TABLE I

PHYSICAL PROPERTIES OF THE LIQUID CRYSTALLINE ANILS

Compound	Smectic range, °C	Nematic range, °C	Anal, % Calcd C	H	N	Found C	H	N
Dianisylideneoctafluorobenzidine		219–370	59.15	2.82	4.93	59.84	3.09	5.16
Dianisylidenebenzidine		252–345[a]						
Di-*p*-propoxybenzylideneoctafluorobenzidine	205–210	210–315	61.54	3.85	4.49	61.68	3.93	4.53
Di-*p*-*n*-propoxybenzylidenebenzidine		252–390	80.67	6.72	5.88	80.60	6.58	6.01
Anisylidene-*p*-aminotetrafluorobenzamide	238–268		55.21	3.06	8.58	55.20	3.46	8.67
Anisylidene-*p*-aminobenzamide	176–195		70.86	5.51	11.02	71.50	5.68	11.20
Benzylideneoctafluorobenzidine		235[b]	61.90	2.38	5.55	61.90	2.45	5.88
O-Propionyl-*p*-hydroxybenzylidene-*p*-trifluoromethoxyaniline	90–136		60.50	4.15	4.15	60.79	4.33	4.19

[a] Reference 2. [b] Not mesomorphic.

octafluorobenzidine has a crystal–nematic transition point at 219–220° and a nematic–isotropic transition point at 370° dec. The di-*p*-*n*-propoxybenzylidene derivative has a crystal–smectic transition at 205°, a smectic–nematic transition at 210°, and a nematic–isotropic transition at 315°. The dibenzylidene derivative is not mesomorphic, as would be expected,[1] owing to a lack of polarizable groups at the terminal positions of the molecule.

Wiegand[2] reports the crystal–nematic point of dianisylidene benzidine to be 252–253° and the nematic–isotropic point to be above 345°. Our results indicate that the substitution of fluorine atoms has little effect on the ability of a molecule to exhibit mesomorphic behavior. However, substitution of fluorine for hydrogen would be expected to increase the lateral interactions between nearest neighbors and therefore increase the smectic thermal stability. We have found this to be the case. Anisylidene-*p*-aminotetrafluorobenzamide has a crystal–smectic transition at 238° and a smectic–isotropic point at 268°. The corresponding unfluorinated compound has a crystal–smectic point at 176° and a smectic–isotropic point at 195°. An even more striking example of the effect of fluorine on the smectic thermal stability is illustrated by the substitution of fluorine in a molecule which exhibits a pure nematic state. Di-*p*-*n*-propoxybenzylidenebenzidine is only nematic from 252 to >390°. However, substitution of fluorine for the eight hydrogen atoms on the benzidine portion of the molecule introduces a smectic state at 205° and in turn decreases the nematic thermal stability. Another interesting example of fluorine increasing the smectic thermal stability is shown by O-propionyl-*p*′-hydroxybenzylidene-*p*-trifluoromethoxyaniline. This material is purely smectic from 90 to 136°, while the corresponding unfluorinated compound is purely nematic from 86–118°.[3] The increased ratio of residual lateral to terminal interactions is due to the strongly polar trifluoromethoxy group, which has a dipole operating perpendicular to the molecular axis.

The physical properties of the new liquid crystalline anils are summarized in Table I. These anils were prepared by the condensation of appropriately substituted benzaldehydes with readily available fluoroaromatic amines.

Acknowledgment.—The authors are indebted to Mr. B. Goydish for the combustion analysis.

[2] C. Wiegand, *Z. Naturforsch.*, **6b**, 240 (1951).

[3] The results of our investigations on this family of anils will be the subject of a future publication.

A Cryoscopic Study of Methanediamines in Sulfuric Acid[1]

J. E. FERNANDEZ AND ROGER SUTOR

Department of Chemistry, University of South Florida, Tampa, Florida

Received July 14, 1966

In connection with studies on the mechanism of the Mannich reaction it became of interest to study the nature of the ionization products of methanediamines in strongly acid media. These compounds as well as hydroxymethylamines have been mentioned as possible intermediates in various proposed mechanisms of the Mannich reaction.[1,2] We now report the results of cryoscopic studies on four methanediamines of formula $R_2NCH_2NR_2$ in concentrated sulfuric acid.

