals, m.p. 110.0–112.0°, which showed no depression in m.p. when admixed with a colorless sample of *N,N*-dimethyl-2,2,2-triphenylethylamine (prepared as indicated in the preparation of 2,2,2-triphenylethyltrimethylammonium iodide). The two compounds moreover gave identical infrared absorption spectra when examined in potassium bromide disks.

Analyses of Products.—Analyses for hydrocarbons in the products from cleavages by sodium was accomplished with the use of a Perkin-Elmer Model 154-C vapor fractometer equipped with a precision gas sampling valve, a 1- or 5-ml. gas sample tube, and 2-m. columns, 0.25 in. in diameter. For separation and analysis of methane and ethane a column packed with silica gel (Perkin-Elmer column "J") was used at 32°. For neopentane a column packed with diatomaceous earth coated with 2,4-dimethyltetrahydrothiophene-1,1-dioxide (Perkin-Elmer column "E") was operated at 33°. For separation and analysis of mixtures of diphenylmethane, 1,1,1-triphenylethane, 1,1,2-triphenylethane, and 1,1,2-triphenylethylene a column packed with diatomaceous earth coated with Apiezon "L" grease (Perkin-Elmer column "Q") was operated at 300°. For separation of mixtures of toluene and diphenylmethane column "Q" was operated at 197°. For separation and analysis of mixtures of triphenylmethane and 1,1,1-triphenylpropane a column packed with silicone grease supported on diatomaceous earth (Perkin-Elmer column "O") was operated at 250°; the identity of these hydrocarbons was confirmed by retention times on column "Q." Empirical calibration curves of peak height *vs.* partial pressure of gas or weight of solid (dissolved in benzene) were prepared from known samples of all hydrocarbon products for which analyses are reported in the present work, save for triphenylethylene, which was ordinarily a minor product and was estimated by assuming its thermal conductivity per mole to be identical with that of 1,1,2-triphenylethane (which was of similar retention time on column "Q"). Analyses for triphenylethylene were also sometimes confirmed by examination of the ultraviolet absorption spectrum of the product in ethyl alcohol solution at 300 m μ , at which wave length triphenylethylene has a molar extinction coefficient of 2.0×10^4 .

Attempted analysis of high molecular weight amines produced in the present work by vapor phase chromatography on column "Q" at 300° was unsuccessful because of thermal decomposition of the amines under the conditions tried. Thus pure samples of *N,N*-dimethyl-2,2,2-triphenylethylamine gave chromatograms having four or five peaks.

The source and purity of chemicals used as standards in these analyses is: 2,2-Dimethylpropane and methane were Phillips Petroleum Co. research grades and were said to be 99.9 and 99.6% pure, respectively. 1,1,1-Triphenylethane, 1,1,2-triphenylethane, and triphenylethylene were highly purified samples previously synthesized¹⁴ in our laboratories. 1,1,1-Triphenylpropane was prepared from ethylmagnesium bromide and triphenylchloromethane.²⁹ Ethylene was C.P. grade (99.0% min. purity) from Matheson Co. Toluene, diphenylmethane, and triphenylmethane were commercial samples whose vapor phase chromatograms indicated 99% or better purity. 1,1-Dimethylcyclopropane, which was used only for qualitative identification, was from Columbia Organic Chemicals, Inc., and was found to be of only about 90% purity according to its vapor chromatogram.

Acknowledgment.—Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the present research.

(29) Cf. M. Gomberg and L. H. Cone, *Ber.*, **39**, 2961 (1906).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 27, N. Y.]

