manner, left 3.58 g of white crystalline material with no significant improvement in melting point (154°) or rotational magnitude $\{[\alpha]^{26}\mathrm{D}\ -71.9 \pm 0.50°$ (*c* 3.08, methanol)} over the singly recrystallized salt. The multiply recrystallized material was treated with cold, 20% aqueous potassium hydroxide solution, followed by extraction of the liberated amine oxide into three 30-ml portions of chloroform. White, crystalline, (+)-*cis*-**amine oxide (16)**, 1.32 g, $[\alpha]^{22}\mathrm{D}\ +2.90 \pm 0.19°$ (*c* 8.07, chloroform), was obtained after removal of the chloroform.

The filtrate obtained from the initial crystallization of the levorotatory salt was reduced to one-half of its volume and kept in the refrigerator overnight. A crop of white crystalline material was obtained: 1.40 g, mp 127–130°, $[\alpha]^{26}\mathrm{D}\ -61.9 \pm 0.60°$ (*c* 2.74, methanol). The filtrate from this crystallization was also reduced to one-half volume, but no crystallization could be induced. Instead the solution was evaporated under reduced pressure to 6.2 g of a residual oil that slowly crystallized to a mass of pale yellow material; mp 88–93°, $[\alpha]^{27}\mathrm{D}\ -37.0 \pm 0.47°$ (*c* 3.45, methanol). The entire quantity was taken up in 30 ml of 20% aqueous potassium hydroxide solution and extracted with three 30-ml portions of chloroform. Evaporation of the combined and dried extracts gave crystalline (very pale yellow) (−)-*cis*-**amine oxide (15)**; 2.0 g, $[\alpha]^{26}\mathrm{D}\ -2.87 \pm 0.20°$ (*c* 14.19, chloroform). Infrared spectra determined from the (+)-*cis*-amine oxide, the (−)-*cis*-amine oxide, and the (±)-*cis*-amine oxide were superimposable.

B. (+)- and (−)-*trans*-N-Methyl-N-neopentyl-4-methylcyclohexylamine Oxides (18 and 17). After a solution of (±)-*trans*-amine oxide (9.18 g, 0.0392 mol) and (−)-D-dibenzoyltartaric acid (14.0 g, 0.0396 mol) in 50 ml of absolute ethanol was kept in the refrigerator overnight, the deposited white crystalline salt was collected and air dried; 14.5 g, mp 151–152°, $[\alpha]^{23}\mathrm{D}\ -66.0 \pm 0.39°$ (*c* 4.57, methanol). This material was recrystallized from 200 ml of absolute ethanol to give 7.93 g of salt; mp 155–156°, $[\alpha]^{23}\mathrm{D}\ -69.0 \pm 0.62°$ (*c* 4.22, methanol). A second recrystallization gave a slight improvement in melting point (155.5–156.0°) and rotatory magnitude $\{[\alpha]^{27}\mathrm{D}\ -72.4 \pm 1.0°$ (*c* 2.77, methanol)}, but no further improvement in these properties was obtained after four additional recrystallizations. The entire quantity of multiply recrystallized material (4.44 g) was taken up in 30 ml of cold 20% aqueous potassium hydroxide solution and extracted with three 30-ml portions of chloroform. The combined extracts were dried (potassium carbonate) and evaporated under reduced pressure to (−)-*trans*-**amine oxide (17)**; 1.02 g, $[\alpha]^{29}\mathrm{D}\ -0.70 \pm 0.05°$ (*c* 11.2, chloroform).

The filtrate from the initial recrystallization above was evaporated to one-half of its volume and kept in the refrigerator overnight. The white crystalline material (1.56 g) obtained had mp 139–141° and $[\alpha]^{23}\mathrm{D}\ -65 \pm 0.45°$ (*c* 3.88, methanol). Reduction to half-volume of the supernatant obtained from this crystallization followed by cooling of the concentrate in the refrigerator overnight failed to give any additional crystallization. Subsequent evaporation of the remaining ethanol, however, provided 4.33 g of crystalline salt; mp 110–112°, $[\alpha]^{23}\mathrm{D}\ -16.5 \pm 0.72°$ (*c* 2.36, methanol). This material was treated with 30 ml of cold 20% aqueous potassium hydroxide solution, followed by extraction with three 30-ml portions of chloroform. Evaporation of the combined and dried chloroform extracts gave (+)-*trans*-**amine oxide (18)**; 0.42 g, $[\alpha]^{27}\mathrm{D}\ +2.35 \pm 0.28°$ (*c* 5.33, chloroform). Infrared spectra determined from each enantiomeric *trans*-amine oxide and from (±)-*trans*-amine oxide were all superimposable.

