The residue from the sublimation was recrystallized several times from benzene-ethanol (500 mg, 6%) and had a melting point of $191-194^{\circ}$ (evac. cap.). The ultraviolet spectrum in ethanol showed two maxima (ϵ_{286} 26,400, ϵ_{250} 31,700) and two minima (ϵ_{286} 25,000, ϵ_{232} 24,700).

Anal. Calcd for $C_{34}H_{25}Cl_2N_3$: C, 74.72; H, 4.57; Cl, 12.98; N, 7.69. Found: C, 74.3; H, 4.9; Cl, 13.1; N, 7.6.

G. Pyrolysis of p-Chlorostyryl Azide IIIb in N-Methylaniline. --p-Chlorostyryl azide IIIb (6.1 g, 34 mmoles) was added to 150 ml of N-methylaniline maintained at ~175°. The total crude product was taken up in benzene and passed through two columns of 120 g of Merck alumina each. The material eluted from the columns was crystallized from cyclohexane: mp 123– 123.5°. The ultraviolet spectrum in ethanol exhibited two maxima (ϵ_{303} 19,500, ϵ_{242} 18,500) and two minima (ϵ_{265} 5200, ϵ_{237} 18,200). This material was identified as 1-methyl-2-(*p*-chlorophenyl)indole (X) by comparison of its properties with those of an authentic sample.³⁰ The yield of X was about 60%.

Synthesis and Azidolysis of 2-Chlorotetramethylguanidine. Synthetic Utility of Hexa- and Tetramethylguanidinium Azide

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2-Chloro- and 2-bromotetramethylguanidine were synthesized by the direct halogenation of 1,1,3,3-tetramethylguanidine. (*Caution*: These compounds are explosive and should not be heated above 50° at atmospheric pressure.) An investigation of halide replacement with sodium azide was undertaken. In acetonitrile, the reaction afforded β -dimethylaminoacrylonitrile in 66% yield. Bis(dimethylamino)carbene and 3,3-bis(dimethylamino)propionitrile are proposed as intermediates in the reaction mechanism. When dimethylformamide was employed in place of acetonitrile, hexamethylguanidinium azide was obtained in 16% yield. This azide is representative of a class of organic azides which possess the property of being both thermally stable and a highly reactive source of azide ion. A synthesis of tetramethylguanidinium azide and its use in an improved synthesis of alkyl azides and 5-substituted tetrazoles is also described.

Although a few N-halo guanidines substituted on the imino nitrogen have been reported,¹ tetrasubstituted guanidine derivatives have not hitherto been described. The present work was undertaken in an effort to synthesize a 2-halotetrasubstituted guanidine and to study the chemistry of this new class of compounds.

2-Chloro- and 2-bromotetramethylguanidine have been obtained by direct liquid-phase halogenation with chlorine and bromine in carbon tetrachloride solution in 76 and 59% yield, respectively. The reaction proceeds readily at 0-10°, and the insoluble tetramethylguanidine hydrohalide by-product separates from solution during the addition of halogen. Initial attempts to apply the preparative procedures to tetramethylguanidine using sodium hypohalite were unsuccessful. It was subsequently shown that 2-halotetramethylguanidine derivatives are sensitive to hydrolysis and must be prepared in nonaqueous systems.

 $2[(CH_3)_2N]_2C \longrightarrow NH + X_2 \longrightarrow$

$$[(CH_3)_2N]_2C \longrightarrow NX + [(CH_3)_2N]_2C \longrightarrow NH_2X^-$$

I, X = Cl
II, X = Br

Compounds I and II are pale yellow liquids which possess a strong ozonelike odor and rapidly oxidize iodide ion to iodine in acetone solution. The N-halo derivatives are quite unstable, each decomposing to some extent on standing at 0° for several weeks. The least stable was II, which turned orange on standing in air at room temperature for 30 min with the separation of a substantial quantity of tetramethylguanidine hydrobromide. Samples of I have been stored for months under refrigeration and protection from light with slight decomposition. The decomposition products of I include the hydrochlorides of a mixture of selfchlorinated products. Caution must be exercised when working with these compounds since explosion results when heated at a temperature above 50° at atmospheric pressure.

