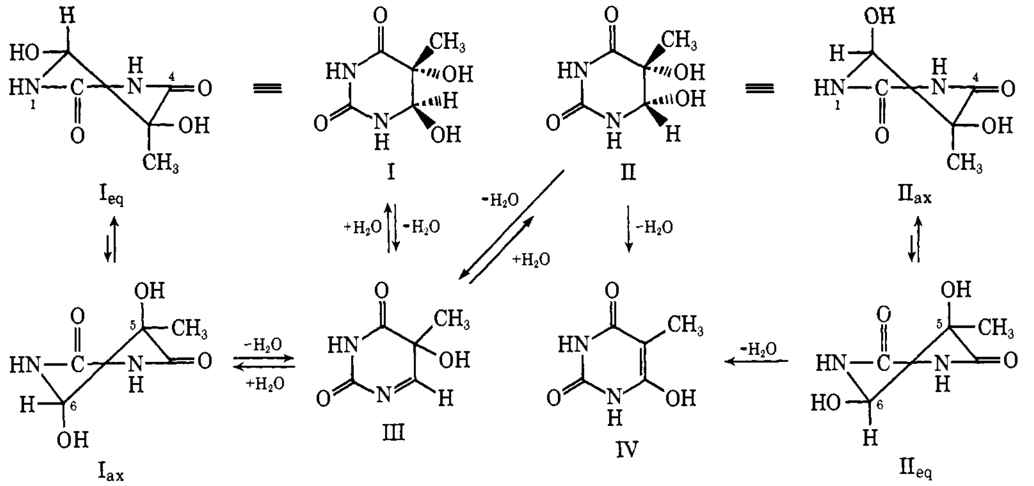
**Scheme I**



only after standing for 5 hr; however, the amount seemed to be very minor at all times.

The major product ($R_f$ 0.39) from II when heated at 90° was isolated and identified as 1,2,3,4-tetrahydro-2,4-dioxy-5-methyl-6-hydroxypyrimidine (5-methylbarbituric acid (IV)) by uv and ir spectra. Thus, the results suggest that the conversion of II to IV is a facile process, but that conversion of II to I is inefficient at best, in contrast to earlier reports.[4a,4e]

On the other hand, when a solution of freshly prepared I (100 mg/15 ml of $H_2O$) was heated at 90° for 30 min, or allowed to stand at 37° for 3 hr, six and five spots, respectively, appeared on tlc. The major products were II (~4%) and III (~4%) in each case with ~85% of I unchanged.

Based on stereochemical considerations, a mechanistic explanation of the above discussed reactions may be given. The most predominant conformer of II was suggested to have an equatorial C(5)OH.[4c] Also, the same C(5)OH configuration may be assigned to I by examining the molecular structure of its analog, thymine–thymine adduct.[9] Thus, the major conformer for I and II may be $I_{eq}$ and $II_{ax}$ with equatorial and axial C(6)OH, respectively, as shown. Since the stereorequirement for a trans elimination process is favored by a trans planar conformation,[10,11] $I_{ax}$ and $II_{eq}$, the minor conformers, are the species favored for dehydration. Thus, in neutral aqueous solutions, II possibly dehydrates at elevated temperature to give IV as the major product. By the same consideration, elimination of water from I should be difficult between C(5)OH and C(6)H, but is possible for C(6)OH and N(1)H to give III.[12] In aqueous solutions, addition of water to III would result in the formation of I or II. Thus I → III → I + II provides a route for the conversion of I to II (see Scheme I). This is a minor process since I, although unstable when dry, is stable in neutral aqueous solutions. On the other hand, II may also form III in the absence of its formation of IV. Although II → III → I is expected, II → IV is a favored process. Thus, the conversion of II to I occurs only in trace quantities. The above results may rule out the possibility of efficient cis and trans isomerization of I and II *via* a common intermediate,[4a,4e] by ring-chain tautomerization.

