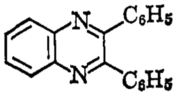
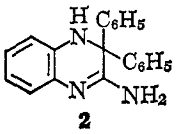
the reaction (*vide infra*) did, in fact, lead to a new product in approximately 30% yield and the recovery of about 60% of unchanged **1**. Data for this new compound A were summarized by Ogg and Bergstrom as follows: the alleged 2,2-diphenyl-3-amino-1,2-dihydroquinoxaline melted at 287° (uncor.), formed a hydrochloride, and was unaffected by nitrous acid or by HCl and ethanol at 150°.


1


2

Anal. Calcd. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.41, 80.28; H, 5.42, 5.50; N, 14.16, 14.11.

This evidence, taken in conjunction with the above analogy, was regarded by Ogg and Bergstrom as good proof for the formulation of A as **2**. The failure of A to react with nitrous acid, despite the presence of both a primary and a secondary amino group, was curious and unexplained.

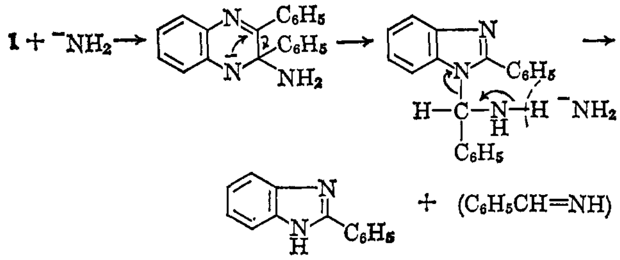
As a consequence of this discrepancy and our general interest in dihydroquinoxalines, we have reinvestigated the "rearrangement" of **1** to **2** and wish to report that the product is in actuality 2-phenylbenzimidazole (**3**), formed by an unusual ring contraction reaction.

Treatment of pure 2,3-diphenylquinoxaline with freshly prepared potassium amide in liquid ammonia in a sealed tube at 140° yielded a crude product, m.p. 260–285°, in 32% yield which, upon rigorous purification, was obtained in the form of colorless needles, m.p. 289–290°, in substantial agreement with the published value. The ultraviolet spectrum of this product (A) showed a distinct bathochromic shift compared with the spectrum of 2,3-diphenylquinoxaline, and was substantially altered by addition of either acid or base. The infrared spectrum of A exhibited diffuse absorption in the range 3010–2500 cm.$^{-1}$, indicative of strong N–H bonding, bands at 698 and 735 cm.$^{-1}$, indicative of a monosubstituted benzene ring, and a band at 760 cm.$^{-1}$, confirming the additional presence in A of a 1,2-disubstituted benzene ring. Otherwise, the spectrum was remarkably simple, especially in the fingerprint region; this feature is often associated with a highly symmetrical molecule. The n.m.r. spectrum of A was similarly nondefinitive, showing only aromatic protons which exhibited complex splitting.

The structure of A was readily determined, however, by inspection of its mass spectrum.[3] The parent peak appeared at m/e 194, with the P + 1 and P + 2 peaks well defined. Microanalysis confirmed the new molecular formula of $C_{13}H_{10}N_2$ (Calcd.: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.25; H, 5.03; N, 14.56); the fortuitous correspondence of these values with those calculated for the alleged $C_{20}H_{17}N_3$ formula is remarkable. It was clear from this result that the "rearrangement" of 2,3-diphenylquinoxaline with amide ion had in actuality resulted in the extrusion of a C_7 fragment. The only possible structure for compound A compatible with this spectroscopic evidence was thus 2-phenylbenzimidazole (**3**), and this conclusion was confirmed by direct comparison (mixture melting point determination and identity of n.m.r., ultraviolet, and infrared spectra) with an authentic sample prepared by the condensation of *o*-phenylenediamine with benzaldehyde in the presence of cupric acetate.[4]

The formation of 2-phenylbenzimidazole (**3**) from 2,3-diphenylquinoxaline (**1**) and potassium amide must involve initial addition of amide ion at C-2 (as postulated by Ogg and Bergstrom), but with subsequent ring contraction, presumably with elimination of benzylidenimine, to give the very stable, symmetrical, observed product **3**, rather than phenyl migration of the benzil acid-rearrangement type.

Attempts to effect ring contraction of **1** to **3** with other bases (potassium hydroxide in water or ethanol, sodium methoxide in methanol, sodium hydride in toluene) were unsuccessful; the efficacy of potassium amide appears to be specific.



