Reaction of Di- and Trisubstituted Chloroiminium Chlorides with Azide Ion. A New "Curtius Type" Rearrangement[1]

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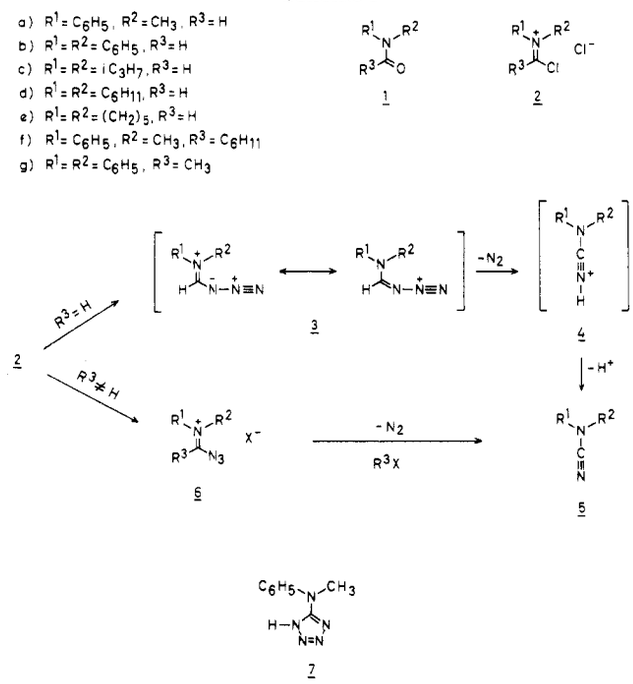
It is shown that disubstituted chloroformiminium chlorides **2** (R^3 = H) react with tetrabutylammonium azide (as well as other azide ion sources) to give the corresponding disubstituted cyanamides **5** presumably via the "Curtius like" rearrangement of an intermediate azidoformiminium salt **3**. Certain trisubstituted chloroiminium chlorides **9** undergo a related reaction with azide ion to give 1-substituted 5-disubstituted aminotetrazoles (**13**) via a trapable carbodiimidinium species **11**. Whereas the disubstituted cyanamide synthesis is a general one, the tetrazole synthesis is limited to those trisubstituted chloroiminium salts (e.g., **9**) where one of the nitrogen atom substituents and the migrating group are both aryl moieties.

The chemistry of organic molecules containing the azido moeity is rich in rearrangement reactions which stem from the propensity of these substances to lose molecular nitrogen.[2] The rearrangement of acyl azides to isocyanates (Curtius reaction[3]) and the reaction of hydrazoic acid with carbonyl compounds (Schmidt reaction[4]) are well known representatives of this general class of transpositions, while the formation of tetrazoles[5] or cyanamides[6] by the pyrolysis of geminal diazides are less frequently encountered members of this group of rearrangements. One rarely observed reaction is the rearrangement of imidoyl azides to carbodiimides.[7] This is because those reactions which are expected to yield the former substances provide tetrazoles instead. In fact, the reaction of imidoyl chlorides with azide ion constitutes one of the most general routes to 1,5-disubstituted tetrazoles and is known as the von Braun–Rudolf synthesis.[8] It occurred to us that one possible method of blocking tetrazole formation, and hence promoting rearrangement in the above instance, would be to utilize a substrate in which the nitrogen atom was disubstituted as is found in the azidoiminium salts **3, 6,** and **10,** derived from the corresponding dichlorides (Vilsmeier–Haack reagents[9]). This publication describes the results of such an investigation.

By analogy to the reactions cited above, it was expected that azidoformiminium salts **3** (Scheme I) would rearrange by the

Scheme I



concurrent loss of molecular nitrogen and migration of hydride from carbon to nitrogen to produce, after the loss of a proton from **4,** an N,N-disubstituted cyanamide. As a first attempt to effect such a transposition, a solution of *N*-methylformanilide (**1a**) in dimethoxyethane (DME) was converted into the chloroiminium salt **2a** with oxalyl chloride, and then solid sodium azide was added below 30 °C. A vigorous reaction, accompanied by considerable gas evolution, ensued. The product mixture, the composition of which depended on the number of moles of sodium azide utilized (Table I), consisted of the starting material **1a,** *N*-methylaniline, *N*-methyl-*N*-phenylcyanamide (**5a**), and the tetrazole **7.** The cyanamide yield was maximal when 2 mol of sodium azide per mole of the iminium salt **2a** was used. Extended reaction periods or higher reaction temperatures favored the formation of the tetrazole at the expense of the cyanamide, a predictable observation in view of the known[10] genesis of tetrazoles from cyanamides and hydrazoic acid.

