N-Cyclohexyl-2-diethylaminoacetamide (XXXVe).—To 29.3 g. of diethylamine in 100 ml. of ethanol, 35.2 g. of 2-chloro-N-cyclohexylacetamide (Ie) was added during about 0.5 hr. at room temperature. The solution was held at 40–45° for 4 hr. and the solvent removed by distillation under reduced pressure. After addition of ether to the liquid residue, there was obtained 18 g. (82.5% of theory) of diethylamine hydrochloride by filtration. Evaporation of the ether gave crude XXXVe (85% yield) which was distilled.

The residue from the distillation of N-cyclohexyl-2-diethylaminoacetamide was heated with acetone and filtered. The white crystalline material, **2,2′-ethyliminobis-(N-cyclohexylacetamide) (XLIIe)** was dissolved in ethanol, filtered and precipitated on the addition of water; m.p. 156–157° (presoftening at 154°). The material was soluble in dilute acid but insoluble in dilute alkali and was chlorine free.

Anal. Calcd. for $C_{18}H_{33}N_3O_2$: C, 66.83; H, 10.28; N, 12.99; neut. equiv., 323.5. Found: C, 67.00; H, 10.33; N, 12.99; neut. equiv., 323.0.

N,N-Diallyl-1,3-dioxo-2-isoindolineacetamide (XXXb).—To 37.0 g. of potassium phthalimide in 250 ml. of dimethylformamide, there was added 34.7 g. of *N,N*-diallyl-2-chloroacetamide at 52–60° during 0.5 hr. The solution was held at 65–70° for 2 hr., cooled to room temperature and poured into 500 ml. of water. The phthalimido derivative was collected on a filter and washed with water, m.p. 100–101°. Recrystallization from aqueous ethanol raised the melting point to 102–103°. XXXa and XXXc were prepared similarly.

4-(Aminoacetyl)-morpholine Hydrochloride (XXXIc).—A solution of 36.6 g. of N-(morpholinocarbonylmethyl)-phthalimide in 500 ml. of absolute ethanol was treated with 10.0 g. of 85% hydrazine hydrate solution and heated at reflux for 2 hr. The solid residue, after removal of the solvent under reduced pressure, was heated at 50° for 10 minutes with 400 ml. of 2 *N* hydrochloric acid.[5] Phthalyl hydrazide (80%) was recovered by filtration at room temperature. The filtrate was concentrated to dryness at 20–25° (20 mm.) and the residue extracted with five 100-ml. portions of absolute ethanol. On cooling 15.0 g. (62% yield) of 4-(aminoacetyl)-morpholine hydrochloride was recovered as non-hygroscopic pearly plates. The melting point was not changed after several recrystallizations from absolute ethanol. XXXIa was prepared similarly and obtained as non-hygroscopic pearly plates.

N,N-Diallyl-2-aminoacetamide (XXXIIb).—N,N-Diallyl-2-aminoacetamide hydrochloride (XXXIb), prepared as described for the morpholine analog, was obtained as an oil which could not be induced to crystallize. It was dissolved in dilute alkali and the solution concentrated to a small volume at 20–25° (20 mm.). The residue was dissolved in ether–acetone mixture, filtered to remove sodium chloride, and after removal of the solvents, the free amine was distilled.

2-Amino-N,N-diethylacetamide (XXXIIa), the free amine, was prepared by passing 23.8 g. of 2-amino-N,N-diethylacetamide hydrochloride (XXXIa) in 150 ml. of water through Amberlite IRA (OH) resin in a 3 × 45 cm. column. The halogen free eluent was concentrated under reduced pressure and the residue distilled. There was obtained 14.7 g. (79% yield) of 2-amino-N,N-diethylacetamide.[9]

N-(Diallylcarbamoylmethyl)-1,3-dioxo-2-isoindolineacetamide (XXXIV).—N,N-Diallyl-2-aminoacetamide (7.4 g.) was chloroacetylated[3] to give 4.5 g. (41% yield) of **N-(diallylcarbamoylmethyl)-2-chloroacetamide (XXXIII)**, b.p. 177° (1.6 mm.). This material was converted to the phthalimido derivative XXXIV by heating at 80–90° for 1 hr. with 7 g. of potassium phthalimide in 100 ml. of dimethylformamide. The cooled mixture was poured into water and the solid collected on a filter and dried, yield 2.0 g. (30%). A sample recrystallized from aqueous ethanol melted at 136–137°.

