73–75° (740 mm)], semicarbazone mp 190° (lit.[9] mp 191°) by the method of Brown and Tsukamoto.[5] The radiochemical purity of **3** is adequately demonstrated by the agreement in the radioactivity values for **3** and **4** and by the excellent activity balances in the degradation products of **3** and **4** as shown in Tables I and II.

Rearrangement of Trimethylacetaldehyde-1-^{14}C and Treatment of 3-Methyl-2-butanone-2-^{14}C (4) with SSPA.—Preparation of the SSPA catalyst and the general experimental procedure have been described previously.[2] A column temperature of 230° was used, and, after one pass of 10 ml of **3** over the catalyst, the 8.7 ml of liquid recovered was shown by glpc and nmr analysis to be free of **3** and to consist entirely of 3-methyl-2-butanone, semicarbazone mp 113° (lit.[10] mp 114°). A 32-ml sample of **3** and the products from its rearrangement were passed repeatedly over the SSPA catalyst at 230°. Samples of the material recovered from passes one, three, six, and nine (Table II) were subjected to glpc and nmr analysis, and were degraded to check for oxygen-function rearrangement of the 3-methyl-2-butanone produced in the first pass. Small amounts of impurities were detected in the later fractions, but these were removed in the work-up and degradation procedures.

Degradation of 3-Methyl-2-butanone-2-^{14}C (4).—Oxidation of **4** to isopropyl acetate and derivative preparation from the ester were carried out as described previously[4,7] except that the more stable, commercially available *m*-chloroperbenzoic acid was used instead of perbenzoic acid. The isopropyl acetate was purified by distillation, bp 88° (740 mm) (lit.[11] bp 91°), and identified by glpc and nmr comparison with an authentic sample. A careful search (glpc analysis) was made for the isomeric ester, methyl isobutyrate, but none was found. Acetanilide, mp 113.5° (lit.[12] mp 114°), and isopropyl 3,5-dinitrobenzoate, mp 122°, (lit.[13] mp 122°), were obtained from the degradation.

Radioactivity Measurements.—The semicarbazones of **3** and **4** and the acetanilide and isopropyl 3,5-dinitrobenzoate derivatives of the degradation products of **4** were assayed for carbon-14 content using a Beckman LS100 liquid scintillation counter, and the external standard ratio method.[14] The results of the activity determinations are given in Tables I and II. The indicated errors are average deviations of three or more measurements of the same sample.

Registry No.—**3**, 24454-13-5; **4**, 24454-14-6.

(9) S. I. Heilbron, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, p 1214.

(10) Reference 9, p 2144.

(11) R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 302.

(12) Reference 11, p 276.

(13) Reference 11, p 280.

(14) For full details of this procedure, see B. W. Palmer, Ph.D. Dissertation, University of Arkansas, Fayetteville, Ark., 1970.

Reaction of 2-(Δ^3-Cyclopentenyl)ethyl Bromide with Tri-*n*-butyltin Hydride. Cyclization to Norbornane[1]

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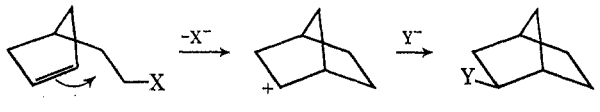
Received January 28, 1970

The reduction of 2-(Δ^3-cyclopentenyl)ethyl bromide (**1**) with tri-*n*-butyltin hydride proceeds with some cyclization to norbornane (**3**). At 130° with dilute hydride the cyclization is appreciable. The cyclization process is discussed in terms of purportedly delocalized intermediates in the analogous cationic process. The conclusion is reached that successful cyclization of 2-(Δ^3-cyclopentenyl)ethyl substrates does not necessarily indicate delocalized *intermediates*. Rather, a favorable geometry in the *transition state* for both cationic and radical (but not the anionic) processes rationalizes the data.

