

curvature deviations (Figures 1, 2, 3) may be attributed to either acetonitrile induced association of  $\text{CH}_3\text{OH}$  units, or to specific  $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$  complexes. More definitive studies of hydrogen bonding in this and other donor-acceptor systems, *e.g.*,  $\text{CH}_3\text{NO}_2$ , DMSO, are in progress in an attempt to resolve this point.

In conclusion, it should be noted that most recent spectral and other studies in this area have been based on the assumed formation of a 1:1 donor-acceptor complex.<sup>24</sup> Our studies reported to date have been limited in scope and cover only the  $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}-\text{CH}_3\text{NO}_2$  systems; however, it is clearly

(24) (a) E. M. Arnett, T. S. S. R. Murty, P. von R. Schleyer, and L. Joris, *J. Amer. Chem. Soc.*, **89**, 5955 (1967). (b) D. Gurka, R. W. Taft, L. Joris, and P. von R. Schleyer, *ibid.*, **89**, 5957 (1967). (c) D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969). (d) R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, 4801 (1969).

evident that the above assumption is not consistent with presently available data for these systems.

**Registry No.**—Methanol, 67-56-1; acetonitrile, 75-05-8.

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## Nitrile Synthesis. The Dehydration of Amides by Silazanes, Chlorosilanes, Alkoxysilanes, and Aminosilanes

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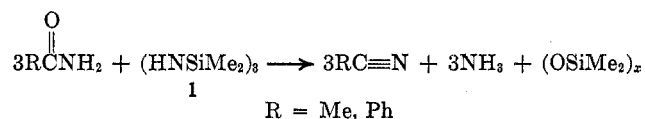
Silazanes, aminosilanes, alkoxysilanes, and chlorosilanes have been found to dehydrate amides to form nitriles at elevated temperatures.

The preparation of nitriles by the dehydration of amides is well known. Reagents used for these dehydrations are either strongly acidic, as, for example, thionyl chloride,<sup>1,2</sup> phosphorus pentoxide,<sup>3</sup> phosphorus oxychloride,<sup>2</sup> zinc chloride- $\alpha,\alpha,\alpha$ -trichlorotoluene,<sup>4</sup> or strongly basic, for example, sodium borohydride<sup>5</sup> and lithium aluminum hydride.<sup>3</sup> The isolation of the products from these reactions is often difficult because of the nature of the by-products.

The reaction of amides with dihalosilanes in the presence of an acid acceptor has been reported to give 2,4-disila-1,3,5-oxadiazine derivatives.<sup>6</sup> Klebe<sup>6</sup> stated that at elevated temperatures nitriles and disiloxanes formed. We wished to determine the utility of this type of dehydration for the preparation of nitriles.

### Results and Discussion

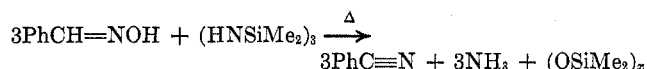
The reaction of hexamethylcyclotrisilazane (1) with benzamide or acetamide at 180-200° gave benzonitrile or acetonitrile in 95 and 85% yields, respectively.



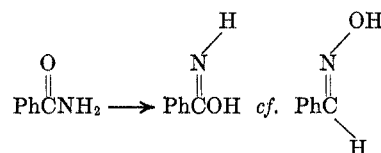
Compound 1 (1 equiv) with benzamide gave a siloxane polymer with a molecular weight  $\bar{M}_w$  of 120,000. The number-average molecular weight  $\bar{M}_n$  was 6800.

- (1) J. C. Thurman, *Chem. Ind. (London)*, 752 (1964).
- (2) B. Rieckborn and F. R. Jensen, *J. Org. Chem.*, **27**, 4609 (1962).
- (3) L. G. Humber and M. A. Davis, *Can. J. Chem.*, **44**, 2113 (1966).
- (4) C. J. Vervanic, U. S. Patent 3,274,229 (1966).
- (5) S. E. Ellzey, C. H. Mock, and W. J. Connick, *J. Org. Chem.*, **32**, 946 (1967).
- (6) J. F. Klebe, *J. Amer. Chem. Soc.*, **90**, 5246 (1968).