Anal. Calcd. for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61; N, 12.31. Found: C, 63.43; H, 5.80; N, 12.14.

(9) G. B. Marini-Bettolo and J. F. Cavalla, *Gazz. chim. ital.*, **84**, 896 (1954).

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

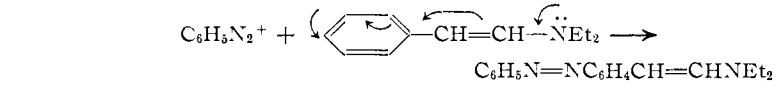
The Reaction of Enamines with Aromatic Diazonium Salts

BY JAMES W. CRARY,[1] OSBORNE R. QUAYLE[2] AND CHAS. T. LESTER

RECEIVED JUNE 4, 1956

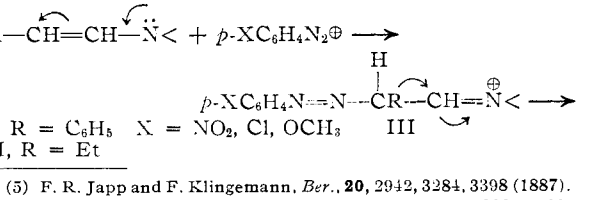
N,N-Diethylstyrylamine and 1-(1-butenyl)-piperidine have been treated with aromatic diazonium salts. Crystalline compounds, identified as the corresponding β-phenylhydrazones of phenylglyoxal and ethylglyoxal, were produced when *p*-nitro-, *p*-chloro- and *p*-methoxybenzenediazonium chloride salts were used. When the behavior of enamines possessing no β-hydrogen was investigated, *p*-substituted phenylhydrazones were the products identified: *viz.*, 1-(β-methylstyryl)-piperidine with 2,4-dinitrobenzenediazonium salt gave acetophenone 2,4-dinitrophenylhydrazone, and 1-(1-isobutenyl)-piperidine with *p*-nitrobenzenediazonium chloride gave acetone *p*-nitrophenylhydrazone. A mechanism for each of these reactions is proposed. The structures of the products were established by synthesis and by comparison of their infrared spectra to compounds of known structure.

N,N-Diethylstyrylamine is a vinylog[3] of N,N-diethylaniline. As such it might be expected to respond to electrophilic attack by a diazonium salt to form a *p*-substituted azo derivative



$$C_6H_5N{=}NC_6H_4CH{=}CHNEt_2$$

However, we have found that, when such a coupling procedure is attempted, the product is a β-phenylhydrazone of a glyoxal. The results of the alkylation of enamines,[4] of the Japp–Klingemann reaction[5] between diazonium salts and β-ketoesters, and of the reaction between diazonium salts and unsaturated anilines and phenol ethers[6] all bear striking relationships to the reactions herein reported. The steps in the production of the β-phenylhydrazones may be rationalized as



I, R = C_6H_5 X = NO_2, Cl, OCH_3 III

II, R = Et

(1) This contribution taken from the Ph.D. Dissertation of J. W. Crary, Emory University, 1955.

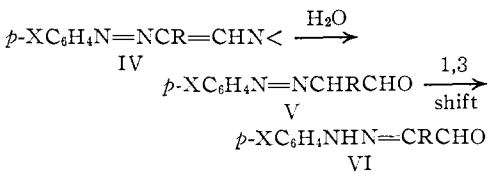
(2) Deceased, December 7, 1954.

(3) R. C. Fuson, *Chem. Revs.*, **16**, 1 (1935).