The above reactions were not always reproducible, presumbaly because of the meager solubility of sodium azide in DME, and consequently trimethylsilyl azide,[11] triethylammonium azide,[12] and tetrabutylammonium azide[13] were examined as more soluble azide ion sources. The cyanamide **5a** was produced in each case, but the yield thereof was the highest (Table I) and by-product formation was the lowest with tetrabutylammonium azide.[14]

The dichlorides **2b–e** were then reacted with tetrabutylammonium azide (2 mol) and the cyanamides **5b–e** were formed in every instance in preparatively useful yields (Table II). The reaction clearly is a general one.

The successful conversion of disubstituted chloroiminium chlorides into the corresponding disbustituted cyanamides was an added impetus to examine the reaction of azide ion with trisubstituted chloroiminium chlorides such as **9** (Scheme II). It was anticipated that the rearrangement of the azidoiminium salts **10** obtained thereby would generate 1-aryl-5-(*N*-alkylanilino)tetrazoles (**13**) via the highly electrophilic alkylcarbodimidinium species[15] **11.** Indeed, the reaction of tetrabutylammonium azide (2.5 equiv) with *N*-methyl-*N*-phenylchlorobenziminium chlorode (**9a**) (1 equiv), in DME solution at 50–60 °C, gave 1-phenyl-5-(*N*-methylanilino)-tetrazole (**13a**) as the principle (57%) product together with minor amounts of 1,5-diphenyltetrazole (**14a**) (8%), *N*-methylaniline (10–13%), and benzaldehyde (10–13%). The structure of **13a** was confirmed by an unambiguous synthesis from the lithium salt of *N*-methylaniline and 1-phenyl-5-chlorotetrazole. Other trisubstituted iminium salts **9b–e** were also converted into the tetrazoles **13** and **14** and other products, the relative amounts of which (Table III) depended on the nature of R^2.

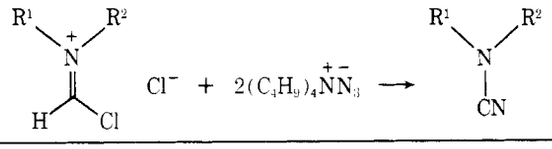
Several aspects of the data recorded in Table III are worthy

Table I. Reaction of *N*-Methyl-*N*-phenylchloroformiminium Chloride (2a) with Various Azide Ion Sources

Azide ion source	Registry no.	Moles azide per mole 2a	Products, %			
			Cyanamide 5a	Tetrazole 7	*N*-Methylaniline	*N*-Methylformanilide (1a)
NaN_3	26628-22-8	1	4	5	52	9
NaN_3		2	39	5	37	11
NaN_3		3	22	2	40	7
$(CH_3)_3SiN_3$	4648-54-8	2	27	*b*	59	*b*
$(C_2H_5)_3NHN_3$	30074-14-7	2	47	5	*b*	5
$(C_4H_9)_4NN_3$	993-22-6	2	75	*a*	9	10

[a] Not detected. [b] Not determined.

Table II. Conversion of Disubstituted Chloroiminium Chlorides into Disubstituted Cyanamides



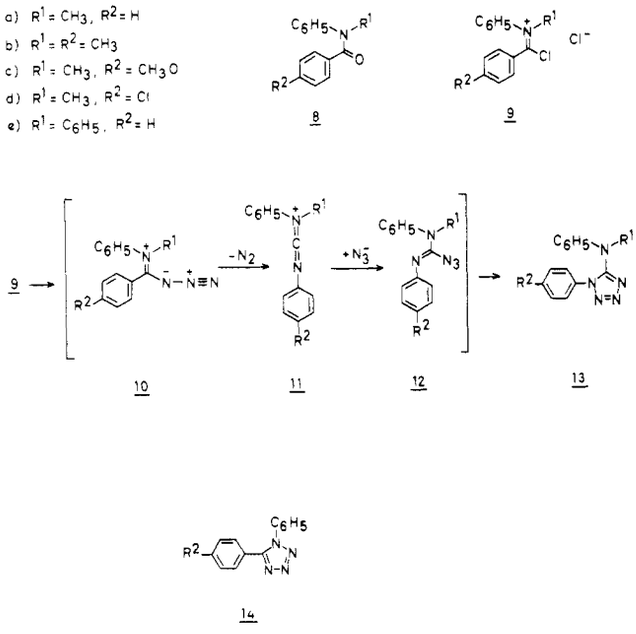
No.	R^1	R^2	Registry no.	% yield	
a	C_6H_5	CH_3	63640-93-7	75	
b	C_6H_5	C_6H_5	63640-94-8	62	
c	*i*-C_3H_7	*i*-C_3H_7	54485-04-0	45	(59)[a]
d	C_6H_{11}	C_6H_{11}	63640-95-9	44	
e		$-(CH_2)_5-$	59611-74-4	21	(41)[a]

[a] Yield by GLC.