Pyrolyses of the Stereoisomeric Amine Oxides. Each pyrolysis was carried out in the heated sample inlet chamber of a gas–liquid partition chromatograph.[24] The pyrolysate was carried out in a helium stream (55 psi, 80 cc/min) onto the column[20] which was maintained at 70°. Repeated runs in each case followed by collection of the peak due to 4-methylcyclohexene provided the olefin in sufficient quantities to corroborate its identity (infrared spectra) and to determine its specific rotation. Pyrolysis data are accumulated in Table II. Calculations of conversion percentages to olefin were based upon actual weights of collected olefin samples and also based upon calibrated area measurements of olefin glpc peaks. In each case, however, the values obtained (Table II) were fairly uncertain because of the hygroscopic character of the amine oxides and the consequent difficulty in knowing the actual weight of a given amine oxide sample during pyrolysis.

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[24] F & M Corporation, Model 500.

Stereochemistry of Deamination of 2-Phenylethylamine

E. I. Snyder[1]

Contribution from the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268. *Received March 14, 1969*

Abstract: Nitrous acid deamination of *erythro*-2-phenylethylamine-1,2-d_2 affords 2-phenylethyl acetate with 52% retention of configuration under conditions where 25–27% label rearrangement occurs with $PhCH_2C^*H_2NH_2$. Deamination of unlabeled amine in CH_3CO_2D results in incorporation of only 0.06 atom of deuterium per molecule. These results are consistent, although not uniquely so, with deamination proceeding *via* three distinct processes, one of which leads to a phenonium ion.

Recently we reported on the relation between the extent of label rearrangement in, and stereochemical course attending, solvolysis of 2-phenylethyl sulfonate esters.[2] In all cases we noted that the per cent retention of configuration in the products was twice the label rearrangement. This result is demanded if a symmetrical phenonium ion is involved and was taken as support for this hypothesis, in contrast to the equilibrating classical ions concept. It seemed important to us to determine the relation between product configuration and label rearrangement in other reactions producing the 2-phenylethyl cation; this paper describes results attending deamination.

In his classic work in the 3-phenyl-2-butyl system, Cram reported[3] on the deamination of the optically active *threo*- and *erythro*-amines. In contrast to the results attending formolysis the deamination products were formed with greatly reduced stereospecificity and considerable hydrogen and methyl group migration. This led Cram to suggest that products were formed, in part, from "hot" carbonium ions whose formation was subject to ground-state conformational control. A considerable fraction of phenonium ions were converted

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[1] Address inquiries to the Midwest Research Institute, Kansas City, Mo. 64110.

[2] R. J. Jablonski and E. I. Snyder, *J. Am. Chem. Soc.*, **91**, 4445 (1969).

[3] (a) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957); (b) D. J. Cram, *ibid.*, **86**, 3767 (1964).

to open ions (a striking contrast to the ion formed solvolytically) and Cram has summarized by saying,[3b] "These results are consistent with the principles of conformational analysis applied to open carbonium ions."

Results

erythro-$PhCHDCHDNH_2$ was prepared by reduction ($LiAlH_4$) of the corresponding azide, which in turn was prepared from *threo*-PhCHDCHDOTs.[2] Deamination in acetic acid under conditions approximating as closely as possible those used in label rearrangement studies[4] afforded a mixture of acetates which was hydrogenolyzed with lithium aluminum hydride. The alcohol mixture was converted to chlorides with triphenylphosphine–carbon tetrachloride. Configurational analysis of the PhCHDCHDCl was performed as described previously[2] utilizing the intensity distributions of the -CHDCl nmr resonances. Since the resonances of $PhCHClCH_3$ (and deuterated counterparts) did not interfere with the -CHDCl signals of the 2 isomer, the chloride mixture did not have to be, and was not, separated. In this way we determined that deamination of *erythro*-$PhCHDCHDNH_2$ afforded 52 ± 3% *erythro*-PhCHDCHDOAc under conditions where 27% label rearrangement occurs.[4]

In a separate experiment $PhCH_2CH_2NH_2$ was deaminated in CH_3CO_2D. 2-Phenylethyl acetate was isolated by vpc and showed 0.06 deuterium atom per molecule.