The instability of I and II precluded an accurate elemental analysis. The characterization and the location of the halogen on the imino nitrogen were evident from infrared spectral studies. The spectra exhibited an absorption band at 6.48 μ attributable to stretching frequency of the >C==NX group and showed the disappearance of N-H stretching at 3.1 μ . A proton nmr spectrum of I consists of two singlets of equal intensities at 2.68 and 2.81 ppm. Starting tetramethyl-guanidine shows two singlets at 5.26 and 2.60 ppm in a ratio of 1:12.

The observed singlets in I could be due to interaction between the chlorine group and one of the dimethylamino groups. Interestingly, the spectrum of dimethyl N-chloroiminocarbonate² has been found to consist of a singlet peak at 3.89 ppm as low as -60° . This difference is attributed to the failure of the methyl protons and the =-NCl group of the iminocarbonate to come into intramolecular proximity to produce a chemical shift.

Further support for the assigned structures of I and II was obtained by treating them with triphenyl-phosphine to give the 1,1,2,2-tetramethyl-3-(triphenyl-phosphoranylidene)guanidinium halide (III).

$$I (II) + (C_6H_5)_3P \longrightarrow \{[(CH_3)_2N]_2C = N = P(C_6H_5)_3\}^+X^-$$
III

The structure of the salt III obtained from II was confirmed by carbon and hydrogen analysis, infrared spectra, and the formation of the corresponding tetramethylguanidine hydrohalide and triphenylphosphine

^{(1) (}a) J. Goerdeler and K. Doerk, Ber., 95, 154 (1962); (b) J. Goerdeler and M. Willig, *ibid.*, 88, 1071 (1955); (c) C. K. Morehouse and R. Glicksman, J. Electrochem. Soc., 104, 467 (1957); (d) G. F. Wright, Can. J. Chem., 80, 62 (1952); (e) I. Kamenski, Ber., 11, 1600 (1878).

⁽²⁾ Synthesized according to the procedure of J. Houben and E. Schmidt, *ibid.*, **46**, 2447 (1913).

oxide on hydrolysis. The ease of hydrolysis of the salt prepared from I precluded the preparation of an analytical sample. Hydrolytic instability of triphenylphosphinimines has been reported.³

Reaction of I with sodium azide in acetonitrile proceeded readily at room temperature with the evolution of 2 moles of nitrogen and the deposition of sodium chloride. Processing of the reaction mixture afforded a crude yellow oil which on standing at room temperature eliminated dimethylamine. Distillation of the resulting oil afforded β -dimethylaminoacrylonitrile (IV) in 66% yield. Evidence for the assigned structure of IV is based on elemental analysis, molecular weight, and infrared and nmr spectral data. The infrared spectrum showed two strong absorption bands at 4.60 and 6.19 μ attributable to conjugated C=N and C=C stretching frequency, respectively. The nmr spectrum exhibited a singlet at 2.90 ppm and two doublets (J =14 cps), the low-field doublet centered at 7.16 and the high-field doublet centered at 3.80 ppm. Although the stereochemistry of IV has not been rigorously established, it may well be the trans isomer as judged by the large splitting of the doublet in the nmr spectrum and the presence of a trans C-H out-of-plane bending vibration at 10.45 μ^4 in the infrared spectrum.⁵

The formation of IV can be reasonably interpreted in terms of the intermediacy of 5,5-bis(dimethylamino)tetrazole (V) arising from nucleophilic attack of the azide ion at the unsaturated imino carbon atom rather than the imino nitrogen atom, since displacements at multiple-bonded atoms are difficult. The reaction could then proceed by elimination of nitrogen from the unstable V to give bis(dimethylamino)carbene (VI). This carbene could then react with



acetonitrile by carbon-hydrogen bond insertion, as would be expected of a nucleophilic carbene,⁶ to give 3,3-bis(dimethylamino)propionitrile (VII) which in turn eliminates dimethylamine to form the final product IV. In a separate experiment, the interme-

$$VI + CH_{3}CN \longrightarrow [(CH_{3})_{2}N]_{2}CHCH_{2}CN \xrightarrow{-(CH_{3})_{2}NH} VII \xrightarrow{(CH_{3})_{2}NCH=CHCN} IV$$

diate formation of VII was demonstrated by conducting the reaction at 0°. Under this condition, VII was obtained as the major product in 50% yield. Conversion of VII to IV occurred readily under slow distillation.