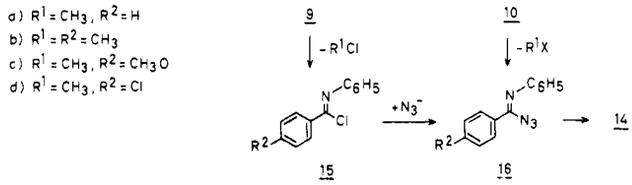
of comment. For example, what is the origin of the 1,5-diaryltetrazoles **14a–d**, *N*-methylaniline, the aromatic aldehydes, and the unsymmetrical urea **18**?

The formation of the 1,5-diphenyltetrazoles **14a–d** can be rationalized in terms of a von Braun type of degradation[16] of **9** and/or **10** (Scheme III). The intermediate imidoyl azide **16** derived directly from **10**, or indirectly via the imidoyl chloride **15**, would then cyclize to **14** in the expected[8] manner. It is probable, however, that the major portion of the 1,5-diaryltetrazole by-product was derived from **15**, which had formed prior to the addition of azide ion. This contention is based on the observation that **15a** and **15d** were formed in 80 and 85% yields (as determined by hydrolysis to the corresponding benzamides) when dimethoxyethane solutions of **9a** and **9d**

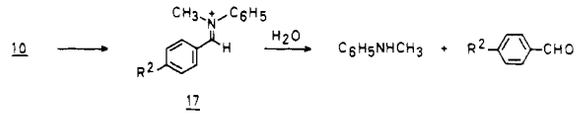
Scheme II



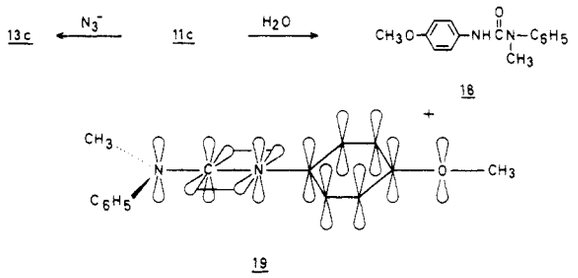
Scheme III



Scheme IV



Scheme V



were heated at reflux temperature (77 °C in Mexico City!) for 24 and 48 h. (The transformation of **8** into **9** required 4–15 h at 60 °C.) Based on the above mechanism, it is not surprising that no 1,5-diphenyltetrazole was formed in the reaction of **9e** with azide ion, since the loss of chlorobenzene from **9e** or phenyl azide from **10e** would be unlikely.

Appreciable amounts of aldehydes and *N*-methylaniline were formed in the reaction of **9a, 9b,** and **9d** with azide ion. In the case of **9a,** at least,[17] equimolar amounts of benzaldehyde and *N*-methylaniline were produced, and this was suggestive of a common intermediate for these substances. Hydrolysis of the iminium salt **17** (Scheme IV) which, in principle, could be derived by hydride transfer from the solvent to **10,** is one plausible[18] source of the above products. Reduction at the chloroiminium salt stage **9** by the solvent is ruled out, because heating **9a** and **9d** in DME gave the corresponding imidoyl chlorides **15a** and **15d** in high yield (see above), and little if any (<3%) of the expected reduction products.

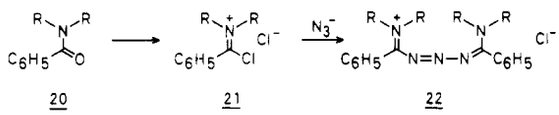
When R^2 was a methoxyl group a considerable amount (42%) of the urea **18** (Scheme V) was isolated. This substance doubtless arose by hydrolysis (during the workup of the reaction) of the carbodimidinium salt **11c,** the reaction of which with azide ion must be slow presumably because of the highly resonance stabilized nature (as shown in **19**) of this species. This latter contention was supported by the isolation of the expected tetrazole **13c** in greater yield (54%), at the expense of the urea (27%), when the reaction was extended from 2 to 24 h. Furthermore, if the reaction was conducted in the presence of excess azide ion (4 mol, see Experimental Section)

Table III. Reaction of Trisubstituted Chloroiminium Chlorides 9 with Tetrabutylammonium Azide

No.	R^1	R^2	Registry no.	Tetrazole 13	Tetrazole 14	$C_6H_5NHR^1$	p-$R^2C_6H_4CHO$	Other
a	CH_3	H	63640-97-1	57	8	10–13	10–13	
b	CH_3	CH_3	63640-98-2	30	4	Present[a]	Present	Start. mat.,[b] 21
c	CH_3	CH_3O	63640-99-3	38	Present[c]	Not det[d]	Not det.	Urea 18, 42 Start. mat., 2
d	CH_3	Cl	63641-00-9	10	28	Present	16	Start. mat., 8
e	C_6H_5	H	63641-01-0	76	0	Not det	Not det	Start. mat., 10

[a] Present by TLC, but percentage not measured. [b] Starting material, i.e., amide 8. [c] Formed in 9% yield together with **13c** when 4 equiv of azide ion was used (see Experimental Section). [d] Not determined.

