The boiling points of the two dienes follow the rather empirical rule that similar homologs boil about 20° apart; however, the "apparent" low boiling points of the two compounds are not too "anomalous," if the C_9F_{16} and $C_{10}F_{18}$ are compared to the fluorocarbons C_7F_{16} (b.p. 82°) and C_8F_{18} (b.p. 102°) and 5° is added for each degree of unsaturation.

Acknowledgments.—The authors wish to thank Dr. Max Rogers of Michigan State University for obtaining n.m.r. spectra on the dienes and assisting in the interpretation of this data. They also wish to thank Dr. T. M. Reed, III, of the University of Florida, for the use of gas chromatographic equipment. Support for this work by the Chemistry Branch of the Office of Naval Research is gratefully acknowledged.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Novel Reductions of N-Nitrosodibenzylamines—A New Reaction[1]

BY C. G. OVERBERGER, JOSEPH G. LOMBARDINO[2] AND RICHARD G. HISKEY

RECEIVED NOVEMBER 29, 1957

N-Nitrosodibenzylamines were reduced by sodium hydrosulfite in basic media or by lithium in liquid ammonia to give an unexpected evolution of nitrogen with formation of hydrocarbon products. For example, reaction of sodium hydrosulfite with *cis*-1-nitroso-2,6-diphenylpiperidine gave *cis*-1,2-diphenylcyclopentane and 1,5-diphenyl-1-pentene while *trans*-1-nitroso-2,6-diphenylpiperidine gave a mixture of *cis*- and *trans*-1,2-diphenylcyclopentane and 1,5-diphenyl-1-pentene. Sodium hydrosulfite reduction of N-nitrosodibenzylamine gave high yields of bibenzyl. The products in almost every case were identical to those isolated from mercuric oxide oxidation of the corresponding N-aminodibenzylamine. A mechanism is suggested which has an identical intermediate for these "abnormal" reductions of nitrosamines and for the mercuric oxide oxidation of the corresponding 1,1-disubstituted hydrazines. Other N-nitrosodialkylamines were reduced readily to dialkylhydrazines by sodium hydrosulfite providing a new, convenient method of reducing nitrosamines.

In the course of a study on the oxidation behavior of 1,1-disubstituted hydrazines it was desirable to obtain *trans*-1-amino-2,6-diphenylpiperidine[3] from *trans*-1-nitroso-2,6-diphenylpiperidines. A wide variety of reducing systems were explored[3] including some methods not previously used for reducing a nitrosamine to a hydrazine. Two of these reducing systems gave especially interesting results with *trans*-1-nitroso-2,6-diphenylpiperidine. Both sodium hydrosulfite in basic media and lithium in liquid ammonia yielded only hydrocarbon products when applied to the *trans*-nitrosamine, prompting a more thorough study of the scope of these novel transformations.

Sodium hydrosulfite in strongly basic media has been reported previously to reduce C-nitro and C-nitroso functions to primary amines.[4a,b] This powerful reducing agent has now been applied to a series of nitrosamines and the results are summarized in Table I.

From these results, it can be seen that nitrosodibenzylamines eliminate nitrogen, whereas mixed benzylalkyl or dialkyl nitrosoamines are reduced to the corresponding hydrazines. An exception to this rule is N-nitrosodiphenylamine which gave diphenylamine; however, the cleavage of the nitrogen–nitrogen bond in N-nitrosodiphenylamine has previously been reported using other reducing agents.[5] It would appear that the sodium hydrosulfite reduction of dialkyl nitrosamines to the corresponding hydrazines is safer and more convenient than any previously reported methods. The products from the nitrosamines I, II and III were identical to those isolated from the mercuric oxide oxidation of the corresponding 1,1-disubstituted hydrazines[3,6] (Table II) suggesting a common intermediate for both the mercuric oxide oxidation of the hydrazines and for sodium hydrosulfite reduction of nitrosamines (see below).

