

Instrument Co.), pH 10 standard buffer (Fisher Chemical Co.), and 0.100 M NaOH. From the spectra of the dye in acidic, neutral, and basic solutions [uv max (0.100 M HCl) 395 m μ (ϵ 9600) and 530 (400); uv max (pH 7 buffer) 530 m μ (ϵ 6850); uv max (0.100 M NaOH) 395 m μ (ϵ 4500) and 530 (13,700)], the dye was calculated to be 53% protonated at pH 7.00. The pK_a is therefore 7.05 \pm 0.03.

π -Cyclopentadienyltetraphenylcobalticinium Cobalt (14).¹⁸— π -Cyclopentadienylcobaltdicarbonyl (6.0 g, 0.35 mol), tetracyclone (13.6 g, 0.35 mol), and 50 ml of xylene were refluxed overnight in a nitrogen atmosphere. The solution was cooled to room temperature and 15.4 g of purple crystals collected. The solid was chromatographed in 3-g portions on a 10 cm \times 30 cm column of alumina. A purple band of tetracyclone was eluted with xylene and an orange band of 14 with chloroform. The crude 14 was recrystallized from chloroform–ligroin: yield 11.0 g (62%); mp 325–326° (lit.¹⁰ 327–329°).

Hydroxy-2,3,4,5-tetraphenylcobalticinium Bromide (15).—A 254-mg sample of 14 (0.5 mmol) was suspended in 30 ml of 48% hydrobromic acid and heated for 30 min at 80–100°, with constant stirring. A gummy oil formed which solidified to a yellow powder. The solution was diluted with 50 ml water and the precipitate collected, yield 244 mg (83%). The crude material was recrystallized from acetone–ether: mp 289–290° dec; ir max (KBr) 3060, 2900–2400 (broad peak possibly due to H–Br bonding), 1600 (w), 1578 (w), 1470, 1430 (C–O stretch), 1410, 1400, 1240, 1170 (s), 1110, 1082, 1030, 1008, 850, 800, 753 (s), 697 (s), 640, 620, 582, 558, 500, 420 cm⁻¹.

Anal. Calcd for C₂₄H₂₆BrCoO: C, 69.28; H, 4.45; Br, 13.56; Co, 10.00; O, 2.71. Found: C, 69.00; H, 4.70; Br, 14.00; Co, 9.98; O, 2.70.

Hydroxy-2,3,4,5-tetraphenylcobalticinium Fluoroborate and Perchlorate.—A 508-mg sample of 14 (1 mmol) was dissolved in 25 ml of chloroform and shaken with 10 ml of 37% fluoroboric acid. The chloroform layer was dried over calcium sulfate. Dropwise addition of ligroin precipitated the product as a fine yellow powder, yield 517 mg (87%). The crude product was recrystallized from acetone–ether, mp 245–250° dec. The ir spectrum of the fluoroborate corresponded to the ir of the bromide except that the broad peak at 2900–2400 cm⁻¹ was shifted to 3500–3200 cm⁻¹, and a broad peak for the BF₄⁻ anion appeared at 1130–950 cm⁻¹.

(18) R. A. Genetti, Ph.D. Thesis, University of Massachusetts, Jan 1969, pp 9–10.

Anal. Calcd for C₂₄H₂₆BCoF₄O: C, 68.48; H, 4.40; Co, 9.88; O, 2.68. Found: C, 68.72; H, 4.65; Co, 9.80; O, 2.70.

The perchlorate salt, mp 253–255° dec, was prepared from 60% perchloric acid by the same procedure.

Anal. Calcd for C₂₄H₂₆ClCoO₃: C, 67.06; H, 4.30; O, 13.14. Found: C, 67.02; H, 4.45; O, 13.10.

Acetoxy-2,3,4,5-tetraphenylcobalticinium Salts (16).—A 152-mg portion of 14 (0.3 mmol) was dissolved in 10 ml of acetyl chloride. The acetyl chloride was evaporated and the residue was dissolved in 30 ml of water and filtered. The acetoxy derivative 16 was precipitated as the hexafluorophosphate salt: ir (KBr) 3120 (cobalticinium C–H), 3060 (phenyl C–H), 2920, 2860, 1785 (s), 1312 (w), 1275 (w), 1600 (w), 1580 (w), 1500 (w), 1450, 1418 (s), 1400, 1370, 1170 (s), 1100, 1085, 1010, 830 (s), 755 (s), 699 (s), 580 (w), 560 (s), 510, 415, and 278 cm⁻¹. The tetraphenylborate was also prepared and recrystallized twice from acetone–ether, mp 235°.