A Comparison of Thermal and Photochemical Rearrangements of Triarylmethyl and Related Azides¹

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RECEIVED OCTOBER 14, 1963

Irradiation of triarylmethyl azides in hexane solution at room temperature by a low pressure mercury vapor lamp has been found to yield qualitatively the same products as the thermal decomposition at 170–190°. The migration aptitudes of substituted phenyl *vs.* phenyl are markedly different, however. The substituent has little, if any, effect in the photochemical reaction, while electron-repelling substituents aid and electron-withdrawing substituents hinder migration in the thermal reaction. Thermal and photochemical reactions of 1,1-diphenylethyl and 2-phenyl-2-propyl azides show similar, but not entirely regular, behavior. The photochemical, but not the thermal, reactions are suggested to involve discrete nitrene intermediates. Whether these nitrenes are singlet or triplet is discussed.

In an earlier investigation of the thermal rearrangement of triarylmethyl azides,³ we noticed an apparent light-promoted decomposition. The present investi-

gation was undertaken to determine the nature of this photochemical process, and to extend the range of compounds studied in the thermal reaction.

(1) This work was supported by the Army Research Office (Durham).
(2) Alfred P. Sloan Foundation Fellow.

(3) W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

Prior to our work only aromatic azides had been photolyzed,⁴ though while it was in progress Barton and Morgan⁵ reported photolyses of various alkyl azides. In cyclohexane, nitrogen loss was accompanied by 1,2-shift of hydrogen to give imines, hydrogen abstraction from solvent to give amines, and ring closure to give pyrrolidines. With *t*-butyl azide, a ring closure to an ethyleneimine occurred.

Photolysis of triphenylmethyl azide in hexane with a low pressure mercury vapor lamp gave benzophenone phenylimine in a yield of 83% based on azide consumed in a photolysis carried to 36% completion. No identifiable products other than imines resulting from 1,2-shifts were isolated in photolyses of any of our azides. In all photolyses an amorphous, red-brown solid formed in the cell. Isolation of this substance in one experiment showed that it constituted only 0.2% of the weight of reactant taken. Its infrared spectrum showed no distinct peaks, and attempts at crystallization failed.

The substituted triphenylmethyl azides were photolyzed in the same fashion. Runs at two different lengths of time were done on each compound to see if any selective destruction of products was occurring. The product mixtures were treated with concentrated sulfuric acid under nitrogen, which hydrolyzed the imines quantitatively to benzophenone plus the *p*-substituted benzophenone, and the unreacted azide to the corresponding triarylcarbinol. The mixture was analyzed by gas chromatography. Results are in Table I. Though triphenylmethyl azide is reported to give only carbinol on treatment with acid,⁶ we did find that the triarylmethyl azides underwent a small amount (<4%) of acid-catalyzed rearrangement to give benzophenones, presumably *via* the imines. A correction was made for the resulting change in product ratio (see Experimental for details), though in most cases the correction was within experimental error.

TABLE I
MIGRATION APTITUDES IN PHOTOLYTIC REARRANGEMENT OF TRIARYLMETHYL AZIDES^a

R in ρ -RC ₆ H ₄	Time of photolysis, hr.	Reaction, %	Migration aptitude, ^b Ar/C ₆ H ₅
Cl	9.5	19.2	1.44
Cl	16	35.8	1.14
CH ₃ O	8	48.3	1.15
CH ₃ O	17	69.6	1.16
NO ₂	8	67.9	1.05
NO ₂	16	73.7	1.01

^a See Experimental for reaction conditions and method of analysis. All photolyses were done in hexane at room temperature except those of the *p*-nitro compound, which were run in 90% hexane-10% ether because of inadequate solubility in pure hexane. ^b Corrected for statistical factor and for small amount of acid-catalyzed rearrangement of unreacted azide during work-up; figure given is average of two or more analyses on same sample. Deviations from mean ran 5-10% of figure given.

Analysis of the products from photolyses of 2-phenyl-2-propyl and 1,1-diphenylethyl azides was more difficult. Hydrolysis was abandoned as a work-up procedure, for the ketones here differ sufficiently in properties for preferential loss to occur, and the azides are more prone to acid-catalyzed rearrangement. Comparison samples of the expected imines were synthesized in the hope of analyzing the products directly by gas chromatography. This hope was realized with

(4) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2435 (1951).