TABLE I

Compound reacted with $Na_2S_2O_4$	Product	Yield, %
N-Nitrosodibenzylamine (I)	Bibenzyl	77
cis-1-Nitroso-2,6-diphenylpiperidine (II)	*cis*-1,2-Diphenylcyclopentane;	56.8
	1,5-diphenyl-1-pentene	21.4
trans-1-Nitroso-2,6-diphenylpiperidine (III)	*trans*-1,2-Diphenylcyclopentane	60.4
	cis-1,2-Diphenylcyclopentane	
	1,5-Diphenyl-1-pentene	19
N-Nitrosobenzylphenylamine	1-Phenyl-1-benzylhydrazine	77
N-Nitrosodiphenylamine	Diphenylamine	80
1-Nitroso-2,6-dimethylpiperidine	1-Amino-2,6-dimethylpiperidine	40

The action of lithium in liquid ammonia on a

TABLE II

Hydrazine oxidized with mercuric oxide	Product	Yield, %	Ref.
1,1-Dibenzylhydrazine	Bibenzyl	83	3, 6
cis-1-Amino-2,6-diphenylpiperidine	*cis*-1,2-Diphenylcyclopentane	65	3
	1,5-Diphenyl-1-pentene	25	
trans-1-Amino-2,6-diphenylpiperidine	*cis*- and *trans*-1,2-Liphenylcyclopentane	71	3
	1,5-Diphenyl-1-pentene	14	

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(1) This is the 22nd in a series of papers concerned with the preparation and decomposition of azo and diazo compounds. For the previous paper in this series, see C. G. Overberger and J. G. Lombardino, THIS JOURNAL, **80**, 2317 (1958). For a preliminary report of this work see C. G. Overberger, J. G. Lombardino and R. G. Hiskey, *J. Org. Chem.*, **22**, 858 (1957). Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., Sept., 1957 (Abstracts p. 38-P).

(2) From a portion of the Dissertation submitted by Joseph G. Lombardino in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger, J. G. Lombardino and R. G. Hiskey, THIS JOURNAL, **79**, 6430 (1957).

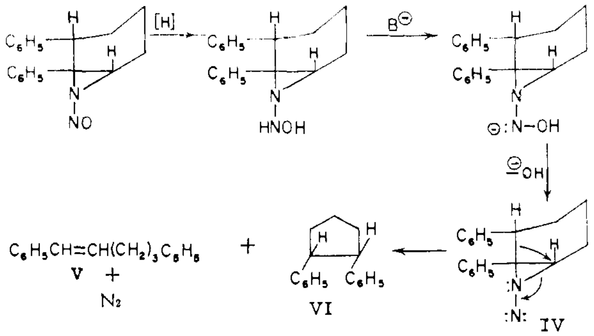
(4) (a) G. T. Redemann and C. E. Redemann, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 69. (b) J. B. Conant and B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 33.

(5) F. W. Schueler and C. Hanna, THIS JOURNAL, **73**, 4996 (1951).

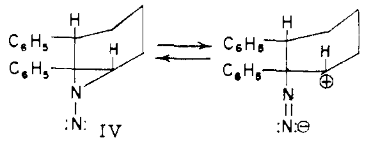
(6) M. Busch and B. Weiss, *Ber.*, **33**, 270 (1900).

nitrosamine has been reported to yield the corresponding hydrazine.[7] When applied to *cis*- and to *trans*-1-nitroso-2,6-diphenylpiperidine, however, the nitrosamine eliminated all of its nitrogen and yielded only hydrocarbon products. From *cis*-1-nitroso-2,6-diphenylpiperidine (II) was obtained 26% of 1,5-diphenyl-1-pentene (V) and 45% of *cis*-1,2-diphenylcyclopentane (VI). From *trans*-1-nitroso-2,6-diphenylpiperidine (III) was obtained 91% of a mixture of *cis*- and *trans*-1,2-diphenylcyclopentane Again, these products are almost identical to those obtained by mercuric oxide oxidation of the corresponding 1-amino-2,6-diphenylpiperidines (Table II). Reaction of N-nitrosodibenzylamine with lithium in ammonia gave a mixture of four products in addition to a small amount of expected bibenzyl (4%). Among these unexpected products were dibenzylamine (15%), benzylamine (37.5%), tribenzylhydrazine (6%) and an as yet unidentified solid containing an azomethine linkage. These products appear anomalous when compared with the very similar *cis*- and *trans*-1-nitroso-2,6-diphenylpiperidines which eliminate all of their nitrogen in this reaction. No simple explanation for these results is evident; however, it should be noted that the products isolated from the reaction of lithium in ammonia with N-nitrosodibenzylamine are very similar to those isolated from the *t*-butyl hypochlorite oxidation of 1,1-dibenzylhydrazine.[8] In addition to the above-mentioned products, tetrabenzyltetrazene was isolated from the *t*-butyl hypochlorite oxidation and Overberger and Marks[8] have suggested that thermal decomposition of the tetrabenzyltetrazene could yield the observed dibenzylamine and benzylamine. In the present work, however, thermal decomposition of an intermediate tetrazene seems less likely at the temperature of liquid ammonia. If tetrabenzyltetrazene were formed by combination of two fragments of an intermediate similar to IV (see below), hydrogenolysis of the tetrazene could also yield benzylamine and dibenzylamine. Direct hydrogenolysis of dibenzylhydrazine and dibenzylamine may also occur to account for the reaction products.