These findings are probably of significance to our understanding of the initial steps of the radiation chemistry of thymine in aqueous solution.

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[9] I. L. Karle, S. Y. Wang, and A. J. Varghese, *Science*, **164**, 183 (1969); I. L. Karle, *Acta Crystallogr. B*, **25**, 2119 (1969). The saturated ring of thymine–thymine adduct is in the half-chair conformation with C(5) 0.4 Å below and C(6) 0.2 Å above the plane of the other four atoms. The C(5)OH is in the equatorial position.

[10] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 189–194.

[11] S. Y. Wang, *J. Amer. Chem. Soc.*, **80**, 6196 (1958); S. Y. Wang, M. Apicella, and B. R. Stone, *ibid.*, **78**, 4180 (1956).

[12] W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, p 183.

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## Nonatetraenyl Anions. The 6-Vinylcycloheptadienyl–Nonatetraenyl Anion Rearrangement

*Sir:*

We wish to report four successful preparative routes to nonatetraenyl anions, two of which involve 6-vinylcycloheptadienyl–nonatetraenyl anion rearrangements.

Nonatetraenyl anion (I, R = H) was prepared in quantitative yield from 1,3,6,8-nonatetraene (II)[1] by metalation with *n*-butyllithium in THF–hexane at −70°. The nmr parameters[2] on structure I (for the parent anion, with R = H) clearly show this anion to exist predominantly in the extended planar conformation, as do the lower vinylogs allyl, pentadienyl, and heptatrienyl anions;[3] since the charge is delocalized over more atoms in I, the chemical shifts of the protons attached to the odd-numbered carbon atoms absorb slightly downfield from the corresponding atoms in heptatrienyl anion. The colors in the series range from none (allyl) through yellow (pentadienyl) and red (heptatrienyl) to blue-black (nonatetraenyl). Unlike heptatrienyl anions, which cyclize to cycloheptadienyl anions at −30°,[3] nonatetraenyl anion is stable at room temperature and could not be induced to cyclize; heating to 70° caused the separation of a black substance of unknown structure.

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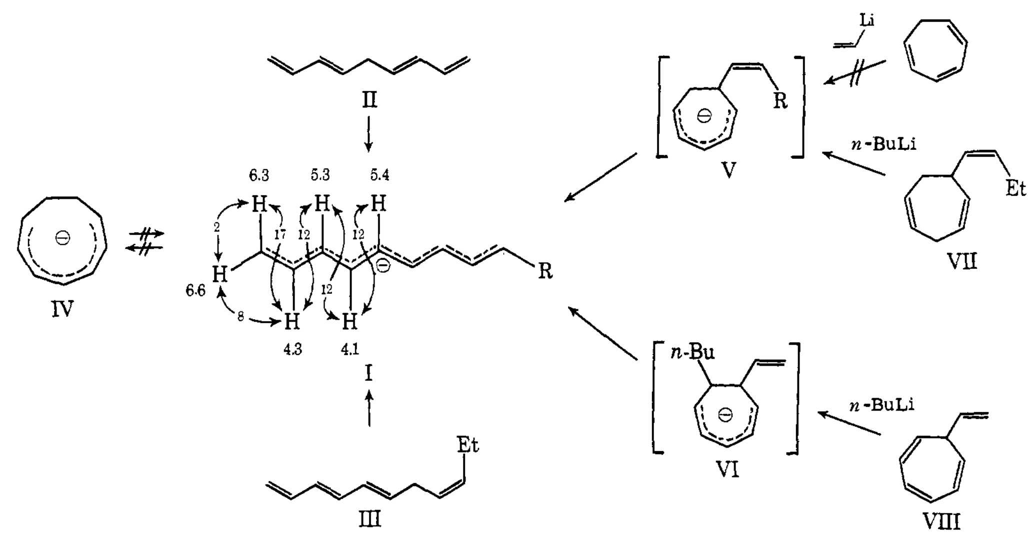
[1] C. H. Hauser, T. W. Brooks, M. I. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963).

