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Alkylhydrazines. III. Dimerization of Certain Substituted 1,1-Dialkyldiazenes to Tetraalkyltetrazenes[1-3]

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The characterization of an unusual class of compounds from the two-electron oxidation of 1,1-dialkylhydrazines in acid is discussed. Spectrophotometric data support the tentative conclusion of $R_2N^+{=}NH$ for the structure of the conjugate acid of the corresponding diazene $R_2N^+{=}N^-$ and suggest the formation of an ion pair $(R_2N^+{=}NH)Cl^-$ or a covalent compound $R_2N^+(Cl)N^-H$ in aqueous hydrochloric acid. A gas–liquid chromatographic technique is used to resolve quantitatively mixtures of certain tetraalkyltetrazenes formed by the neutralization of acid solutions containing at least two different 1,1-dialkyldiazenium ions. The dimerization of 1,1-dimethyldiazenium and 1,1-diethyldiazenium ions resulted in the random formation of tetramethyltetrazene, 1,1-diethyl-4,4-dimethyltetrazene and tetraethyltetrazene as a function of the initial mole ratio of 1,1-dimethylhydrazine and 1,1-diethylhydrazine. Chromatographic data are given for cases of two, three and four component mixtures of 1,1-dialkylhydrazines which resulted in the formation of three, six and ten component mixtures of tetraalkyltetrazenes. All data conformed to a random distribution of products corresponding to the multinomial expansion for n equal to two $(r + s + \ldots + z)$.[2]

Introduction

Although the mechanism for the oxidation of 1,1-dialkylhydrazines with alkali halates in acid medium was partially resolved previously,[1] the nature of the 1,1-dialkyldiazenium ion, $R_2N^+{=}NH$,[4] is still not completely understood. In brief, the pertinent experimental data[1] for the formation of the ionic intermediate, $R_2N^+{=}NH$, could be summarized as: (1) spectrophotometric evidence denoting the absence of tetraalkyltetrazenes in the initially oxidized solution of 1,1-dialkylhydrazines unless the acid solution is first neutralized; (2) the quantitative reduction of the oxidized species by stannous chloride in acid solution to a 1,1-dialkylhydrazine under conditions that would not reduce the corresponding tetraalkyltetrazene; (3) the isolation of the compound, $(CH_3)_2N^+{=}NHClO_4^-$, in preliminary experiments by the reaction of iodine, silver perchlorate and 1,1-dimethylhydrazine in anhydrous ether; and (4) the formation of 1,1-diethyl-4,4-dimethyltetrazene as well as tetramethyltetrazene and tetraethyltetrazene from equal molar solutions of 1,1-dimethylhydrazine and 1,1-diethylhydrazine oxidized separately, mixed, and coupled through careful neutralization of the resultant solution.

The present paper considers the possible structure of the species formed by the two-electron oxidation of 1,1-dialkylhydrazines in acid; the mechanism of their dimerization to tetraalkyltetrazenes, and the resolution of mixtures of tetraalkyltetrazenes formed by the neutralization of solutions containing at least two different 1,1-dialkyldiazenium ions in the originally acid solution.

Experimental

Materials.—The 1,1-dimethylhydrazine was obtained from Westvaco Chemicals. The 1,1-diethylhydrazine and 1,1-di-*n*-propylhydrazine were prepared originally by the reduction of the corresponding nitrosodialkylamine with lithium aluminum hydride in ether.[5] The 1,1-dialkylhydrazines were purified either by fractional distillation or by converting them to the oxalate salt by precipitation from ether. These salts were recrystallized from 95% ethanol. Other 1,1-dialkylhydrazines were available more recently from Commercial Solvents Corporation. General methods of synthesis for tetraalkyltetrazenes by oxidation of 1,1-dialkylhydrazines were considered previously.[1]

Other materials were reagent grade chemicals and were employed without further purification.

Ultraviolet Analysis of Tetraalkyltetrazenes.—The ultraviolet data for tetramethyltetrazene, 1,1-diethyl-4,4-dimethyltetrazene and tetraethyltetrazene in absolute ethanol and basic aqueous solution are given in Table I. Since the absorption spectra of tetraalkyltetrazenes in aqueous solution are a function of pH,[1] all measurements were made after adjusting the pH of the solution to about 12. Linear standard calibration curves (absorbance *vs.* p.p.m. of pure tetraalkyltetrazene) were used for the analysis of the data. In absolute ethanol the absorption peaks were used for these calibration curves; in aqueous solution measurements were