Scheme VI



a) R = CH_3
b) R = C_6H_5

for an extended period of time (46 h), the only products isolated were the tetrazoles **13c** (50%) and **14c** (9%).

It is significant that, of the trisubstituted azidoiminium salts **10**, the yield of rearrangement derived products was the greatest when the migrating group was 4-methoxyphenyl (i.e., **10c**). This is a forseeable result if the reactions described herein are mechanistically analogous to the Curtius, Schmidt, Beckmann, etc., rearrangements.[19]

The successful rearrangement reactions described to this point were those in which the migrating group was either hydrogen or an aryl moiety. It was of interest to determine if the reaction would also occur when the group to be transposed possessed a lesser migratory aptitude. Therefore, the chloroiminium chloride **2f**, derived from *N*-methyl-*N*-phenylcyclohexanecarboxamide, was reacted with tetrabutylammonium azide in the usual manner. A mixture of products resulted, from which *N*-methylaniline (61%) and *N*-methyl-*N*-phenylcyanamide (**5a**, 32%) were isolated. No *N*-cyclohexyl-*N*-methylanilinotetrazole was, however, present in this mixture. The iminium salt **2g**, obtained from diphenylacetamide (**1g**), reacted in an analogous fashion to give diphenylcyanamide (**5b**, 33%), but no 1-methyl-5-diphenylaminotetrazole. No cyclohexene was detectable (as 1,2-dibromocyclohexane) in the reaction of **2f** with azide ion, and therefore the formation of the cyanamides probably takes place via a fragmentation mechanism where the alkyl moiety is lost by a nucleophilic displacement reaction.

A further limitation of the above tetrazole synthesis was encountered for those substrates in which the nitrogen atom did not bear at least one aryl group. For example, the chloroiminium chlorides **21** (Scheme VI) gave orange red salts which could not be obtained analytically pure. Structure **22** has tentatively been assigned to these substances on the basis of the colored nature thereof, as well as literature precedent[20] and a less than satisfactory elemental analysis of the cyclohexyl compound **22b**.

Finally, it is worthy of note that heterocyclic quaternary azidoiminium tetrafluoroborates derived from pyridine, quinoline, isoquinoline, and benzothiazole have been reported[20,21] to be isoable, crystalline substances with thermal stabilities considerably in excess of those observed for the azidoiminium salts described herein.

Experimental Section

The melting points were determined in a Mel-Temp melting point apparatus and are not corrected. The infrared spectra were measured with a Perkin-Elmer Model 237 grating infrared spectrophotometer. The NMR spectra were obtained with a Varian T-60 spectrometer. The ultraviolet spectra were recorded on a Perkin-Elmer Model 402 ultraviolet–visible spectrophotometer. The gas–liquid partition chromatographic analyses were effected using a Hewlett-Packard Model 5750 Research chromatograph using a 6 ft × ⅛ in. SE-30 column and a flame ionization detector. The mass spectra were measured with an Atlas CH-4 spectrometer.

The reactions with the chloroiminium chlorides were carried out in anhydrous 1,2-dimethoxyethane in a nitrogen atmosphere. The apparatus used was flame dried in an atmosphere of nitrogen.

The starting amides were synthesised by known procedures, and the physical constants thereof were identical with those recorded in the literature.

The disubstituted cyanamides were prepared[22] from the appropriate secondary amine and cyanogen chloride or cyanogen bromide.

Tetrabutylammonium Azide. To a 40% tetrabutylammonium hydroxide solution (130 g, 0.2 mol) was added sodium hydroxide (4 g, 0.1 mol), sodium sulfate (28.4 g, 0.2 mol), and sufficient distilled water to give a total volume of 200 mL. A solution of sodium azide (26 g, 0.4 mol) in water (50 mL) was added, and the product was extracted with dichloromethane and worked up in the manner described by Brändström et al.[13] The solid tetrabutylammonium azide was stored in a tightly stoppered brown bottle in a desiccator containing calcium chloride. The azide is very hygroscopic and weighings were performed as rapidly as possible. The weighed samples were redried in high vacuum prior to addition to the reaction mixtures.

Preparation of the Chloroiminium Chlorides. (A) From the Tertiary Amides and Oxalyl Chloride. All of the chloroiminium chlorides except that derived from *N,N*-diphenylacetamide were prepared by the following method.