The following mechanism is proposed for the nitrogen elimination reactions of dibenzyl-type nitrosamines with either sodium hydrosulfite or lithium in liquid ammonia

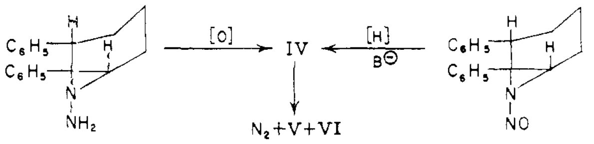


In this scheme, B^- is hydroxyl ion in the sodium hydrosulfite reductions and amide ion in the lithium–ammonia reductions. It has been previously pointed out[3] that structure IV may be in the equilibrium shown and that this gives rise to the olefin structure V by elimination of nitrogen and a proton.

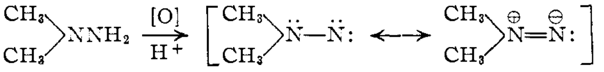


The stereospecific elimination of nitrogen by a concerted process to give VI with retention of configuration at the benzyl carbon has also previously been discussed.[3]

It should be noted that the intermediate IV is identical to that proposed for the mercuric oxide oxidation of 1-amino-2,6-diphenylpiperidines[3] and the identical products obtained in both cases lend further support to a common intermediate in both reactions.



An intermediate such as IV previously has been discussed in the literature. Kenner and Knight[9] have suggested a similar intermediate for the Busch and Weiss[6] oxidation of 1,1-dibenzylhydrazine. McBride and Kruse[10] have presented evidence for the existence of the conjugate acid of the intermediate VII from oxidation of 1,1-dimethylhydrazine.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!NNH_2 \xrightarrow[H^+]{[O]} \left[\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\ddot{N}-\ddot{N}: \longleftrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\overset{\oplus}{N}=\overset{\ominus}{N}:\right]$$

VII

Carpino[11] also has suggested an intermediate such as IV for the decomposition of 1,1-dibenzyl-2-arylsulfonhydrazides in basic media. Thus, it is suggested that all the aforementioned reactions, including sodium hydrosulfite or lithium in ammonia reduction of dibenzylnitrosamines, mercuric oxide oxidation of dibenzylhydrazines and basic decomposition of dibenzyl sulfonhydrazides have a common intermediate such as IV.

Experimental

Preparation of Nitrosamines.—N-Nitrosodibenzylamine was prepared according to the procedure of Overberger, *et al.*,[12] by the nitrosation of dibenzylamine, m.p. 60–61° (m.p. 61°).[12]

The preparation of *cis*- and *trans*-1-nitroso-2,6-diphenylpiperidine has been described previously.[3]

N-Nitrosobenzylphenylamine and N-nitrosodiphenylamine were Eastman Kodak Co. organic chemicals.

A sample of 1-nitroso-2,6-dimethylpiperidine[12] was kindly furnished by Dr. B. Marks.

Reaction of N-Nitrosodibenzylamine with Sodium Hydrosulfite.—A solution of 3.4 g. (0.015 mole) of N-nitrosodi-

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[7] R. C. Cookson and M. E. Trevett, *J. Chem. Soc.*, 2089 (1956).

[8] C. G. Overberger and B. S. Marks, THIS JOURNAL, **77**, 4104 (1955).

[9] J. Kenner and E. C. Knight, *Ber.*, **69**, 341 (1936).

[10] W. R. McBride and H. W. Kruse, THIS JOURNAL, **79**, 572 (1957).