(5) D. H. R. Barton and L. R. Morgan, Jr., *Proc. Chem. Soc.*, 206 (1961); *J. Chem. Soc.*, 622 (1962).

(6) J. H. Boyer, F. C. Canter, J. Hamer, and R. K. Putney, *J. Am. Chem. Soc.*, **78**, 325 (1956).

2-phenyl-2-propyl azide, but with 1,1-diphenylethyl azide the column temperatures required were high enough to cause thermal rearrangement of unreacted azide. The procedure eventually chosen was reduction of the imine-azide mixture with lithium aluminum hydride to an amine mixture which was analyzed by gas chromatography. This procedure left substantially unchanged the ratio of isomeric imines in a simulated product mixture. Results of these photolyses are given in Table II. The figures are undoubtedly less reliable than those of Table I, as the imines are difficult to handle and sensitive to hydrolysis.

TABLE II
MIGRATION APTITUDES IN PHOTOLYTIC REARRANGEMENT OF 1,1-DIPHENYLETHYL AND 2-PHENYL-2-PROPYL AZIDES^a

Reactant	Time of photolysis, hr.	Reaction, %	Migration aptitude, ^b Ph/Me
Ph ₂ MeCN ₃	8	20.4	2.45
Ph ₂ MeCN ₃	17	24.0	1.87
Ph ₂ MeCN ₃	30	32.3	2.22
		Average	2.18
PhMe ₂ CN ₃	10	37.0	0.96
PhMe ₂ CN ₃	10	29.6	1.03
PhMe ₂ CN ₃	10	26.4	0.89
PhMe ₂ CN ₃	20	51.0	0.95
		Average	0.96

^a See Experimental for details of reaction conditions and methods of analysis. All photolyses were done in hexane at room temperature. ^b Corrected for statistical factor. Each figure represents an entirely separate run, and is the average of two or more analyses. Deviations from mean ran 10-15% in most cases.

Finally, the thermal rearrangements of 2-phenyl-2-propyl and 1,1-diphenylethyl azide were studied for comparison with the photolyses. The procedure employed was direct injection of the azide into a gas chromatographic apparatus at a column temperature sufficient to cause rapid thermal rearrangement. An obvious disadvantage is that reaction conditions are less well defined than when the pyrolysis and analysis are conducted separately. The reproducibility, however, is much better. Evidently there is less opportunity for hydrolysis or decomposition of the imines in the direct procedure. Results of these thermal rearrangements are given in Table III.

TABLE III
MIGRATION APTITUDES IN THERMAL REARRANGEMENT OF 1,1-DIPHENYLETHYL AND 2-PHENYL-2-PROPYL AZIDES^a

Reactant	<i>t</i> , °C. ^b	Reaction, %	Migration aptitude, ^c Ph/Me
Ph ₂ MeCN ₃	223	100	2.36
PhMe ₂ CN ₃	192	83	4.05

^a Performed by injecting sample of azide directly on gas chromatograph; see Experimental for details. ^b Column temperature. ^c Corrected for statistical factor. Each figure is the average of two or more runs. Deviations from mean ran 5-10% of figure given.

The migration aptitudes in Table I differ little for phenyl and substituted phenyl groups. Such differences as there are lie in the direction of slightly greater migration aptitudes for the substituted phenyl groups, regardless of the electronic nature of the substituent. This is in contrast to the results of the thermal reaction, where electron-repelling substituents aided and electron-withdrawing substituents hindered migration.³ The migration aptitudes in the thermal rearrangement for those substituents included in the present study were *p*-methoxyl, 2.5; *p*-chloro, 0.4; and *p*-nitro, 0.2. Though the spread is not large, its direction is unmistakable.