The so-called "π route" (1) to the 2-norbornyl and related cations is well documented.[2] The ring closure



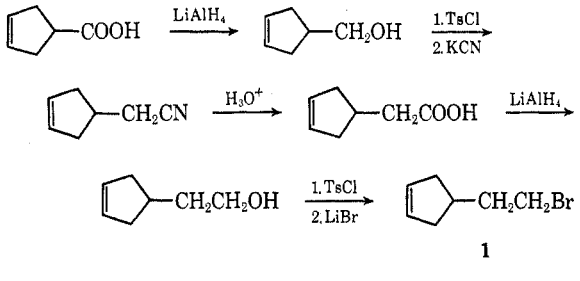
(1)

observed in spite of the considerable steric strain involved (estimated[3] at 9–19 kcal mol^{-1}) has been taken[2b] as evidence for the special stability associated with the 2-norbornyl cation, a stability commonly attributed to its supposed nonclassical nature.

Although ring closure of carbon radicals is likewise well documented,[4] we have found no such study extant comparable to eq 1. In line with our interest in possible nonclassical radicals,[5] we studied the 2-(Δ^3-cyclopentenyl) ethyl radical (**1**·) to seek ring-closed products.

Results and Discussion

2-(Δ^3-Cyclopentenyl)ethyl bromide (**1**) was prepared from the corresponding tosylate by treatment with lithium bromide in dry acetone (eq 2). The synthetic



(2)

sequence proceeded from 3-cyclopentene-1-carboxylic acid and utilized known procedures (see Experimental Section). Bromide **1** so prepared was characterized by

(1) Taken from the M.S. Thesis of S. N. M., Loyola University of Chicago, 1969.

(2) (a) R. G. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (d) H. L. Goering and W. D. Closson, *ibid.*, **83**, 3511 (1961); (e) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

(3) Bartlett and Bank[2b] give the strain energy of the norbornyl ring as "about 19" kcal mol^{-1} and quote a privately communicated estimate from H. J. Dauben, Jr., as 9.49 kcal mol^{-1}. From heat of combustion data, 18.5 kcal mol^{-1} appears most reliable: A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(4) For recent references, *cf.* (a) D. L. Struble, A. L. J. Beckwith, and G. E. Green, *Tetrahedron Lett.*, 3701 (1968); (b) M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, **4**, 1603 (1968).

(5) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962); J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967).

TABLE I

REACTION OF 1 WITH TRI-n-BUTYLTIN HYDRIDE[a]

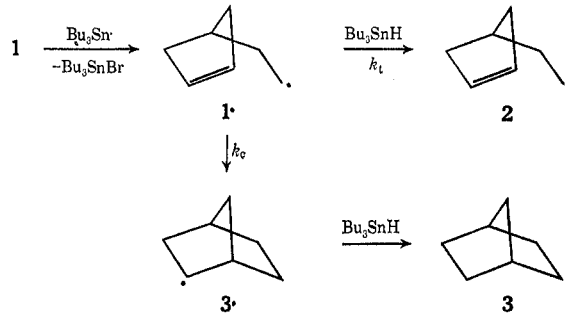
Bu_3SnH, M	Temp, °C	Product composition[b,c] 4-Ethylcyclopentene (2)	Norbornane (3)
0.100	93[d]	93	7
0.050	93	86	14
0.025	93	80	20
0.100	130[e]	82	18
0.050	130	75	25
0.025	130	59	41

[a] Bromide 1 was in threefold excess in all runs. [b] Only traces at most of norbornane were formed at 40° (AIBN initiated) at the three concentrations of Bu_3SnH used. [c] The conversions allowed were small (*ca.* 10–20%) so as to simplify the kinetics (see Text) and to prevent loss of 2 through addition of Bu_3SnH. Several runs were made at each temperature and the percentages are ± 1%. [d] AIBN initiated. [e] Di-*t*-butyl peroxide initiated.

combustion analysis and consonant spectra.[6] To produce 1·, we chose the excellent process developed by Kuivila, *viz.*, reduction with tri-*n*-butyltin hydride.[7]

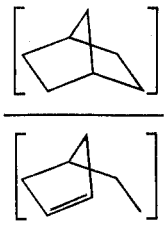
The reduction of 1 was patterned after the study by Walling, *et al.*,[8] of 6-bromo-1-hexene. The results are gathered in the Table I.