[11] L. A. Carpino, *ibid.*, **79**, 4427 (1957).

[12] C. G. Overberger, B. S. Marks, L. Palmer and N. Byrd, *ibid.*, **77**, 4100 (1955).

benzylamine and 100 ml. of a 1:1 mixture of ethanol and 20% aqueous sodium hydroxide solution was prepared at 58°. A tube was attached to the condenser so as to lead evolved gases into a 1-liter graduate filled with water and inverted in a beaker of water. The solution was stirred under a stream of nitrogen for 0.5 hour and then 5.25 g. (0.030 mole) of sodium hydrosulfite was placed in a solids addition tube and the system sealed. The solid was added in one portion and after 10 minutes nitrogen began to evolve. After approximately 4 hours, the theoretical volume of nitrogen, 367 ml., had been evolved. The reaction mixture was added to an equal volume of salt solution, extracted three times with ether and the ether layers dried over magnesium sulfate. On removal of solvent and recrystallization of the residual solid, there was obtained 2.10 g. (77%) of bibenzyl, m.p. 53–54°. A mixture melting point with a sample of authentic bibenzyl, m.p. 51.5–52.5°, melted at 53.0–54.5°.

In another experiment, 25 g. of N-nitrosodibenzylamine was reduced and the products distilled in an attempt to detect side products, but only bibenzyl could be identified.

Reaction of *cis*-1-Nitroso-2,6-diphenylpiperidine with Sodium Hydrosulfite.—A solution of 3.0 g. (0.0113 mole) of *cis*-1-nitroso-2,6-diphenylpiperidine (m.p. 67–69°)[3] and 100 ml. of a 1:1 mixture of ethanol and 20% aqueous sodium hydroxide was prepared. The solution was maintained at 58° in a water-bath and stirred under a stream of nitrogen for 30 minutes. Then 4.35 g. (0.025 mole) of sodium hydrosulfite was placed in the solids addition tube and the system sealed. The solid was added in one portion and after approximately 7 minutes, the evolution of nitrogen gas was observed. After 4.5 hours the theoretical amount of nitrogen, 276 ml., had been evolved. The reaction was poured into an equal volume of salt water, extracted with two 100-ml. portions of Skellysolve B, b.p. 60–70°, and the extracts dried over magnesium sulfate. The solvent was reduced to approximately 50 ml., the residual solution passed through 100 g. of neutral alumina (Woelm, activity one) using dry Skellysolve B as eluent and eight 100-ml. fractions collected. All fractions were combined and evaporated to dryness under vacuum to yield a clear liquid, a mixture of isomeric material weighing 1.97 g. (79%). A comparison of the quantitative infrared spectrum of this liquid with that of an authentic[13] mixture of *cis*-1,2-diphenylcyclopentane, m.p. 46–47°,[14] and 1,5-diphenyl-1-pentene[15] showed identical absorption peaks. The intensity of the peak at 10.37 μ indicated[3] that 21.4% of the liquid was 1,5-diphenyl-1-pentene.

The sample used for infrared analysis was combined with the main portion of liquid and the combined material dissolved in 10 ml. of acetic acid. To this was added a solution of 0.68 g. (0.0029 mole) of 2,4-dinitrobenzenesulfenyl chloride in 4 ml. of warm acetic acid. On standing, the yellow solution deposited a yellow solid, m.p. 112.5–114.5°. A mixture melting point with the 2,4-dinitrobenzenesulfenyl chloride derivative of authentic 1,5-diphenyl-1-pentene, m.p. 113–115°,[3] was not depressed, m.p. 113–115°.

The filtrate was evaporated to dryness, then placed under high vacuum in a desiccator over potassium hydroxide pellets for 12 hours. The residual red oil was extracted several times with dry Skellysolve B and the extracts chromatographed through neutral alumina (Woelm, activity one). The first six 50-ml. fractions yielded 1.42 g. (56.8%) of *cis*-1,2-diphenylcyclopentane, m.p. 43–45° (46°).[13,14] A mixture melting point with authentic[13] *cis*-1,2-diphenylcyclopentane, m.p. 46–47°, was not depressed, m.p. 43.5–46°.