Anal. Calcd for C₆₀H₄₈BCoO₂: C, 82.75; H, 5.56; O, 3.68; Co, 6.77. Found: C, 82.80; H, 5.60; O, 3.68; Co, 6.76.

Registry No.—1, 12427-42-8; 2, 12427-48-4; 3, 12427-51-9; 4, 12427-47-3; 5, 12427-49-5; 6, 12427-45-1; 7, 12427-50-8; 8, 12427-46-2; 9, 12427-43-9; 9 (tetraphenylborate), 12427-55-3; 9 (diazo derivative), 12427-56-4; 10, 12427-41-7; 11, 12427-53-1; 15, 12427-59-7; 16, 12427-63-3; 16 (tetraphenylborate), 12427-62-2; 10 (tetraphenylborate), 12427-54-2; hydroxy-2,3,4,5-tetraphenylcobalticinium (BF₄), 12427-58-6; hydroxy-2,3,4,5-tetraphenylcobalticinium (perchlorate), 12427-60-0.

Acknowledgments.—We wish to thank W. Michael Minihane for his assistance in measuring the uv spectra and pK values for the compounds reported. We also wish to thank the National Science Foundation (Science-Faculty Fellowship), the Research Corporation (Frederick Gardner Cottrell Grant), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research program.

Intermolecular Hydrogen Bonding between Nitriles and Methanol. A Nuclear Magnetic Resonance Study

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Received September 4, 1969

The addition of alkyl- and aryl nitriles to methanol, with or without CCl₄ dilution, prolongs the residence time for exchange of the –OH proton. The inhibition of –OH exchange is sufficient to allow detection of J_{HCOH}. Studies of binary and ternary (CCl₄) mixtures of acetonitrile and methanol showed a marked variability in the –OH resonance position with increasing CH₃CN concentration. The observed spectral changes support prior postulations of a strong –CN–HO– hydrogen-bonding interaction, and appear to indicate changes in the equilibrium concentration of CH₃OH–CH₃CN associates over a broad range of binary and ternary (CCl₄) solution concentrations.

Studies of intermolecular –CN–HO– hydrogen bonding have been centered primarily on the elucidation of infrared hydroxyl frequency shifts ($\Delta\nu_{OH}$) for binary and ternary (CCl₄) mixtures of nitriles with alcohols and phenols.¹ The $\Delta\nu_{OH}$'s observed for methanol or phenol interacting with a wide variety of nitriles correlated well with Taft σ^* parameters,² however, even under carefully controlled experimental conditions it is evident that the magnitude of $\Delta\nu_{OH}$ is not necessarily

a measure of hydrogen-bonding acceptor strength.^{2,3} Consequently, no definite conclusions could be reached regarding the acceptor strengths of nitriles relative to other known hydrogen-bonding bases.

Recently, we have been concerned with solvent–solute interactions traceable through changes in the –OH and –CH₃ resonances of methanol,⁴ e.g., suppression of –OH exchange and the concentration dependence of the –OH resonance for both binary and ternary

(1) (a) S. S. Mitra, *J. Chem. Phys.*, **36**, 3286 (1962). (b) A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 371 (1963).

(2) A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 866 (1963).

(3) A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 1715 (1963).

(4) N. F. Heffinger and P. A. Clarke, *J. Org. Chem.*, **34**, 2572 (1969).