- (3) H. Zimmer and G. Singh, J. Org. Chem., 29, 1579 (1964).
 (4) S. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 34.
- (5) Synthesis of the *cis* isomer has been recently reported by F. Scotti

(c) Symmetry of the holm in the both for the product of F and E. J. Frazza, J. Org. Chem. 29, 1800 (1964).
 (c) H. W. Wanzlick, Angew. Chem. Intern. Ed. Engl., 1, 75 (1962).

The proposed carbene intermediate could not be trapped with electron deficient olefins or other compounds expected to undergo carbon-hydrogen insertion. Either tarry reaction products were formed or the compounds were reactive with I alone. Some new reactions of I were observed during the latter investigation and will be reported at a later date. Neither tetrakis(dimethylamino)ethylene nor trimethylacetamidine which could arise by coupling and rearrangement of the carbene, respectively, were detected in the reaction products.

When acetonitrile was replaced by DMF in the reaction of I with sodium azide, an unidentified nondistillable and noncrystallizable crude red oil was obtained as the major product and hexamethylguanidinium azide (VIII) as a minor product in 16% yield.



The following data support the structure of VIII: (1) elemental analysis; (2) infrared spectrum: strong absorption bands at 5.07 (N₃⁻), 6.31, and 6.41 μ (>C=N<); (3) ultraviolet spectrum: $\lambda_{\max}^{C_2H_3OH} 222 \text{ m}\mu$ $(\epsilon 18,406)$; (4) nmr spectrum: inconclusive results were obtained in that various runs under identical conditions gave two absorption bands with varying intensities; however, in most runs the nmr spectrum (in deuteriochloroform) showed the expected two singlets (a strong singlet at 3.07 and a weak singlet at 3.04 ppm); and (5) derivatives.

The position of the azide stretching frequency in the infrared region of VIII is of interest. The linear N3 frequency in simple aliphatic azides is found as a sharp, absorption band appearing quite consistently at wave lengths between 4.65 and 4.70 μ .⁷ The azide ion in inorganic azides, such as sodium azide, absorb in the same wavelength range but the band is somewhat broad. However, the azide ion stretching frequency of VIII is shifted to a strong, sharp absorption band at 5.07 μ which is in accord with the shift to longer wavelengths expected for a strongly ionic compound. This high ionic character is attributed to high resonance stabilization of the cation of VIII.

The saltlike character of VIII was demonstrated by reaction with sodium tetraphenylborate in aqueous solution to give hexamethylguanidinium tetraphenylborate (IX) and sodium azide. An infrared spectrum of IX showed the complete absence of an absorption band attributable to azide, and this represented the only major difference on comparison with an infrared spectrum of VIII.



⁽⁷⁾ See ref 4, p 263.

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TABLE I Azides

]	RN3			
Halide	Product	Yield, %	Reaction time, min	Bp (mm) Found	or mp, °C— Lit.
β -Bromoethylbenzene	β -Azidoethylbenzene	100	90	52-54(0.65)	$43(0.5)^{a}$
Benzyl chloride	Benzyl azide	91	60	85 (11)	82.5 (16.5)
1-Chlorohexane	1-Azidohexane	60	240	150 - 152	156-157 (758)
Ethyl α -chloroacetate	Ethyl α -azidoacetate	89	60	40-42(2.5)	$44-46 (2.0)^d$
Benzhydryl bromide	Benzhydryl azide ^e	81	60	100-101(0.3)	$122-123(1,7)^{\prime}$
2,3,5,6-Tetramethyl-1,4- xylylene dichloride ⁹	2,3,5,6-Tetramethyl-1,4- xylylene diazide ^h	96	90	116–117	