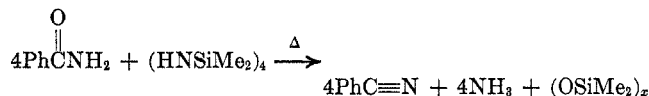
The reaction of 1 with *syn*-benzaloxime also formed benzonitrile in good yield. An analogy between the



reaction of benzaloxime and benzamide can be seen if benzamide is written in another tautomeric form.

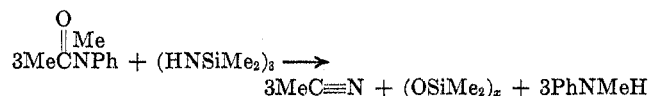
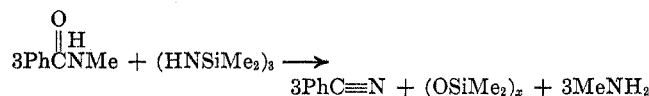


Octamethylcyclotetrasilazane also dehydrated benzamide to form benzonitrile in good yield. In order to

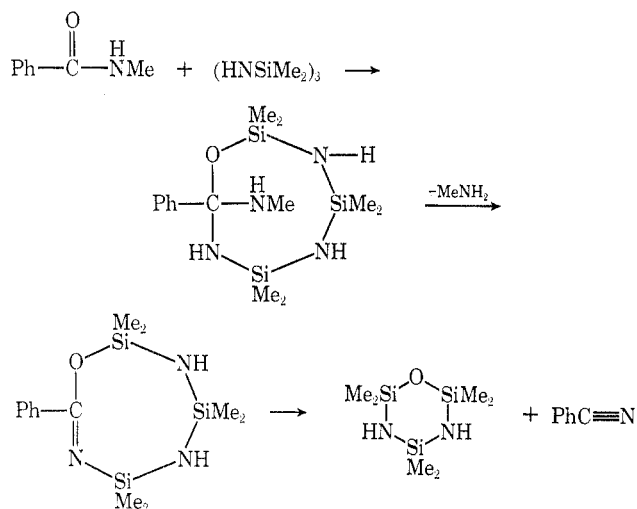


extend the scope and determine the limitations of the dehydration of amides by 1, some N-substituted amides were examined.

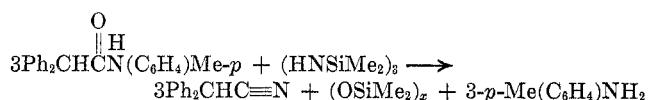
*N*-Methylbenzamide with 1 gave benzonitrile in 43% yield. *N*-Methylacetamide gave a 27% yield of acetonitrile. These yields should not be considered the maximum obtainable, because the reactions were not allowed to go to completion. These *N*-methylamides required prolonged heating above 200° for reaction.



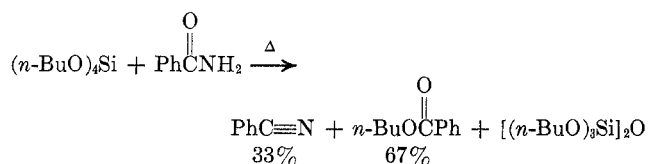
A plausible route for the formation of nitriles from *N*-methylamides is as follows.



The reaction of benzamide with *N,N*-dimethylamino-hexyldimethylsilane formed benzonitrile and *sym*-dihexyldimethylsiloxane after prolonged heating above 200°. *N*-(*p*-Methylphenyl)diphenylacetamide with **1** gave diphenylacetone nitrile rapidly and in good yield, 73%.



Benzamide with phenylmethyldichlorosilane or phenyltrichlorosilane gave benzonitrile with the liberation of hydrogen chloride. Phenylmethyldimethoxysilane and benzamide gave benzonitrile, *sym*-diphenyldimethyl-dimethoxydisiloxane, and a small amount of methyl benzoate. Tetra-*n*-butoxysilane with benzamide gave a 33% yield of benzonitrile and a 67% yield of



*n*-butyl benzoate. The products obtained in this reaction can be explained as due to the dehydration of 1 mol of benzamide to form 1 mol of water and 1 mol of benzonitrile. Each mole of water then reacted with 2 mol of tetrabutoxysilane to yield 1 mol of hexa-*n*-butoxydisiloxane and 2 mol of *n*-butyl alcohol. Each mol of *n*-butyl alcohol then formed 1 mol of *n*-butyl benzoate.