TABLE I

ULTRAVIOLET ABSORPTION DATA FOR TETRAALKYLTETRAZENES

DATA FOR ABSOLUTE ETHANOL

Tetrazene	Max., mμ	Molar absorptivity, ε
Tetramethyl-	277	8980
1,1-Diethyl-4,4-dimethyl-	280	8770
Tetraethyl-	285	8160
1,1-Dimethyl-4,4-di-*n*-propyl-	281	8780
Tetra-*n*-propyl-	287	8860

DATA FOR BASIC AQUEOUS SOLUTION

Tetrazene	Molar absorptivity, ε 277 mμ	248 mμ	Ratio (277/248)
Tetramethyl-	7280	5340	1.364
1,1-Diethyl-4,4-dimethyl-	6260	6140	1.019
Tetraethyl-	4530	7490	0.604

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

(2) W. H. Urry, H. W. Kruse and W. R. McBride, *ibid.*, **79**, 6568 (1957).

(3) Presented before the Division of Inorganic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 7–12, 1958.

(4) The nomenclature, 1,1-dialkyldiazene for $R_2N^+{=}N^-$ and 1,1-dialkyldiazenium ion for $R_2N^+{=}NH$ is tentatively proposed for these compounds based on their formal relationship to the unsaturated hydronitrogens with the type formula, N_nH_n [L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951; L. F. Audrieth, *J. Chem. Ed.*, **7**, 2055 (1930)]. Although the term diimide has been generally accepted for HN=NH, this nomenclature is neither consistent with the homologous members of the series, triazene, tetrazene, etc., or readily amenable to use with substituted compounds or ionic species. Furthermore, S. H. Bauer [THIS JOURNAL, **69**, 3104 (1947)] and others have used the term difluorodiazine for the configuration $F_2N^+{=}N^-$. This latter terminology might in certain circumstances be confused with ring-structure nomenclature. L. A. Carpino [*ibid.*, **79**, 4427 (1957)] has suggested the term azamine for the parent compound, $H_2N^+{=}N^-$, but offers no details for the systematic naming of substituted compounds. The present authors will continue to use the terminology derived from the relation of these compounds to the hydronitrogens until such time as the nomenclature for these compounds is clarified.

(5) H. Zimmer, L. F. Audrieth, M. Zimmer and R. A. Rowe, *ibid.*, **77**, 790 (1955).

TABLE II

CHROMATOGRAPHIC SEPARATION AND ANALYSIS OF TETRAALKYLTETRAZENES

	Experiment number								
	1	2	3	4	5	6	7	9	10
Mole ratio (DMH/DEH)	1/1	2/1	1/2	1/1	1/1	3/1	1/3	1/1	1/1
Tetramethyltetrazene									
Elution time, min.	3.3	3.2	3.4	3.3	3.2	3.2	3.4	3.3	3.2
Analyses. p.p.m.									
Ethanol	5.65	9.80	2.12	5.05	5.14	13.15	1.26	1.90	0.922
Aqueous	5.35	9.89	(2.38)	5.25	5.24	13.30	(1.36)	1.94	(1.100)
1,1-Diethyl-4,4-dimethyltetrazene									
Elution time. min.	6.3	6.4	6.3	6.3	6.3	6.4	6.1	6.3	6.2
Analyses. p.p.m.									
Ethanol	13.90	12.40	10.70	13.35	11.90	11.47	9.30	5.07	2.38
Aqueous	13.65	12.60	10.85	13.25	12.25	11.55	9.80	5.05	(2.63)
Tetraethyltetrazene									
Elution time. min.	12.3	12.3	12.3	12.3	12.5	12.2	12.2	12.3	12.1
Analyses. p.p.m.									
Ethanol	9.55	4.40	13.65	7.44	6.80	2.91	17.00	(2.96)	1.36
Aqueous	9.30	(4.88)	13.88	(8.70)	7.05	2.92	17.70	2.85	(1.48)

made at 277 and 248 mμ. The absorbance ratio at these two wave lengths was useful in establishing purity of the resolved tetraalkyltetrazenes, especially tetramethyltetrazene, 1,1-diethyl-4,4-dimethyltetrazene and tetraethyltetrazene. In general, measurements were made in both aqueous and absolute ethanol solutions. If the concentration of tetraalkyltetrazenes was low, preference was given to absorbance measurements in absolute ethanol. In all other cases the agreement between the analyses was quite good, approximately 2%. Other considerations did not justify further refinement of the spectrophotometric techniques.

All measurements were made at room temperature with a Cary Model 11 MS recording spectrophotometer using 1-cm. cells.