(4) G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

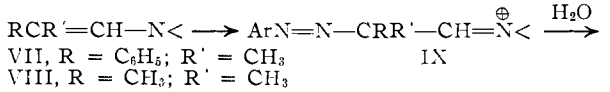
(5) F. R. Japp and F. Klingemann, *Ber.*, **20**, 2942, 3284, 3398 (1887).

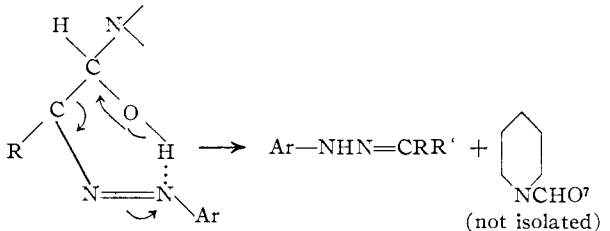
(6) (a) A. Quilico and N. Freri, *Gazz. chim. ital.*, **58**, 380 (1928); *C. A.*, **23**, 597 (1929); **59**, 600 (1929); **24**, 599 (1930); **60**, 606 (1930); *C. A.*, **25**, 932 (1931); (b) A. Quilico and E. Fleischner, *ibid.*, **59**, 39 (1929); **23**, 3675 (1929).

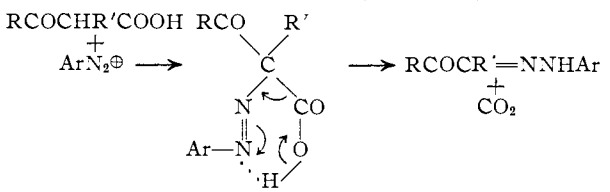


As indicated this reaction also has been successfully applied to 1-(1-butenyl)-piperidine (II), a totally aliphatic enamine. The β-phenylhydrazones prepared by this procedure are recorded in Table I.

If the above rationale is sound, an enamine with no β-hydrogen could not undergo the necessary shift II → III or IV → V to produce a β-phenylhydrazone of a glyoxal. Accordingly, the enamines 1-(β-methylstyryl)-piperidine (VII) and 1-(1-isobutenyl)-piperidine (VIII) were treated with diazonium salts. Phenylhydrazones of acetophenone and acetone were formed







Some difference in behavior between VII and VIII was noted. At the conclusion of the reaction of VII, XII was isolated directly. However, in the case of VIII an oil was isolated which changed to XIII only after treatment with acid.[8]

The structures of the β-phenylhydrazones were established in most cases by synthesizing the α-hydrazones, showing them to be different from the products of the reactions between the enamine and diazonium salt, and converting both the α- and β-phenylhydrazones to the same osazone by treating each with the proper phenylhydrazine.[9] The compounds involved are shown in Tables II and III.

Those compounds whose identities were not established as described above were identified by using infrared spectral data. From a comparison of the curves of known compounds the assignments indicated in Table IV were used.[10]

Experimental[11]

Preparation of the Enamines.—I, II and VIII were prepared in yields of 62, 53 and 45%, respectively, by the method of Mannich and Davidsen.[12] VIII was prepared, by the same procedure, from piperidine and hydratropic aldehyde, b.p. 119–120° at 2 mm., crude yield 77%. *Anal.* Calcd. for $C_{14}H_{12}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 84.10; H, 9.45; N, 6.60.

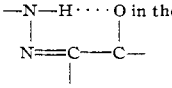
Preparation of Diazonium Salts.—The amine (0.01 mole) was diazotized using 3 ml. of concd. hydrochloric acid and 0.01 mole of sodium nitrite in sufficient ice and water to make 40–50 ml. of solution. 2,4-Dinitroaniline was diazotized in a special manner.[13]

