compounds, and lattice sizes. Vaughan,[9] however, has described a new, denser hexagonal U_2N_3 (La_2O_3 type), which occurred in a mixture of nitrides obtained on heating massive U in N_2 between 500 and 915°. Evans[10] has suggested that this is a coherency structure, but Trzebiatowski, *et al.*,[11] have found that annealing the cubic Mn_2O_3-type U_2N_3 at temperatures $>1000°$ led to a new denser U_2N_3 phase. Recently Bugh and Bauer[12] have stated that only the three compounds found by Rundle occur and that the solubility of N_2 in solid U is <1 p.p.m. They believe the solubility range of UN to be "fairly limited," which would correlate with Cater's[13] observations on US and the general belief for UC,[14] also that UN_2 needs high pressures to form although oxygen contamination may improve the stability of the higher U_2N_3–UN_2 regions.

In their note[1] D and G's observations included (a) that UN_2 could be readily prepared by passing NH_3 over UH_3 while raising the temperature to 1000°; (b) that heating UN_2 in a tantalum crucible in argon for 4 hr. at 1200 and 1900° gave $UN_{1.33}$ and $UN_{1.22}$, respectively, while heating *in vacuo* for 3 hr. at 1950° gave $UN_{1.04}$—these three latter phases had identical NaCl lattices; (c) that studies on sintered powders of UN (up to 83% density[15]) gave electrical resistivities of 0.9–1.4×10^{-4} ohm cm. between 300 and 1300°K. and a thermoelectric power of $+50$ μv./°K. at room temperature rising to $+100$ μv./°K. at 700°K. and falling back to $+50$ μv./°K. at 1300°K.

The present writers, having failed to obtain such high electrical conductivities with UN compacts prepared from N_2,[16] have attempted to reproduce the results of D and G and to examine the occurrence and stability of hexagonal U_2N_3.

Experimental Method and Results

D and G[15] prepared their UN_2 by converting a weighed amount of the metal to the hydride and passing NH_3 gas (purified through BaO and a hot UN column) over it at 800–850° for 24 hr. followed by a short heating at 1000° and cooling in NH_3 to room temperature. The composition was determined by chemical analysis for U. Oxygen contents were 0.38–0.42%.

On repeating this procedure, except for the substitution of CaH_2 and UH_3 as drier and oxygen purifier, respectively, of the initial gas, the writers have obtained $UN_{1.80}$ consistently. Duplicate analyses were completed on three different batches. The use of N_2 instead of NH_3 also gave $UN_{1.80}$. At lower temperatures smaller ratios were obtained. The lattice constant of $UN_{1.80}$ was 10.568 ± 0.002 Å. The U content was determined by oxidation to U_3O_8 before exposure to the atmosphere, although other samples remained unchanged in weight on standing for 50 hr. in air. Oxygen contents were $<0.2\%$. The only visible difference between the powders was size, batches prepared from NH_3 being much finer.

Heating either powder for 1 hr. at 1100° at a pressure of $\sim 10^{-2}$ mm. led to the formation of the hexagonal La_2O_3-type U_2N_3, the ratio being confirmed by analysis. The lattice size agreed with Vaughan's figures of $a = 3.69 \pm 0.01$ and $c = 5.83 \pm 0.01$ Å. This compound was stable in air at room temperature. Between 1150 and 1200° it broke down *in vacuo* to give UN. On heating in an argon or helium atmosphere the conversion was about 50° higher. It appeared that the UN_{2-x} on losing N_2 assumed the hexagonal U_2N_3 structure directly and despite frequent attempts the writers failed to obtain a Mn_2O_3-type X-ray pattern.

For powders heated above 1200° in argon or *in vacuo*, the only product was UN. Up to 1700° the product was stoichiometric ($UN_{1.0 \pm 0.02}$) but above this temperature the analyses were inconsistent, some experiments giving results as low as $UN_{0.8}$ at 1850°. This latter material may, however, be $UN_{1.0} + U$ since the chemical analysis made no distinction. The UN lattice spacings were all 4.888 ± 0.002 Å. When hot pressing, at 5000 p.s.i. in molybdenum-lined graphite dies, the powders prepared *via* NH_3 gave much denser compacts than those prepared *via* N_2, 90% of the theoretical density being easily achieved at 1650°. With these compacts, the room temperature thermoelectric powers of $+52$ μv./°C. and electrical resistivities of 1.1–1.4×10^{-4} ohm cm. closely approached those reported by D and G.