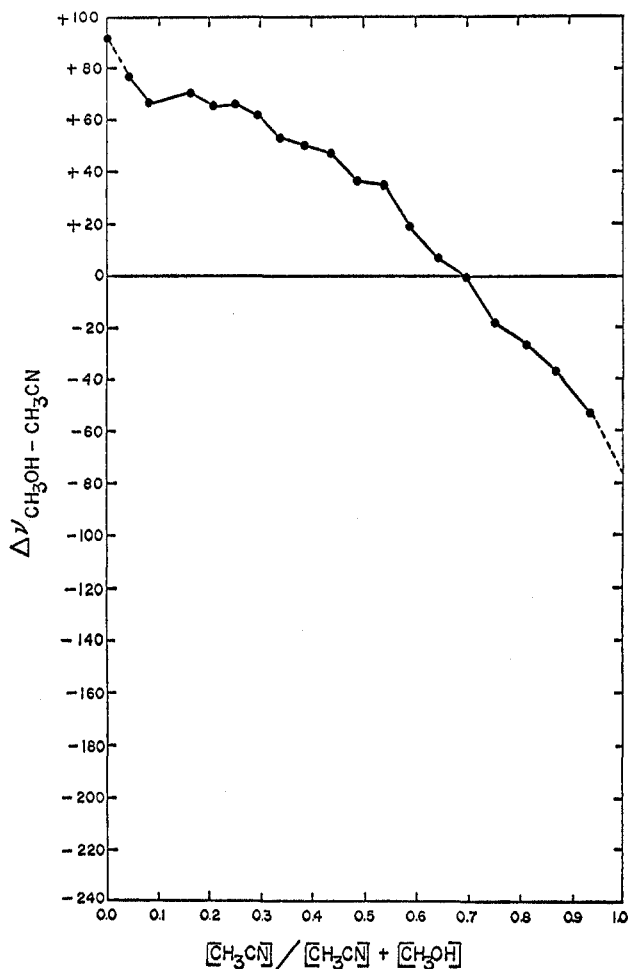


Figure 1.—Effect of CH_3CN on $\Delta\nu_{\text{CH}_3\text{OH}}$. Negative values correspond to shifts of the $-\text{OH}$ proton upfield of the $-\text{CH}_3$ resonance of methanol.

(CCl_4) mixtures of proton donor and acceptor species. A cursory examination of the $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ system revealed $-\text{OH}$ shift and exchange retardation effects similar to those previously cited in support of hydrogen bonding interactions between alcohols and other proton acceptor species, *e.g.*, acetone,^{5,6} DMSO ,⁵ CH_3NO_2 .⁴ These preliminary observations prompted the more extensive dilution studies reported here for $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ mixtures. In broad agreement with prior infrared and nmr investigations,^{1,2,7} the present nmr study provides additional support for a strong $-\text{CN}-\text{HO}-$ hydrogen-bonding interaction.

Experimental Section

Instrumentation.—Nmr spectra were obtained at $32 \pm 1^\circ$ using a Varian A-60 spectrometer equipped with a variable temperature probe. Chemical shifts were measured using the CH_3 resonance of methanol and/or 1–5% tetramethylsilane (TMS) as internal references; side-band techniques were used as a check. Calibration of the instrument was accomplished with an audio signal generator (Hewlett-Packard 205AG) monitored by a frequency counter (Hewlett-Packard 5244L) operated in the period mode. After warm-up, the drift and instability of the instrument were better than one part in 10^6 . Spectrometer drift during 1 hr approached ± 0.2 cps.

(5) W. Drinkard and D. Kivelson, *J. Phys. Chem.*, **62**, 1494 (1958).

(6) P. L. Corio, R. L. Rutledge and J. R. Zimmerman, *J. Mol. Spectrosc.*, **3**, 592 (1959).

(7) A. Loewenstein and Y. Margalit, *J. Phys. Chem.*, **69**, 4152 (1965).