Reactions of I and II with Diazonium Salts.—The enamine (0.01 mole) was dissolved in cold dilute hydrochloric acid (1.5 ml. of concentrated acid and 5–10 g. of ice), the resulting solution added to the diazonium salt solution and the reaction medium adjusted as rapidly as possible to *p*H 5–6 by the addition of sodium acetate solution. The solids which separated, either immediately or on standing (occasionally overnight), were isolated by filtration, washed with water, dried and crystallized from 95% ethanol. The crystalline products isolated in this manner are listed in Table I. The diazonium salts prepared from aniline, *p*-aminophenol and sulfanilic acid failed to give crystalline products. In addition to the β-*p*-chlorophenylhydrazone of phenylglyoxal, the reaction of I and *p*-chlorobenzenediazonium chloride also produced a small amount, 0.08 g., of a compound tentatively identified as *p*-chlorophenylformazan of benzaldehyde, m.p. 179–180°. *Anal.* Calcd. for $C_{19}H_{14}Cl_2N_4$: C, 61.80; H, 3.82; N, 15.2. Found: C, 61.62; H, 3.64; N, 14.9. The origin of this compound is obscure. It has been reported that some phenylhydrazones will react with diazonium salts to give formazans.[14]

(7) A mechanism similar to this can be written for the reaction of an alkylated β-ketoacid and a diazonium salt (F. R. Japp and F. Klingemann, *Ann.*, **247**, 218 (1888)).

(8) In the rearrangement of XI the product lacks the possibility of stabilization, by conjugation of —C=N— with a benzene ring, that exists for X. Additional acid may therefore be needed to initiate the rearrangement of XI, presumably by attack on the nitrogen bound to the aryl group.

(9) This method failed with the *p*-methoxyphenylhydrazone of phenylglyoxal. It was possible to prepare both the α- and the β-derivative and show that they were different but, although the β-hydrazone yielded the osazone, the α-isomer failed to react with the *p*-methoxyphenylhydrazine.

(10) All of the spectra of the β-derivatives of phenylglyoxal and ethyl glyoxal showed strong bands in carbonyl region at 5.9 μ. Since no absorption in this region was observed with the hydrazones of acetophenone and methyl ethyl ketone, this wave length was assigned to the aldehyde carbonyl of the glyoxal. This is above the upper limits of assignment for unconjugated aliphatic aldehydes (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 114–116, 226–228, 313–314). However, if one may assume conjugative interaction between the carbon to nitrogen double bond and the aldehyde group or "conjugate chelation" (R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949)) of the following type  in the hydrazone of glyoxals (N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3336 (1949)), the assignment is reasonable. The weak band in the region of 3 μ is attributed to the nitrogen to hydrogen bond (H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determinations of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949). The assignment of a frequency to the carbon to nitrogen double bond offered some difficulty. Bellamy (see reference above) assigns 5.92–6.10 μ as the region for unconjugated acyclic carbon to nitrogen double bonds. The absorption at 6.22 μ in the hydrazones of acetophenone and methyl ethyl ketone was so strong that this was assigned to the carbon–nitrogen double bond in these compounds. This same band appeared in the β-hydrazones of phenylglyoxal and ethylglyoxal. However in both of these classes of compounds the band at 6.22 μ became progressively narrower and less intense as the *p*-substituent was varied from nitro to chloro to methoxyl. This band at 6.22 μ was therefore assigned to the benzene nucleus and a band in the 6.4 μ region was assigned to the carbon to nitrogen double bond. This latter band remained constant in intensity relative to the carbonyl throughout all the glyoxal derivatives examined.

(11) All m.p.'s and b.p.'s reported are uncorrected. The analsyes reported were performed by Drs. G. Weiler and F. B. Straus of Oxford, England.

(12) C. Mannich and H. Davidsen, *Ber.*, **69B**, 2106 (1936).

(13) G. T. Morgan and E. D. Evans, *J. Chem. Soc.*, **115**, 1139 (1919).

(14) L. Mester and A. Major, THIS JOURNAL, **78**, 1403 (1956).