Clearly, the "π route" to ring closure occurs in the radical case also.[9] The most economical[10] pathway from 1 to products is given in eq 3. With the low



(3)

conversions allowed in this work, one may consider that $[Bu_3SnH] \cong$ constant. Following an approach used in similar situations,[11] one may then derive eq 4.

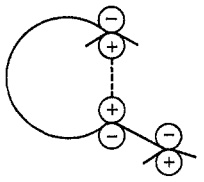


$$= k_c/k_t \cdot \frac{1}{[Bu_3SnH]} \quad (4)$$

From the data in the Table, $k_c/k_t \cong 19 \times 10^{-3}$ at 130°, whereas at 93° this ratio is understandably smaller, 7.3×10^{-3}. An Arrhenius treatment of these ratios indicates that the cyclization of 1· to 3· has an energy barrier *ca.* 7.6 kcal mol^{-1} above that for the transfer process leading to 2. Carlsson and Ingold[12] have found rate constants of 10^5–10^6 M^{-1} sec^{-1} for chain transfer with organotin hydrides at 25° (a calculated energy barrier of 6.8–8.2 kcal mol^{-1}); so the barrier involved in the cyclization of 1· to 3· is *ca.* 14–16 kcal mol^{-1}. While we have no direct evidence on the overall enthalpy change associated with this ring closure, we judge it to be modestly exothermic. An approximate calculation[13] gave $\Delta H \cong -9$ kcal mol^{-1}.

Such a cyclization in spite of the strain involved might be viewed as evidence for unusual stability in 3·, as has been the claim for the analogous cationic process.[2b] No available evidence supports this view, however. Indeed, the consensus is that 3· is a classical radical devoid of extraordinary stabilization *via* 1, 6-σ or other electronic delocalization.[14] We therefore conclude that cyclization of 2-(Δ^3-cyclopentenyl)ethyl substrates to norbornyl products does not *per se* require nonclassicality in the cyclized intermediate.[15]

An explanation for the cyclization centers on the mechanism proposed by Struble, *et al.*,[4] namely, an interaction of the radical center with the π^* orbital of the double bond along a line vertical with one of the olefinic carbon atoms (5). Such a vertical bond-forming path



(5)

helps to explain the curious fact[4] that such cyclizations preferentially form five-membered rather than the thermodynamically preferred six-membered ring products even at the expense of a primary radical intermediate. In the case of 1· such a path (6) could involve a transition state (i or i′ equally) utilizing vertical bond formation *or* possibly the symmetric one (ii) also shown which does not. Interestingly, the analogous cyclization of the 2-(Δ^3-cyclopentenyl)ethyl anion does not occur.[6] Simple molecular orbital calculations[16] indicate that a tricentric transition state involving two or three electrons is favored when triangular (as would be ii). With

(6) E. A. Hill, R. J. Thiessen, A. Doughty, and R. Miller, *J. Org. Chem.*, **34**, 3681 (1969), reported this without analysis. Their sample was prepared from the corresponding alcohol and phosphorus tribromide in pyridine and contained some impurities, among them norbornyl bromide (~5%). Our material showed no contamination (glpc and spectra). Otherwise their reported properties and spectra for 1 agree with ours (see Experimental Section).

(7) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Amer. Chem. Soc.*, **84**, 3584 (1962); L. W. Menapace and H. G. Kuivila, *ibid.*, **86**, 3047 (1964); H. G. Kuivila, *Accounts Chem. Res.*, **1**, 1299 (1968).

(8) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 536 (1966).

(9) An *ionic* cyclization of 1 *via* catalysis by tri-*n*-butyltin bromide is improbable (it did not occur at 40°). Indeed, such a complication has been sought and found absent in a sensitive substrate system by Kuivila.[7]

(10) A "concerted cyclization" of 1 directly to 3 has not been included. Though Walling, *et al.*,[8] suggested such a step, Struble, *et al*,[4] found it to be absent in work somewhat related to the present.

(11) F. H. Seubold, Jr., *J. Amer. Chem. Soc.*, **75**, 2532 (1953).

(12) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 1055 (1968). We used a frequency factor of 10^{11} M^{-1} sec^{-1} to calculate the energy of activation, E_{act}.