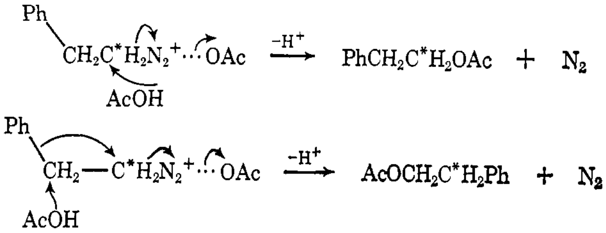
Discussion

The problem of data interpretation must take into account (1) the problem of the mechanism of deamination in general and (2) the problem of the nature of the cation.

White has suggested that nitrous acid deaminations take a mechanistic course similar to that exhibited by decomposition of the related N-nitrosoamides.[5] This process is characterized by ion-pair formation, expulsion of nitrogen, and ion-pair collapse in a time short compared to rotation of the cation. Thus most of the product is formed intramolecularly with considerable net *retention* of configuration. However, this general scheme is based on data obtained from secondary and tertiary alkylamines. It seems inapplicable to the nitrous acid deamination of primary alkylamines, where Streitwieser has previously noted[6] that butyl acetate is formed with 69% net *inversion* of configuration. Furthermore, decomposition of primary alkyl N-nitrosoamides is known to be mechanistically atypical since both Streitwieser[7] and White[8] have shown that diazoalkanes are important intermediaries. On this basis it seems reasonable to us that most, if not all, primary alkyl substitution product is formed by a combination of direct displacement on the diazonium ion, $RCH_2N_2^+$, and reaction of the intermediate diazoalkane with acidic solvents.[9]

Our observation for 2-phenylethylamine deamination that about 50% of 2-phenylethyl acetate is formed with *retention* of configuration contrasts strongly with the dominant inversion which is probably characteristic of "normal" primary alkylamines. This seems, to us, to be *prima facie* evidence for atypical structural features at some point along the deamination reaction coordinate of the title compound. Diazoalkane formation cannot account for the observed extent of retention, since deamination in DOAc gives little $PhCH_2CHDOAc$.

We must now address ourselves to the question of extensive label rearrangement accompanying deamination of 2-phenylethylamine. If deamination of the latter occurs by a process which we consider typical for that of primary amines, *viz.*, backside solvent displacement on a diazonium ion pair, then rearrangement could arise from the following competing processes. However, it is not at all obvious what driving force would permit the second displacement to compete, since the products are structurally (and energetically) degenerate. Furthermore, this process predicts roughly 70% over-all inversion in deamination of $PhCHDCHDNH_2$, and is therefore incompatible with experimental observation.



Another possible mode of label rearrangement is that of rapid equilibration of open, classical cations, $PhCH_2C^*H_2^+ \rightleftarrows {}^+CH_2C^*H_2Ph$. However, Friedman recently has suggested[10] that for primary aliphatic amines ". . . carbonium ions are not formed by unimolecular fission of the corresponding diazonium ion." Insofar as this statement is valid it precludes equilibrating primary cations as the origin of label rearrangement and demands the presence of a different kind of cation.

Our data seem to be in complete accord with the reactions shown in Scheme I, although others can be formulated. The 25–27% label rearrangement means 50–54% of the reaction occurs by path 1; incorporation of 0.06 deuterium atom per molecule when the reaction is run in DOAc means 6% occurs by path 3; the remaining 40–44% of reaction occurs by path 2. Assuming complete retention *via* (1), complete inversion by (2), and equal amounts of inversion and retention in (3) lead to the prediction that product should be formed with 53–57% retention, 43–47% inversion. The observation of 52% retention agrees fairly well with the predicted value. Note the parallel between concurrent paths in solvolysis and deamination. The solvolysis reaction occurs in part *via* direct ionization to the phenonium ion, analogous to path 1 in deamination, and in part *via* a backside solvent displacement, analogous to path 2 of deamination.

The validity of this scheme is subject to additional experimental verification by measuring the stereochemistry at *each* side-chain carbon atom independently.

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(4) J. L. Coke, *J. Am. Chem. Soc.*, **89**, 135 (1967); J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953).

(5) E. H. White and D. J. Woodcock in "Chemistry of the Amino Group," S. Patai, Ed., Interscience Publishers, N. Y., 1968, Chapter 8, especially p 462 ff.

(6) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).