Results on phenyl *vs.* methyl migration aptitudes (Tables II and III) are somewhat less regular. Phenyl migration is clearly preferred in the thermal, but not in the photochemical, decomposition of 2-phenyl-2-propyl azide. In contrast, there is little difference between the thermal and photochemical migration aptitudes with 1,1-diphenylethyl azide, phenyl migration being preferred in both cases. In all of our reactions the preference for phenyl over methyl is far less than it is in carbonium-ion rearrangements.⁷

The pattern of all the thermal rearrangements is that of migration to an electron-deficient nitrogen atom, or nitrene



We argued earlier that the departure of nitrogen and the migration were probably concerted, as the wide variations in energy and entropy of activation found in the thermal decomposition of the triarylmethyl azides seemed inconsistent with a mere inductive effect of the aryl group. Though extensive rate studies were not done on the thermal decompositions in the present work,⁸ there are no reasons for suspecting a different mechanism with them.

The different patterns of results in the thermal and photochemical reactions make it evident that the mechanisms must be different. The first step of the photochemical reaction would be absorption of light accompanied by a transition to an electronically-excited singlet state of the azide. Among the numerous paths this intermediate might follow are: direct loss of nitrogen, with or without aryl participation or conversion to a lower excited state (probably triplet), followed by nitrogen loss, again with or without aryl participation.

In order to limit somewhat the area for discussion, we will assume that nitrogen loss from the azide (either singlet or triplet) occurs without aryl participation. The amount of energy absorbed by the azide is more than sufficient to break the nitrogen-nitrogen bond, and any appreciable degree of aryl participation seems unlikely if there is no energetic advantage to be gained from it. The possible paths to a nitrene then are: singlet azide \rightarrow triplet azide \rightarrow triplet nitrene or singlet azide \rightarrow singlet nitrene \rightarrow triplet nitrene. The actual rearrangement step could involve either a singlet or a triplet nitrene.

If we assume a singlet nitrene, we can say that the low selectivity in the migration arises from its very high energy and consequent lack of discrimination. The apparent small preference for substituted phenyl over phenyl would, in this picture, be a simple matter of experimental error. In addition, one must assume that this highly excited species would rearrange before it could suffer collisional deactivation by solvent molecules.

Explanation of the migration aptitudes is somewhat easier with a triplet nitrene. A radical-type rearrangement could explain the small preference for substituted phenyl, as all of the *p*-substituents used should increase the ability of the phenyl group to bear an odd electron. There is also independent evidence for triplet nitrenes. Though the compounds we used have not been examined, some organic azides give e.p.r. signals attributable to triplet nitrenes after irradiation in a rigid glass at 77°K.⁹ Barton and

Morgan⁵ observed loss of optical activity on photochemical cyclization of (+)-4-methylhexyl azide to 2-ethyl-2-methylpyrrolidine. This they took as evidence against direct insertion in the C-H bond of a singlet nitrene, and for a diradical intermediate arising from a triplet nitrene.

For these reasons, we feel that the triplet nitrene is the most likely intermediate in our photochemical rearrangements. Other mechanisms cannot be excluded, but are distinctly less likely.

Experimental¹⁰

Preparation of Triarylmethyl Azides.—The procedure of Saunders and Ware³ was followed in all cases. Triphenylmethyl azide was obtained as a solid, m.p. 64.5–65° (lit.³ 64–65°). Diphenyl-(*p*-nitrophenyl)-methyl azide, (*p*-anisyl)-diphenylmethyl azide, and (*p*-chlorophenyl)-diphenylmethyl azide were obtained as oils, and used as such. Examination of the infrared spectra revealed no apparent impurities except a trace of hydroxyl-containing material, presumably unreacted carbinol.

1,1-Diphenylethyl Azide.—The procedure of Gudmundsen and McEwen¹¹ was employed. Material of b.p. 92.5–98° (0.7 mm.) (lit.¹¹ 112–115° (1 mm.)) was chromatographed on alumina with petroleum ether and the fractions showing strong azide absorption at 4.82 μ and no absorption from 1,1-diphenylethylene at 11.18 μ were taken as pure product.