Chromatographic Apparatus and Procedure.—The Perkin–Elmer Model 154 Vapor Fractometer was used for the gas–liquid chromatographic separation of the tetraalkyltetrazenes after suitable modification of the instrument. The sample collection line was replaced with an asbestos covered 1/8 in. o.d. copper tube whose orifice was closed with a piece of sintered stainless steel from a filter crucible to permit a greater dispersion of the gas bubbles. The detector response was recorded on a 5 mv. Leeds and Northrup Speedomax G recorder which had a 1 sec. full scale response and a chart speed of 1/2 in./min.

All data were obtained by the use of a polyethylene glycol column (10% by wt. on 20–35 mesh C-22 firebrick, 43 in. in length). The column was prepared as follows: The polyethylene glycol (av. mol. wt. of 400, Gemex Chemical Company) without further purification was dissolved in *n*-pentane and suitably mixed with the firebrick support. The solvent was then evaporated carefully under vacuum while the flask was agitated to provide an even coating of the solid support. A 1/4 in. o.d. stainless steel tube, plugged at one end with glass wool, was filled with the treated firebrick while the column was vibrated mechanically to ensure proper packing of the support material. With this polyethylene glycol column, a pressure differential of 2 lb. was sufficient to allow a helium flow of approx. 80 ml./min. through the column. These conditions permitted the complete separation of tetramethyl-, 1,1-diethyl-4,4-dimethyl- and tetraethyltetrazene in an interval of 20 min. at 70°.

In all experiments a 0.010-ml. sample of tetraalkyltetrazenes was introduced through the septum of the instrument using a 0.050-ml. Hamilton Miniature No. 705 microsyringe. An estimate of the reproducibility of the volume of liquid delivered by the microsyringe was determined by a calibration procedure with water. A mean of six determinations of 0.0100-ml. samples was 0.01001 g. with a standard deviation of 0.00032 g., or an error of about 3.2%. Since preliminary work did not suggest that the reproducibility of the peak height as a function of the amount of tetraalkyltetrazene was as good as that desired, a procedure was developed for the recovery and analysis of the resolved effluent fractions of the tetraalkyltetrazenes utilizing their absorption spectra in the ultraviolet. The effluent fractions were collected in 20 ml. absolute ethanol contained in a 20 by 135 mm. test-tube since recovery of the tetraalkyltetrazenes in distilled water was not feasible because of their limited solubility. During the experiments, the collectors were changed in order to effect maximum separation of the individual components. This usually meant that the collectors were changed as the recorded trace of the detector response indicated the appearance of an additional component. The effluent fractions in absolute ethanol were transferred to a 25-ml. volumetric flask and diluted to volume. For the subsequent ultraviolet analysis, 5-ml. aliquots were diluted to both 25 ml. with absolute ethanol and to 50 ml. with distilled water after the addition of 2.5 ml. of 0.1 *N* NaOH.

Oxidation Reactions of 1,1-Dimethylhydrazine and 1,1-Diethylhydrazine in Acid.—The data for the oxidation experiments of mixtures of 1,1-dimethylhydrazine and 1,1-diethylhydrazine and the subsequent separation and analysis of the several tetraalkyltetrazenes formed in the reaction are given in Table II. The ultraviolet analyses are recorded as p.p.m., g. $\times 10^{-6}$/cm.^{3}; the dilutions correspond to those described for determinations in aqueous solution. In experiments 1 to 7 the effect of the mole ratio of 1,1-dimethylhydrazine (DMH) and 1,1-diethylhydrazine (DEH) on the relative amounts of tetramethyltetrazene (TMT), 1,1-diethyl-4,4-dimethyltetrazene (DEDMT) and tetraethyltetrazene (TET) is determined. Experiments 9 and 10 are multiple component systems in which mixtures of three and four 1,1-dialkylhydrazines are oxidized. These particular experiments are considered in detail later. Consideration of the oxidation of 1,1-dialkylhydrazines[1] require that the temperature, acid concentration and time of the reaction be so chosen as to minimize the decomposition of the diazo-like intermediate prior to the neutralization of the solution. The general procedure for the experiments is given below.