^a P. A. S. Smith and B. B. Brown, J. Am. Chem. Soc., **73**, 2435 (1951). ^b T. Curtius and G. Ehrhart, Ber., **55**, 1559 (1922). ^c K. Henkel and F. Weygand, *ibid.*, **76**, 812 (1943). ^d M. O. Forster and H. E. Fierz, J. Chem. Soc., **93**, 72 (1908). ^e Prepared by Dr. Seymour Yolles of this laboratory. ^f C. H. Gudmundsen and W. E. McEwen, J. Am. Chem. Soc., **79**, 329 (1957). ^e Obtained from Dr. E. L. Martin of the Central Research Department of this company. ^h Anal. Calcd for C₁₂H₁₆N₆: C, 59.00; H, 6.60; N, 34.40. Found: C, 58.88; H, 6.55; N, 34.20.

TABLE II

		1 11						
		5-Substituti	ed Tetrazoles					
R-C N-N H								
		React	ion		°C			
R	Yield, %	Time, hr	Temp, °C	Found	Lit.			
C_6H_5	75	3	100	216 dec	213-215 dec ^a			
C_6H_5	100	6	125	214 dec	213-215 dec ^a			
$C_6H_5CH_2$	94	6.5	120	123-124	123-125°			
$4-CH_{3}OC_{6}H_{4}$	30	3	100	231-232	228 ^b			
$(CH_3)_2N$	83	7	100	240	235-240°			
$1,4-(-C_6H_4-)$	100	1.5	120	309 (explodes)	>300 decª			
^a See ref 8. ^b W.	Lossen and J. Colman,	Ann., 298, 107 (1897).	• K. A. Jensen an	d C. Pedersen, Acta Chem.	Scand., 15, 991 (1961).			

Additional chemical evidence in support of structure c VIII was provided by its reaction with organic halides. For example, VIII reacted with ethyl α -bromoacetate h in dichloromethane in an exothermic reaction to give ethyl α -azidoacetate and hexamethylguanidinium bro-

mide in 54 and 93% yield, respectively. In view of the stability and reactivity of VIII, it was desirable to investigate other more readily available substituted guanidinium azides as a stable, soluble source of azide ion in common low-boiling organic solvents. Because of the ease of preparing tetramethylguanidinium azide (X) from the reaction of tetramethylguanidine and hydrazoic acid, it was the reagent of choice.



The guanidinium azide (X) reacted in refluxing chloroform with alkyl halides to form the corresponding alkyl azides in high yield at short reaction times. Reaction with the more reactive halides, in particular the alkyl bromides, was exothermic and required cooling at the initial stages. The solubility of X in chloroform simplifies product isolation. Addition of ether to the reaction mixture causes precipitation of tetramethylguanidine hydrochloride by-product leaving the desired alkyl azide in chloroform-ether solution. The use of chloroform as a solvent also appears to enhance the rate of halide displacement. Since X is soluble in chloroform, it probably exists in this solvent as discrete anions which would be efficient at displacing the halide atom of the alkyl halide.

Table I summarizes the yields of purified product azides obtained from the reaction of X with a variety of alkyl halides in refluxing chloroform. The results shown in Table I demonstrate the general versatility and simplicity of the reaction for the synthesis of heatsensitive organic azides.

Further, 5-substituted tetrazoles are formed in excellent yield by heating X and nitriles in the absence of a solvent at temperatures of $100-125^{\circ}$. Table II lists the yields and reaction conditions for the synthesis of various 5-substituted tetrazoles made by the procedure. This procedure eliminates the need to remove highboiling solvents such as DMF as required by current approaches to 5-substituted tetrazoles.⁸

Experimental Section⁹

2-Chlorotetramethylguanidine (I).—Liquid chlorine (22.8 ml, 0.5 mole) in 30 ml of carbon tetrachloride was added to a solution of 115.1 g (1 mole) of tetramethylguanidine in 700 ml of carbon tetrachloride during 1 hr while the reaction temperature was maintained at 0 to 10°. When the addition was complete, the mixture was stirred at room temperature for 1 hr. The precipitated tetramethylguanidine hydrochloride was collected by filtration, washed with additional solvent, and dried; yield 75.0 g (100%), mp 202-205°. Recrystallization from ethanol raised the melting point to 207-210°.