2-Phenyl-2-propyl Azide.—The procedure of Gudmundsen and McEwen¹¹ was again used, with 2-phenyl-2-propanol as starting material. The colorless oil obtained was chromatographed on alumina with petroleum ether. Fractions with strong azide absorption at 4.76 μ and no hydroxyl or terminal methylene bands were taken as pure material.

Benzophenone Methylimine.—The reaction of benzophenone dichloride with methylamine followed the procedure of Curtin and Hauser.¹² The crude product from evaporation of the ether extract was purified by gas chromatography on a column of 20% Apiezon L on Chromosorb P at 211°. The imine was very easily hydrolyzed, its infrared spectrum showing a trace of benzophenone even immediately after purification.

Acetophenone Phenylimine.—Acetophenone diethyl ketal¹³ (0.09 mole) was heated with aniline (0.12 mole) under a 6-in. helix-packed column. When distillation of ethanol was complete, and the temperature of the vapor had risen to 100°, the mixture was distilled at reduced pressure. A fraction boiling at 170° (15 mm.) solidified to a yellow solid, m.p. 37–38° (lit.¹⁴ 41°).

Acetophenone Methylimine.—A solution of 6 g. of acetophenone and 6 g. of methylamine in 300 ml. of methanol was heated in a sealed tube at 90° for 12 hr. The reaction mixture was taken up in ether, dried over magnesium sulfate, and the solvents removed by distillation. The yellow oil was purified by gas chromatography on a 12-ft. column of Ucon Polar on Chromosorb P at a temperature of 140°. The product showed imine absorption in the infrared at 6.12 μ .¹⁵ It contained a trace of acetophenone, as shown by a small peak at 5.95 μ . The imine is reported¹⁶ to have b.p. 96° (10 mm.).

Acetone Phenylimine.—The procedure was the same as that for acetophenone phenylimine, using 0.17 mole of acetone diethyl ketal¹³ and 0.19 mole of aniline. The imine distilled at 121–133° (15 mm.) (lit.¹⁷ 227–229° (760 mm.), 78° (10 mm.)). Further purification was effected by gas chromatography on a 12-ft. column of Ucon Polar on Chromosorb P at 140°. The product showed imine absorption in the infrared at 6.05 μ ¹⁵ and a trace of carbonyl absorption.

N-(1-Phenylethyl)-aniline.—Acetophenone phenylimine was reduced by the procedure of Billman and Dising.¹⁸ The reaction mixture was diluted with water and extracted with ether. The extract was dried over potassium hydroxide and then evaporated. The crude product was used as such in gas chromatographic comparisons. Its infrared spectrum showed N-H absorption at 2.98 μ and absorption due to aromatic amine at 6.26 μ , with no carbonyl or imine peaks.

Methylbenzhydramine.—Reduction of benzophenone methylimine was performed in the same manner as that of acetophenone phenylimine. The crude product was used as such in

(10) Melting points and boiling points are uncorrected.

(11) C. H. Gudmundsen and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 329 (1957).

(12) D. Y. Curtin and J. W. Hauser, *ibid.*, **83**, 3474 (1963).

(13) L. Claisen, *Ber.*, **40**, 3908 (1907).

(14) L. Claisen, *ibid.*, **29**, 2931 (1896).

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 267.

(16) K. Kindler, *Ann.*, **431**, 225 (1923).

(17) P. Riehm, *ibid.*, **238**, 1 (1887); R. Kuhn and H. Schretzmann, *Chem. Ber.*, **90**, 557 (1957).

(18) J. H. Billman and A. C. Dising, *J. Org. Chem.*, **22**, 1068 (1957).

(7) W. H. Saunders, Jr., and R. H. Paine, *J. Am. Chem. Soc.*, **83**, 882 (1961).

(8) Mr. S. Weinreb established that decompositions of 2-phenyl-2-propyl and 2,2-diphenylethyl azides at 180 and 190° were first order, and that the latter reacted almost twice as fast as the former. The activation energies and entropies for the two compounds did not differ within the rather wide experimental error (± 1.6 kcal. and 3.5 e.u., respectively).