The use of silicon functionality for the dehydration of amides offers several advantages over conventional dehydrating agents. The choice of silazanes, alkoxy-silanes, and chlorosilanes allows the reaction to be run under mildly basic, neutral, or acidic conditions. The nitriles if volatile can be distilled from the siloxane polymer and if solid they can be removed by filtration. If silazanes or chlorosilanes are used the reaction may be followed by the ammonia or hydrogen chloride that is liberated. The use of hexamethylcyclotrisilazane offers an advantage of a low equivalent weight therefore providing good volume efficiency.

## Experimental Section

**Reagents and Analyses.**—*N*-(*p*-Methylphenyl)diphenylacetamide, mp 176–177°, was prepared from *p*-toluidine and diphenylacetyl chloride using a published procedure.<sup>7</sup>

Benzaldehyde, *p*-toluidine, *N*-methylacetanilide, and diphenylacetic acid were obtained from Eastman Organic Chemicals and were used without further purification. Benzoyl chloride and hydroxylamine hydrochloride were Baker Analyzed Reagent grade and were used without purification.

Hexamethylcyclotrisilazane, bp 149° (200 mm),  $n_D^{25}$  1.4472 [lit.<sup>8</sup> bp 188° (756 mm),  $n_D^{20}$  1.448], and octamethylcyclotrisilazane, bp 174° (60 mm) [lit.<sup>8</sup> bp 225° (756 mm)], were prepared from dimethyldichlorosilane and ammonia. *n*-Butyl silicate, bp 134–136° (5 mm),  $n_D^{25}$  1.4106 (lit.<sup>9</sup>  $n_D^{20}$  1.4128), was prepared from ethyl silicate. All other silanes were available from Dow Corning Corporation and were >95% pure by glc analysis and were used without further purification. Benzonitrile, *n*-butyl alcohol, *n*-butyl benzoate, benzoic acid, and 1,3,5-triphenyltriazine were identified by comparison of their ir spectra with standards. In addition, their boiling points and melting points gave the correct values.

The ir spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. The <sup>1</sup>H nmr spectra were obtained on a Varian Associates Model A-60 using CCl<sub>4</sub> as a solvent. The glc analyses were obtained on an 8 ft × 0.125 in. stainless steel column packed with 26% Dow Corning SGM-11 on Chromosorb W, 80–100 mesh, using an F & M Scientific Model 5750 research chromatograph.

**Acetonitrile from Acetamide and Hexamethylcyclotrisilazane (1).**—A mixture of 30 g (0.5 mol) of acetamide (Fisher Scientific Co.) and 100 g (0.46 mol, 1.37 equiv) of **1** was heated to 120–130° for 64 hr and to 170° for an additional 24 hr. Acetonitrile distilled from the mixture: 17.4 g, (85%); bp 80°;  $n_D^{25}$  1.3434 (lit.<sup>10</sup>  $n_D^{20}$  1.3441). Residue from the distillation, 96 g, had a neutral equivalent of 130. The theoretical value was 110. The difference was probably due to external moisture which caused some loss of NH<sub>3</sub>.

**Benzonitrile from Benzamide and 1.**—A mixture of 60 g (0.5 mol) of benzamide (mp 130–132°) and 100 g (0.46 mol) of **1** was heated at 84–110° for 30 hr and 130° for 18 hr. Distillation then gave 51 g, bp 70–73° (10 mm), which was 85% benzonitrile by glc area per cent. The remainder of the peaks seen by glc analysis corresponded to several siloxane moieties. The yield based on 48.5 g is 94%.

A mixture of 12.1 g (0.1 mol) of benzamide and 7.5 g (0.034 mol, 0.102 equiv) of **1** was heated at 220° for 20 hr. At the end of this time the rate of evolution of ammonia was very slow. The product was distilled to give 9.6 g, 91%, bp 70° (~10 mm), of benzonitrile which was pure by glc analyses. The residue was taken up in hexane and filtered to remove 350 mg, 3.3%, of 1,3,5-triphenyltriazine, mp 234–236°. The siloxane polymer contained no peaks by glc analysis corresponding to cyclic dimethylsiloxanes and the neutral equivalent was 4120. The calculated neutral equivalent for the excess silazane used is 2740. The difference in neutral equivalent corresponds to 17 mg of water.