[2] Chemical shifts are in $\tau$ units; coupling constants are in hertz.

[3] R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), and references therein.



To explore another possible route to nonatetraenyl anions, tetraene III, a constituent of algae of the genus *Dicytopteris*,[4] was mixed with *n*-butyllithium in THF–hexane. Approximately equal amounts of metalation product I (R = Et) and products of addition of butyllithium to the conjugated triene system were obtained, as judged from the relative heights of the mass spectral peaks at *m/e* 157 and 213 after quenching with $D_2O$ followed by hydrogenation. Thus, under these metalation conditions, a 1,3,6,8-tetraene (*e.g.*, II) is a more suitable precursor for a nonatetraenyl anion than is a 1,3,5,8-tetraene (*e.g.*, III).

Since the nonatetraenyl anions I (R = H, Et) showed no tendency to cyclize, several ring-opening routes for their preparation were investigated. 1,3,6-Cyclononatriene[5] did not react with *n*-butyllithium in THF–hexane, presumably due to poor overlap in the developing anion, but was metalated at room temperature by *n*-butyllithium in TMEDA–hexane, producing a tan powder which could be the lithium salt of IV solvated by TMEDA.[6] This dissolved in THF-$d_8$ to give a deep red solution, which could not be induced by heating to ring open to I (R = H), but decomposed in an unknown manner at 90°. If this anion is IV then the energy barrier for the nonatetraenyl–cyclononatrienyl anion rearrangement is at least 25 kcal/mol.

Routes involving the ring opening of 6-vinylcycloheptadienyl anions V and VI were more successful. V (R = H) could not be prepared in high concentration by adding vinyllithium to cycloheptatriene, evidently because V adds to cycloheptatriene faster than does vinyllithium. VII, however, is obtainable from *Dictyopteris* extracts,[4] and, as expected, metalates preferentially in the secondary position to yield V (R = Et), which opens, even at −30°, to I (R = Et); protonation followed by hydrogenation gives undecane, identified by mass spectral and glpc comparison with an authentic sample. Also, the reaction of 7-vinylcycloheptatriene (VIII)[7] with *n*-butyllithium in THF–hexane at −30° gave I (R = *n*-Bu), no doubt *via* VI; protonation and hydrogenation gave tridecane, identified by mass spectral and glpc comparison with an authentic sample.

Thus, the 6-vinylcycloheptadienyl–nonatetraenyl rearrangement favors the open form, in contrast to the heptatrienyl–cycloheptadienyl rearrangement.[3,8] The major factor responsible for this difference is probably the greater delocalization energy of I (2.63 $\beta$, from HMO calculations) as compared to heptatrienyl anion (2.06 $\beta$); since the delocalization energy of cycloheptadienyl anion is 1.46 $\beta$, 1.17 $\beta$ would be lost if I cyclized, whereas only 0.60 $\beta$ is lost when heptatrienyl anion cyclizes. In the former cyclization, the delocalization energy lost would more than offset the energy gained in forming a new carbon–carbon single bond.

Though the position of equilibrium in the cyclononatrienyl–nonatetraenyl anion rearrangement is unclear, it appears (if the anion described above is IV) that the activation energy for this rearrangement may be much larger than that for the heptatrienyl–cycloheptadienyl and 6-vinylcycloheptadienyl–nonatetraenyl anion rearrangements. This could be rationalized by noting that the latter two rearrangements involve a Möbius array[9] of seven $\pi$ orbitals in the all-cis conformation of the open form as the transition state is approached, whereas the former (unobserved) rearrangement requires considerable loss of overlap as the transition state is approached from either the open or closed form.

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(4) J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

(5) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971).

(6) It could also be the lithium salt of the homoaromatic dianion (*cf.* R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4729 (1966); M. Ogliaruso, R. Rieke, and S. Winstein, *ibid.*, **88**, 4731 (1966); T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966)); the nmr spectrum is unusual and not yet fully understood. This substance will be the subject of a further communication.