Reaction of *trans*-1-Nitroso-2,6-diphenylpiperidine with Sodium Hydrosulfite.—The reaction of *trans*-1-nitroso-2,6-diphenylpiperidine[3] with sodium hydrosulfite was carried out as described above for the *cis* isomer. Chromatographing the reaction products in Skellysolve B yielded 83% of the theoretical amount of isomeric products. A quantitative infrared spectra was identical with that of an authentic mixture of *cis*- and *trans*-1,2-diphenylcyclopentane[3,13] and 1,5-diphenyl-1-pentene.[15] From the intensity of the absorption at 10.37 μ[3] it was estimated that 19% of the mixture was 1,5-diphenyl-1-pentene. Treatment of the mixture with 2,4-dinitrobenzenesulfenyl chloride in acetic acid followed by chromatography using Skellysolve B removed the olefin and gave 1.58 g. (63%) of a white solid, m.p. 50–60°. Attempts to fractionate this mixture of 1,2-diphenylcyclopentanes by crystallization, failed.

Reaction of N-Nitrosobenzylphenylamine with Sodium Hydrosulfite.—As previously described for the reaction of N-nitrosodibenzylamine, a solution of 5.0 g. (0.0235 mole) of N-nitrosobenzylphenylamines, m.p. 57–58°, was prepared in 50 ml. of 20% aqueous sodium hydroxide and 75 ml. of ethanol. After stirring the solution under a nitrogen atmosphere at 58° for 30 minutes, 8.2 g. (0.047 mole) of sodium hydrosulfite was added in one portion to the closed system. No significant gas evolution was noted over 12 hours after which the reaction was poured into water, extracted with ether and the extracts dried over magnesium sulfate. Evaporation of the solvent yielded 3.6 g. (77%) of 1-phenyl-1-benzylhydrazine. A hydrochloric acid salt was prepared in ether, m.p. 170–173° (167°).[16]

Reaction of N-Nitrosodiphenylamine with Sodium Hydrosulfite.—Into 5.0 g. (0.025 mole) of N-nitrosodiphenylamine (m.p. 66–67°) dissolved in 50 ml. of ethanol and 50 ml. of 20% aqueous sodium hydroxide solution, heated to 60° and stirred magnetically, was passed a stream of nitrogen gas. Then, 8.78 g. (0.051 mole) of sodium hydrosulfite was added in one portion and heating and stirring continued for five hours. The reaction was then poured into 300 ml. of water, extracted twice with ether and the extracts dried over magnesium sulfate. On complete evaporation of solvent under high vacuum, 3.4 g. (80%) of diphenylamine as white plates was obtained which on recrystallization from an ethanol–water mixture melted at 53.2–54.4° (m.p. 53.9°).[17]

A sulfuric acid salt of the product was prepared in ether, m.p. 124.5–126° (m.p. 123–125°).[17]

Reaction of *cis*-1-Nitroso-2,6-dimethylpiperidine with Sodium Hydrosulfite.—Under conditions identical to those used for the reaction of N-nitrosodiphenylamine with sodium hydrosulfite, 2.24 g. (0.0157 mole) of *cis*-1-nitroso-2,6-dimethylpiperidine[12] and 6.0 g. (0.036 mole) of sodium hydrosulfite yielded, after drying an ether solution of the product and treatment with picric acid in ether, 2.2 g. (39.8%) of the picric acid salt of 1-amino-2,6-dimethylpiperidine, m.p. 167.5–169°. A mixture melting point with the picric acid salt of authentic 1-amino-2,6-dimethylpiperidine,[12] m.p. 167–168°, melted at 167–169°.

Reduction of *cis*-1-Nitroso-2,6-diphenylpiperidine with Lithium in Ammonia.—To 0.26 g. (0.0375 g. atom) of lithium ribbon dissolved in 100 ml. of liquid ammonia was added dropwise with stirring a solution of 2.0 g. (0.0075 mole) of *cis*-1-nitroso-2,6-diphenylpiperidine dissolved in 50 ml. of dry ether and 10 ml. of dry dioxane. After complete addition, color changes from blue to white and then from violet to red were evident. The red solution was stirred an additional 1.5 hours and then hydrolyzed with 25 ml. of ethanol followed by 100 ml. of water. The white reaction mixture was poured into water and extracted twice with ether and dried. Removal of the solvent followed by chromatography of the residue on alumina gave 1.17 g. (71%) of a liquid mixture of isomeric materials. An infrared spectrum of the mixture showed it to be identical to a mixture of authentic *cis*-1,2-diphenylcyclopentane[13] and 1,5-diphenyl-1-pentene.[15] The intensity of the absorption at 10.37 μ indicated that 26% of the mixture was 1,5-diphenyl-1-pentene.