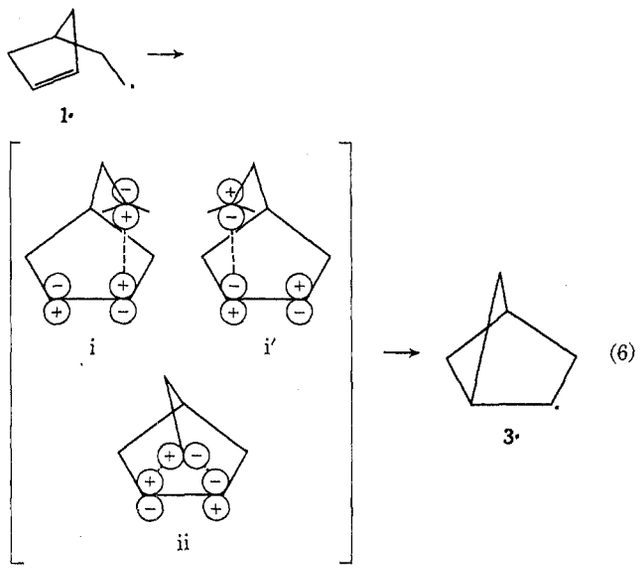
(13) Modeled after the calculation of Hill, *et al.*, for the anionic case.[6] However, the radical cyclization involves formation of a 2° radical, estimated as *ca.* 3.5 kcal mol^{-1} *more* stable than a 1° radical; so instead of $\Delta H = -2.8$ kcal mol^{-1} as in the carbanion,[6] we obtain a value of -8.8 kcal mol^{-1} for the radical. Otherwise, the treatment is the same.

(14) *Cf.* D. I. Davies and S. J. Cristol, "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Elek-Academic Press, London, 1965, Chapter 5.

(15) It should be mentioned that radicals do not always cyclize. Certain strained radicals undergo ring opening [J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966)], or fail to close [N. O. Brace, *ibid.*, **32**, 2711 (1967)].

(16) *Cf.* W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 266–267 and references therein.

four electrons, a linear transition state is favored. One may view the *cationic* and *radical* cyclization of 2-(Δ^3-



(6)

cyclopentenyl)ethyl substrates as examples of the first cases, while the absence of cyclization in the *anionic* instance illustrates the last, as a linear arrangement of the three centers involved is sterically impossible.

Experimental Section

Melting and boiling points are uncorrected. Combustion analyses were performed by the microanalytical laboratories of the Universal Oil Products Co., Des Plaines, Ill. Gas–liquid partition chromatography (glpc) was carried out on F & M Model 720 and Varian Autoprep A-700 instruments. Infrared, nmr and mass spectra were determined on Beckman IR-5A, Varian A-60A and Consolidated Engineering Type 21-103C instruments.

3-Cyclopentene-1-carboxylic Acid.—The acid was prepared from diethyl 2-vinylcyclopropane-1,1-dicarboxylate by the method of Schmid and Wolkoff:[17] bp 75–77° (2.2 mm) [lit.[18] bp 83–85° (2 mm)]; δ^{neat} 12.13 s (COOH), 5.64 s (–CH=CH–), 3.1 m (>CH–), 2.7 distorted d ($-CH_2-$); λ^{neat} 3.0–4.2, 5.9 (COOH), 6.2, 14.5 (–CH=CH–).

Δ^3-Cyclopentenylcarbinol.—The above acid was reduced to the oily carbinol with lithium aluminum hydride[19] in 95% crude yield: δ^{neat} 5.61 s (–CH=CH–), 5.13 t (–OH, slow exchange), 3.44 m ($-CH_2OH$), 2.2–2.0 m (other H's); λ^{neat} 3.0, 9.3, 9.6 ($-CH_2OH$), 3.3, 6.2, 14.9 (–CH=CH–). The crude carbinol was converted to the **tosylate** in the usual way with tosyl chloride in pyridine: 90%; mp 30–31.5°; λ^{neat} 7.35, 8.4, 8.5 ($-OSO_2-$).