(7) This substance was prepared from vinylmagnesium chloride and 7-methoxycycloheptatriene by G. A. Gladkovskii, S. S. Skorokhodov, S. G. Sylvina, and A. S. Khachaturov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7, 1273 (1963); we substituted vinyllithium (Alfa Inorganics, Inc.) for the Grignard reagent.

(8) K. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1984 (1969).

(9) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964); H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

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## Micellar Control of the Nitrous Acid Deamination Reaction. A Unique Salt Effect on Stereochemistry

*Sir:*

In contrast to micellar effects on reaction rates,[1] little is known about micellar control of stereochemistry. We discovered micellar alteration of the stereochemistry of alcohol formation in the deamination of amines.[2] Others have reported stereoselective hydrolyses of chiral esters catalyzed by chiral micelles,[3] and micellar enhancement of the mutarotation of 2,3,4,-6-tetramethyl-$\alpha$-D-glucose.[4]

Now, we demonstrate that stereochemical modification of the deamination reaction *requires both alkylammonium micelles and certain relatively hydrophobic counterions.* Moreover, whereas the counterion identity is crucial to the product-forming step, which determines stereochemistry, micellar catalysis of the rate-determining nitrosation step[5] displays only a mild dependence on counterion.

*l*-2-Aminooctane was deaminated at various concentrations in 1.59 *M* aqueous $NaNO_2$, at pH 4, adjusted with $HClO_4$ or HCl.[6,7] The reaction stereochemistry was determined[8] (to ±1%) from the optical purities of the gc-isolated product 2-octanol and the initial 2-aminooctane. We also determined pseudo-first-order rate constants ($k_{obsd}$) for these deaminations.[9]

Twenty-five experiments are represented in Figure 1, which relates the reaction stereochemistry and $k_{obsd}$ to $F_m$, the fraction of the initial 2-octylammonium ions which are micellized.[10] Mechanistically, each perchlorate stereochemical result is the "weighted average" of a micellar deamination and a much slower nonmicellar deamination. This function is only approximately linear in $F_m$, but can be calculated within 2% by treating the reaction as the sum of a micellar fraction ($F_m$),[10] with characteristic stereochemistry of 6% net retention, and a nonmicellar fraction ($1 - F_m$), with characteristic stereochemistry of 24% net inversion.

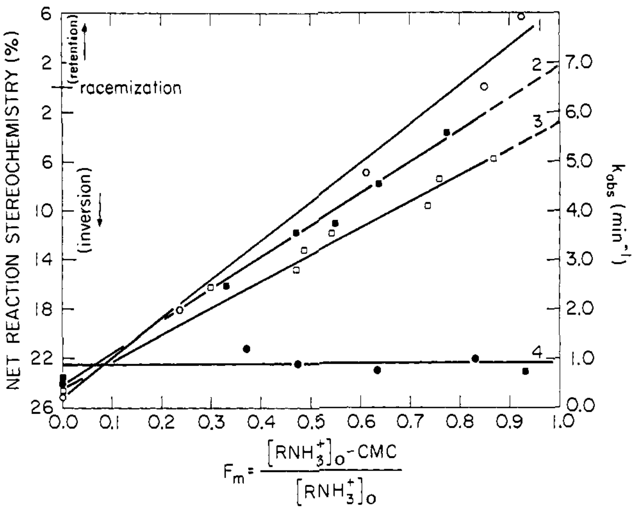

Figure 1. The stereochemistry and kinetics of the nitrous acid deamination of 2-aminooctane: curve 1, stereochemistry, perchlorate counterions; curve 2, kinetics, chloride counterions; curve 3, kinetics, perchlorate counterions; curve 4, stereochemistry, chloride counterions. The rate constants, as shown on the right-hand ordinate, have been arbitrarily multiplied by 10.0.