**Benzonitrile from Benzamide and Octamethylcyclotetrasilazane.**—A mixture of 12.1 g (0.1 mol) of benzamide and 14.0 g (0.048 mol, 0.19 equiv) of octamethylcyclotetrasilazane was heated at 220° for 4.5 hr. The mixture was distilled to give 9.1 g, bp 87–88° (27 mm), which was 83% benzonitrile by glc area per cent with the remainder of the material appearing as several siloxane peaks, yield 71%.

**Benzonitrile from Benzaldoxime and 1.**—A mixture of 13.0 g (0.11 mol) of *syn*-benzaldoxime (mp 27–33°) and 10 g (0.046 mol, 0.137 equiv) of **1** was heated at 210° for 6 hr. The mixture was distilled to give 9.4 g of material, bp 59–63° (8 mm), which in addition to siloxanes contained 85% benzonitrile; the yield is 72%.

**Benzonitrile from Phenyltrichlorosilane and Benzamide.**—A mixture of 10.5 g (0.05 mol) of phenyltrichlorosilane and 6.0 g (0.05 mol) of benzamide was heated to 240–260° for 40 hr. The

(7) C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, **75**, 657 (1953).

(8) S. D. Brewer and C. P. Haber, *ibid.*, **70**, 3888 (1948).

(9) B. A. Arbuzov and T. G. Shavsha, *Dokl. Akad. Nauk SSSR*, **68**, 859 (1949).

(10) R. R. Driesbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2877 (1949).

mixture was then distilled to give 2.5 g, 47.6%, of pure benzonitrile. A toluene solution of the residue when analyzed by glc contained benzonitrile and nothing else except solvent. Hydrogen chloride was detected during the reaction.

**Benzonitrile from *N,N*-dimethylaminodimethylhexylsilane and Benzamide.**—A mixture of 18.7 g (0.1 mol) of *N,N*-dimethylaminodimethylhexylsilane and 6.05 g (0.05 mol) of benzamide was heated to 235°. At the melting point of benzamide, dimethylamine was liberated rapidly. After 4 hr at 235° an ir spectrum of the mixture indicated some benzonitrile by a small absorption at 4.5  $\mu$ . There was also a broad absorption at 1060  $\text{cm}^{-1}$  corresponding to the SiOSi structure of *sym*-dihexyltetramethyldisiloxane. Ammonium sulfate, 0.5 g, was added and benzonitrile was slowly distilled from the mixture. A total of 5.4 g of distillate was obtained which was 95% benzonitrile by glc area per cent. The yield based on 5.1 g is 96%. Coinjection of this residue with an authentic sample indicated by glc most of the residue was *sym*-dihexyltetramethyldisiloxane.

**Reaction of *N*-(*p*-Methylphenyl)diphenylacetamide with Hexamethylcyclotrisilazane.**—A mixture of 16 g (0.05 mol) of *N*-(*p*-methylphenyl)diphenylacetamide, mp 176–177°, and 11.0 g (0.05 mol) of 1 was heated at 240° for 4 hr. The evolution of ammonia was noticed at the melting point of the amide and after 4 hr at 240° the rate of ammonia evolution had greatly decreased. The product was triturated with benzene and hexane to give 3.0 g, 18.7%, of starting material, mp 167–174°. Benzene and hexane were removed from the solution *in vacuo* and after filtration 7.1 g of solid, mp 69–70°, corresponding to a 73% yield of diphenylacetoneitrile was obtained. A portion of this material was recrystallized (ether–pentane): mp 74–75°; ir ( $\text{CCl}_4$ ) 2250  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ); nmr 5.10 (s, 1.0, C—H), 2.75 (s, 10.0, Ar—H). The filtrate did not contain a significant amount of hexamethylcyclotrisilazane or *p*-toluidine by glc analysis but did contain at least 13 broad peaks. The filtrate was taken up in ether and washed with cold dilute hydrochloric acid. The acidic aqueous extract was neutralized with potassium hydroxide and *p*-toluidine was extracted with ether. The ethereal solution was dried over sodium sulfate and after removing the volatiles *in vacuo* 2.75 g, 52%, of *p*-toluidine, mp 37–40°, mixture melting point undepressed, was obtained.