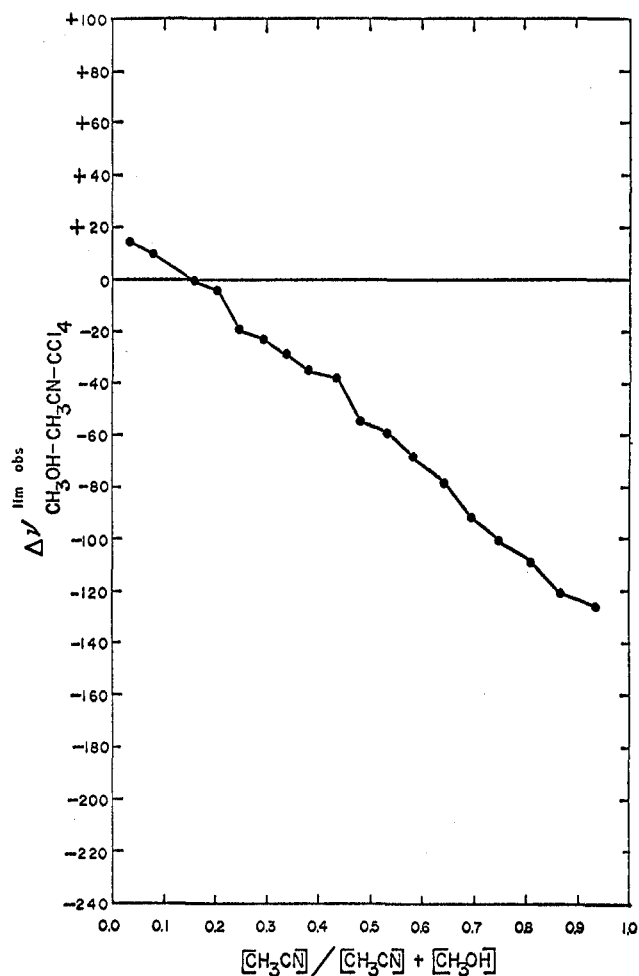


Figure 2.—The relationship between the limiting observed 60-MHz values, $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\text{lim obs}}$ and the acetonitrile concentration; considering only concentrations of active species in plotting the abscissa.

Sample Preparation.—Samples preparation and accuracy are as noted previously.⁴ Purification of acetonitrile was according to literature procedures,⁸ other nitriles were “shelf variety” dried over CaSO_4 . Methanol (Fisher) was purified as previously noted;⁴ “Spectral Grade” CCl_4 (Fisher) was stored over CaSO_4 . No detectable impurities were noted in the high gain nmr spectra of the materials used. Temperatures were measured using a sealed sample of purified methanol. Duplicate $-\text{OH}$ shift determinations on the same sample, or duplicate determinations on duplicate samples (random selection at ten concentrations for points indicated in Figures 1 and 2 showed a maximum variation of ± 0.5 Hz. The filled circles in Figures 1 and 2 represent ± 1.0 Hz.

Bulk samples of neat methanol exhibiting splitting in the nmr spectrum sufficient to allow the determination of J_{HCOH} at probe temperature (32°) have been repeatedly prepared in this laboratory. However, methanol exhibiting broadened $-\text{OH}$ and $-\text{CH}_3$ singlets neat or on dilution to 0.05 *M* with CCl_4 was used for the present study. As a consequence, the observation of induced splitting of the $-\text{OH}$ and $-\text{CH}_3$ resonances of methanol serves as a diagnostic test for retardation of $-\text{OH}$ exchange. Purified methanol exhibiting either type of spectrum showed no significant differences in chemical shifts (*i.e.*, greater than 1.0 Hz at 60 MHz) for the $-\text{OH}$ and $-\text{CH}_3$ resonances.

Results and Discussion

Minimal concentrations of acetonitrile in methanol produced an nmr spectrum exhibiting three broadened singlets at τ 2.03, 3.38 and 4.67 ppm. The major peaks

(8) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **7**, 1161 (1965).

(relative intensities 1:3) assignable to the $-\text{OH}$ and $-\text{CH}_3$ resonances showed no discernable fine structure as the acetonitrile concentration was increased to $[\text{CH}_3\text{CN}]/[\text{CH}_3\text{CN}] + [\text{CH}_3\text{OH}] = 0.7$ (ca.). Here, the methanol resonances merged to a singlet due to "accidental" equivalence of the $-\text{OH}$ and $-\text{CH}_3$ protons. Higher acetonitrile concentrations shifted the $-\text{OH}$ resonance upfield of the $-\text{CH}_3$ resonance, spin-spin coupling ($J_{\text{HCOH}} = 5.2$ Hz)⁹ became apparent and was detected in the spectra of all remaining binary $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ mixtures studied (Table I). The modifica-

to the $-\text{CN}-\text{HO}-$ interaction. Other nitriles, *e.g.*, propionitrile, benzyloxy, β -chloropropionitrile, *o*-tolunitrile and *p*-tolunitrile, were also tested over limited concentrations in methanol. Each nitrile at concentrations approaching a molar excess induced splitting of the methanol $-\text{CH}_3$ and $-\text{OH}$ resonances;¹¹ coalescence of the $-\text{OH}$ and $-\text{CH}_3$ peaks was also observed at higher nitrile concentrations. Thus, the observed phenomenon which is indicative of a strong hydrogen bonding interaction, appears to be general for nitrile-alcohol interactions.