3

Experimental

Reaction of 2,3-Diphenylquinoxaline with Potassium Amide in Liquid Ammonia. Formation of 2-Phenylbenzimidazole (3).—2,3-Diphenylquinoxaline[5] was treated with potassium amide, and the crude product was separated from unchanged starting material as previously described.[2] It was recrystallized from ethanol, with the use of Norit, then sublimed at 260° (0. 1 mm.) and the sublimate was recrystallized three times from ethanol to give colorless needles, m.p. 289–290° (lit.[4] m.p. 290°).

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[3] We are deeply indebted to Dr. Frank Hochgesang of the Socony Oil Co., Paulsboro, N. J., for the determination of the mass spectrum.

[4] R. Weidenhagen, *Chem. Ber.*, **69**, 2263 (1936).

[5] R. W. Bost and E. E. Towell, *J. Am. Chem. Soc.*, **70**, 904 (1948).

Substituent Effects on the Long-Range Nitrogen-14 Coupling in Alkylammonium Salts[1]

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The H^1–N^{14} long-range coupling in ammonium salts has been noted by several workers.[3–8] In general, these authors have attributed the existence of this

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[1] The authors are indebted to the National Cancer Institute for Public Health Service Grant CA-07110-1 which supported this investigation.

[2] National Institutes of Health Predoctoral Fellow, 1963–1965.

[3] H. C. Hertz and W. Spalthoff, *Z. Elektrochem.*, **63**, 1096 (1959).

[4] J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *J. Chem. Phys.*, **38**, 1260 (1963).

[5] E. Bullock, D. G. Tuck, and E. J. Woodhouse, *ibid.*, **38**, 2318 (1963).

[6] M. Franck-Neumann and J. M. Lehn, *Mol. Phys.*, **7**, 197 (1963).

[7] E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963).

[8] Private communication from G. Fraenkel, Department of Chemistry, The Ohio State University.

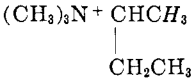
unusual coupling of N^{14} with hydrogen on the β-carbon to the presence of a highly symmetrical electric-field gradient around nitrogen. This symmetry results in an increase in the spin-lattice relaxation time (T_1), since the nucleus in its excited spin state can no longer transfer energy to the surrounding molecular environment through the interaction of its quadrupole with fluctuating field gradients. When T_1 increases within certain limits, the "decoupling" of the long-range interaction between N^{14} and H^1 become negligible and the H^1–N^{14} coupling constant (J_{NH}) becomes measurable.[9]

Although the existence of the H^1–N^{14} long-range coupling is well documented, relatively little is known about the requirements for a highly symmetrical electric-field gradient around nitrogen.[10] Having available a variety of alkylammonium salts, we decided to investigate the effect of substituents and hybridization on the H^1–N^{14} coupling.

As noted in Table I, replacement of the ethyl groups of tetraethylammonium iodide by methyl groups resulted in a gradual increase in the coupling constant between nitrogen and the hydrogen on the β-methyl group. The average increment was *ca.* +0.12 c.p.s./replaced ethyl group. Substitution of the methylene hydrogens of the ethyl group had an opposite effect in that the coupling constant was decreased. Thus, substitution of the first hydrogen by an alkyl group, as has been done in isopropyltrimethylammonium iodide, resulted in a decrease of the coupling constant by *ca.* 0.30 c.p.s. Replacement of the second hydrogen as in *t*-butyltrimethylammonium iodide caused an additional decrease of *ca.* 0.10 c.p.s. In general there is a trend for electron-inducing substituents to decrease the H^1–N^{14} coupling constant. However, this pattern holds only for saturated alkyl substituents, and even in this group the correlation between coupling constant and the σ* value of substituent groups was poor. Cases such as allyltriethylammonium iodide give much smaller coupling constants than would be predicted on the basis of inductive effects. Thus it appears that inductive effects do play some part in determining the size of the coupling constant but that this is not the major factor. In line with these results we found that several N-ethylpyridinium salts and N-ethylanilinium salts showed no detectable splitting due to H^1–N^{14} coupling.