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.70; H, 6.36.

Δ^3-Cyclopentenylacetonitrile.—The tosylate above (107 g) was refluxed for 16 hr in 90% aqueous ethanol with potassium cyanide (53.6 g). The material was poured into water and extracted with ether. Upon processing the ether extracts, the nitrile was obtained as a sweet-smelling oil: 38.1 g, 86%; bp 91–93° (30 mm); $n^{20}D$ 1.4988; d^{20}_4 0.9453; δ^{neat} 5.65 s (–CH=CH–), 2.8–1.7 m (all other H's); λ^{neat} 4.45 (CN).

Anal. Calcd for C_7H_9N: C, 78.46; H, 8.46. Found: C, 78.40; H, 8.53.

Δ^3-Cyclopentenylacetic Acid.—The nitrile was hydrolyzed to this acid as described for a related case[2a] with alcoholic potassium hydroxide. The crude acid was used directly in the next step. Acid-catalyzed alcoholysis of the nitrile to the ethyl ester caused partial isomerization of the Δ^3 double bond to the Δ^2 position and is not recommended.

2-(Δ^3-Cyclopentenyl)ethanol.—Reduction of the above acid to the alcohol was achieved with lithium aluminum hydride in the usual way: 80%; bp 85–87° (15 mm); δ^{neat} 5.62 s (–CH=CH–), 4.9 s (–OH), 3.58 t ($-CH_2CH_2OH$), 2.4–1.7 m (other H's); λ^{neat} 3.0, 9.4 ($-CH_2OH$), 3.3, 6.2, 14.5 (–CH=CH–); lit.[2c] bp 82–85° (15 mm). The **tosylate** was obtained from the alcohol, tosyl chloride, and pyridine as a crude oil. Analysis by nmr indicated a purity of 89%, the remainder being pyridine. By this method Bartlett, *et al.*, obtained a crude tosylate of 88.7% purity.[2c]

2-(Δ^3-Cyclopentenyl)ethyl Bromide (1).—Dry acetone was distilled from potassium permanganate and potassium carbonate. The above tosylate (38.3 g, 0.144 mol) and lithium bromide (36 g) were refluxed in this acetone (1400 ml) protected from moisture. Magnetic stirring prevented serious bumping. The acetone was removed on a rotary evaporator and the residual oil was taken up in ether. The ether material was washed well with water and brine and dried. Distillation afforded **1** as a colorless oil that was best stored over anhydrous potassium carbonate: 16.8 g, 67%; bp 71–72° (15 mm); $n^{20}D$ 1.4988; d^{20}_4 1.3066; δ^{neat} 5.63 s (–CH=CH–), 3.30 t ($-CH_2CH_2Br$), 2.7–1.7 m (other H's); λ^{neat} 3.3, 3.4, 6.2, 6.9, 7.4, 7.9, 8.2, 14.5; lit.[6] for less pure material, bp 68–70° (15 mm), $n^{23}D$ 1.4967, essentially same spectra. Analysis by glpc, ir, and nmr indicated no *exo*-2-norbornyl bromide in our sample.

Anal. Calcd for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 47.91; H, 6.44.

4-Ethylcyclopentene (2).—2-(Δ^3-Cyclopentenyl)ethyl tosylate was reduced to **2** with lithium aluminum hydride in ether under reflux for 2 days. The hydrocarbon was isolated by preparative glpc using 15% Carbowax 20M on Chromosorb A, 5 ft × $^3/_8$ in, 120° (rearrangement occurred >150°): δ^{neat} 5.58 s (–CH=CH–), 2.2 m (other ring H's), 1.4 broad q further split ($-CH_2CH_3$), 0.9 distorted t ($-CH_2CH_3$, the spectrum illustrates virtual coupling); λ^{neat} 3.26, 3.51, 6.2, 6.85, 7.25, 10.75, 14.5, *inter alia* (identical with that published[20]).