A preliminary indication of the apparent stability of the $-\text{CN}-\text{HO}-$ interaction was obtained by diluting the $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ mixtures exhibiting fine structure in the CH_3OH portion of the spectrum with CCl_4 .¹² Additional changes in spectral patterns due to displacement of the $-\text{OH}$ resonance were observed, however, J_{HCOH} could still be determined at total methanol concentrations less than 0.06 *M*. Since portions of the purified methanol sample at much lower concentrations in CCl_4 did not exhibit multiplet structure,¹³ the observed retardation in $-\text{OH}$ exchange for the dilute ternary mixtures is clearly induced by the added nitrile and supports prior evidence for a strong $-\text{CN}-\text{HO}-$ interaction. Evidence supporting the latter conclusion was also apparent from the general shape of the binary dilution curve (Figure 1).

For the total range of binary $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ mixtures studied (Figure 1), $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}}$ ¹⁴ reflected the expected upfield displacement of the $-\text{OH}$ resonance to give an extrapolated shift ($\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}}^{\infty}$) of 165 Hz, *i.e.*, 72 Hz upfield of the methanol $-\text{CH}_3$ resonance. The direction and magnitude of $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}}^{\infty}$ are consistent with variations in the $-\text{OH}$ resonance of alcohols previously reported for the addition of hydrogen bonding acceptor species, *e.g.*, DMSO,⁵ acetone.^{5,6} Some attempts have been made to relate shifts observed for binary systems to the relative strengths of hydrogen bonds formed between various donor-acceptor pairs.^{5,15} However, owing to the observed variability in the $-\text{OH}$ resonance displacement (Figure 1), any comparison in hydrogen bond strengths for this relative to other reported systems appeared premature. Especially in view of the fact that prior observations of maxima in binary curves for alcohols interacting with proton acceptor species, *e.g.*, acetone,^{5,6} DMSO,⁵ nitromethane,⁴ have been cited as evidence for complex formation. Spectral and freezing point data have also been reported which specifically indicate the complexation of acetonitrile with various proton donors, *e.g.*, phenol,^{1b} pyrrole,^{1a} CHCl_3 ,¹⁶ and *t*-butyl alcohol.¹⁷ If, as the present data appear to indicate, a consistent (albeit qualitative) explanation for the variability in the

TABLE I

OBSERVED AND EXTRAPOLATED SHIFTS (HERTZ)^a OF THE $-\text{OH}$ RESONANCE FOR $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ MIXTURES

$[\text{CH}_3\text{CN}]/$ $[\text{CH}_3\text{CN}] +$ $[\text{CH}_3\text{OH}]$	$\Delta\nu$ ($\text{CH}_3\text{OH}-$ CH_3CN)	$\Delta\nu_{\text{lim}}^{\text{obs } b}$ ($\text{CH}_3\text{OH}-$ $\text{CH}_3\text{CN}-\text{CCl}_4$)	$\Delta\nu_{\infty}^{c, d}$ ($\text{CH}_3\text{OH}-$ $\text{CH}_3\text{CN}-\text{CCl}_4$)
0.019			-95.0 ^e
0.039	+77.4	+14.9	-15.5
0.079	+67.0	+11.4	-21.0
0.161	+71.0	0.0	-34.3
0.204	+65.6	-3.9	-31.0
0.249	+66.7	-19.4	-58.0
0.293	+62.0	-23.4	-50.0
0.339	+53.5	-29.3	-62.5
0.386	+50.5	-36.1	-74.5
0.436	+47.7	-37.3	-66.0
0.486	+36.8	-53.8	-89.5
0.536	+35.3	-57.7	-95.0
0.588	+19.0	-65.2	-101.5
0.643	+7.8	-78.0	-119.0
0.698	0.0	-90.2	-135.0
0.753	-18.0	-100.8	-142.0
0.814	-26.5	-108.6	-137.5
0.873	-37.0	-121.4	-152.0
0.938	-52.5	-127.2	-150.0
0.968			-193.0 ^e

^a The internal shift of the $-\text{OH}$ resonance was measured relative to the methyl resonance of methanol. No appreciable shift (*ca.* >1.0 Hz) of the methanol CH_3 resonance relative to TMS was observed. ^b Limiting observed values are based on the dilution of 0.05 ml of the corresponding binary mixture with 0.95 ml of CCl_4 . The $[\text{CH}_3\text{CN}]/[\text{CH}_3\text{CN}] + [\text{CH}_3\text{OH}]$ ratio is maintained although the concentration of CH_3OH varies from 1.2 to 0.06 *M*. ^c Extrapolation values were obtained from a series of six dilutions in CCl_4 for each $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ mixture indicated. The total variation in the CCl_4 concentration was from 0 to *ca.* 95 mol %. ^d It should be noted that this abbreviation does not signify a constant, but depends upon the relative concentrations of active species. ^e Determined using 100-MHz instrumentation and are included in Figure 3 only.