TABLE I

β-PHENYLHYDRAZONES OF GLYOXALS, R-C(CHO)=N-NH-C_6H_4-X-*p*

R	X	M.p., °C.	Yield, %	Analyses, % Calculated C	H	N	Found C	H	N
Phenyl	NO_2	186–187	94	62.45	4.12	15.6	61.89	4.51	15.4
Phenyl	Cl	147–148	90	64.99	4.29	10.83	65.09	4.32	10.7
Phenyl	CO_2H	246–248	89	67.15	4.51	10.4	66.67	4.51	9.95
Phenyl	OCH_3	137–139	76	70.84	4.44	11.0	70.74	5.64	10.9
Ethyl	NO_2	196–197	41	54.29	5.01	19.0	54.01	5.26	20.0
Ethyl	Cl	165–166	65	57.01	5.26	13.3	57.01	5.37	13.1
Ethyl	OCH_3	123–125	53	64.06	6.84	13.6	63.71	6.71	12.9

TABLE II

α-PHENYLHYDRAZONES OF GLYOXALS, R-CO-CH=N-NH-C_6H_4-X-*p*

R	X	M.p., °C.	Recrystn. solvent	Analyses, % Calculated C	H	N	Found C	H	N
Phenyl	NO_2	199[a]	Xylene	62.45	4.12	15.6	62.86	4.30	15.9
Phenyl	Cl	176	95% ethanol	64.99	4.29	10.8	65.43	4.57	10.9
Phenyl	CO_2H	281	Glacial HOAc	67.15	4.51	10.4	67.31	4.42	10.0
Phenyl	OCH_3	114	95% ethanol	70.84	5.55	11.0	71.00	5.86	11.1
Ethyl	NO_2	228[b]	95% ethanol	...	..	..	...	..	..

[a] E. Bamberger and D. Schmidt, *Ber.*, **34**, 2015 (1901), report 199°. [b] E. D. Vanus-Danilova and V. F. Kozimirova (*J. Gen. Chem.* (*U.S.S.R.*), **16**, 2099 (1946); *C. A.*, **42**, 110 (1948)) report 227°.

TABLE III

PHENYLOSAZONES OF GLYOXALS, HC=NNHC_6H_4X-*p*

RC=NNHC_6H_4X-*p*

R	X	M.p., C.	Recrystn. solvent	Analyses, % Calculated C	H	N	Found C	H	N
Phenyl	NO_2	346[a]	Nitrobenzene	59.40	3.99	20.9	59.81	4.06	21.0
Phenyl	Cl	200	95% ethanol	62.67	4.21	14.6	62.67	4.29	14.7
Phenyl	CO_2H	324	Glacial HOAc[b]	65.66	4.51	13.9	65.26	4.53	13.8
Phenyl	OCH_3[c]	138	95% ethanol	62.67	4.21	14.6	62.43	4.25	14.8
Ethyl	NO_2	285	Nitrobenzene	53.93	4.53	23.6	54.39	4.61	22.0

[a] A. F. Straus, *Ann.*, **393**, 282 (1912), reports 310°. [b] No good recrystallization solvent was found. The osazone was formed in glacial HOAc medium from which it crystallized immediately. [c] Prepared from phenylglyoxal β-(*p*-methoxyphenylhydrazone) only.

TABLE IV

INFRARED ASSIGNMENTS OF PHENYLHYDRAZONES

Compound	Functional group absorption, μ C=O	C=N	N—H
A. Acetophenone			
1, *p*-Nitrophenylhydrazone[a,b]	..	6.22	2.95
2, *p*-Chlorophenylhydrazone[a,c]	..	6.22	2.96
B. Methyl ethyl ketone			
1, *p*-Nitrophenylhydrazone[a,d]	..	6.22	2.96
C. Phenylglyoxal			
1, β-*p*-Nitrophenylhydrazone[a,b]	5.88	6.37	3.00
2, β-*p*-Chlorophenylhydrazone[a,b]	5.92	6.40	3.00
3, β-*p*-Methoxyphenylhydrazone[b,e]	5.95	6.42	3.00
D. Ethylglyoxal			
1, β-*p*-Nitrophenylhydrazone[a,b]	5.88	6.35	2.96
2, β-*p*-Chlorophenylhydrazone[b,e]	5.92	6.37	2.96
3, β-*p*-Methoxyphenylhydrazone[a,e]	5.95	6.39	2.96

[a] Structure established by synthesis. [b] Compound dissolved in chloroform. [c] Compound dissolved in carbon disulfide. [d] Compound dissolved in carbon tetrachloride. [e] Structure not established by synthesis.

