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 $\Delta m$ in the molality of the diamine, $\nu$ 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 $\mu$[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

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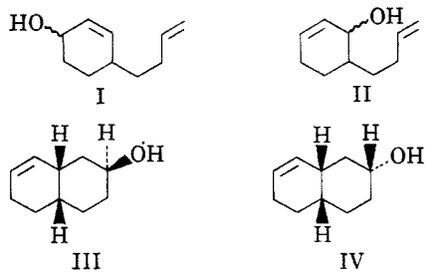
In a recent publication from our laboratory,[2] it was reported that the butenylcyclohexenol (I), as well as its isomer (II), on treatment for a few minutes at room temperature with formic acid, underwent stereoselective cyclization in high yield to produce the formate of $\Delta^7$-*cis,anti*-2-octalol (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.




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 $\mu$, which are characteristic of the *cis,syn* but not of the *cis,anti* isomer. There was only weak absorption at 9.9 $\mu$ 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 $\mu$ were observed, and no appreciable absorption was found at 9.70 $\mu$ attributable to the acetate of the *cis,anti* isomer.

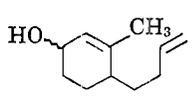
(1) Part VIII: W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *J. Am. Chem. Soc.*, **87**, 5148 (1965).

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

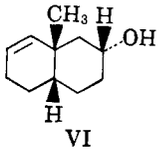
(3) W. S. Johnson and K. E. Harding, to be reported.

(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).

Vapor phase chromatography on a 150-ft capillary Castorwax column failed to give good resolution of a mixture of *cis,anti*- and *cis,syn*-2-decalol. This proximity of retention times apparently accounts for the error that was previously made in distinguishing between the two epimers. The *cis,anti* and *cis,syn* acetates, however, are nicely resolved on this column at 130°, showing retention times of 43.0 and 45.25 min, respectively. Analysis of the acetates derived from the hydrogenated cyclization products showed relative peak areas at these respective retention times of 16 and 84% for the product derived from I, and 17 and 83% for the product derived from II. Peak enhancement experiments confirmed the identity of these peaks with those of authentic materials. This analysis also showed that less than 2% of the total decalyl acetates corresponded to the *trans*-2-decalyl acetates in either of the reaction products. This result constitutes evidence that the significant amounts of *trans*-decalols formed in the previous study[2] did indeed arise from isomerization during hydrogenation over palladium. In the present study we chose platinum catalyst since it is known[5] to be less effective than palladium in promoting this type of isomerization. Now it becomes evident that these cyclizations are essentially stereospecific with respect to the ring fusion, and that the two isomers I and II give, within experimental error, identical cyclization product distributions.



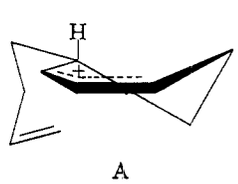

V



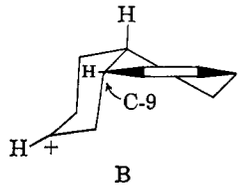

VI

By analogy to the results described above it appears most probable that the major product of the cyclization of the homologous dienol V is the *cis,syn*-methyloctalol (VI) rather than the previously presumed[1] *anti* epimer. The 9-methyl-2-decalol, mp 72–74°, produced on hydrogenation of VI[1] is therefore now regarded as the *cis,syn* isomer.

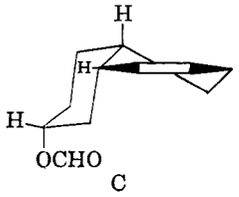
The foregoing conclusions are consistent with a more satisfying mechanistic interpretation than previously advanced. If the allylic cation, generated from either dienol I or II, is envisaged as reacting in its more favored conformation A with the butenyl side chain equatorial, then the new bond can form in such a way




A




B




C

(quasi-axial development) to give the most favorable orbital overlap in the transition state.[6] The *cis,syn* product (C) arises in one or more of the following ways: (a) concerted attack by solvent as ion A undergoes cyclization; (b) attack by solvent on a bridged cation derived from A; (c) preferred equatorial attack by solvent on the intermediary bicyclic solvated cation B. We believe that a significant part of the process occurs by pathway c, because the attack of solvent is not stereospecific. The formation of the less preponderant *cis,anti* isomer can be envisaged as the result of some higher energy axial attack by solvent on cation B and/or equatorial attack by solvent on the flipped form of B. Apparently this flipping mechanism is not of major importance, because of the results of the cyclization of the homologous dienol V[1] which we have also reexamined in more detail. Hydrogenation of the product over platinum catalyst, followed by acetylation, gave material which on vapor phase chromatographic analysis at 147° exhibited two peaks corresponding to those produced by an authentic mixture of the epimeric *cis*-9-methyl-2-decalyl acetates.[1] These peaks were found at retention times of 26.2 and 27.8 min in a ratio of 97 to 3. These presumably (see above) correspond to the *syn* and *anti* epimers, respectively. This percentage of the *anti* isomer is significantly lower than in the case of the demethyl series (see above), a result which is compatible with the view that attack by solvent on the cation B, or on the 9-methyl homolog, plays a significant role in both cases. The effect of the 9-methyl group would be to raise the activation energy of axial attack on the cation, because of the development of a 1,3-diaxial interaction between the angular methyl group and the attacking solvent in the transition state. If the *anti* epimer were produced mainly by equatorial attack on the flipped form of cation B, the presence of the 9-methyl group, which is known to lower the energy barrier of the flipping process in a related system,[7] would be expected to result in a higher proportion of *anti* epimer than in the demethyl case.

### Experimental Section

Samples of 4-($\Delta^3$-butenyl)-$\Delta^2$-cyclohexenol (I), 6-($\Delta^3$-butenyl)-$\Delta^2$-cyclohexenol (II), and 4-($\Delta^3$-butenyl)-3-methyl-$\Delta^2$-cyclohexenol (V) from the original studies[1,2] were used. The specimen of the dienol I had discolored after being stored for 3 years; therefore it was evaporatively distilled at 110° (0.75 mm) prior to use. In the case of dienol V, which had been stored for 2 years, it was necessary to purify the material by chromatography on acid-washed alumina, followed by evaporative distillation at 105° (0.06 mm). The cyclizations were performed on a 10.7-mg scale for substance I, a 46.5-mg scale for II, and a 13.4-mg scale for V. The procedures for the cyclization and lithium aluminum hydride treatment were the same as those already described.[1,2] The crude products were hydrogenated as previously described except that platinum oxide was employed in place of palladium-on-carbon catalyst. The hydrogenated products were acetylated by treatment with acetic anhydride in pyridine at room temperature. The vapor phase chromatographic analyses were performed on a Perkin-Elmer gas chromatograph, Model 810, equipped with a hydrogen flame ionization detector. A 150 ft × 0.01 in. column packed with Castorwax was employed, and nitrogen was used as the carrier gas. Peak areas were calculated by the method of Bartlet and Smith.[8]

(5) *Cf. inter alia* J-F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Am. Chem. Soc.*, **83**, 3874 (1961); see also F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, **1**, 255 (1962).

(6) H. L. Goering and R. R. Josephson, *J. Am. Chem. Soc.*, **84**, 2779 (1962); see also H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963) H. L. Goering and U. Mayer, *ibid.*, **86**, 3753 (1964).

(7) J. T. Gerig and J. D. Roberts, *ibid.*, **88**, 2791 (1966).

(8) J. C. Bartlet and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960).