Clearly, deamination reactions are accelerated by 2-octylammonium micelles whatever the counterion, but the stereochemistry of 2-octanol formation is altered only when micelles are present *and* perchlorate is the counterion. The following experiments highlight the need for both micelles and specific anions in order to control stereochemistry.[12]

(a) Solutions containing excess 2-decylammonium and low concentrations of 2-octylammonium ions were deaminated, affording 2-octanol with up to 5.4% net retention. In these experiments, 2-decylammonium micelles provided a template for 2-aminooctane deamination, which therefore occurred with a stereochemistry characteristic of $F_m > 0.9$. However, perchlorate was necessary; parallel experiments with chloride counterions gave 2-octanol with 21–22% ("normal") net inversion.

(b) Inclusion of $NaClO_4$ in $NaNO_2$–HCl deaminations shifted the stereochemistry toward increased retention. Added perchlorate did not affect $NaNO_2$–$HClO_4$ deaminations.

(c) Deaminations ($[RNH_3^+]_0 >$ cmc) which used $NaNO_2$–HBr, or which occurred in excess (micellar) 2-octyltrimethylammonium bromide solutions, *did not* afford 2-octanol with enhanced retention, although $k_{obsd}$ was augmented.

(d) Fluoroborate and *p*-tosylate resembled perchlorate in eliciting stereochemical micellar control. At $F_m \sim 0.8$, $NaNO_2$–$HBF_4$ and $NaNO_2$–*p*-$CH_3C_6H_4SO_3H$ deaminations gave 2-octanol with 15 and 7% net inversion, respectively. At $F_m \leq 0$, 23% net inversion was observed in each case.

The rate of nitrosation of *free* amine by $N_2O_3$ determines the rate of deamination[13] and $k_{obsd}$ can be shown

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[1] Reviews include: E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970); E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969); and H. Morawetz, *Advan. Catal.*, **20**, 341 (1969).

[2] R. A. Moss and D. W. Reger, *J. Amer. Chem. Soc.*, **91**, 7539 (1969).

[3] C. A. Bunton, L. Robinson, and M. F. Stam, *Tetrahedron Lett.*, 121 (1971). See also, C. A. Bunton, L. Robinson, and M. F. Stam, *J. Amer. Chem. Soc.*, **92**, 7393 (1970).

[4] E. J. Fendler, J. H. Fendler, R. T. Medary, and V. A. Woods, *Chem. Commun.*, 1497 (1971).

[5] R. A. Moss and C. J. Talkowski, *Tetrahedron Lett.*, 703 (1971).

[6] Protonation of the amine exceeds 99% under these conditions; 2-octylammonium perchlorate or chloride is the 2-aminooctane "reservoir."

[7] General deamination procedures appear in ref 2, and in R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

[8] R. A. Moss, D. W. Reger, and E. M. Emery, *ibid.*, **92**, 1366 (1970).

[9] Methodological details appear in ref 5.

[10] $F_m = ([RNH_3^+]_0 - \text{cmc})/[RNH_3^+]_0$, where 0 denotes initial concentration, and cmc the critical micelle concentration for $RNH_3^+$ under simulated reaction conditions. Details of the cmc determinations[11] are available on request, and will be published in full. The dependence of 2-octylammonium cmc on $[RNH_3^+]_0$ (0.08–0.6 *M*) was small. Best values, used to calculate $F_m$, were 0.058 (perchlorate counterions) and 0.09 *M* (chloride counterions).

[11] Related determinations appear in R. A. Moss and W. L. Sunshine, *J. Org. Chem.*, **35**, 3581 (1970).

[12] Details will appear in the full paper.

[13] J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961); T. W. J. Taylor, *J. Chem. Soc.*, 1099 (1928); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p 294; and J. H. Dusenbury and R. E. Powell, *J. Amer. Chem. Soc.*, **73**, 3266 (1951).