To a solution of the amide (0.11 mol) in anhydrous dimethoxyethane (10–20 mL), maintained in an atmosphere of dry nitrogen, was added (at room temperature) oxalyl chloride (1.0 mL, 0.016 mol) via a hypodermic syringe. The formation of the chloroformiminium chlorides was usually complete after 4 h at room temperature. The trialkylchloroiminium chlorides formed much more slowly, and heating at 60 °C for 4–15 h was required before consumption of the amide was complete. The progress of the reactions could be followed by the rate of gas evolution, or by TLC examination of an aliquot which had been quenched with excess *n*-butylamine. Most of the chloroiminium chlorides were only partially soluble in dimethoxyethane, and the precipitation of a white solid during the course of the reaction was another indicator of the formation of the desired salt.

(B) Preparation of the Chloroiminium Chloride 2g. The reaction of *N,N*-diphenylacetamide with oxalyl chloride in the manner described above gave a new substance which was not converted into the starting amide with water. A second equivalent of oxalyl chloride had to be added to complete the consumption of the starting material. The reaction was poured into water and extracted with dichloromethane, and the extract was dried over sodium sulfate. The extract was passed through a short column of silica gel, then removal of the solvent in vacuo left a solid, which on crystallization from hexane–dichloromethane gave a solid which decomposed with gas evolution at 113–137 °C. This substance was identified as 5-diphenylamino-2,2-dichloro-3(2*H*)-furanone on the basis of the elemental analysis, spectroscopic properties, and literature precedent:[23] IR ($CHCl_3$) 1718, 1610, 1670 cm^{-1}; NMR ($CDCl_3$) δ 4.57 (s, 1 H), 7.00–7.50 (m, 10 H); MS *m/e* (rel intensity) 323 (5), 322 (5), 321 (21), 320 (7), 319 (29), 258 (10), 256 (30), 193 (20), 164 (18), 161 (62), 159 (100), 77 (46), 46 (65).

Anal. Calcd. for $C_{16}H_{11}Cl_2NO_2$: C, 60.03; H, 3.44; Cl, 22.15; N, 4.38. Found: C, 60.18; H, 3.53; Cl, 22.05; N, 4.29.

To prepare the iminium salt **2g,** a 12.5% solution of phosgene in benzene (50 mL) was added to *N,N*-diphenylacetamide (1.16 g, 0.0055 mol), and the solution was left at room temperature for 3 days. The solvent was removed in vacuo with careful maintainance of anhydrous conditions. Anhydrous dimethoxyethane (20 mL) was added to the residue, and this solution was then reacted with tetrabutylammonium azide (see below).

Reaction of *N*-Methyl-*N*-phenylchloroformiminium Chloride 2a with Sodium Azide. To the chloroiminium chloride **2a,** prepared from 1.5 g (0.011 mol) of *N*-methylformanilide, was added finely pulverized sodium azide (1.45 g, 0.022 mol) in one portion. A vigorous gas evolution commenced in a short while, and the reaction temperature began to rise. The reaction temperature was not permitted to exceed 30 °C by occasional cooling with a water bath. After 5 h, the mixture was partitioned between water and ether, the aqueous phase was extracted with ether, and the combined extracts were washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and saturated sodium chloride solution. The extract was dried over magnesium sulfate and then concentrated in vacuo. The residue was subjected to column chromatography on silica gel (30 g) using benzene and then benzene–ethyl acetate (8:1) as the eluting solvents. The cyanamide-containing fractions were evaporated to give *N*-methyl-*N*-phenylcyanamide (0.57 g, 39%, pure by TLC), which after distillation, bp 85–87 °C (0.2 mm), yielded the pure substance, mp 29–30 °C (lit.[24] 28 °C), identical with an authentic specimen.

Later chromatographic fractions afforded the starting material (0.16 g, 11%) and 5-(*N*-methylanilino)tetrazole (**7,** 0.09 g, 5%), mp 133–135 °C (lit.[10a] 139 °C).

Basification of the aqueous acidic phase described above, followed by ether extraction, gave crude (0.43 g, 37%) *N*-methylaniline.

General Procedure for the Reaction of the N,N-Disubstituted Chloroformiminium Chlorides 2 with Tetrabutylammonium Azide. To the chloroiminium chloride (0.011 mol) was added a solution of tetrabutylammonium azide (6.39 g, 0.0224 mol) in anhydrous dimethoxyethane (15 mL) in a dropwise manner, the temperature being maintained at ≤30 °C as described above. Gas evolution commenced immediately after the addition of the azide solution was started, and the precipitation of a white solid usually began shortly thereafter. This solid redissolved when the addition was completed or after warming of the mixture to 40 °C. The reactions were stirred at room temperature for 4–13 h, or in the case of **2c** and **2e,** the temperature was maintained at 40 °C for 1–2 h. The reactions were worked up as described for the sodium azide reaction, and the crude product was separated from contaminants by column chromatography on silica gel. Final purification of the cyanamide was achieved by distillation in vacuo and/or by crystallization from a suitable solvent. The cyanamides were identical with authentic specimens prepared in the manner previously referred to.