Norbornane (3).—Norbornadiene (freshly distilled) was hydrogenated over palladium on charcoal at 50 psig to produce **3**. The nmr spectrum was free from olefinic contamination and the mass spectrum agreed with a published spectrum.[21]

Reactions of 1 with Tri-*n*-butyltin Hydride.—Tri-*n*-butyltin hydride [BTH, bp 73–75° (1 mm)] was prepared as reported.[22] Azobisisobutyronitrile (AIBN) was recrystallized from methanol, mp 100–102°. Di-*t*-butyl peroxide (DTBP) was freshly distilled, bp 51° (90 mm). Solutions of **1**, BTH, initiator (AIBN or DTBP) were made in benzene in a 30:10:1 ratio in the concentrations given in Table I. The benzene was distilled from sodium spheres. The solutions in ampoules were degassed by four freeze–thaw cycles and sealed. After a heating period, the contents were analyzed by glpc (Apieson L, 50–55°). The reaction at 40° (AIBN used) required 48 hr to show the desired conversion to products (10–20%), while at 93° (AIBN again used) 20 hr was sufficient. The study at 130° (DTBP used) needed only 15 hr. The composition of the product (**2** + **3**, no other products) was determined by glpc using calibration data from known mixtures. A larger scale run at 130° allowed the isolation of **3** as a pure product, identical *via* ir, nmr, and mass spectra and glpc behavior with an authentic sample. Several runs were made at each temperature and concentration. The data at 93 and 130° were closely duplicable (±1%), whereas at 40° the production of **3** was always just in trace amounts. Attempts to determine such small amounts quantitatively were not made.

Registry No.—3-Cyclopentene-1-carboxylic acid, 7686-77-3; Δ^3-cyclopentenylcarbinol, 25125-21-7; Δ^3-

(17) G. H. Schmid and A. W. Wolkoff, *J. Org. Chem.*, **32**, 254 (1967). This method involves, in part, the pyrolytic rearrangement of the cyclopropane diester at 400–425° to Δ^3-cyclopentene-1,1-dicarboxylic ester. We found at 425–460° that the cyclopentene product was accompanied by some diethyl 2-butenylidenemalonate (15%). Details of this aspect of the work are available upon request.

(18) K. C. Murdock and R. B. Angier, *ibid.*, **27**, 2395 (1962).

(19) J. Meinwald, P. G. Gassman, and J. K. Crandall, *ibid.*, **27**, 3366 (1962).

(20) S. Pinchas, J. Shabtai, J. Herling, and E. Gil-Av, *J. Inst. Petrol.*, London, **45**, 311 (1959).

(21) American Petroleum Institute, Project 44, "Mass Spectral Data," Vol V, Serial No. 1466.

(22) H. G. Kuivila and O. F. Beumel, *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

cyclopentenylcarbinol tosylate, 25125-22-8; Δ^3-cyclopentenylacetonitrile, 21860-24-2; 2-(Δ^3-cyclopentenyl)-ethanol, 766-01-8; **1**, 25125-25-1; **2**, 3742-38-9; **3**, 279-23-2; tri-*n*-butyltin hydride, 688-73-3.

Acknowledgment.—We thank the staffs of the microanalytical and spectral laboratories of the Universal Oil Products Co. for their cooperation and technical assistance.

Notes

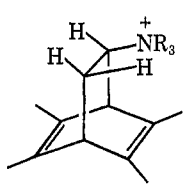
Nitrogen-15 Magnetic Resonance Spectroscopy. X. Angular Dependence of Vicinal ^{15}N–H Coupling Constants in Amino Acids[1,2]

ROBERT L. LICHTER AND JOHN D. ROBERTS

Contribution No. 3987 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

Received February 10, 1970

In contrast to the extensive investigations of the dependence of vicinal proton–proton and proton–fluorine coupling constants on dihedral angle, relatively little is known about the angular dependence of vicinal proton–nitrogen couplings in saturated systems. The principal reasons for this are experimental difficulties associated with the quadrupole-induced relaxation of ^{14}N and the relatively small magnitudes of ^{14}N–H coupling constants. However, Terui, Aono, and Tori[3] have recently demonstrated a geometrical dependence of the vicinal ^{14}N–H coupling in compounds of types **1** and **2** for dihedral angles of 0, 60, and 120°. More



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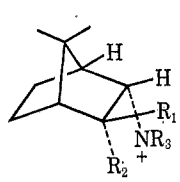

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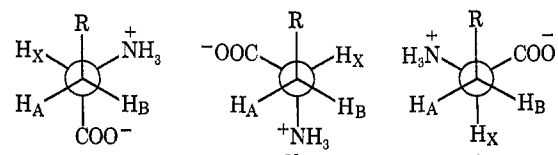
recently, Bothner-By and Cox[4] have reported values of *gauche* and *trans* ^{14}N–H coupling constants derived from aliphatic isocyanides, which agree well with those determined by Terui and coworkers.