⁽⁸⁾ W. G. Finnegan, R. A. Henry, and R. Lofquist, J. Am. Chem. Soc., 80, 3908 (1958).

⁽⁹⁾ Boiling points and melting points are uncorrected. Nmr spectra were taken on a Varian Associates 60-Mc high-resolution nmr spectrometer. Infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer.

Anal. Calcd for $C_{5}H_{14}ClN_{3}$: C, 39.60; H, 9.31. Found: C, 39.84; H, 9.47.

The filtrate from the original reaction mixture was concentrated under reduced pressure at room temperature. [Caution: Care should be taken to avoid "hot spots" during this operation otherwise an explosion will result. We found the use of a warmwater bath (30°) satisfactory during the stripping process and an oil bath for subsequent vacuum distillation. Efficient stirring must also be employed.] The residual oil distilled *in vacuo*: yield 57.1 g (76%) of I, bp 50° (0.1 mm). Anal. Calcd for C₈H₁₂ClN₈: Cl, 23.70. Found: Cl, 23.35.

Anal. Calcd for $C_5H_{12}CIN_5$: Cl, 23.70. Found: Cl, 23.35. **2-Bromotetramethylguanidine** (II).—The experimental procedure was identical with that used in the preparation of 2chlorotetramethylguanidine. Tetramethylguanidine hydrobromide was obtained in quantitative yield. Crystallization from ethanol-ether afforded a white product in 79% yield, mp 186– 187.5°.

Anal. Calcd for $C_5H_{14}BrN_3$: C, 30.62; H, 7.20; Br, 40.75; N, 21.43. Found: C, 30.62; H, 7.18; Br, 41.07; N, 21.95.

Evaporation of the solvent from the filtrate and distillation of the oil afforded II in 59% yield, bp 72° (0.35 mm). (*Caution:* This compound is explosive. Do not heat above 50° at atmospheric pressure.)

Anal. Calcd for $C_{5}H_{12}BrN_{8}$: Br, 41.18. Found: Br, 39.88. 1,1,2,2-Tetramethyl-3-(triphenylphosphoranylidene)guanidinium Bromide (III).—A solution of freshly distilled 2-bromotetramethylguanidine (7.8 g, 0.04 mole) in 100 ml of anhydrous ether was added, with stirring, to a solution of 10.5 g (0.04 mole) of triphenylphosphine in 100 ml of anhydrous ether over a period of 5–10 min. After stirring the reaction mixture for 15 min, the precipitated solid product was collected by filtration, washed thoroughly with ether to remove any unreacted starting material, and dried: yield 17.2 g (94%). Three crystallizations from methanol-ether and one from chloroform-benzene afforded 16.3 g (89%) of white product: mp 230–231.5°; infrared,

6.60 (s) (>C=N<) and 9.07 μ (s) (>N=P<).¹⁰ Anal. Calcd for C₂₃H₂₇BrN₃P: C, 60.53; H, 5.96. Found: C, 60.73; H, 5.93.

1,1,2,2-Tetramethyl-3-(triphenylphosphoranylidene)guanidinium chloride was prepared from 2-chlorotetramethylguanidine in the manner used for the bromide salt: yield 71%, mp $170-173.5^{\circ}$. The extreme hygroscopicity of the chloride salt precluded an accurate elemental analysis.

 β -Dimethylaminoacrylonitrile (IV).—A mixture of 4.5 g (0.03 mole) of 2-chlorotetramethylguanidine and 2.0 g (0.03 mole) of sodium azide in 10 ml of anhydrous acetonitrile was stirred at ambient temperature by means of a magnetic stirrer for 24 hr. The reaction mixture was protected from light by means of aluminum foil to retard decomposition of the starting guanidine. There was no apparent heat of reaction, and, during this time, 2 moles of nitrogen gas (identified by mass spectrometry) was collected over water. The reaction mixture was then filtered free of sodium chloride, and the filtrate was concentrated under re-duced pressure. The yellow oil obtained at this point contained a pronounced aniline type odor; however, on standing approximately 20-45 min, the characteristic odor of a low molecular weight amine became progressively more evident. Distillation furnished 1.9 g (66%) of colorless product, bp 68-70° (0.2 mm), n^{25} D 1.5337. An analytical sample was obtained by distillation through a 28-in. spinning-band column: bp 47-48° (0.10 mm).