Previous cryoscopic studies on dibasic compounds, $X(CH_2)_nY$, have been reported where X and Y are ether or amino groups and $n \geqq 2$. These compounds generally have van't Hoff *i* factors of about 3 which indicates that they behave as simple difunctional bases[3] (eq 1).

$$X(CH_2)_nY + 2H_2SO_4 \longrightarrow [XH(CH_2)_nYH]^{2+} + 2HSO_4^- \quad (1)$$

In the compounds which we now report, the nitrogen atoms are separated by only one methylene group. These methanediamines exhibit van't Hoff *i* factors near 4 at approximately 0.02 *m* concentrations (Table I). The simplest explanation for these results involves dissociation of the monoprotonated moiety to form the resonance-stabilized aminocarbonium ion (eq 2).

$$\begin{aligned} &R_2NCH_2NR_2 + 2H_2SO_4 \longrightarrow \\ &\qquad [R_2NHCH_2NHR_2]^{2+} + 2HSO_4^- \rightleftharpoons \\ &\qquad R_2N^+HCH_2NR_2 + HSO_4^- + H_2SO_4 \longrightarrow \\ &\quad R_2N^+H_2 + 2HSO_4^- + [R_2\ddot{N}{-}CH_2^+ \longleftrightarrow R_2N^+{=}CH_2] \quad (2) \end{aligned}$$

Such aminocarbonium ions have been suggested previously[4] as intermediates in the Mannich reaction.

[1] A Study of the Mannich Reaction. VIII. For previous papers, see J. E. Fernandez and W. I. Ferree, *Quart. J. Florida Acad. Sci.*, **29**, 13 (1966); J. E. Fernandez and J. M. Calderazzo, *J. Chem. Eng. Data*, **10**, 402 (1965); J. E. Fernandez, J. S. Fowler, and S. J. Glaros, *J. Org. Chem.*, **30**, 2787 (1965).

[2] (a) J. H. Burkhalter, J. N. Wells, and W. J. Mayer, *Tetrahedron Letters*, 1353 (1964); (b) J. E. Fernandez, *ibid.*, 2889 (1964); (c) E. C. Wagner, *J. Org. Chem.*, **19**, 1862 (1954); (e) B. Reichert, "Die Mannich Reaktion," Springer-Verlag, Berlin, 1959.

[3] R. J. Gillespie and J. A. Leisten, *Quart. Rev.* (London), **8**, 40 (1954).

[4] (a) S. V. Liebermann and E. C. Wagner, *J. Org. Chem.*, **14**, 1001 (1949); (b) E. R. Alexander and E. J. Underhill, *J. Am. Chem. Soc.*, **71**, 4014 (1949); H. Hellmann and G. Opitz, *Chem. Ber.*, **89**, 81 (1956); *Angew. Chem.*, **68**, 265 (1956).

Table I

Cryoscopic Data for Methanediamines in Sulfuric Acid

Compound	Factor[a]
Tetramethylmethanediamine	3.9 ± 0.2
Tetraethylmethanediamine	4.1 ± 0.5
Tetra-*n*-propylmethanediamine	3.7 ± 0.5
Methanedi(N-piperidine)	3.4 ± 0.3

[a] The values given represent averages of at least five determinations with mean deviations.

More recently, nmr evidence was presented for the existence of such ions in the condensation of secondary amines and formaldehyde in 70% H_2SO_4.[5]

Experimental Section

Apparatus.—The freezing point cell consisted of a heavy-walled, 50-ml, erlenmeyer flask with a 10-in.-long neck through which was sealed a Beckman-type differential thermometer. A second neck consisting of a 10–30 ₸ joint was used for the introduction of sample and solvent. The mixture was stirred with a glass-enclosed, magnetic stirring bar. The entire apparatus was immersed in a glass wool jacketed container to ensure slow and even warming of the frozen solutions.

Calibration of the thermometer was carried out by plotting the melting point of various fuming H_2SO_4–H_2O mixtures to determine the maximum freezing point.[6] This maximum temperature was taken as the melting point of pure H_2SO_4.

Melting Point Determinations.—Melting points were determined by cooling the solution rapidly in ice–water and inducing crystallization of the supercooled liquid by touching the side of the cell with a piece of Dry Ice. The solid mass was then allowed to warm until nearly all had melted. When only a few crystals remained, the solution was cooled slowly and with stirring to ensure even crystal growth. After about half of the mixture was solid, the freezing bath was replaced by the insulated jacket and the mixture was allowed to warm with vigorous stirring. During the warming period, the temperature was plotted against time to obtain a warming curve. The melting point was taken as the intersection of the two straight lines corresponding to before and after complete melting.[7] In this way, melting points were reproducible to within a few hundredths of a degree.