In connection with other studies, we have determined the proton magnetic resonance (pmr) chemical shifts and coupling constants for a series of ^{15}N-enriched amino acids. The H–C–C–H couplings in these spectra have been used to estimate the populations of the staggered rotational isomers **3a–3c**[5–9] and these, in conjunction with the N–C–C–H couplings, have been used to estimate the geometrical dependence of the vicinal N–H couplings. These couplings are much easier to measure with ^{15}N because ^{15}N ($I = 1/2$) has no quadrupole moment and a slightly larger magnetogyric ratio than ^{14}N (see Figure 1).



3a **3b** **3c**

If we denote the fractional populations of **3a–c** by p_a, p_b, and p_c, respectively, and *trans* and *gauche* proton–proton coupling constants by J_t^H, J_g^H, respectively, the observed coupling constants are given by eq 1 and 2. With the knowledge that $p_a + p_b + p_c$

$$J_{BX} = p_a J_t^H + (p_b + p_c) J_g^H \quad (1)$$

$$J_{AX} = (p_a + p_c) J_g^H + p_b J_t^H \quad (2)$$

$= 1$, the populations are given by

$$p_a = \frac{J_{BX} - J_g^H}{J_t^H - J_g^H} \quad (3)$$

$$p_b = \frac{J_{AX} - J_g^H}{J_t^H - J_g^H} \quad (4)$$

$$p_c = 1 - p_a - p_b \quad (5)$$

From eq 6 and 7, the *trans* and *gauche* vicinal ^{15}N–H

$$J_{NB} = (p_a + p_b) J_g^N + p_c J_t^N \quad (6)$$

$$J_{NA} = p_a J_t^N + p_c) J_g^N \quad (7)$$

$$J_g^N = \frac{p_c J_{NA} - p_a J_{NB}}{p_c - p_a} \quad (8)$$

$$J_t^N = \frac{J_{NB}(1 - p_a) - J_{NA}(p_a + p_b)}{p_c - p_a} \quad (9)$$

coupling constants are then given by eq 8 and 9. Evaluation of these expressions requires a knowledge of J_t^H and J_g^H. Pachler[5] has suggested 13.6 and 2.6 Hz, respectively, on the basis of a variety of experiments. These values have been discussed and supported by Cavanaugh[7] and will be used in the subsequent discussion.

The experimental data on which the calculations are based are given in Table I. Chemical shifts and coupling constants were assigned on the assumption that

(1) Part IX: W. Bremser, J. I. Kroschwitz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 6189 (1969).

(2) Supported by the Public Health Service, Grant No. 11072, from the Division of General Medical Sciences and by the National Science Foundation.

(3) Y. Terui, K. Aono, and K. Tori, *J. Amer. Chem. Soc.*, **90**, 1069 (1968).

(4) A. A. Bothner-By and R. H. Cox, *J. Phys. Chem.*, **73**, 1830 (1969).

(5) K. G. R. Pachler, *Spectrochim. Acta*, **19**, 2085 (1963); **20**, 581 (1964).

(6) H. Ogura, Y. Arata, and S. Fujiwara, *J. Mol. Spectrosc.*, **23**, 76 (1967).

(7) J. R. Cavanaugh, *J. Amer. Chem. Soc.*, **89**, 1558 (1967); **90**, 4533 (1968).

(8) F. Taddei and L. Pratt, *J. Chem. Soc.*, 1553 (1963).

(9) R. B. Martin and R. Mathur, *J. Amer. Chem. Soc.*, **87**, 1065 (1965).