tions in the appearance of the nmr spectrum of methanol, observed under conditions of "slow" exchange of the hydroxyl proton, are expected owing to changes in the $J/\Delta\nu$ ratio as the $-\text{OH}$ resonance is shifted upfield.¹⁰ Corresponding changes have been noted in the spectra of methanol^{5,9} and other alcohols³ for interactions with strong hydrogen bonding acceptor species, *e.g.*, acetone, DMSO, and, more recently, CH_3NO_2 .⁴ To our knowledge, this constitutes the first report of nitrile induced suppression of proton exchange in methanol attributable

(9) D. Kivelson and M. G. Kivelson, *J. Mol. Spectrosc.*, **2**, 518 (1958) also reported $J_{\text{HCOH}} = 5.2$ Hz and a complete interpretation of the spectral changes encountered in the acetone-methanol system; W. B. Moniz, C. F. Poranski, Jr., and T. N. Hall, *J. Amer. Chem. Soc.*, **88**, 190 (1966) have reported the solvent dependency of this parameter for various alcohols.

(10) For example see P. Laszlo in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. III, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, London, 1967.

(11) Observation of fine structure in the ambient temperature spectrum of a specially purified neat sample of methanol has been reported by E. Krakower and L. W. Reeves [*Trans. Faraday Soc.*, **59**, 2528 (1963)]. No significance can be attached to the apparent concentration dependence of the effect observed here.

(12) For a discussion of the major limitations to the use of carbon tetrachloride as an inert diluent see ref 10.

(13) See Experimental Section.

(14) Throughout this communication, $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}}$ and $\Delta\nu_{\text{CH}_3\text{OH}-\text{CCl}_4}^{\infty}$ signify the extrapolated or infinite dilution shifts (hertz at 60 MHz) for the $-\text{OH}$ proton of methanol in the indicated solvent. $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}}$ and $\Delta\nu_{\text{CH}_3\text{OH}-\text{CCl}_4}$ refer to observed shifts.

(15) C. P. Rader, *J. Amer. Chem. Soc.*, **91**, 3248 (1969).

(16) T. Matsuto and Y. Kudera, *J. Phys. Chem.*, **70**, 4087 (1966).

(17) C. Lussan, *J. Chim. Phys.*, **60**, 1100 (1963).

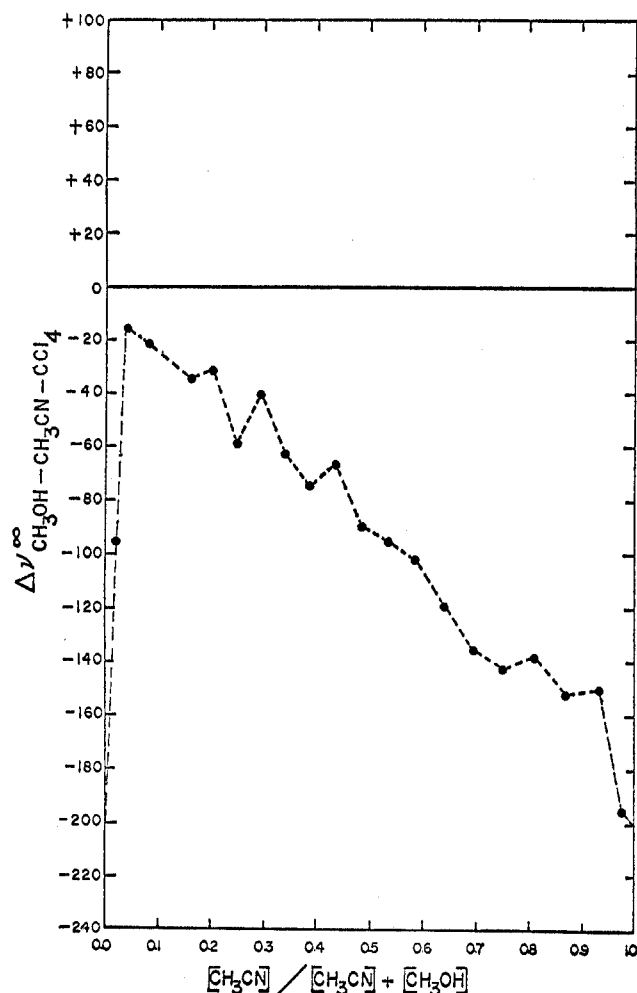


Figure 3.—The relationship between $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\infty}$ and the acetonitrile concentration. The CCl_4 concentration was assumed to be constant; only the concentrations of active species were considered in plotting the abscissa.