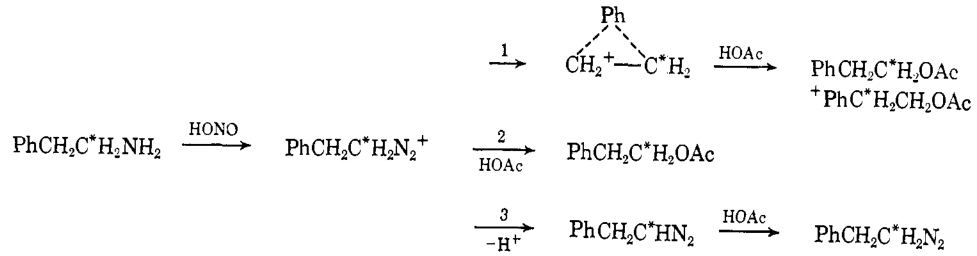
(7) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957).

(8) E. H. White and C. Aufdermarsh, Jr., *ibid.*, **83**, 1174 (1961).

(9) However, it is claimed[6] that diazoalkane formation accounts for no more than 1% of the product in nitrous acid deamination of *n*-$BuNH_2$.

(10) J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Am. Chem. Soc.*, 90, 4468 (1968).

Scheme I



Such an experiment and the predicted results are shown below. Assuming a unit isotope effect for diazoalkane

$$\begin{array}{lll} PhCD_2CHDNH_2 \longrightarrow & PhCD_2CHDOAc \ + & PhCHDCD_2OAc \\ \text{active} & 37\text{–}41\%\ \text{retention} & 100\%\ \text{inversion} \end{array}$$

formation, noting that the product resulting from deuterium loss in HOAc would be the nonanalyzable $PhCD_2CH_2OAc$, and assuming 52% passes through (1), the extent of retention in $PhCD_2CHDOAc$ would be

$$\frac{(0.26 + 0.015)100}{(0.26 + 0.015) + (0.42 + 0.015)} = 39\%$$

Such an experiment was attempted, but unfortunately proved to be unfeasible. Thus, the (*R*)-O-methylmandelate ester of $PhCD_2CH_2OH$ in various solvents shows a sharp singlet for the diastereotopic[11] $-CH_2O-$ protons, the chemical shift difference (at 60 MHz) estimated to be less than 2.5 Hz (see Experimental Section). Similarly, the same alcohol in (+)-1-α-naphthylethylamine remained a sharp singlet.[12]

We note that our explanation is not in accord with some work of Collins,[13] who has shown that in deamination of various amines some phenyl migration occurs with retention at the migration terminus and who can consistently rationalize his results in terms of equilibrating open ions. This observation was used to argue in favor of equilibrating classical ions as opposed to the bridged cation. We also note that insofar as our interpretations are valid it places restrictions on the "hot" carbonium ion concept.[14] It suggests that, in the 2-phenylethyl system at least, such a carbonium ion is "hot" only insofar as it is chemically indiscriminate to nucleophiles, but that the structure of the cation closely resembles that formed in "cooler" solvolysis reactions.[15] The Streitwieser hypothesis[16] still seems capable of accounting for increased rearrangement, etc., accompanying deamination relative to solvolysis.

Experimental Section

erythro-**2-Phenylethyl-1,2-*d*₂ Azide.** To a solution of 10.0 g (0.036 mol) of *threo*-2-phenylethyl-1,2-d_2 tosylate[2] in 60 ml of 95% ethanol at reflux was added 4.6 g (0.071 mol) of NaN_3 in 10 ml of water. Another portion of azide (2.3 g in 5 ml of water) was added after 1 hr and the solution was heated under reflux for 25 hr. The cooled solution was diluted with water and extracted with ether (three 90-ml portions), and the ether solutions were dried ($MgSO_4$). Solvent was removed *in vacuo* and the residue was distilled (1.0–0.5 mm), bp 55–50°, 4.96 g (92%). An undeuterated sample had $n^{25}\mathrm{D}$ 1.5298 (lit.[17] $n^{25}\mathrm{D}$ 1.5308).

erythro-**2-Phenylethylamine-1,2-*d*₂.** A 4.7-g portion of azide was reduced with 0.6 g of lithium aluminum hydride in a total of 50 ml of absolute ether at ambient temperature over 1.5 hr. The mixture was decomposed by the method of Micovic,[18] ether was distilled at reduced pressure, and amine collected at 79–80° (8 mm), 3.12 g (80%).