TABLE I

N.M.R. SPECTRA OF ACYCLIC QUATERNARY AMMONIUM IODIDES

Compound[a]	J_{NH}, c.p.s.[b]	Std. dev.	Multiplicity
$(CH_3CH_2)_4N^+$	1.80	0.03	Tripled triplet
$(CH_3CH_2)_3N^+CH_3$	1.85	0.01	Tripled triplet
$(CH_3CH_2)_2N^+(CH_3)_2$	2.01	0.02	Tripled triplet
$CH_3CH_2N^+(CH_3)_3$	2.15	0.01	Tripled triplet
$(CH_3)_3N^+C(CH_3)_3$	1.74	0.04	Tripled singlet
$(CH_3)_3N^+CH(CH_3)_2$	1.83	0.04	Tripled doublet
 $(CH_3)_3N^+\underset{\displaystyle CH_2CH_3}{\underset{\vert}{CH}}CH_3$	1.87	0.01	Tripled doublet
$(CH_3)_3N^+CH_2CH_3$	2.15	0.01	Tripled triplet
$(CH_3CH_2)_3N^+CH_2CH{=}CH_2$	1.50	0.03	Tripled triplet
$(CH_3CH_2)_3N^+CH_2CH_2CH_2CH_3$	1.80	0.02	Tripled trip'et
$(CH_3CH_2)_3N^+CH_2CH_2CH_3$	1.78	0.07	Tripled triplet
$(CH_3CH_2)_3N^+CH_2CH_3$	1.80	0.03	Tripled triplet

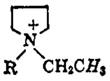
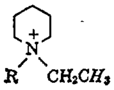
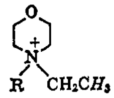
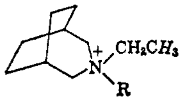
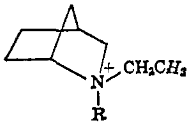
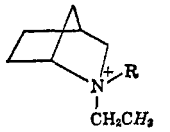
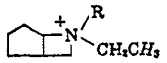
[a] The hydrogens coupled with the nitrogen are italic. [b] See Experimental.

A second phase of our studies was concerned with N,N-dialkyl heterocyclics. Again we found that the N-methyl-N-ethyl derivatives had larger coupling constants than the corresponding N,N-diethyl salts. This was as anticipated on the basis of inductive effects. As shown in Table II, the relatively unstrained five-, six-, and seven-membered nitrogen heterocyclics all exhibited comparable coupling constants. An unusual effect occurred with N-methyl-N-ethyl-6-azabicyclo[3.2.0]heptyl iodide in which the nitrogen of the tetraalkylammonium salt was part of a four-membered ring. In this case the bond angles to nitrogen and hence the hybridization about nitrogen was altered. In view of this change it might be anticipated that the symmetry of the electrical field around the quaternary nitrogen would be disturbed. Indeed this seems to be the case since this compound exhibits no H^1–N^{14} long-range coupling.

Our results indicate that the type of ammonium salts in which H^1–N^{14} long-range coupling can occur is extremely limited. In general this phenomenon appears to be restricted to tetra*alkyl*ammonium salts in which the hybridization of the bonds to nitrogen are sp^3. Apparently, slight distortion from a tetrahedral

TABLE II

N.M.R. SPECTRA OF
CYCLIC QUATERNARY AMMONIUM IODIDES

Compound	R	J_{NH}, c.p.s.	Std. dev.
	CH_3	1.90	0.04
	C_2H_5	1.88	0.04
	CH_3	1.75	0.06
	C_2H_5	1.67	0.06
	CH_3	1.75	0.03
	C_2H_5	1.69	0.06
	CH_3	1.79	0.04
	H	No spin–spin coupling[a]	
	CH_3	1.82	0.03
	C_2H_5	1.62	0.03
	CH_3	1.80	0.07
	C_2H_5	1.62	0.03
	CH_3	No spin–spin coupling	

[a] Attempts to prepare the N,N-diethyl derivative yielded the trialkylammonium hydriodide. As noted for all other hydriodides no splitting occurs.

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[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 102, 215, 225; also see L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, pp. 8–13, 72.

[10] For a discussion of N^{14} coupling, see W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963).

configuration results in a sufficiently large change in the symmetry of the electric-field gradient of the nitrogen that the spin-lattice relaxation time of N^{14} becomes comparable with the reciprocal of the spin-spin coupling constant and decoupling occurs.

Experimental

All spectra were measured in D_2O using a Varian A-60 n.m.r. spectrometer. All values were measured from five to nine times, each measurement being made on a different day.

All compounds were rigorously purified. The preparation of the new compounds listed in this study will be published separately.