In the case of **5c** and **5e,** the reaction mixtures were subjected to quantitative analysis by GLC at 81 °C (before workup) using *N*-cyanopiperidine (**5e**) and diisopropylcyanamide (**5c**), respectively, as internal standards.

1-Phenyl-5-(*N*-methylanilino)tetrazole (13a) by the Amination of 1-Phenyl-5-chlorotetrazole. A solution of freshly distilled *N*-methylaniline (1.20 g, 0.0122 mol) in anhydrous tetrahydrofuran (25 mL), maintained in a nitrogen atmosphere, was cooled in a dry ice–acetone bath and ethereal methyllithium (6.5 mL of a 1.8 M solution) was added. The mixture was left to come to room temperature, and then solid 1-phenyl-5-chlorotetrazole (1.80 g, 0.01 mol) was added. After 2 h, ethanol (2 mL) and then water (2 mL) were added and the solution was concentrated in vacuo. The residue was partitioned between dichloromethane and water. The organic extracts were washed in turn with hydrochloric acid (3 N), water, and saturated salt solution. The extract was dried over sodium sulfate, and after removal of the solvent in vacuo the residue was crystallized from ether–hexane to give the tetrazole (1.85 g, 74%): mp 73.5–74.5 °C; UV (CH_3OH) 230, 265 nm (ε 10 000, 5010); IR (KBr) 1597, 1563 cm^{-1}; NMR ($CDCl_3$) δ 3.50 (s, 3 H), 6.57–7.00 (m, 5 H), 7.08 (s, 5 H); MS *m/e* (rel intensity) 251 (28), 223 (31), 222 (62), 118 (16), 106 (69), 105 (16), 104 (17), 91 (54), 79 (22), 78 (86), 77 (100), 65 (18), 46 (30).

Anal. Calcd. for $C_{14}H_{13}N_5$: C, 66.91; H, 5.21; N, 27.87. Found: C, 66.86; H, 5.26; N, 28.08.

Reaction of the Trisubstituted Chloroiminium Chlorides 9 with Tetrabutylammonium Azide. Formation of the Tetrazoles 13. 1-Phenyl-5-(*N*-methylanilino)tetrazole (13a). A solution of tetrabutylammonium azide (7.81 g, 0.0275 mol), in dry dimethoxyethane (20 mL), was added to a suspension of the trisubstituted chloroiminium salt **9a** (0.011 mol) in dimethoxyethane (20 mL) at 50–60 °C over a 2-min period. Vigorous gas evolution accompanied by a change in the color of the solution to dark red-orange was observed. The color faded as the reaction progressed and after 0.5 h at the above temperature the solution was poured into water. The products were extracted into ether, and the extract was washed successively with dilute hydrochloric acid, water, and saturated salt solution. The ether solution was dried over magnesium sulfate and evaporated in vacuo. Crystallization of the residue from hexane–ethyl acetate (4:1) gave the tetrazole **13a** (1.58 g, 57%), mp 74–75 °C, identical with the material prepared as described above.

The mother liquor from the above crysatllization was subjected to preparative TLC on silica gel using hexane–ethyl acetate (3:1) as the developing solvent. There was thus obtained an oil (0.12 g, 10%), identified as benzaldehyde by direct comparison of its spectral properties to those of a pure specimen, and a solid which after crystallization from methanol had mp 141–143 °C (lit.[25] 144–145 °C). This latter substance, obtained in 8% yield, was shown to be 1,5-diphenyltetrazole by direct comparison with an authentic sample.

The aqueous acidic phase from above was basified and extracted with ether. The extract was passed through a short column of silica gel to give, after evaporation of the solvent, pure *N*-methylaniline (0.15 g, 13%).

1-(4-Methylphenyl-5-(*N*-methylanilino)tetrazole (13b). The reaction of **9b** with tetrabutylammonium azide was carried out as described for **9a,** and following an identical workup there was obtained the tetrazole **13b,** mp 155–157 °C (ether–hexane), in about 30% yield: UV (CH_3OH) 233, 255 (sh) nm (ε 12 000, 6800); IR ($CHCl_3$) 1595, 1553, 1516 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 3 H), 3.47 (s, 3 H), 6.58–7.13 (m, 9 H); MS *m/e* (rel intensity) 265 (27), 237 (21), 236 (34), 132 (28), 107 (38), 106 (100), 105 (61), 104 (26), 91 (25), 79 (26), 78 (23), 77 (70), 65 (17), 46 (27).

Anal. Calcd. for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.85; H, 5.64; N, 26.37.

In addition, there was isolated 21% of the starting amide and 4% of 1-phenyl-5-(4-methylphenyl)tetrazole (**14b**), which had mp 131–133 °C (lit.[8] 136 °C) after crystallization from hexane–ethyl acetate.