Deamination. To a stirred solution of 2.34 g of amine described above in 50 ml of glacial acetic acid was added 1.4 g of sodium nitrite in small portions over 0.5 hr. The solution was stirred at ambient temperature for 21 hr, then concentrated *in vacuo*. The residue was poured into sufficient iced 10% sodium hydroxide to make the mixture basic and extracted with ether (three 60-ml portions), and the ether layer was washed with two 35-ml portions of 5% HCl. From the ether solution there was isolated 1.75 g of mixed acetates; the aqueous acid wash afforded 0.55 g of unreacted amine. The mixed acetates were hydrogenolyzed with lithium aluminum hydride and the resulting mixed alcohols were converted to chloride as previously described.[2] Analysis by nmr[2] showed that the 2-phenylethyl-1,2-d_2 chloride was 52 ± 3% *threo*. Since chloride formation involves inversion of the alcohol this means the original acetate was 52 ± 3% *erythro* configuration.

A 0.975-g portion of undeuterated amine was deaminated in 20 ml of CH_3CO_2D (99% isotopic purity) with 0.56 g of sodium nitrite under conditions as described above. After work-up, 2-phenylethyl acetate was collected by glpc (10 ft × 0.25 in. cyanosilicone XF1150, 156°). Analysis for deuterium content[19] showed 0.51 atom % excess deuterium, or 0.06 deuterium per molecule.

2-Phenylethyl (*R*)-O-Methylmandelate. 2-Phenylethanol-1,1-d_2 was prepared by reduction of methyl phenylacetate by $LiAlD_4$. The (*R*)-O-methylmandelate ester was prepared as described by Dale and Mosher,[20] bp 134° (0.2 mm). An undeuterated sample had the correct analysis. *Anal.* Calcd for $C_{17}H_{18}O_2$: C, 75.53; H, 6.71. Found: C, 74.93; H, 6.88. Solutions of the deuterated mandelate in CCl_4, benzene, and pyridine showed only a singlet (upon deuterium decoupling) for the benzylic protons of the alcohol portion. Small couplings to the aromatic protons led to line widths of *ca.* 1.5 Hz in all cases. If the diastereotopic protons were to give an AB pattern, we should have been able to resolve a separa-

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[11] K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, pp 1–38; M. Raban and K. Mislow, *Tetrahedron Letters*, 3961 (1966).

[12] W. H. Pirkle, *et al.*, *J. Am. Chem. Soc.*, **88**, 1837, 4294 (1966); **89**, 5485 (1967); M. Raban and K. Mislow in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 199 ff.

[13] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957); B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961); B. M. Benjamin and C. J. Collins, *ibid.*, **83**, 3662 (1961).

[14] It does not seem that our data are compatible with conformational control from a diazonium ion. Since 18% of the product is 1-phenylethyl acetate and 82% is 2-phenylethyl acetate[4] one could partition the reaction as follows (assuming 26% phenyl migration).

$$\begin{array}{lll} PhCH_2\overset{*}{C}H_2N_2^+ \longrightarrow & Ph\overset{+}{C}H\overset{*}{C}H_3 & 18\% \\ \longrightarrow & {}^+C\overset{*}{H_2}CH_2Ph & 0.26 \times 82 = 21\% \\ \longrightarrow & PhCH_2\overset{*}{C}HN_2 & 0.06 \times 82 = 5\% \\ \xrightarrow{SOH} & PhCH_2\overset{*}{C}H_2OS & 0.68 \times 82 = 56\% \end{array}$$

If hydride and phenyl migration are conformationally controlled then the energy differences between the conformers with Ph, N_2^+ *trans* and *gauche* oriented must be approximately 0.5 kcal/mol⁻¹. This is about the same value found for the conformational energy difference of $PhCH_2CH_2NH_2$ in methanol, where the amino group is believed to be heavily solvated (W. F. Bayne, unpublished results). However, for the above scheme to be compatible with the over-all observed retention of configuration of 2-phenylethyl products requires that the solvent displacement step proceed with 34% retention, 66% inversion. This does not seem reasonable to us.

[15] A similar statement was previously made by Streitwieser.[6]

[16] A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

[17] P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2435 (1951).

[18] V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

[19] J. Nemeth, Urbana, Ill.

[20] J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, **90**, 3732 (1968).

tion of 1.5 Hz between the central lines. Assuming a typical geminal coupling constant of *ca.* 12 Hz, this means $\delta_{AB} \sim 6$ Hz for the benzylic protons in the solvents studied.

2-Phenylethanol-2,2-d_2 was prepared as described[21] and converted into the (*R*)-O-methylmandelate ester. Deuterium-decoupled spectra in pyridine and carbon tetrachloride showed only a singlet for the $-CH_2O$ protons, with half-width of *ca.* 0.6 Hz; the line width in benzene was 1.0 Hz. Assuming natural line widths of 0.4 Hz (appropriate to our spectrometer) the observed line width of 0.6 Hz implies that the central lines of the AB pattern are separated by less than 0.2 Hz. With $J_{AB} = 12$ Hz this means $\delta_{AB} \leqslant 2.2$ Hz. Spectra of the alcohol itself in (+)-α-naphthylamine also showed a sharp singlet of line width 0.7 Hz.