**Reaction of *N*-Methylbenzamide with 1.**—A mixture of 6.75 g (0.05 mol) of *N*-methylbenzamide and 11.0 g (0.05 mol) of 1 was heated at 220–240° for 48 hr and slowly distilled over 16 hr to give 3.0 g of distillate which was 70% benzonitrile by glc analysis. Other peaks corresponded to several siloxane compounds. The yield based on 2.1 g is 42%.

**Reaction of *N*-Methylacetanilide with 1.**—A mixture of 14.9 g (0.1 mol) of *N*-methylacetanilide and 7.5 g (0.03 mol) of 1 was heated to 240–260° for 64 hr. The mixture became dark over this period and a basic gas was detected by pH paper. After 64 hr, the product was distilled over a 3-hr period to give 2.2 g of material which was 50% acetonitrile by glc area per cent. The

distillate contained several higher boiling components and had an amine odor.

**Reaction of *n*-Butyl Silicate with Benzamide.**—A stirred mixture of 13.2 g (0.05 mol) of *n*-butyl silicate and 6.05 g (0.05 mol) of benzamide was refluxed at 200° for 44 hr during which time there was no reaction. Three drops of (2-phenylpropyl)methyldichlorosilane was added. The mixture was refluxed an additional 48 hr when glc analysis indicated the presence of *n*-butyl alcohol, benzonitrile, *n*-butyl benzoate, *n*-butyl silicate, and hexa-*n*-butoxydisiloxane. Distillation at 10 mm gave the following fractions: 400 mg, bp 70–73°, benzonitrile; 4.6 g, bp 73–120°, 30% benzonitrile–70% *n*-butyl benzoate; 2.8 g, bp 120–128°, 90% *n*-butyl benzoate–10% *n*-butyl silicate; 1.0 g, bp 128–141°, 50% *n*-butyl benzoate–50% *n*-butyl silicate. The residue, 8.0 g, was 50% *n*-butyl silicate and 50% higher boiling product, presumably hexa-*n*-butoxydisiloxane. The yield of *n*-butyl benzoate based on 6.05 g is 65%, of benzonitrile based on 1.78 g is 34%.

**Reaction of Methylphenyldichlorosilane with Benzamide.**—A mixture of 1.2 g (10 mmol) of benzamide and 2 ml (12.3 mmol) of methylphenyldichlorosilane was heated at 160–180° for 16 hr. The reaction was two phases and after 16 hr at 160–180° the temperature was increased to 220°. The evolution of hydrogen chloride was observed at this temperature and the mixture was held at this temperature for 28 hr. Analysis by glc contained a peak corresponding to benzonitrile. Estimated conversion based on the ratio of glc area per cents of the peaks corresponding to benzonitrile and starting phenylmethyldichlorosilane was 70%. An ir spectrum of this mixture had an absorption at 4.5  $\mu$  indicative of  $\text{C}\equiv\text{N}$ .

**Reaction of Methylphenyldimethoxysilane with Benzamide.**—A solution of 1.2 g (10 mmol) of benzamide in 5 ml (27.5 mmol) of methylphenyldimethoxysilane was refluxed for 120 hr. At this time, a glc analysis showed the presence of benzonitrile and a small peak corresponding to methylbenzoate eluting near phenylmethyldimethoxysilane. There was an absorption at 4.4  $\mu$  in the ir spectrum for  $\text{C}\equiv\text{N}$ . In addition there was a small absorption at 5.75  $\mu$  ( $\text{C}=\text{O}$ ) corresponding to methylbenzoate. The final mixture was neutral. Distillation gave 900 mg of material which was 50% benzonitrile, 40% methylphenyldimethoxysilane, and 10% methyl benzoate by glc area per cent.

**Registry No.**—1, 1009-93-4; acetamide, 60-35-5; benzamide, 55-21-0; octamethylcyclotetrasilazane, 1020-84-4; benzaldoxime, 932-90-1; phenyltrichlorosilane, 98-13-5; *N,N*-dimethylaminodimethylhexylsilane, 25913-89-7; *N*-(*p*-methylphenyl)diphenylacetamide, 4107-01-1; *N*-methylbenzamide, 613-93-4; *N*-methylacetanilide, 579-10-2; *n*-butyl silicate, 4766-57-8; methylphenyldichlorosilane, 149-74-6; methylphenyldimethoxysilane, 3027-21-2.