Anal. Calcd for $C_5H_8N_2$: C, 62.47; H, 8.39; N, 29.19; mol wt, 96. Found: C, 62.45; H, 8.85; N, 29.74; mol wt (ebullioscopic in ethylene chloride), 104.

The low-boiling fraction was collected in a gas trap immersed in a Dry Ice-acetone bath during distillation. The liquid product was identified as dimethylamine by means of its hydrochloride salt, mp $170-172^{\circ}$.

3,3-Bis(dimethylamino)propionitrile (VII).—A mixture of 15.0 g (0.1 mole) of 2 chlorotetramethylguanidine and 6.8 g (0.105 mole) of sodium azide in 60 ml of anhydrous acetonitrile was stirred at 0° for 28 hr while protecting the mixture from light. The reaction mixture was then allowed to stand at room temperature for 24 hr. The salt was removed by filtration, and the filtrate evaporated to give a yellow oil. Distillation afforded 7.0 g (50%) of colorless product VII, bp 40-42° (0.25-0.30 mm), and 0.9 g (9%) of IV, bp 72° (0.20 mm). The product possessed the strong characteristic odor of dimethyl-

(10) See ref 4, p 323.

amine and showed the presence of an absorption band in the infrared region at 4.45 μ , attributable to unconjugated C=N stretching frequency. The facile elimination of dimethylamine precluded an accurate elemental analysis. Slow redistillation of a sample of VII afforded IV, yield 79%, bp 77-78° (0.45 mm).

Hexamethylguanidinium Azide (VIII).—To a suspension of 3.3 g (0.05 mole) of sodium azide in 25 ml of freshly distilled, anhydrous DMF was added 7.0 g (0.047 mole) of 2-chlorotetramethylguanidine at one time. The reaction mixture was magnetically stirred at ambient temperature for 24 hr in the dark. During this time, there was a slow but steady evolution of nitrogen (1 mole/mole of I). Filtration afforded 3.4 g (100%) of salt. The yellow filtrate was concentrated by distillation under reduced pressure (0.1 mm) while avoiding excessive heating (>60°). The solid pot residue was collected by filtration, washed with several small portions of cold, dry acetone, and dried: yield 1.5 g (16%) of white hygroscopic product, mp 150–153°. Several crystallizations from chloroform-benzene raised the melting point to 157.5–159.5°.

Anal. Calcd for C7H18N6: N, 45.12. Found: N, 45.20.

Hexamethylguanidinium Tetraphenylborate (IX).—To a solution of 0.26 g (1.4 mmoles) of hexamethylguanidinium azide in 10 ml of water was added at one time, with swirling, a solution of 0.68 g (2.0 mmoles) of sodium tetraphenylborate in 20 ml of water. The mixture was heated to 50° to ensure completion of reaction and then allowed to stand at room temperature for 24 hr. The water was evaporated by means of a stream of nitrogen gas and the crude white product was washed with a mixture of methanol-water (1:1) and filtered. The product was washed thoroughly with water and finally crystallized from acetonitrile-water and dried: yield 0.48 g (78%), mp 340–343° dec. An analytical sample was prepared by recrystallization from acetonitrile: mp 345–347° dec; infrared, 6.31 (s) and 6.41 μ (m) (>C=N<).

Anal. Calcd for C₃₁H₃₈BN₃: C, 80.33; H, 8.26; N, 9.07. Found: C, 80.54; H, 8.43; N, 9.22. Tetramethylguanidinium Azide (X).—A dried ether solution

Tetramethylguanidinium Azide (X).—A dried ether solution of hydrazoic acid (prepared by adding 80 ml of concentrated HCl to a cold solution (0°) of 66 g (1.0 mole) of sodium azide in 200 ml of water over 30 min and then extracting with ether) was added to a solution of 115.2 g (1.0 mole) of tetramethylguanidine in 700 ml of ether over a period of 3 hr while maintaining the temperature at 0°. After complete addition, the mixture was allowed to stand at ambient temperature for 12 hr. Subsequently, the ether was decanted from the solid product. The product was slurried with two 100-ml portions of ether, crystallized from chloroform-ether, and dried: yield 130.1 g (86%) of a white hydroscopic solid, mp 90–93°. The infrared spectrum contained bands at 4.95 (N₃⁻), 6.0 (C=N), 3.61 (NH₂⁺), and 3.00–3.25 μ (NH₂).