concentration dependence of the $-\text{OH}$ shifts (Figure 1) can be based on changes in the equilibrium concentration of a series $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ associates, the complicated nature of binary curves may effectively mask any reliable measure of the bonding interaction. Furthermore, any conclusions regarding relative hydrogen bond strengths based upon data for binary solutions, whether for the interaction of a specific acceptor, *e.g.*, DMSO,¹⁵ with alcohols showing varying degrees of association or to compare various acceptor species with a single alcohol (*e.g.*, methanol)⁵ may be untenable.

In an attempt to clarify the mode of complex formation for the present system, more comprehensive dilution studies of the $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ system were carried out. The limiting observed shifts ($\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\text{lim obs}}$ and $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\infty}$ for each mixture (diluted with CCl_4 as previously noted) plotted *vs.* $[\text{CH}_3\text{CN}] / [\text{CH}_3\text{CN}] + [\text{CH}_3\text{OH}]$ appear as Figures 2 and 3, respectively. Both the low and high acceptor ends of Figure 3 are obtained by extrapolation. Extrapolation of the high acceptor end of this curve using Varian A-60 data was not feasible; however, data obtained from 100-MHz instrumentation allowed an extrapolation at this end of the curve of 200 Hz upfield of the $-\text{CH}_3$ resonance of methanol.¹⁸

The overall upfield displacements of $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\text{lim obs}}$ and $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\infty}$ relative to $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}}$ show the expected disruption of the "residual" $-\text{OH}-\text{O}-$ bonded structure of the alcohol. However, in that $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\infty}$ for each mixture does not approach $\Delta\nu_{\text{CH}_3\text{OH}-\text{CCl}_4}$ as a limiting value, *i.e.*, 200 Hz upfield of the $-\text{CH}_3$ resonance of methanol, one further indication of $-\text{CN}-\text{HO}-$ hydrogen bonding is obtained.¹⁹

Perhaps the more interesting and important feature of the ternary curves (Figures 2 and 3) is the repeated occurrence of maxima in the $-\text{OH}$ displacement with increasing acceptor concentration, *i.e.*, at average values²⁰ of $[\text{CH}_3\text{CN}] / [\text{CH}_3\text{CN}] + [\text{CH}_3\text{OH}] = 0.05, 0.15, 0.25, 0.4, 0.55, 0.7, \text{ and } 0.85$ (*ca.*).²¹ The retention of these maxima in the latter curves under conditions expected to minimize alcohol autoassociation cannot be easily explained without invoking the formation of $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ aggregates, *i.e.*, consistent with preliminary indications of complexation derived from Figure 1. Accepting the maxima, or for that matter minima, in these curves as indicative of stoichiometric $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$ aggregates having defined geometries presents many intriguing questions. A particular case in point is the initial reversal in $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\text{lim obs}}$ and $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\infty}$ at $[\text{CH}_3\text{CN}] / [\text{CH}_3\text{CN}] + [\text{CH}_3\text{OH}] = 0.05$ (*ca.*); the latter cannot be expected to correspond to a specific complex having the corresponding 20:1 molar ratio of $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$. Consequently, it has been necessary to use a more reasonable working model for hydrogen bonding in this system based, in part, upon suppressed dissociation of methanol aggregates, *i.e.*, that in undergoing a hydrogen-bonded interaction with CH_3CN , the $-\text{OH}-\text{O}-$ bonded structure of the alcohol is stabilized and does not exhibit the "expected" $-\text{OH}$ displacement on dilution with an inert solvent, *e.g.*, CCl_4 .²² Past the initial maximum, the general upfield shift of the $-\text{OH}$ resonance with increasing relative concentration of the nitrile can then be ascribed to a decrease in the average number of methanol units possibly associated with an acetonitrile unit.¹⁸ It is also evident, however, that even the simplest explanation for the "sawtooth" curves presented here (Figure 2 or 3) must be modified to include complex formation; otherwise, a gradual diminishment in the $\text{CH}_3\text{OH} / \text{CH}_3\text{CN}$ ratio, even if these species are interacting, might not be expected to exhibit any obvious maxima in the $-\text{OH}$ displacement.²³ The present data do not allow any firm conclusions as to which of the observed