To 20 ml. of 12.2 *N* HCl (0.244 mole) in a suitably cooled, 200-ml. tall-form beaker equipped with a stirrer and thermometer, sufficient chopped ice was added with stirring to form a slurry at −10°. Aliquots of 0.77 ml. of 1,1-dimethylhydrazine (0.0100 mole) and 1.11 ml. of 1,1-diethylhydrazine (0.0100 mole) were pipetted dropwise into the slurry. The pipet used in these experiments was a 1-ml. pipet graduated in 0.01-ml. divisions. The total number of moles of 1,1-dialkylhydrazine used in each experiment was 0.0200 mole which required 0.0400 equiv. of oxidant. A 40-ml. aliquot of 1.000 *N* $KBrO_3$ (0.0400 equiv.), cooled to about 0°, was added to the acid solution over a 1-min. period while the solution was kept between −5 and 0° by additions of ice. The appearance of a yellow color at or near the end-point was indicative of a slight excess of bromine in solution. The total volume of solution was approx. 100 ml. After a 1-min. interval 30 ml. of 10.0 *N* NaOH (0.300 mole), cooled to 0°, was added dropwise over a 1-min. period to the initially acid solution. The temperature toward the end of the neutralization normally rose to about 5° even with the additions of ice to the solution. The appearance of the solution gradually changed from colorless, to reddish momentarily, then to a white turbid solution on the initial separation of the tetraalkyltetrazene phase. After the addition was complete,

the stirrer and thermometer were removed and rinsed with distilled water. The final volume of the solution was between 150 and 175 ml. The aqueous solution was extracted three times with 25–30 ml. portions of *n*-pentane after which the aqueous solution was diluted to 250 ml. and scanned in the ultraviolet region to determine the effectiveness of the extractions with *n*-pentane. No tetraalkyltetrazenes were left in the aqueous solution. The combined *n*-pentane extractions were placed in a tared flask attached to a Vigreux column and the *n*-pentane was distilled off slowly by gradually heating the flask in a water bath to 90–100°. The *n*-pentane distillate and washings from the Vigreux column were combined and diluted to 100 ml. The total loss of tetraalkyltetrazene in the *n*-pentane distillate (assumed to be tetramethyltetrazene) was approximately 0.010 g. Although the theoretical yield of tetramethyltetrazene would be 0.581 g. based on the total amount of 1,1-dimethylhydrazine oxidized, in this experiment with a 1:1 mole ratio of 1,1-dimethylhydrazine to 1,1-diethylhydrazine only one third of the 1,1-dimethylhydrazine would be converted to tetramethyltetrazene, 0.194 g. This corresponds to a loss of 5.2% of the theoretical amount of tetramethyltetrazene. Since the assumption was made that this loss was only tetramethyltetrazene, this value would correspond to a maximum loss. After the completion of the distillation of the *n*-pentane, the flask was removed, cooled and reweighed for an estimate of the total tetraalkyltetrazene fraction (which contained some residual solvent). The yield of tetraalkyltetrazenes remaining in the flask, corrected for the *n*-pentane, was approx. 95% of theory. The tetraalkyltetrazene mixture was then suitable for the chromatographic separation.

In experiment 5 the 1,1-dialkylhydrazines were oxidized separately, mixed and then neutralized to form the mixture of tetraalkyltetrazenes. Although this work had been performed previously in a qualitative manner, it was desirable to repeat the work with the present techniques. The analyses of the separated fractions for this experiment are given in Table III. The summation of the absorbance measurements in aqueous solution for the three fractions is within 3% of the absorbance of an unresolved aliquot dissolved directly into the absolute ethanol and diluted in a similar manner. The calculations for the relative mole ratios of the tetraalkyltetrazenes are also given. The p.p.m. of the resolved tetraalkyltetrazene was divided by its mol. wt. to arrive at the relative total moles of tetraalkyltetrazene formed in the reaction. The mole fraction of each component was then calculated and these fractions reduced to whole numbers for a direct comparison of the multinomial or binomial coefficients for a random distribution of products. For the data in Table III, the expected products should be in the ratios of 1:2:1 since the initial mole ratio of reactants was 1:1. Two additional calculations were used as a control on the experimental technique and the resolution of the tetraalkyltetrazene mixture. The first is based on the fact that the relative ratio of the 1,1-dialkylhydrazine constituents present in the tetraalkyltetrazenes should be equal to that initially introduced in the reaction. In Table III the apparent total moles of 1,1-dimethylhydrazine is $2 \times 4.51 + 8.49 = 17.51$, and for 1,1-diethylhydrazine is $2 \times 4.09 + 8.49 = 16.67$. The mole fraction of the constituents calculated in this manner is 0.512 and 0.488, respectively. Thus, the ratio of the mole fractions, 1.049, indicates that no major systematic error existed in the experimental procedure such as preferential volatilization, decomposition of the oxidation intermediate, or grossly impure 1,1-dialkylhydrazines. A second criterion was the ratio of the absorbance of the aqueous tetraalkyltetrazene fractions at 277 and 248 mμ compared to the ratio for the pure components. The ratio for TMT was 0.327/0.251 = 1.303 (theory 1.364); for DEDMT was 0.526/0.512 = 1.027 (theory 1.019); and for TET was 0.197/0.307 = 0.642 (theory 0.604). However, in the latter case, the effect of the 10% ethanol upon the absorbance was sufficient to change the ratio from 0.604 to 0.650. For this particular experiment the estimated yield of tetraalkyltetrazenes was 97.3%.