Anal. Calcd for C₅H₁₄N₈: C, 37.96; H, 8.92. Found: C, 38.28; H, 8.98.

Reaction of Guanidinium Azides with Alkyl Halides.—The azides prepared by the reaction of tetramethylguanidinium azide with alkyl halides in refluxing chloroform are given in Table I. The general procedure employed is illustrated by the reaction of hexamethylguanidinium azide and ethyl α -bromacetate. To a solution of 3.7 g (0.02 mole) of hexamethylguanidinium azide in 40 ml of dichloromethane was added a solution of 3.3 g (0.02 mole) of ethyl α -bromacetate in 15 ml of dichloromethane over a period of 5 min. The temperature of the reaction mixture rose to 32° during the addition and maintained itself at this temperature for 10 min after the addition was complete. It was then heated at a gentle reflux for 5 min and concentrated by means of a stream of nitrogen gas. Ether (50 ml) was added, and the precipitated hexamethylguanidinium bromide collected by filtration, washed with several portions of ether, and dried: yield 4.2 g (93%), mp 302-303° dec. Crystallization of this salt from chloroform-benzene afforded 4.0 g (89%) of product, mp 319-323° dec.

Anal. Calcd for $C_7H_{18}BrN_3$: C, 37.51; H, 8.09; Br, 35.65. Found: C, 37.72; H, 8.22; Br, 35.24.

The filtrate from the original reaction mixture was concentrated under reduced pressure to give a crude, pale yellow oil. Distillation gave 1.4 g (54%) of ethyl α -azidoacetate, bp 43° (2.0 mm), lit.¹¹ bp 44-46° (2.0 mm) infrared 4.75 μ (s) (N₃).

⁽¹¹⁾ M. O. Forster and H. E. Fiery, J. Chem. Soc., 93, 72 (1908).

Reaction of Tetramethylguanidinium Azide with Nitriles to Give 5-Substituted Tetrazoles .- The tetrazoles prepared are shown in Table II. One general procedure for the synthesis and isolation of the tetrazoles was employed. This procedure is illustrated by the preparation of 5-dimethylaminotetrazole. A mixture of 3.5 g (0.05 mole) of dimethylcyanamide and 7.9 g (0.05 mole) of tetramethylguanidinium azide was stirred and heated at 100° for 7 hr. The reaction mixture was cooled to room temperature, dissolved in 30 ml of water, and acidified with glacial acetic acid (concentrated hydrochloric acid was used with all the other tetrazoles listed in Table II). (Caution:

Some hydrazoic acid could be evolved on acidification.) The precipitated product was collected, washed with cold water, and dried: yield $4.7 \text{ g} (83\%) \text{ mp } 238^{\circ}$ dec. Recrystallization from ethanol gave 4.0 g (71%), mp 240° dec.

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Oxidation of Active Hydrogen Compounds with 2-Chlorotetramethylguanidine

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Oxidative condensation of certain active hydrogen compounds was accomplished by reaction with 2-chlorotetramethylguanidine in nonaqueous systems. In general, methylene compounds afforded ethylenes while methine and sterically hindered methylene derivatives gave ethanes. Triethyl 1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate and tetramethylguanidinium pentacyanopropenide were obtained when ethyl cyanoacetate and malononitrile, respectively, were employed in the reaction. In contrast, a-bromo-p-nitrotoluene alkylated 2-chlorotetramethylguanidine to give 1, 1-di(p-nitrotolyl)tetramethylguanidinium perbromide.