Conclusions

(1) The room temperature thermoelectric data of D and G can be reproduced. (2) $UN_{2.0}$ is not readily prepared at normal pressures. (3) Hexagonal U_2N_3 exists as a stable phase. (4) The existence of a UN phase with an appreciable excess of nitrogen is very doubtful.

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[10] P. E. Evans, *J. Am. Ceram. Soc.*, **45**, 305 (1962).

[11] W. Trzebiatowski, R. Troe, and J. Leciejewicz, *Bull. acad. polon. sci., Sér. sci. chim.*, **10**, 395 (1962).

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[13] E. D. Cater, P. W. Gilles, and R. J. Thorn, *J. Chem. Phys.*, **35**, 608 (1961).

[14] B. R. T. Frost, *J. Nucl. Mater.*, **10**, 265 (1963).

[15] R. Didchenko, private communication.

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Silicon Imidazolidines

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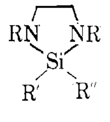
We have recently reported the preparation of spiro silaimidazolidines by the reaction of silicon tetrachloride with N,N′-disubstituted ethylenediamines.[1] We now report the synthesis of a series of monocyclic silaimidazolidines.



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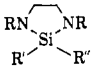
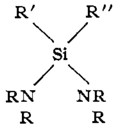
[1] C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964).

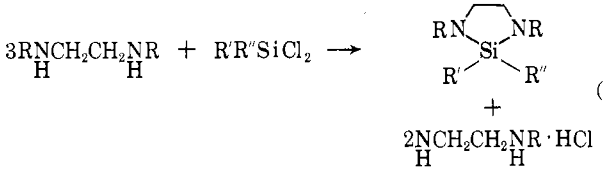
TABLE I[a]

SILICON IMIDAZOLIDINES AND OTHER NEW SILYLAMINES

	R′	R″	R	B.p. or m.p. (uncor.)	Ref. index $n^{30}D$	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found	Si, % Calcd.	Si, % Found	Mol. wt. Calcd.	Mol. wt. Found
I	CH_3	CH_3	CH_3	131° (740 mm.)		49.94	49.90	11.18	10.91	19.41	19.50	19.47	19.67		
II	CH_3	CH_3	C_2H_5	162–163° (740 mm.)	1.4408	55.76	55.96	11.70	11.75	16.26	16.36	16.30	16.00	172	171[b]
III	CH_3	CH_3	n-C_3H_7	81° (8 mm.)	1.4447	59.93	59.92	12.07	12.20	13.98	14.15	14.02	14.05	200	221[b]
IV	CH_3	CH_3	C_6H_5	124–126° (m.p.)		71.61	71.55	7.51	7.58	10.39	10.63	10.47	10.21	268	281[d]
V	CH_3	CH_3	p-$CH_3C_6H_4$	104–106° (m.p.)		72.92	73.00	8.16	8.17	9.45	9.17	9.47	9.31	297	298[d]
VI	CH_3	CH_3	p-$CH_3OC_6H_4$	169–172° (m.p.)		65.81	66.00	7.36	7.58	8.52	8.54	8.55	8.57	328	311[d]
VII	CH_3	C_6H_5	CH_3	110° (11 mm.)	1.5155	64.00	63.90	8.79	8.82	13.57	13.55	13.61	13.65	206	184[b]
VIII	CH_3	C_6H_5	C_2H_5	140–141° (14 mm.)	1.5075	66.60	66.40	9.46	9.61	11.95	11.92	11.98	11.85	234	240[e]
IX	C_6H_5	C_6H_5	CH_3	175° (10 mm.)	1.5683	71.61	71.42	7.51	7.75	10.39	10.31	10.47	10.49	268	267[b]
															
X	C_6H_5	CH_3	C_2H_5	152° (14 mm.)	1.4935	68.09	68.22	10.67	10.69	10.59	10.42	10.65	10.16	264	280[e]
XI	C_6H_5	C_6H_5	CH_3	168° (10 mm.)	1.5568	71.08	70.90	8.20	8.00	10.36	10.60	10.39	10.50	270	281[c]

[a] Melting points were measured on a Townson and Mercer Type 5 melting point block and are uncorrected. Analyses were done by Schwarzkopf Microanalytical Laboratory. [b] Determined ebullioscopically in benzene. [c] Determined cryoscopically in benzene. [d] Determined by vapor phase osmometry in benzene. [e] Determined by the Rast method.