Reduction of *trans*-1-Nitroso-2,6-diphenylpiperidine with Lithium in Ammonia.—Reduction was carried out as described above for the *cis* isomer except that the white solution obtained after complete addition was allowed to stand overnight at room temperature. Hydrolysis and extraction followed by removal of the solvent yielded 1.52 g. (91.5%) of a liquid whose infrared spectrum was identical with that of a mixture of authentic *cis*- and *trans*-1,2-diphenylcyclopentane.[3,13] Attempts to fractionate this mixture chromatographically were unsuccessful.

Reaction of N-Nitrosobenzylphenylamine with Lithium in Ammonia.—In a similar manner, reduction of 3.0 g. (0.014 mole) of N-nitrosobenzylphenylamine with 0.49 g. (0.07 g. atom) of lithium afforded an oil which on treatment with dry hydrochloric acid in ether solution yielded 2.52 g. (76%) of benzylphenylamine hydrochloride, m.p. 213.5–

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[13] F. Japp and G. Lander, *J. Chem. Soc.*, **71**, 131 (1897).

[14] H. A. Weidlich, *Ber.*, **71**, 1601 (1938).

[15] C. G. Overberger and J. J. Monagle, THIS JOURNAL, **78**, 4470 (1956).

[16] A. Michaelis and B. Phillips, *Ann.*, **252**, 287 (1889).

[17] I. Heilbron, "Dictionary of Organic Compounds," Oxford Univ. Press, New York, N. Y., 1953, p. 402.

215° (214–216°).[18] A mixture melting point with an authentic sample of the hydrochloric acid salt of benzylphenylamine, m.p. 214.5–216°, melted at 213–215°.

Reaction of N-Nitrosodibenzylamine with Lithium in Liquid Ammonia.—To a stirred solution of 1.54 g. (0.22 g. atom) of lithium dissolved in 250 ml. of liquid ammonia was added dropwise a solution of 10.0 g. (0.044 mole) of N-nitrosodibenzylamine in 125 ml. of dry ether and 25 ml. of dry dioxane. External cooling was removed and after 10 minutes color change from blue to white then from orange to bright red was observed. The red reaction was stirred for 1.5 hours and then hydrolyzed with 50 ml. of ethanol followed by 50 ml. of water. The reaction mixture was poured into 500 ml. of water, extracted with ether and the extracts dried over magnesium sulfate. Removal of solvent yielded 5.0 g. of residue.

At this point, in another experiment, 6% of tribenzylhydrazine, m.p. 82.5–84° (m.p. 86°)[8] was isolated by crystallization from the residue. A picrate salt was prepared in ether, m.p. 138–140.5 (m.p. 140–141°).[8]

The mixture was extracted with dry Skellysolve B several times and the extracts chromatographed through neutral alumina (Woelm, activity one). A Skellysolve B-insoluble material was recrystallized from ethanol, 0.50 g., m.p. 205–207°. This solid contains nitrogen and an infrared spectrum exhibited a strong absorption at 6.08 μ, probably C=N.[19] The solid reacts slowly with a methanolic hydrochloric acid solution of 2,4-dinitrophenylhydrazine to give an orange derivative, m.p. 118–121°. The solid was not further characterized.

The first 25-ml. fraction obtained from the column, using dry Skellysolve B as eluent, yielded 0.32 g. (4%) of bibenzyl, m.p. 50–51.5°; a mixture melting point with authentic bibenzyl melted at 50–52°. The next three fractions yielded 1.75 g. (37.5%) of benzylamine, whose picrate salt prepared in ether, melted at 197–200° (195–199°).[20] A mixture melting point with the picrate salt of authentic benzylamine melted at 197.5–200°. A yellow band was removed from the column, using dry methanol as eluent, yielding 1.3 g. (15%) of dibenzylamine, whose picrate salt prepared in ether melted at 139–141°. A mixture melting point with the picrate salt of authentic dibenzylamine prepared in ether melted at 138.5–140°.