TABLE III

ANALYSIS OF DATA FOR EXPERIMENT 5

ULTRAVIOLET ANALYSIS IN AQUEOUS SOLUTION

Sample	Component	Absorbance measurements 277 mμ (p.p.m.)	248 mμ (p.p.m.)
32	TMT	0.327 (5.24)	0.251
33	DEDMT	0.526 (12.25)	0.512
34	TET	0.197	0.307 (7.05)
	Total	1.050	1.070
50	Mixture	1.080	1.101

CALCULATION OF MOLE RATIO OF TETRAALKYLTETRAZENES

Component	Total moles analyzed	Mole fraction	Mole ratio Found	Theory
TMT	5.24/116.17 = 4.511	0.264	1.056	1.00
DEDMT	12.25/144.22 = 8.494	.497	1.988	2.00
TET	7.05/172.27 = 4.092	.239	0.956	1.00

Oxidation of 1,1-Dialkylhydrazines in Multiple Component Systems.—The experimental technique employed for the oxidation of 1,1-dialkylhydrazines in multiple component systems was essentially the same as that described above. The procedure was extended to three and four component systems with the intent to test the chromatographic method on more complex systems as well as to consider further the coupling mechanism of a greater number of 1,1-dialkylhydrazines. Experiment 9 is the oxidation of 1,1-dimethyl-, 1,1-diethyl- and 1,1-di-*n*-propylhydrazine in equal mole ratios. The chromatographic separation partially resolved all six of the tetraalkyltetrazenes formed in this reaction. The isomeric pair, tetraethyltetrazene and 1,1-dimethyl-4,4-di-*n*-propyltetrazene (DMD*n*-PT), was not completely resolved although a shoulder indicated the presence of two components. Experiment 10 is similar in all respects to 9 except that 1,1-di-*n*-butylhydrazine was added as the fourth component. Of the three isomeric pairs, only the 1,1-diethyl-4,4-di-*n*-propyltetrazene (DED*n*-PT) and the 1,1-di-*n*-butyl-4,4-dimethyltetrazene (D*n*-BDMT) were not resolved.

The analysis of tetramethyltetrazene, 1,1-diethyl-4,4-dimethyltetrazene and tetraethyltetrazene was given previously in Table II. In experiment 9 it was possible to resolve the isomeric pair, tetraethyltetrazene and 1,1-dimethyl-4,4-di-*n*-propyltetrazene, by the solution of simultaneous equations based on their absorption curves in aqueous solution. Ultraviolet data for the analysis of the components in experiment 9 are given in Table IV. Since it became obvious after the conclusion of the experiment that only 86.6% of the expected absorbance was given by the summation of the several effluent fractions, it was necessary to make a rather arbitrary assumption. It was assumed that the difference of the two values (14.00 − 12.13 = 1.87) represented the tetra-*n*-propyltetrazene which was not collected in the time interval allowed. In experiment 10, no attempt was made to determine quantitatively more than the first three tetraalkyltetrazenes given in Table II.

TABLE IV

ABSORPTION DATA IN ABSOLUTE ETHANOL FOR EXPERIMENT 9

Samples	Components	Max., mμ	Absorbance	p.p.m./10
50	TMT	278	1.46	1.90
51	DEDMT	281	3.09	5.07
55	TET, DMD-*n*-PT	283	4.20	8.65[a]
56, 61, 62	DED-*n*-PT	285	3.38	7.57
	Total		12.13	
153	Mixture	282	14.00	
	T-*n*-PT (by difference)		1.87	4.77

[a] TET was 2.85, DMD-*n*-PT was 5.80.