A Preparation of Aroyl and Acyl Formamidinium Salts

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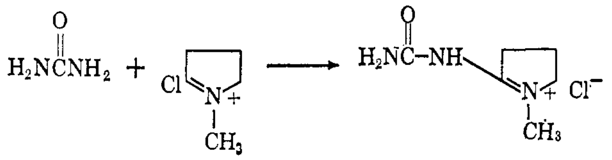
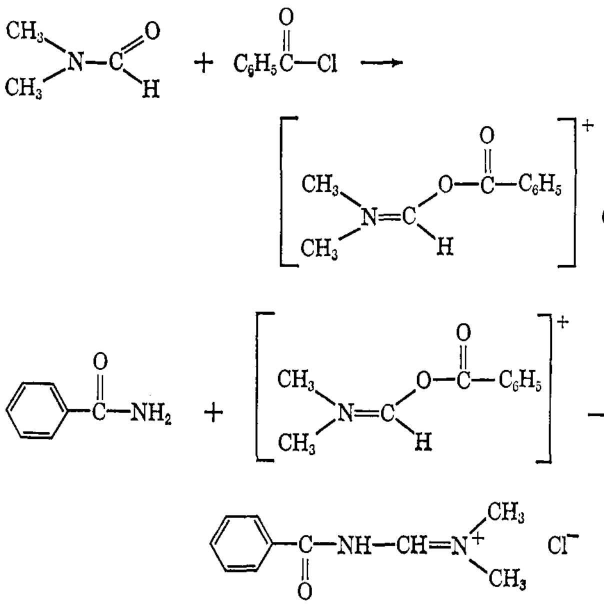
Received March 19, 1965

In a recent review on amido chlorides, Eilingsfeld, Seefelder, and Weidinger[1] comment that urea and its derivatives react with amido chlorides to produce amidinium salts (eq. 1). The preparation and physical properties of a number of these urea derivatives from thionyl chloride and dimethylformamide has been disclosed in the German patent literature.[2] However, Eilingsfeld states[1] that carboxamides do not undergo the corresponding reaction but rather undergo dehydration to nitriles when treated with acid chlorides or carbamido chlorides.[1,3]


(1)

While this appears to be true for such acid chlorides as phosgene, phosphorus oxychloride, and thionyl chloride, it has now been found that the use of benzoyl chloride or acetyl chloride leads to good yields of formamidinium salts.

A solution of carboxamide, *e.g.*, benzamide, in dimethylformamide was cooled to 5° and 1.1 equiv. of benzoyl chloride was slowly added. After spontaneously warming to room temperature and stirring overnight, the reaction mixture was poured into a mixture of benzene and ether and refrigerated. A 68% yield of N-benzoyl-N′,N′-dimethylformamidinium chloride was obtained. This reaction can probably be interpreted in the same fashion as the amido chloride reactions except that benzoate anion is the leaving group rather than chloride ion, as illustrated in eq. 2. Acetyl chloride was equally effective in this reaction; however, when ethyl chloroformate was used, no identifiable product was obtained.


(2)

Vapor phase chromatographic examination of the filtrate from the reaction showed that in no case was dehydration to nitrile entirely absent. Benzonitrile was produced in amounts varying from 20 to 80% as the solvent was changed from neat dimethylformamide to 50% dioxane.

Elemental analysis, n.m.r. spectroscopy and hydrolysis to the known N-formylamides served to identify the products. Table I lists several examples of the reaction.

The reaction between urea and dimethylformamide may also be carried out using benzoyl chloride or acetyl chloride rather than phosgene or thionyl chloride. With urea and benzoyl chloride, a 92% yield of N,N-dimethyl-N′-carbamidoformamidinium chloride, m.p. 191–192° dec. (lit.[2] 190–192° dec.), was obtained, and aniline, benzoyl chloride, and dimethylformamide gave an 81% yield of N,N-dimethyl-N′-phenylformamidinium chloride, m.p. 243–244° dec. (lit.[4] 239–241°).

Although Bredereck[4] prepared N,N-dimethyl-N′-phenylcaprinamidine from aniline, phosphorus oxychloride, and N,N-dimethylcaprinamide, the substitution of N,N-dimethylacetamide for N,N-dimethylformamide in the present study was unsuccessful. The reaction between benzamide, benzoyl chloride, and N,N-dimethylacetamide gave tribenzamide as the only identified product. N-Benzoylurea was obtained when urea was used in a reaction with N,N-dimethylacetamide.

Experimental

Preparation of Formamidinium Chlorides.—A solution of 0.1 mole of amide in 50 ml. of freshly distilled dimethylformamide was prepared. After solution was complete, the solution mixture was cooled to 0–5° and 16 g. of benzoyl chloride was slowly added without allowing the temperature to rise above 5°. After the benzoyl chloride was added, the temperature was maintained below 10° for an additional 2 hr. The reaction mixture was allowed to spontaneously warm to room temperature and was stirred for an additional 16 hr.

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(1) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

(2) K. H. Beyer, H. Eilingsfeld, and H. Weidinger, German Patent 1,110,625 (1961).

(3) R. Greenhalgh, British Patent 488,036 (1938).

(4) H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Ber.*, **92**, 837 (1959).