The picrate salt of authentic dibenzylamine was prepared by adding excess saturated picric acid in ether to an ether solution of the amine. Three separate preparations of this salt using various samples of dibenzylamine all yielded a yellow solid, m.p. 140°. The previously reported[8] picrate of dibenzylamine could not be duplicated. An analytical sample was prepared by recrystallization from ethanol to yield yellow needles, m.p. 140–141° (93–94°).[8]

Anal.[21] Calcd. for $C_{20}H_{18}N_4O_7$: C, 56.34; H, 4.25; N, 13.14. Found: C, 56.48; H, 4.61; N, 13.19.

Acknowledgment.—We wish to gratefully acknowledge the support of this work by the National Science Foundation, Grant NSF-1453.

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[18] W. S. Emerson and P. M. Walters, THIS JOURNAL, **60**, 2023 (1938); K. Brand, *Ber.*, **42**, 3460 (1909).

[19] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 226.

[20] G. Jerusalem, *J. Chem. Soc.*, **95**, 1283 (1909).

[21] Analyses by Schwarzkopf Laboratories, New York, N. Y.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Pyrolysis of Pyruvic Acid Hydrazones[1]

BY J. H. BOYER AND L. R. MORGAN, JR.

RECEIVED DECEMBER 30, 1957

Thermal decarboxylation of pyruvic acid hydrazones (I) through zwitterions provides a basis for understanding the formation of both acetaldehyde and, in some cases, biacetyl derivatives. When the hydrazone terminal nitrogen is weakly basic, zwitterions of type III predominate and decarboxylation leads to the formation of corresponding acetaldehyde and biacetyl hydrazones. The formation of the phenylhydrazone (X) of α-acetylquinoline upon decarboxylation of pyruvic acid phenylhydrazone (Ib) in quinoline establishes the presence of an intermediate (VIb) capable of reacting with cationoid reagents. For those hydrazones in which terminal nitrogen is more strongly basic, it is proposed that decarboxylation proceeds through β,γ-azobetaines (IV) with the formation of acetaldehyde but not of biacetyl hydrazones. With the respective loss of ammonia and aniline, the bis-hydrazone at 170° and the bis-phenylhydrazone of biacetyl at 300° undergo ring-closure condensation into 4,5-dimethyltriazole and 2-phenyl-4,5-dimethyltriazole. The latter also is obtained from the monophenylhydrazone monoxime of biacetyl at 200°. At 160° a mixture of α- and β-acetaldehyde phenylhydrazones is transformed quantitatively into the β-modification (lower melting).

A bis-phenylhydrazone (VIII) of biacetyl was reported in 1888[2] as a product from thermal decarboxylation of pyruvic acid phenylhydrazone (Ib). The present work, undertaken to explain its formation, developed into an investigation on the thermal decarboxylation of five pyruvic acid hydrazones. Other products from Ib included carbon dioxide, ammonia and the phenylhydrazones Vb of acetaldehyde.[2] These have now also been obtained by carrying out the decarboxylation in inert solvents. From pyruvic acid dinitrophenylhydrazone (Ic) the best yield (60%) of biacetyl, isolated as its bis-dinitrophenylhydrazone, and the lowest yield of acetaldehyde, isolated as its dinitrophenylhydrazone, have been obtained. In contrast only the corresponding acetaldehyde derivatives are obtained from pyruvic acid hydrazone (Ia), α-methyl-α-phenylhydrazone (Id) and diphenylhydrazone (Ie).

Interpretation of the data has been based upon an ionic process for thermal decarboxylation of carboxylic acids as an established rule and the prediction that decarboxylation of a zwitterion will require less activation energy than of a corresponding acid anion.[3] The ratio (II/III) of the two zwitterionic forms for pyruvic acid hydrazones is dependent upon relative basicities of the hydrazone nitrogen atoms. For those hydrazones with weakly basic terminal nitrogen, zwitterions III may predominate in decarboxylation. It is predicted that hydrazones I with no demonstrable basicity at terminal nitrogen will decarboxylate exclusively through zwitterions of type III. For those hydrazones in which the terminal nitrogen is appreciably basic an additional equilibrium with an

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[1] Partial support of this work under a National Institutes of Health Grant No. CY-2895-CY is gratefully acknowledged.

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