Reaction of VII with Diazonium Salts.—The same reaction conditions as described above were used. With 2,4-dinitrophenyldiazonium salt, VII produced 2.9 g., 97%, of the 2,4-dinitrophenylhydrazone of acetophenone, m.p. and mixture m.p. with authentic sample, 246–247°. The *p*-nitrophenylhydrazone, 87%, m.p. and mixture m.p. 185–186°, and the *p*-carboxyphenylhydrazone, 95%, m.p. and mixture m.p. 249–250°, of acetophenone were similarly prepared from the reaction of VII with the appropriate diazonium salt.

Reaction of VIII with Diazonium Salts.—When *p*-nitrophenylbenzenediazonium chloride and VIII were allowed to react according to the general procedure, a red oil was formed which did not solidify on standing. However, when poured into concentrated hydrochloric acid, it quickly precipitated the solid *p*-nitrophenylhydrazone of acetone, m.p. and mixture m.p. (after crystallization), 148–150°. The reaction of *p*-chlorobenzenediazonium chloride and VIII also resulted in an uncrystallizable oil, which produced crystals, m.p. 78–82°, on heating with dilute hydrochloric acid; reported m.p. of *p*-chlorophenylhydrazone of acetone, 84°.[15]

Coupling in Non-aqueous Media.—*p*-Nitroaniline (1.4 g., 0.01 mole) was dissolved in 25 ml. of absolute ethanol containing 1.7 ml. (0.03 mole) of concd. sulfuric acid in a 150-ml. flask. After cooling to 0°, 2 ml. (0.01 mole) of *n*-butyl nitrite[16] in 10 ml. of absolute ethanol was added. When the diazonium salt separated from solution, a cold solution of 1.8 g. (0.01 mole) of I in 10 ml. of absolute ethanol was added, followed immediately by 5 ml. of diethylamine in 10 ml. of absolute ethanol. After standing one hour, the solution was poured into 200 ml. of water. A brown solid precipitated (1.5 g., 56% yield). After filtering, drying and recrystallizing from 95% ethanol, this product had a m.p. and mixture m.p. with β-*p*-nitrophenylhydrazone of phenylglyoxal, of 184–186°.

Sodium *p*-nitrophenyl-*anti*diazoate (2.5 g., 0.013 mole), prepared as previously described,[17] was coupled with I (2.2 g., 0.013 mole) at 0° in 100 ml. of glacial acetic acid. The

(15) E. Bamberger, *Ber.*, **30**, 218 (1897).

(16) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 108.

(17) C. Schraube and C. Schmidt, *Ber.*, **27**, 518 (1894).

solution was immediately diluted with 200 ml. of water. The yellow solid which precipitated, 1.8 g., 66%, after crystallization was identified as the β-*p*-nitrophenylhydrazone of phenylglyoxal.

Preparation of α-Phenylhydrazones of Glyoxals.—The four α-phenylhydrazones of phenylglyoxal were prepared from sodium benzoylacetate by reaction with the proper diazonium salt.[18] Similarly, *p*-nitrobenzenediazonium chloride was treated with sodium propionylacetate,[19] according to a procedure described for sodium acetoacetate,[20] to produce the α-*p*-nitrophenylhydrazone of ethylglyoxal. The α-derivatives are recorded in Table II.