(18) Preliminary studies using 100-MHz instrumentation for the study of this and other proton donor-acceptor systems, *e.g.*, CH_3NO_2 , show that extrapolations of the 60-MHz data reported herein are reliable indications of trends but do not provide limiting values of use for critical comparisons of hydrogen bonding interactions. Additional studies are in progress based on the use of more sensitive 100-MHz instrumentation.

(19) In the absence of hydrogen bonding one would expect $\Delta\nu_{\text{CH}_3\text{OH}-\text{CH}_3\text{CN}-\text{CCl}_4}^{\infty}$ to approach the extrapolated shift for the $\text{CH}_3\text{OH}-\text{CCl}_4$ system.

(20) A complete definition of the maxima would require many more points than have been determined in this study.

(21) These maxima appear not only in the binary and ternary curves shown here, but also in the entire family of ternary curves resulting from approximately six incremental dilutions for each binary mixture indicated in Table 1.

(22) We have previously observed the occurrence of similar maxima in ternary curves for the $\text{CH}_3\text{OH}-\text{CH}_3\text{NO}_2$ system. Comparative studies for these two systems are in progress.

(23) The autoassociation curve for methanol shows only a "smooth" displacement of the $-\text{OH}$ resonance without any marked deviations; for further discussion see ref 10.

curvature deviations (Figures 1, 2, 3) may be attributed to either acetonitrile induced association of CH_3OH 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.*, CH_3NO_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.²⁴ 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.

Acknowledgments.—We are grateful to Dr. R. K. Kullnig of Sterling Winthrop Research Institute for assistance in obtaining 100-MHz nmr data and to the administrators of the Petroleum Research Fund, American Chemical Society (PRF No. 1037-G1), for partial support of this research. We also wish to thank the Materials Branch of NASA for supplying funds to purchase a Varian A-60 nmr spectrometer and Dr. J. Kuder for samples of high purity acetonitrile. One of us, P.A.C., is grateful for an NDEA Fellowship for the period of 1968-1969.

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

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Received April 7, 1970

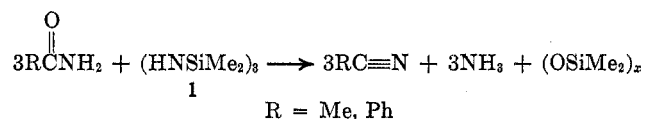
Silazanes, aminosilanes, alkoxysilanes, and chlorosilanes have been found to dehydrate amides to form nitriles at elevated temperatures.

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,^{1,2} phosphorus pentoxide,³ phosphorus oxychloride,² zinc chloride- α,α,α -trichlorotoluene,⁴ or strongly basic, for example, sodium borohydride⁵ and lithium aluminum hydride.³ 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.⁶ Klebe⁶ 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

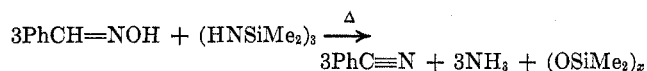
The reaction of hexamethylcyclotrisilazane (1) with benzamide or acetamide at 180-200° gave benzonitrile or acetonitrile in 95 and 85% yields, respectively.



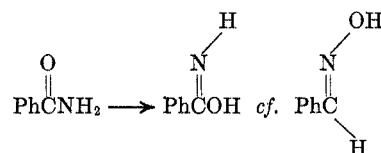
Compound 1 (1 equiv) with benzamide gave a siloxane polymer with a molecular weight \bar{M}_w of 120,000. The number-average molecular weight \bar{M}_n was 6800.

- (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).

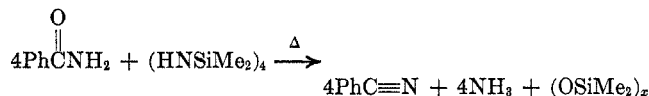
The reaction of 1 with *syn*-benzaldoxime also formed benzonitrile in good yield. An analogy between the



reaction of benzaldoxime 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*-Methylacetanilide 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.