1-(4-Methoxyphenyl)-5-(*N*-methylanilino)tetrazole (13c). The reaction with **9c** was effected in the usual way, and after workup the crude product was triturated with ether to give the tetrazole **13c** (38%) which, after crystallization from methanol, had mp 154–156 °C: UV (CH_3OH) 238, 260 (sh) nm (ε 11 500, 6890); IR ($CHCl_3$) 1595, 1555, 1515 cm^{-1}; NMR ($CDCl_3$) δ 3.47 (s, 3 H), 3.67 (s, 3 H), 6.48–7.05 (m, 9 H).

Anal. Calcd. for $C_{15}H_{15}N_5O$: C, 64.04; H, 5.37; N, 24.90. Found: C, 63.87; H, 5.38; N, 24.76.

The mother liquors from above were chromatographed on a column of silica gel (hexane–ethyl acetate). In addition to the starting material (2%), *N*-methyl-*N*-phenyl-*N'*-(4-methoxyphenyl)urea (**18**) was isolated in 42% yield. It had mp 99–100.5 °C after crystallization from water, and was identical with an authentic sample prepared from *N*-methylaniline and 4-methoxyphenyl isocyanate in hot benzene: UV (CH_3OH) 233 nm (ε 16 600); IR ($CHCl_3$) 3440, 1666, 1619, 1600, 1510 cm^{-1}; NMR ($CDCl_3$) δ 3.27 (s, 3 H), 3.67 (s, 3 H), 6.62 (d, 2 H, J = 9.2 Hz), 7.05 (d, 2 H, J = 9.2 Hz), 7.25 (m, 5 H).

Anal. Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.57; H, 6.51; N, 10.62.

If the reaction was allowed to proceed for 24 h, the yield of the tetrazole **13c** was 54% and that of the urea was 27%. If at the end of 22 h, 2 mol of sodium azide was added and the reaction was continued for a further 24 h (60 °C), the tetrazole **13c** (50%) and 1-phenyl-5-(4-methoxyphenyl)tetrazole (**14c,** 9%) were the only products formed. The latter compound was isolated from the mother liquors obtained from the crystallization of **13c.** After crystallization from hexane–ethyl acetate it had mp 107–109 °C (lit.[26] 110 °C).

1-(4-Chlorophenyl)-5-(*N*-methylanilino)tetrazole (13d). The product mixture, obtained in the standard manner, was separated into its components by preparative TLC on silica gel (hexane–ethyl acetate, 70:30). In this way there was isolated 4-chlorobenzaldehyde (16%), starting material (8%), 1-phenyl-5-(4-chlorophenyl)tetrazole (28%), mp 155–156 °C (lit.[27] 155.5 °C, after crystallization from methanol), and the desired tetrazole **13d** (10%). This substance had mp 165–167 °C after crystallization from methanol: UV (CH_3OH) 232, 260 (sh) nm (ε 15 900, 6220); IR ($CHCl_3$) 1603, 1592, 1554 cm^{-1}; NMR ($CDCl_3$) δ 3.50 (s, 3 H), 6.57–7.11 (m, 9 H).

Anal. Calcd. for $C_{14}H_{12}ClN_5$: C, 58.85; H, 4.23; Cl, 12.41; N, 24.51. Found: C, 58.80; H, 4.09; Cl, 12.24; N, 24.42.

1-Phenyl-5-(diphenylamino)tetrazole (13e). In addition to the starting material (10%) the only other substance formed in this reaction was the tetrazole **13e** (76%). After crystallization from ethyl acetate, it had mp 161–163 °C: UV (CH_3OH) 265 nm (ε 12 900); IR ($CHCl_3$) 1595, 1525 cm^{-1}; MS *m/e* (rel intensity) 313 (29), 285 (19),

284 (45), 169 (25), 168 (100), 167 (52), 77 (40), 46 (26).

Anal. Calcd. for $C_{19}H_{15}N_5$: C, 72.82; H, 4.83; N, 22.33. Found: C, 72.72; H, 4.87; N, 22.09.

Reaction of the Trisubstituted Chloroiminium Chloride 2f with Tetrabutylammonium Azide. The salt **2f** was prepared on a 0.022-mol scale. After the addition of the azide solution (0.055 mol) at 50–60 °C, stirring was continued at this temperature for 15 h. The solvent was distilled at atmospheric pressure, and the distillate was collected in a receiver cooled with a dry ice–acetone bath. The final pot temperature was 160 °C. The distillate was reacted with excess bromine at 0 °C, the solvent and excess bromine were removed in vacuo at room temperature (20 mm), and the residue was examined by GLC. There was no detectable 1,2-dibromocyclohexane present in this mixture.