A number of N-halo compounds are known to undergo a variety of interesting reactions.¹ A few examples of oxidation of organic compounds by N-haloamides and imides have been previously reported. The compounds studied included primary and secondary alcohols, $^{2-8}$ α -amino acids, 9 and cyclic systems. $^{10-18}$

This paper describes a study of the oxidation of compounds containing active hydrogen atoms by 2chlorotetramethylguanidine (I) and reports on the reaction of I with α -bromo-*p*-nitrotoluene.

Certain active hydrogen compounds have been found to undergo oxidative condensation on treatment with I to produce ethylenes, ethanes, and a cyclopropane. The reactions proceed smoothly at room temperature in a nonaqueous solvent or neat with the precipitation of tetramethylguanidine hydrochloride by-product during the reaction.

The results of the reactions studied are summarized in Table I. Yields are based on purified compounds and products were identified by elemental analysis, physical constants, and infrared spectrum.

Diethyl malonate, phenylacetonitrile, p-chlorophenylacetonitrile, and *p*-nitrophenylacetonitrile each gave the corresponding ethylene upon treatment with an equimolar amount of I. On the other hand, both bis(pnitrophenyl)methane and diphenylacetonitrile reacted with I in a 2:1 molar ratio, respectively, to give the

- (2) R. D. Chattaway and K. J. P. Orton, Ber., 32, 3573 (1899). (3) J. Blair, W. R. Logan, and G. T. Newbold, J. Chem. Soc., 2443
- (1956).
 - (4) C. A. Grob and H. M. Schmidt, Experientia, 5, 199 (1949).
 - (5) M. F. Hebbelynck and R. H. Martin, ibid., 5, 69 (1949).
 - (6) M. J. Leconte and C. Dufour, Compt. Rend., 234, 1887 (1952).
 - (7) L. F. Fieser and S. Raiagopalan, J. Am. Chem. Soc., 71, 3935 (1949).
 (8) L. F. Fieser, W. P. Schneider, and W.-Y. Huang, *ibid.*, 75, 124 (1953).

(9) A. Schonberg, R. Mousbascher, and M. Z. Barakat, J. Chem. Soc.,

- 2504 (1951).
 - (10) R. A. Barnes, J. Am. Chem. Soc., 70, 145 (1948).
 - R. A. Barnes and G. R. Buckwalter, *ibid.*, **73**, 3858 (1951).
 T. A. Geissman and E. Hinreiner, *ibid.*, **73**, 782 (1951).

 - (13) T. A. Geissman and T. G. Halsall, ibid., 73, 1280 (1951).

ethanes. The general reactions giving ethylene and ethane are shown by eq 1 and 2, respectively.



$$2[(CH_{\delta})_{2}N]_{2}C = \dot{N}H_{2}CI^{-}$$

$$(p-O_{2}NC_{6}H_{\delta})_{2}CHCH(C_{6}H_{\delta}NO_{2}-p)_{2}$$

$$2(p-O_{2}NC_{6}H_{\delta})_{2}CH_{2} + I \longrightarrow + (2)$$

$$[(CH_{\delta})_{2}N]_{2}C = \dot{N}H_{2}CI^{-}$$

The reaction with both ethyl cyanoacetate and malononitrile proceeded rapidly and exothermally in benzene and tetrahydrofuran solution, respectively. Unexpectedly, the former gave triethyl 1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (II). The product

$$3I + 3CH_2(CN)CO_2C_2H_5$$

$$\begin{array}{c} CO_2 C_2 H_5 \quad CO_2 C_2 H_5 \\ \hline CN \quad CN \quad + \quad 3 \underline{[CH_3]_2 N]_2 C} = \overset{+}{N} H_2 C I^{-1} \\ \hline CO_2 C_2 H_5 \\ II \end{array}$$

from the reaction with malononitrile was tetramethylguanidinium pentacyanopropenide (III).

$$[(CN)_2C = C(CN)C(CN)_2]^-[((CH_3)_2N)_2C = NH_2]^+$$
III

Evidence in support of III was obtained from elemental analysis and comparison of infrared and ultraviolet spectra with an authentic sample prepared by the reaction of malononitrile with tetracyanoethylene

⁽¹⁾ S. S. Navikov, V. V. Sevost'yanova, and A. A. Fainzil'berg, Russian Chem. Rev., 31, 671 (1962).