Spectrophotometric Data for 1,1-Dialkyldiazenium Ions and Ion-pair Formation.—A typical procedure for the oxidation of the 1,1-dialkylhydrazines was as follows: A 1.00-ml. aliquot of acid solution containing 0.00112 mole of 1,1-dimethylhydrazine was added to 30 ml. of 12.2 *N* HCl cooled to 0°, and the solution titrated potentiometrically with 22.25 ml. of 0.1000 *N* $KBrO_3$ over an interval of 5 min. The solution was diluted to 100 ml. in a volumetric flask and 25-ml. aliquots withdrawn and added to 100 ml. flasks to which different amounts of 12.2 *N* HCl had been added. The solutions were kept at 0°, diluted to volume and scanned several times in the ultraviolet region. The absorption data

for the 1,1-dimethyldiazenium ion at several wave lengths is given in Table V. At a total concentration of approximately 0.0028 *M*, the absorbance was directly dependent upon the concentration of hydrochloric acid. The extrapolated values give a hypothetical absorption for zero acid concentration. Additional data establish that this absorption is dependent upon the chloride ion concentration and is essentially independent of the hydrogen ion concentration. The latter experiments which were carried out in aqueous perchloric acid show the linear dependence of the absorbance of the 1,1-dimethyldiazenium ion with concentration. Qualitatively, this characteristic absorption band at about 280 mμ was observed with acid solutions of other 1,1-dialkyldiazenes. Although ion-pair formation of 1,1-dimethyldiazenium ion most likely does not occur in sulfuric acid, it was observed in hydrochloric, acetic and several other acids.

TABLE V

SPECTROPHOTOMETRIC DATA FOR 1,1-DIMETHYLDIAZENIUM ION AND ITS ION-PAIR FORMATION

Concentration, *N*			Absorbance			
$(CH_3)_2N^+=NH \times 10^3$	H^+	Cl^-	320 mμ	300 mμ	280 mμ	250 mμ
2.8	0.90	0.90	0.115	0.292	0.385	0.53
2.8	3.30	3.30	.140	.371	.539	1.19
2.8	5.70	5.70	.182	.436	.639	1.82
2.8	8.10	8.10	.230	.495	.754	2.42
2.8[a]	(0.00)	(0.00)	(.095)	(.280)	(.360)	(0.300)
5.0	4.38	4.38	.280	.725	1.085	>2.3
5.0	0.12	4.37	.300	.720	1.085	>2.3
2.5	4.40	0.00	.075	.240	0.375	0.240
5.0	4.54	.00	.150	.470	0.700	0.455
7.5	4.67	.00	.215	.700	1.055	0.713
10.0	4.24	.00	.260	.740	1.495	0.940

[a] Above data extrapolated to zero *N* HCl.

Discussion

During the last few years the oxidation of hydrazine has been considered by Cahn and Powell[6] and Higginson and Wright.[7] More recently, Rosseinsky[8] reinvestigated the oxidation of hydrazine by iron(III) in acid solution and discussed the mechanisms suggested by previous authors. One of the most noticeable facts of this previous work is the failure of the authors to consider or discuss possible ionic intermediates formed in the oxidation of hydrazine although, for the most part, much of the work was carried out in strongly acid media. These results are in contrast to the present work with the oxidation of 1,1-dialkylhydrazines in which the 1,1-dialkyldiazenium ion, the protonated species $R_2N^+=NH$, is surprisingly stable.

Although the following conclusions are somewhat tentative, the spectrophotometric data do suggest an interesting series of reactions for the 1,1-dialkyldiazenes, $R_2N^+=N^-$, in acid solution. If one assumes that the reason that the two-electron oxidation intermediate of 1,1-dialkylhydrazines does not form tetraalkyltetrazenes, $R_2NN=NNR_2$, in acid solution under the previously described conditions[1] is stabilization due to the protonation of this intermediate, then the resonance structure for such an intermediate would most likely be between $R_2N^+=NH$ and $R_2\ddot{N}-\overset{+}{\underset{\cdot\cdot}{N}}:H$. The more probable structure should be the 1,1-dialkyldiazenium ion with the nitrogen–nitrogen double bond rather than an open sextet arrangement. However, such a structure should exhibit some absorption in the ultraviolet region at about 280 mμ. The spectrophotometric data in Table V demonstrate that these solutions do show absorption in the ultraviolet region that can best be ascribed to the 1,1-dialkyldiazenium ion. Furthermore, the absorption band for the 1,1-dialkyldiazenium ion is near 280 mμ. The molar absorptivity of the 1,1-dimethyldiazenium ion in 4.5 *M* perchloric acid is approximately 150. The relationship between the absorbance and the chloride ion concentration, especially at the lower wave lengths, suggests the formation of an ion pair $(R_2N^+=NH)Cl^-$ or a covalent compound $R_2N^+(Cl)N^-H$ in aqueous hydrochloric acid. The absorption spectra of the covalent compound would be expected to be similar to that of the 1,1-dialkylhydrazines rather than that of the 1,1-dialkyldiazenium ions. This seems to be the case. In a qualitative manner, it was substantiated that other 1,1-dialkyldiazenes in perchloric acid also exhibit this characteristic absorption band and form ion-pairs with chloride and other ions.