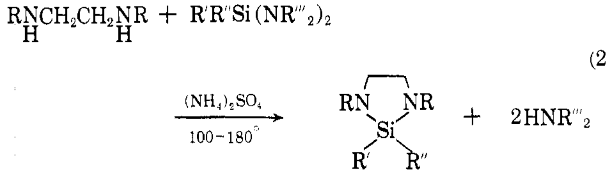
The general applicability of the amine chloride type reaction (1) was questioned by Lienhard, who reported that the reaction of dimethyldichlorosilane with N,N′-dimethylethylenediamine yielded a "complicated reaction mixture" and that the five-membered cyclic compound (R = R′ = R″ = CH_3) could be obtained only by the amine exchange reaction.[2] Kummer and Rochow found that the presence of the trimethylsilyl group (R = $Si(CH_3)_3$) greatly facilitated formation of the five-membered rings, and by allowing silicon tetrachloride and organohalosilanes to react with N,N′-bis(trimethylsilyl)ethylenediamine or its lithium salt, these workers prepared various trimethylsilyl silaimidazolidine derivatives.[3] The preparation of the spiro compounds by the general amine chloride reaction reopened the possibility of forming these compounds by simple reaction of diorganoethylenediamines with diorganodihalosilanes.



(1)

Indeed, we have found that the reaction of dimethyldichlorosilane with N,N′-dimethylethylenediamine does give the silaimidazolidine in fair yield (10–20%). Silaimidazolidine was formed under the following conditions: (a) dimethyldichlorosilane in benzene was added to a mixture of the diamine and triethylamine in benzene at 60–70° (mole ratio of 1:1:3, respectively); (b) dimethyldichlorosilane in benzene was added to a mixture of the diamine and triethylamine in benzene at −10° (same ratio); (c) dimethyldichlorosilane in benzene was added to the diamine in benzene at 80° (mole ratio 1:4, respectively).

Additional cyclic compounds (whose physical properties and analyses are given in Table I) were prepared by the amine exchange reaction (2). This method, although requiring preparation of the starting silanediamine, produces an essentially quantitative yield of pure silaimidazolidine under the proper conditions (removal of the displaced HNR‴$_2$). Ammonium sulfate serves as a catalyst.



(2)

The N-alkyl compounds were purified by fractional distillation, and the N-aryl derivatives were recrystallized from benzene–hexane. Structure assignments were based on infrared and nuclear magnetic resonance spectra, molecular weight, and C, H, N, and Si analytical data. N.m.r. spectra of the 2,2-dimethyl and 2,2-diphenyl derivatives show a single peak for the bridge methylene protons, indicating either planarity of the ring or rapid inversion of tetrahedral nitrogen.[4]

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(2) F. A. Henglein and K. Lienhard, *Makromol. Chem.*, **32**, 218 (1959); K. Lienhard, Dissertation, Technische Hochschule Karlsruhe, 1959.

(3) D. Kummer and E. G. Rochow, *Z. anorg. allgem. Chem.*, **321**, 21 (1963).

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Compounds I–VIII were prepared by exchange of the appropriate diamine with dimethylbis(diethylamino)silane or methylphenylbis(diethylamino)silane. N,N′-di-*o*-tolylethylenediamine gave no reaction with dimethylbis(diethylamino)silane at a temperature of 180° and neither could the N,N′-di-*o*-tolyl derivative be obtained by reaction with dimethylbis(dimethylamino)silane. The reluctance of this diamine to react was also observed in the preparation of the spiro compounds[1] and is probably associated with the steric hindrance of the *o*-methyl group or the strain which it imposes on the product ring. N,N′-Di-*p*-nitrophenylethylenediamine also failed to react with dimethylbis(diethylamino)silane at 200°. This can be attributed to the low basicity of the diamine or the high temperature (and consequent possible decomposition of the silylamine) necessary to melt the diamine. The 2,2-diphenyl derivative was prepared by reaction of diphenylbis(dimethylamino)silane with N,N′-dimethylethylenediamine. It is curious that the isomeric compounds IV and IX which differ only by the placement of the phenyl and methyl substituents have such strikingly different physical properties: the N-phenyl compound melts at 124–126°, while the N-methyl isomer is a liquid at room temperature, b.p. 175° (10 mm.), freezing point *ca.* 23°.