(9) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

gas chromatographic comparisons. Its infrared spectrum showed N-H absorption at 3.11 μ and no carbonyl or imine absorption.

1,1-Diphenylethylamine.—1,1-Diphenylethyl azide was reduced with lithium aluminum hydride by the procedure of Boyer.¹⁹ The crude product was used as such in gas chromatographic comparisons. Its infrared spectrum showed N-H absorption at 3.10 μ and slight absorption at 11.2 μ (probably from a trace of 1,1-diphenylethylene, whose terminal methylene absorbs at this wave length).

Photolysis of Azides.—A solution (ca. 3% by weight) of the azide in hexane was placed in a cylindrical cell with quartz windows of ca. 12-ml. capacity. The solution was irradiated with light from a Hanovia SC 2537 low-pressure mercury vapor lamp (Hanovia Chemical and Manufacturing Co., Newark, N. J.). No filters were used, but ca. 96.5% of the ultraviolet light emitted by the lamp is claimed to be at 2537 Å. Times of reaction and work-up procedures are described below or tabulated for specific cases. A phenomenon common to all the photolyses was the collection on the quartz window near the light source of a small amount of amorphous, red-brown solid. In one case this was investigated. It constituted only 0.2% of the starting material by weight, and showed no distinct peaks in its infrared spectrum. It did seem to slow the photolyses in their later stages by absorbing part of the light.

Isolation of Products in Photolysis of Triphenylmethyl Azide.—Photolysis of 202.9 mg. of triphenylmethyl azide in 12 ml. of hexane for 2.5 hr. was followed by chromatography on alumina. Elution with 19:1 hexane-benzene gave 129.1 mg. (64%) of unreacted azide. Elution with benzene gave 55.1 mg. (83% of unrecovered azide) of benzophenone phenylimine. Further elution with benzene and finally with chloroform gave only 5 mg. of a red solid and 1.8 mg. of an orange-red oil. Recovered azide plus imine accounted for 93% of the starting material.

Products from Photolysis of 1,1-Diphenylethyl Azide.—The reaction mixture (12 ml. containing ca. 0.06 g. of product and 0.2 g. of azide) was diluted with 20 ml. of ether and added slowly to 0.2 g. of lithium aluminum hydride in ether. The solution was refluxed for 4 hr. and treated cautiously with water until the solid salts had precipitated. The clear solution was decanted, combined with ether washings of the residue, and dried over potassium hydroxide. After partial concentration, the solution was analyzed by gas chromatography on a column of 20% Apiezon L on Chromosorb P at 211°. Results are given in Table II.

A control reduction was performed on a simulated reaction mixture. The calculated ratio of the two imines was 1.13:1, found 1.07:1. The calculated ratio of imines to azides was 0.58:1, found 0.36:1.

Products from Photolysis of 2 Phenyl-2-propyl Azide.—The hexane solution containing the product imines and unreacted

azide was kept carefully protected from atmospheric moisture until it was analyzed. Samples of the solution were analyzed directly by gas chromatography on a column of 20% Ucon Polar on Chromosorb P at 140°. These conditions were shown to result in no thermal rearrangement of the azide. Peak positions were established by comparison of retention times with those of authentic samples.

Products from Photolysis of Triarylmethyl Azides.—A 2-neck flask equipped with a pressure-equalizing dropping funnel and containing 5 ml. of concentrated sulfuric acid was heated in an oil bath to 150°. A nitrogen atmosphere was maintained by using the funnel top as a nitrogen inlet and the other neck as outlet. The hexane solution of photolysis products was added rapidly through the dropping funnel with stirring. The flask was then removed from the oil bath, and crushed ice was added with stirring. The hydrolysis products were extracted with three 20-ml. portions of ether and the extracts dried over magnesium sulfate. The solution was analyzed by gas chromatography on a column of 20% Apiezon L on Chromosorb P at temperatures of 205–230°.