The subsequent portion of the discussion will be devoted to the dimerization reaction to form 2-tetrazene linkages, $\rangle$—NN=NN—$\langle$, by the neutralization of the 1,1-dialkyldiazenium ions, $R_2N^+=NH$. The mechanism of the coupling reaction is believed to occur through the formation of the conjugate base of the 1,1-dialkyldiazenium ions formed on two-electron oxidation of 1,1-dialkylhydrazines in acid solution.

$$H_2O + R_2N^+=NH \rightleftharpoons R_2N^+=N^- + H_3O^+ \quad (1)$$

followed by

$$R_2N^+=N^- + R_2N^+=NH \longrightarrow R_2N^+HN=NNR_2 \quad (2)$$

This mechanism differs, for the most part, from the earlier consideration[1] in that the coupling reaction is thought to be the reaction between the 1,1-dialkyldiazenium ion and the 1,1-dialkyldiazene. Previously, the opinion was held that coupling did not occur until the *p*H of the solution was between 3 and 5. It has now been shown that if the concentrations of the ionic intermediate are 0.20 *M* or higher, rather than approx. 0.01 *M* as previously considered, then the formation of tetraalkyltetrazenes may occur in 0.1 to 1.0 *N* hydrochloric acid solutions. Since the rate of the coupling reaction to form tetraalkyltetrazenes, eq. 2, is proportional to the second power of the total concentration of the intermediate in solution, the effect of its concentration on the rate of formation of tetraalkyltetrazenes is readily apparent. This increase in concentration is an important factor in the quantitative conversion of the oxidized intermediate to tetraalkyltetrazenes. Furthermore, recent evidence has shown that if the ionic intermediate in low concentration is added to strongly basic sodium hydroxide solutions, the formation of tetraalkyltetrazenes, as a product of the reaction, is decreased or almost eliminated. The low yield of tetraalkyltetrazenes by this inverted neutralization technique is additional evidence which suggests that the ionic reaction for the formation of tetraalkyltetrazenes, eq. 2, is correct.

Quantitative data for the formation of 1,1-diethyl-4,4-dimethyltetrazene as well as tetra-

(6) J. W. Cahn and R. E. Powell, THIS JOURNAL, **76**, 2568 (1954).
(7) W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1551 (1955).
(8) D. R. Rosseinsky, *ibid.*, 4685 (1957).

TABLE VI

DISTRIBUTION OF TETRAALKYLTETRAZENES AS A FUNCTION OF THE MOLE RATIO OF 1,1-DIMETHYLHYDRAZINE AND 1,1-DIETHYLHYDRAZINE

No.	Reactants DMH	Reactants DEH	Found TMT	Found DED-MT	Found TET	Calculated TMT	Calculated DED-MT	Calculated TET
1	1.00	1.00	0.95	1.94	1.11	1.00	2.00	1.00
			0.97	1.92	1.10			
2	2.00	1.00	3.88	3.95	1.17	4.00	4.00	1.00
3	1.00	2.00	0.95	3.89	4.16	1.00	4.00	4.00
4	1.00	1.00	0.97	2.06	0.96	1.00	2.00	1.00
5[a]	1.00	1.00	1.06	1.99	0.96	1.00	2.00	1.00
6	3.00	1.00	8.66	6.06	1.28	9.00	6.00	1.00
7	1.00	3.00	0.98	5.95	9.07	1.00	6.00	9.00
9[b]	1.00	1.00	0.98	2.06	0.98	1.00	2.00	1.00
10[c]	1.00	1.00	0.95	1.97	1.03	1.00	2.00	1.00

[a] In this experiment the 1,1-dialkylhydrazines were oxidized separately, the solutions mixed and then neutralized to form the tetraalkyltetrazenes. [b] Three reactants in equal mole ratio, 1,1-dimethyl-, 1,1-diethyl- and 1,1-di-*n*-propylhydrazine. [c] Four reactants in equal mole ratio, all in *b* and in addition 1,1-di-*n*-butylhydrazine.