Preparation of Phenylosazones of Glyoxals.—The reaction of phenylglyoxal[21] with the appropriate phenylhydrazine and the reaction of the α- and β-phenylhydrazones of the glyoxals were all done in the usual manner.[22] *p*-Methoxyphenylhydrazine was prepared by the method of Blaike and Perkin.[23] The other hydrazines were prepared by a method described for phenylhydrazine.[24]

Infrared Absorption Spectra.—The spectra were determined as solutions in carbon tetrachloride, carbon disulfide and chloroform. A Perkin-Elmer double beam, self-recording instrument, with rock salt optics throughout the region studied, was employed. Sodium chloride cells of 0.111 mm. and 0.215 mm. were used.

Acknowledgment.—We wish to express our appreciation to W. A. Blanchard and W. C. Bailey who determined the infrared spectrograms and to Drs. Leon Mandell and J. H. Goldstein who helped in their interpretation.

(18) E. Bamberger and A. Schmidt, *Ber.*, **34**, 2015 (1901).

(19) A. Brandstrom, *Acta Chem. Scand.*, **5**, 820 (1951).

(20) F. D. Chattaway and D. R. Ashworth, *J. Chem. Soc*, 930 (1934).

(21) W. Madelung and M. E. Oberwegner, *Ber.*, **65**, 931 (1932).

(22) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(23) K. G. Blaike and W. H. Perkin, *J. Chem. Soc.*, **125**, 313 (1924).

(24) Reference 16, Coll. Vol. I, p. 442.

EMORY UNIVERSITY, GEORGIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, AND THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. X. Rearrangement During the Deamination of 1,2,2-Triphenylethylamine with Nitrous Acid[1]

BY WILLIAM A. BONNER AND CLAIR J. COLLINS

RECEIVED MAY 25, 1956

1,2,2-Triphenylethylamine, alternately labeled with radioactive carbon at carbon-1 and in the 1-phenyl nucleus, has been prepared and subjected to deamination with nitrous acid. 1,2,2-Triphenylethanol constituted over 95% of the product from these deaminations. The extent of isotope position isomerization attending the deaminations has been determined by oxidation of the carbinol products to benzophenone and benzoic acid, followed by radioactivity assay of these fragments. The net phenyl migration accompanying deamination of the carbon-1 labeled amine could be related to that observed during deamination of the 1-phenyl labeled amine using simple kinetic expressions based on the assumption of equilibrating classical 1,2,2-triphenylethylcarbonium ions as the sole reaction intermediates. The present radiochemical results thus lend strong support to the theory of equilibrating classical ions previously proposed to rationalize radiochemical data from tosylate solvolyses and dehydration reactions in the 1,2,2-triphenylethyl system.

Introduction

We have reported in earlier papers[2] the radiochemical results of the solvolytic and elimination reactions of multiply-labeled derivatives of 1,2,2-triphenylethanol (I). The reactions so studied could be divided into two classes depending upon

$Ph_2C^*CHOHPh$ (Ia) $\qquad Ph_2CHCHOHPh^*$ (Ic)

$^*Ph_2C{=}CHPh^*$ (IIcd) $\qquad Ph_2^*C{=}^*CHPh$ (IIab)

whether or not the radiochemical isomerizations were complete. Thus the acid-catalyzed elimination reactions[2c] of Ia and Ic and their acetates yielded the olefins IIab and IIcd, respectively, which possessed statistical distributions of their radioactive labels. The isotope position isomerization of the acetates[2d] of Ia and Ic likewise proceeded to a statistical conclusion. In contrast, the acetolyses[2c] and hydrolyses[2c] of the tosylates of Ia and Ic, as well as the *p*-toluenesulfonic acid-catalyzed dehydrations (in xylene) of Ia and Ic, yielded products whose labels were not distributed statistically. Further, in all of the reactions studied there was a higher percentage rearrangement of the phenyl label than of the chain label.

The concept of bridged ions as intermediates[3] in certain molecular rearrangements very satisfactorily accounts for the stereochemistry and kinetics observed, particularly in those cases studied by Cram[3c] in which the rate-determining ionization is assisted by the migrating group. The observed radiochemical[2c,d] results for the rearrangement of 1,2,2-triphenylethanol and its derivatives, in contrast, are best explained by assuming that the

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