The pot residue from above was diluted with water and extracted with dichloromethane. The extract was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and saturated salt solution. The organic phase was dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel. The cyanamide was eluted with hexane–benzene–ethyl acetate (5:4:1) and several more polar products were removed from the column with ethyl acetate. The crude *N*-methyl-*N*-phenylcyanamide (1.15 g) was distilled in vacuo as before to give a pure specimen (0.94 g, 32%) identical with the material prepared from **2a.**

Basification of the acidic fraction from above gave, after ether extraction and the usual manipulation, nearly pure *N*-methylaniline (1.43 g, 61%).

Reaction of the Chloroiminium Chloride 2g with Azide Ion. To a solution of the iminium salt **2g** (0.0055 mol), prepared from **1g** and phosgene as described above, was added a dimethoxyethane solution of tetrabutylammonium azide (0.014 mol) and the resultant was heated at reflux temperature for 18 h. The solution was poured into water and extracted with dichloromethane. The dried (sodium sulfate) extract was evaporated in vacuo, and the residue was chromatographed on a column of silica gel using hexane–benzene (4:1) as the eluting solvent. The first fractions contained diphenylamine, the cyanamide **5b** (0.350 g, 35%), identical with the material prepared from **2b,** was eluted next, and this substance was followed by the starting material (0.50 g, 43%).

Reaction of 21b with Azide Ion. Synthesis of 22b. To a suspension of the iminium salt **21b** (0.0055 M) in dimethoxyethane (10 mL) was added a dimethoxyethane solution of tetrabutylammonium azide (0.015 mol) at 50–60 °C in the usual manner. A red-orange solid precipitated immediately. This substance was collected by filtration and dried in vacuo. It could not be recrystallized, and therefore a sample was dried in vacuo for analysis. The substance thus obtained had mp 210 °C dec, gave positive Beilstein and silver nitrate tests, and decomposed, with gas evolution and the formation of *N,N*-dicyclohexylbenzamide, on treatment with aqueous ethanolic potassium hydroxide. A mass spectrum of the red salt could not be obtained: UV (CH_3OH) 382 nm (ϵ 40 800); IR ($CHCl_3$) 1560 cm^{-1}; NMR ($CDCl_3$) δ 0.83–2.17 (m, 36 H), 2.40–3.10 (m, 4 H), 3.24–3.96 (m, 4 H), 6.53–6.77 (m, 4 H), 6.87–7.33 (m, 6 H).

Anal. Calcd. for $C_{38}H_{30}ClN_5$: C, 74.05, H, 8.83; N, 11.37. Found: C, 73.00; H, 8.80; N, 11.40.

The above data are not inconsistent with structure **22b.**

Acknowledgment. We are greatful to a referree for suggesting the mechanism of formation of the urea **18** from **11c.**

Registry No.—**1a,** 93-61-8; **1b,** 607-00-1; **1c,** 3700-30-3; **1d,** 2269-63-4; **1e,** 2591-86-8; **1f,** 23824-50-2; **1g,** 519-87-9; **2f,** 63641-02-1; **2g,** 63641-03-2; **13a,** 63641-04-3; **13b,** 63641-05-4; **13c,** 63641-06-5; **13d,** 63641-07-6; **13e,** 63641-08-7; **18,** 59849-55-7; **22b,** 63641-09-8; oxalylchloride, 79-37-8; 5-diphenylamino-2,2-dichloro-3(2*H*)-furanone, 636-41-10-1; phosgene, 75-44-5; *N*-methyaniline, 100-61-8; 1-phenyl-5-chlorotetrazole, 14210-25-4.

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Reaction of Di- and Tribromotetrahydro-4*H*-pyran-4-ones with Bases

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The reaction of 3,5-dibromotetrahydro-4*H*-pyran-4-ones (**1a,b**) with morpholine in HMPA gave enamino ketones **2a,b** and **3a,b** as the major products. The reaction of 3,3,5-tribromotetrahydro-4*H*-pyran-4-ones (**5a,b**) with silver acetate in acetic acid gave a mixture of bromo α-diketones **8a,b** and their enol acetates **9a,b** exclusively. Furthermore, dehydrobromination of **8a,b** with DBU or Dabco gave corresponding 3-hydroxy-4*H*-pyran-4-ones **10a,b.** However the reaction of diethyl 3,3,5-tribromotetrahydro-4*H*-pyran-4-one-2,6-dicarboxylate (**5c**) with silver acetate in acetic acid afforded bromo α-diketones **8c,** diethyl 3-hydroxy-4*H*-pyran-4-one-2,6-dicarboxylate (**10c**), and diethyl 3,5-dibromo-4*H*-pyran-4-one-2,6-dicarboxylate (**11**).

Of the simple tetrahydro-4*H*-pyran-4-ones, only a few have received attention in the literature with respect to their oxidation product.

In this paper, we wish to report the formation of tetrahydro-4*H*-pyran-3,4-diones and their derivatives from 3,5-dibromo- or 3,3,5-tribromotetrahydro-4*H*-pyran-4-ones.