Acknowledgment. This work was supported by National Science Foundation Grant GP-7939. Acknowledgment is made to the donors of the Petroleum Research Fund for partial support of this research.

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[21] W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).

Electron Spin Resonance Studies of Nitronylnitroxide Radicals with Asymmetric Centers[1]

Robert W. Kreilick,[2a] J. Becher,[2b] and Edwin F. Ullman[2c]

Contribution from the Department of Chemistry, University of Rochester,
Rochester, New York 14627, and Synvar Research Institute,
Palo Alto California 94304. Received March 24, 1969

Abstract: We have investigated the esr spectra of two nitronylnitroxide radicals with substituents containing asymmetric centers. The asymmetric center is bonded to a methylene group adjacent to the heterocyclic ring. The methylene protons are magnetically nonequivalent and exhibit different hyperfine coupling constants. Some of the peaks in the esr spectra are observed to broaden with decreasing temperature. The temperature dependence of the spectra is explained by a model involving hindered interconversion of conformers.

Investigations of π-electron organic radicals with aliphatic substituents have produced information about the mechanism of coupling to the aliphatic protons.[3] Couplings to the first group of protons on the aliphatic chain have been shown to depend on the twist angle between the 2p orbital on the unsaturated carbon and the plane defined by the two carbon atoms and the hydrogen. The empirical relation which has been used to relate the coupling constant (a_i), the twist angle (θ), and the spin density at the unsaturated carbon (ρ_2) is given by

$$a_i = [B_0 + B\cos^2\theta]\rho_2 \qquad (1)$$

B_0 and B are constants with values estimated to be +3 and +45 G.

Rotation about the carbon–carbon single bond is normally rapid at room temperature and the observed spectrum is a time average of the various conformations available for a given molecule. If one considers a methylene group bonded to the unsaturated carbon, one will observe the normal three-line spectrum from coupling to two equivalent hydrogens. The magnitude of the coupling constant will depend on the values of the angles in the various conformations which are averaged by rotation. If rotation is slow one may observe the spectrum from a given conformation in which the twist angles for the two protons and their respective coupling constants are different. At intermediate rates of rotation, the inner lines in this four-line spectrum may be broadened.[4] This line broadening results from partial time averaging of the energy levels responsible for these transitions.

We have investigated the nmr and esr spectra of the nitronylnitroxide radicals shown in Figure 1. The asymmetric center bonded to the α-carbon atom makes the two α-hydrogens geometrically nonequivalent. These two hydrogens may therefore have different average twist angles in the various conformations. Rotation about the C_2–C_α bond will not interchange the two sets of twist angles and the protons will be nonequivalent. In the limit of rapid conformational interconversion, the coupling to the two nuclei will result from a time average of the different sets of twist angles.

We have examined the esr spectra of these radicals in toluene and in aqueous solutions of different pH. In most cases different couplings were observed from the two α-methylene hydrogens. Variable temperature studies conducted with toluene as the solvent showed a broadening of some of the lines with decreasing temperature.

Experimental Section

The nmr spectra were taken on a JEOLCO 4H-100 nmr spectrometer equipped with a 35-Hz broad line unit. Esr spectra were taken on a JEOLCO 3BSX esr spectrometer.

2-(2′-Phenylpropyl)-1,3-dioxy-4,4,5,5-tetramethyldihydroimidazole (1). 3-Phenylbutyraldehyde[5] (1.0 g, 6.75 mmole) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane[6] (1.0 g, 6.75 mmole) in

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[1] Synvar Research Institute Contribution No. 8: Studies of Stable Free Radicals. V.

[2] (a) University of Rochester; (b) Synvar Postdoctoral Fellow, 1968–1969; (c) Synvar Research Institute.

[3] F. Yamauchi and R. W. Kreilick, *J. Amer. Chem. Soc.*, **91**, 3429 (1969); E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962); C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960).

[4] G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6636 (1967); J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1156 (1962).

[5] J. V. Braun, A. Grabowski, and G. Kirschbaum, *Ber.*, **46**, 1266 (1913).

[6] M. Lamchen and T. W. Mittag, *J. Chem. Soc., C*, 2300 (1966).