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CONTRIBUTION FROM THE CHEMISTRY RESEARCH SECTION
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Difluoramine: Preparation of Difluorodiazine and Addition Compounds with Alkali Metal Fluorides

BY EMIL A. LAWTON, DONALD PILIPOVICH,
AND R. D. WILSON

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Difluoramine is amphoteric, as witnessed by its formation of a complex with boron trichloride[1] and the formation of 1:1 complexes with weak bases such as alkyl ethers.[2] We have found that difluoramine also forms complex compounds with the more basic alkali metal fluorides. At higher temperatures, difluoramine is converted smoothly and in excellent yield to difluorodiazine as in eq. 1.[3] With the ready availability of difluoramine from urea,[4] this method constitutes the most convenient laboratory synthesis of difluorodiazine. Of the other methods which have been recently reviewed by Colburn,[5] the most convenient preparation mentioned involved the electrolysis of ammonium bifluoride to form N_2F_2 in 5–10% yields as a by-product in the synthesis of NF_3.

$$2MF + 2HNF_2 \longrightarrow 2MF\cdot HF + N_2F_2 \qquad (1)$$

The alkali metal fluorides effective in the dehydrofluorination of difluoramine to difluorodiazine at ambient temperatures are potassium fluoride, rubidium fluoride, and cesium fluoride. Two isomeric forms of N_2F_2 are formed and are the *cis* and *trans* isomers reported previously.[6] No evidence for a third form has been observed.

In connection with our investigation of the conversion of HNF_2 to N_2F_2, evidence was obtained that clearly showed the formation of molecular complexes of alkali metal fluorides and HNF_2. Elucidation of the structure of these complexes by low-temperature infrared techniques has been completed in this laboratory and will be reported separately.[7]

Reproducible dissociation pressures for $KF\cdot HNF_2$ and $RbF\cdot HNF_2$ were measured and, as predicted from the relative basicities of the alkali fluorides, the stability of the complexes formed varied as follows: $CsF > RbF > KF > NaF$. In fact, no evidence was found for any interaction of difluoramine with NaF, CaF_2, or NiF_2 down to −80°.

A complete study of the $CsF–HNF_2$ system was not carried out because of the explosive properties of the complex. Condensing difluoramine over CsF and allowing some difluoramine to escape from the system resulted in a dissociation pressure of about 1.5 mm. at −65.8°, a higher pressure than the 0.8 mm. observed with RbF at this temperature. However, removal of about 50% of the complexed difluoramine caused an abrupt drop in the dissociation pressure to less than 0.05 mm. On warming, this complex invariably exploded before it reached 0°.

In addition to the gas–solid reaction shown in (1) it was found that aqueous KF (pH 8.6) effected the smooth dehydrofluorination of HNF_2. A nominally 25% solution of KF in water consumed HNF_2 rapidly with the formation of both isomers of N_2F_2 in approximately 75% yield, as in the equation

$$2F^- + 2HNF_2 \longrightarrow 2HF_2^- + N_2F_2$$

It is interesting to note, however, that experiments carried out with HNF_2 and standard buffer solutions ($Na_2B_4O_7–K_3PO_4$) at pH 8.0 and 9.0, respectively, resulted in only 20% yields.

These results indicate that F^- may be particularly effective in the dehydrofluorination reaction, but ex-

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(2) E. A. Lawton and J. Q. Weber, *ibid.*, **85**, 3595 (1963).

(3) E. A. Lawton and D. Pilipovich, U. S. Patent 3,109,711 (1963).

(4) Difluoramine is released in high yield by adding sulfuric acid drop-by-drop to the fluorinated urea liquids, described by Lawton and Weber,[2] or to difluorourea: E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

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