Various control experiments were performed. The hydrolysis under the above conditions of a weighed sample of pure benzophenone phenylimine dissolved in hexane gave 97% of benzophenone. Triphenylmethyl azide was subjected to the hydrolysis procedure and gave 1.6% of benzophenone. The same treatment applied to (*p*-nitrophenyl)-diphenylmethyl azide gave less than 4% of benzophenone plus *p*-nitrobenzophenone. In calculating migration aptitudes given in Table I, it was assumed that 4% of the unreacted azide underwent acid-catalyzed rearrangements in all cases. Migration aptitudes obtained by McEwen for benzhydryl azide²⁰ were assumed to apply, and the amounts of benzophenone and substituted benzophenone formed in the acid-catalyzed reaction calculated as percentages of total reaction (photolytic plus acid catalyzed). These percentages were then subtracted from the observed percentages of the two ketones. The correction to the migration aptitudes was less than 0.10 in all but one case, the photolysis of *p*-chlorophenylidiphenylmethyl azide for 9.5 hr., where it was +0.16.

Thermal rearrangements of 1,1-diphenylethyl and 2-phenyl-2-propyl azides were performed by injecting the azide directly into the gas chromatograph, the reaction apparently occurring mainly on the column as the extent of conversion paralleled the column temperature. Peaks were identified by comparison with authentic samples of the expected imines. For 1,1-diphenylethyl azide a 10-ft. column of 20% silicone on Fluoropak 80 was used with the injector at 230°, the column at 223°, and the detector at 252°. For 2-phenyl-2-propyl azide a 12-ft. column of 20% Ucon Polar on Chromosorb P was used with the injector at 216°, the column at 192°, and the detector at 226°.

(19) J. H. Boyer, *J. Am. Chem. Soc.*, **73**, 5865 (1951).

(20) R. F. Tietz and W. E. McEwen, *ibid.*, **77**, 4007 (1955).

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

Kinetics of Hydrolysis of N,N'-Diarylformamidines in Alkaline Dioxane Solutions

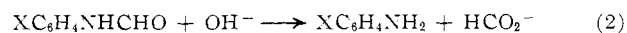
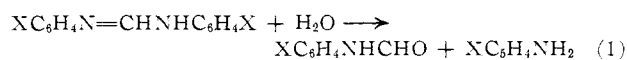
BY ROBERT H. DEWOLFE

RECEIVED SEPTEMBER 7, 1963

The effects of aryl substituents, temperature, solvent polarity, and hydroxide ion concentration on the rate of hydrolysis of N,N'-diarylformamidines were studied. Amidines having electron-releasing aryl substituents hydrolyze in alkaline solutions at a rate which is almost independent of the hydroxide ion concentration and of the structure of the aryl group. Amidines having electron-withdrawing substituents undergo hydrolysis by two processes, one of which appears to be independent of hydroxide ion concentration, and another whose rate is a nonlinear function of hydroxide ion concentration. The nonlinear concentration dependence of the hydroxide ion-catalyzed reaction is shown to be a result of partial conversion of the amidines to unreactive conjugate bases in alkaline solutions. The mechanisms of the hydrolysis reactions are discussed.

The kinetics of hydrolysis of N,N'-diarylformamidines in buffer solutions and solutions of strong acids have been studied previously.^{1,2} In acidic solutions, the kinetic data for hydrolysis of the diarylformamidines and N,N'-diarylacetamidines³ are rationalized equally well by a mechanism involving nucleophilic attack by water or other bases on the hydrated amidinium ion, or by a general base-catalyzed attack by water on the amidinium ion.⁴

Diarylformamidines also hydrolyze under alkaline conditions, yielding arylamines and formanilides as the initial reaction products. The formanilides may, depending on reaction conditions and the structure of the aryl group, hydrolyze at a rate comparable to that of the amidine



The present study was undertaken to obtain information on the effect of structure and reaction conditions

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