methyltetrazene and tetraethyltetrazene from equal molar solutions of 1,1-dimethylhydrazine and 1,1-diethylhydrazine oxidized separately, mixed and coupled through careful neutralization of the resultant solution was given in Table III. Calculations for the distribution of these tetraalkyltetrazenes as a function of mole ratios of 1,1-dimethylhydrazine and 1,1-diethylhydrazine are listed in Table VI. The distribution of tetraalkyltetrazenes formed in the oxidation of multiple component systems with three and four 1,1-dialkylhydrazines is given in Tables VI and VII. All data, within experimental error, conform to a random distribution of products corresponding to the multinomial expansion, $(r + s + \ldots + z)^n$ for n equal to two. The oxidation of the 1,1-dialkylhydrazines for two, three and four component mixtures resulted in the formation of three, six and ten component mixtures of tetraalkyltetrazenes.

TABLE VII

TETRAALKYLTETRAZENES FORMED IN MULTIPLE COMPONENT SYSTEMS

Tetrazene	Elution time, min.	Mole ratios Found 9	Found 10	Calcd. 9 and 10
Tetramethyl-	3.3	0.92	0.95	1.00
1,1-Diethyl-4,4-dimethyl-	6.3	1.97	1.97	2.00
Tetraethyl-, 1,1-dimethyl-4,4-di-*n*-propyl-	12.3			
Tetraethyl-	12.3	0.93	1.03	1.00
1,1-Dimethyl-4,4-di-*n*-propyl-	13.5	1.89	2.06	2.00
1,1-Diethyl-4,4-di-*n*-propyl-, 1,1-di-*n*-butyl-4,4-dimethyl-	24.9			
1,1-Diethyl-4,4-di-*n*-propyl-	25.5	2.12		2.00
1,1-Di-*n*-butyl-4,4-diethyl-	40.6			
Tetra-*n*-propyl-	48.2	1.17		1.00
1,1-Di-*n*-butyl-4,4-di-*n*-propyl-	74.0			
Tetra-*n*-butyl-	143.0			

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Haloboranes with Organocyclosiloxanes. II. Boron Fluoride with Methyl and Ethyl Trimer and Tetramer[1-3]

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The reactions of boron fluoride with the cyclosiloxanes, $(R_2SiO)_3$ and $(R_2SiO)_4$, where R is methyl or ethyl, give the products: $(R_2SiO)_n \cdot nBF_3$, $(R_2SiFO)BF_2$, $(R_2SiFO)_3B$, $(R_2SiF)_2O$, R_2SiF_2 $(R_2SiO)_3$, by a series of disproportionation reactions. With the exception of the coördination complexes, the intermediate fluorine compounds disproportionate much more readily than the corresponding chlorine compounds. *sym*-Tetramethyldifluorodisiloxane disproportionates slowly but completely at room temperature with the evolution of gaseous dimethyldifluorosilane and the formation of hexamethylcyclotrisiloxane. A reaction sequence which accounts for the exclusive formation of trimeric cyclosiloxane from the disproportionation of *sym*-tetraalkyldihalodisiloxanes is proposed. Steric factors involving the size of the boron halide molecule as well as the availability of the oxygens of the siloxanes strongly influence the rate of the initial reaction between boron halides and organocyclosiloxanes.

The reactions of boron chloride with hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane[4] were described in a previous paper from these Laboratories.[1] Through a series of disproportionations these reactions were found to produce, in sequence, dialkylchlorosiloxydichloroboranes, $(R_2SiClO)BCl_2$; tris-(dialkylchlorosiloxy)-boranes, $(R_2SiClO)_3B$; *sym*-tetraalkyldichloridisiloxanes, $(R_2SiCl)_2O$; dialkyldichlorosilanes and hexaalkylcyclotrisiloxanes.

The analogous reactions of boron fluoride with these alkylcyclosiloxanes and the relative disproportionation tendencies of the intermediate fluorine and chlorine compounds have now been studied and the results are reported in the present paper.

Experimental

Reagents and Procedures.—Most of the reagents used, the reaction apparatus and the methods of purification and characterization used have been described previously.[1] Boron fluoride, technical grade from the Matheson Company was passed through sulfuric acid saturated with boric oxide.

(1) Previous paper, THIS JOURNAL, **80**, 1103 (1958).

(2) Abstracted from portions of the June 1958 doctoral dissertation of Rev. Thomas Ostdick, O.S.B. Presented in part at the New York Meeting of the American Chemical Society, September, 1957.

(3) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

(4) The four cyclic compounds will be referred to as methyl trimer, methyl tetramer, ethyl trimer and ethyl tetramer.