Solutions.—Solvent samples were prepared by adding either water or 30% fuming H_2SO_4 to concentrated H_2SO_4 in the cell to obtain a solvent of the desired melting point. After measuring the melting point and weight of the solvent, a quantity of methanediamine was added to the cold solvent to make the concentration near 0.02 *m*, and several determinations were made of the melting point.

Van't Hoff *i* factors were calculated from the equation[8] below

$$i = \frac{\Delta\nu}{\Delta m \times 6.154(1 - 0.0047\nu)}$$

where $\Delta\nu$ is the lowering of the melting point of the solution due to the increment Δm in the molality of the diamine, ν is the total melting point depression, and 6.154 is the molal freezing point constant for sulfuric acid.

Methanediamines.—The methanediamines were prepared from the corresponding secondary amines and formaldehyde and distilled through a Vigreux column: tetramethylmethanediamine,[9a] bp 83–84° (760 mm); tetraethylmethanediamine,[9b] bp 162–164° (760 mm); tetrapropylmethanediamine,[9c] bp 226.5° (760 mm); methanedi(N-piperidine),[9d] bp 88° (4.6 mm). Purity was confirmed by the absence of any N–H absorption near 1.53 μ[10] using the pure liquid.

---

[5] N. C. Deno [*Chem. Eng. News*, **42** (45), 88 (1964)] refers to unpublished work by Skell and de Luis.

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 279.

[7] A. R. Glasgow, B. J. Mair, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **26**, 594 (1941).

[8] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **55**, 1900 (1933).

[9] (a) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957); (b) L. Henry, *Bull. Acad. Roy. Med. Belg.*, **26**, 200 (1893); **29**, 355 (1895); (c) L. Henry, *ibid.*, **26**, 204 (1893); (d) H. G. Johnson, *J. Am. Chem. Soc.*, **68**, 12 (1946).

[10] W. Kaye, *Spectrochim. Acta*, **6**, 257 (1954).

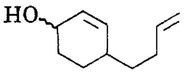
Olefinic Cyclizations.
IX.[1] Further Observations on the Butenylcyclohexenol System

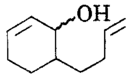
William S. Johnson and Kenn E. Harding

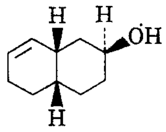
Department of Chemistry, Stanford University, Stanford, California 94305

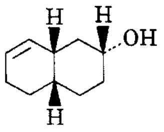
Received August 3, 1966

In a recent publication from our laboratory,[2] it was reported that the butenylcyclohexenol (I), as well as its isomer (II), on treatment for a few minutes at room temperature with formic acid, underwent stereoselective cyclization in high yield to produce the formate of Δ^7-*cis,anti*-2-octalol (III). The *cis* fusion of the rings was established unequivocally, and the *anti* relationship of the hydrogen atoms at C-2 and C-9 was assigned on the basis of a hydrogenation experiment to give what appeared to be mainly *cis,anti*-2-decalol. The preliminary results of some related studies,[3] as well as theoretical considerations (see below), led us to suspect that this latter configurational assignment was incorrect. In the present paper, we have reexamined the matter and have shown that the product of the aforementioned cyclization experiments is really a mixture consisting of the *cis,anti*- and the *cis,syn*-octalols (III and IV), predominantly the latter.


I


II


III


IV

The cyclization of dienol I and of dienol II was carried out as previously described[2] and, after treatment with lithium aluminum hydride to cleave the formate residue, the product was hydrogenated over platinum catalyst. The infrared spectra of the resulting two substances were nearly identical with each other and very similar to that of authentic *cis,syn*-2-decalol.[4] In particular, these spectra showed strong bands at 9.51, 9.73, and 10.52 μ, which are characteristic of the *cis,syn* but not of the *cis,anti* isomer. There was only weak absorption at 9.9 μ owing to the latter isomer. The hydrogenation products were acetylated by treatment with acetic anhydride and pyridine. The infrared spectra of these acetates were nearly identical with each other and quite similar to that of the acetate of authentic *cis,syn*-2-decalol.[4] The characteristic bands at 9.55 and 9.73 μ were observed, and no appreciable absorption was found at 9.70 μ attributable to the acetate of the *cis,anti* isomer.

---

[1] Part VIII: W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *J. Am. Chem. Soc.*, **87**, 5148 (1965).

[2] W. S. Johnson, W. H. Lunn, and K. Fitzi, *ibid.*, **86**, 1972 (1964).

[3] W. S. Johnson and K. E. Harding, to be reported.

[4] We are indebted to Professor W. G. Dauben for providing us with pure, authentic comparison materials. See W. G. Dauben, R. C. Tweit, and C. Mannerkantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).