was identified by its pmr spectrum. The product's vpc retention time was equal to that of an authentic sample of methylferrocene. Pmr analysis indicated that approximately 0.6 atom of deuterium had been incorporated into the molecule. Mass spectral analysis of the m/e 200 and 201 peaks corrected for natural isotopic abundance indicated the incorporation of 0.55 atom of deuterium.

Preparation of 2,5-Dideuterioethylferrocene.—N,N-Dimethylaminoethylferrocene (2.57 g, 10 mmol) along with 25 ml of anhydrous ether were placed in a flame-dried, round-bottom flask equipped with a magnetic stirrer, gas inlet, and reflux condenser. n-Butyllithium (10 ml, 15 mmol) was added under an argon atmosphere and the solution was stirred at room temperature for 2 hr,[8] after which time the reaction mixture was hydrolyzed with 1 ml of deuterium oxide. The resulting mixture was stirred for 30 min, diluted with ether, and dried over anhydrous MgSO₄. The dried ethereal solution was stripped of its solvent, yielding a red oil. The lithiation and deuteration of this oil was repeated twice, yielding 2,5-dideuteriodimethylaminoethylferrocene (2.40 g, 95%). Pmr analysis of the resulting amine indicated that *ca.* 1.8–2.0 atoms of deuterium were incorporated into the molecule.

The above deuterated amine (2.40 g, 9.4 mmol) was treated with excess methyl iodide (2.48 g, 20 mmol) at room temperature. Upon cooling, precipitation of the ammonium salt occurred. Subsequent isolation and air drying afforded 1.85 g (50%) of the methiodide. In a 250-ml flask sodium (2 g, 87 mmol) was dissolved in about 150 ml of ammonia and the blue solution obtained was poured over the methiodide (1.8 g, 4.5 mmol) contained in another 250-ml flask. After about 45 sec ammonium chloride was added followed by water. The reaction mixture was extracted with ether. Evaporation of the ether left a crude oil which was chromatographed on activated alumina. The first band was eluted with petroleum ether and yielded 2,5-dideuterioethylferrocene (0.50 g, 5%), identified by its pmr spectrum and by comparison of its retention time at 187° with that of an authentic sample of ethylferrocene.[12] A second band was eluted with petroleum ether–benzene, and was identified by its ir and pmr spectra as 2,5-dideuteriovinylferrocene (0.223 g, 22%), mp 51–52.5° (lit.[3] mp 51–52°). The pmr spectrum was identical in appearance with that reported by Rausch and Siegel,[3] although chemical shifts varied slightly.

Chloromercuration of *tert*-Butylferrocene.—*tert*-Butylferrocene (1.8 g, 7.4 mmol) was dissolved in ether in a 250-ml flask, to which was added an ether–hexane solution of mercuric acetate (2.5 g, 9.7 mmol). After about 16 hr lithium chloride (0.5 g, 12 mmol) was added in ether solution. The heterogeneous mixture was stripped and chromatographed on alumina III with benzene–ether. A small band of *tert*-butylferrocene was eluted first followed by a larger band which yielded 3,1'-di(chloromercuri)-*tert*-butylferrocene (0.30 g, 8.5%), a brown sold which melted at 163–166°. A portion of this material (0.184 g, 0.26 mmol) was added to about 30 ml of ether in a 100-ml flask. To this heterogeneous mixture was added about 3 ml of *n*-butyllithium solution upon which the solid material dissolved immediately. After the resulting solution was allowed to sit for 1 hr, excess deuterium oxide was added and the resultant mixture was extracted twice with ether. The crude ether extracts were stripped of solvent and purified by vapor phase chromatography, yielding 3,1'-dideuterio-*tert*-butylferrocene (retention time equal to that of an authentic sample of *tert*-butylferrocene[13]). The 60-MHz pmr spectrum of this compound was consistent with the incorporation of approximately 1.6 atoms of deuterium. The 100-MHz and 220-MHz spectra indicated that approximately 1.1 of these deuterium atoms were in the unsubstituted ring, and 0.6 of these were in the 3,4 positions, with essentially no deuterium incorporation in the 2,5 position. Mass spectral analysis of the m/e 242, 243, and 244 peaks corrected for natural isotopic abundance indicated that 70% of the molecules contained two atoms of deuterium, that 13% of the molecules contained one deuterium, and that 17% of the molecules contained no deuterium.

The Conformational Analysis of 1-Butene

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The temperature dependences of two nmr spectral parameters have been utilized in the conformational analysis of *1,1,4,4,4-d₅*-1-butene (1). The three-bond vinyl-allylic coupling constant and the chemical shift of the methylene protons were observed to have a small but real temperature dependence which was correlated with the cis–skew conformational equilibrium of 1. A qualitative estimate of the enthalpy difference between the two conformers was made on the basis of the coupling constant data. It was concluded that the cis conformer is more stable than the skew one by 100 ± 50 cal/mol with $\Delta S = 1.376$ eu.

A wide variety of open-chain organic compounds containing a single bond between tetrahedral and trigonal carbon atoms have been shown to exist as a mixture of rotational conformers.[1b] The majority of these compounds contain one or more heteroatoms and the effect of unsaturation on the conformational equilibrium is not clear. In the case of propene, microwave spectroscopy has confirmed that the most stable conformation is that in which a methyl carbon–hydrogen bond is eclipsed with the carbon–carbon double bond.[2] Various spectroscopic methods (infrared,[3] Raman,[3,4]

nuclear magnetic resonance,[5] and microwave[6]) have been applied to establish the conformational preference of the ethyl group in 1-butene (1). The nmr work of Bothner-By[5a,b] and coworkers suggested that two conformers, the cis (1a) and skew (1b) forms, were present in about equal proportions. Kondo,[6] *et al.*, confirmed the existence of 1a and 1b from a detailed microwave study of 1-butene and estimated 1b to be more stable than 1a by 150 ± 150 cal/mol. Empirical and theoretical estimates of the enthalpy difference for eq 1 are -400 and -690 cal/mol, respectively.[5c,7]

(1) (a) Correspondence concerning this article should be addressed to E. W. G., Center for Applied Research in Environmental Sciences, P.O. Box P, St. Michaels, Md. 21663. (b) G. J. Karabutsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).

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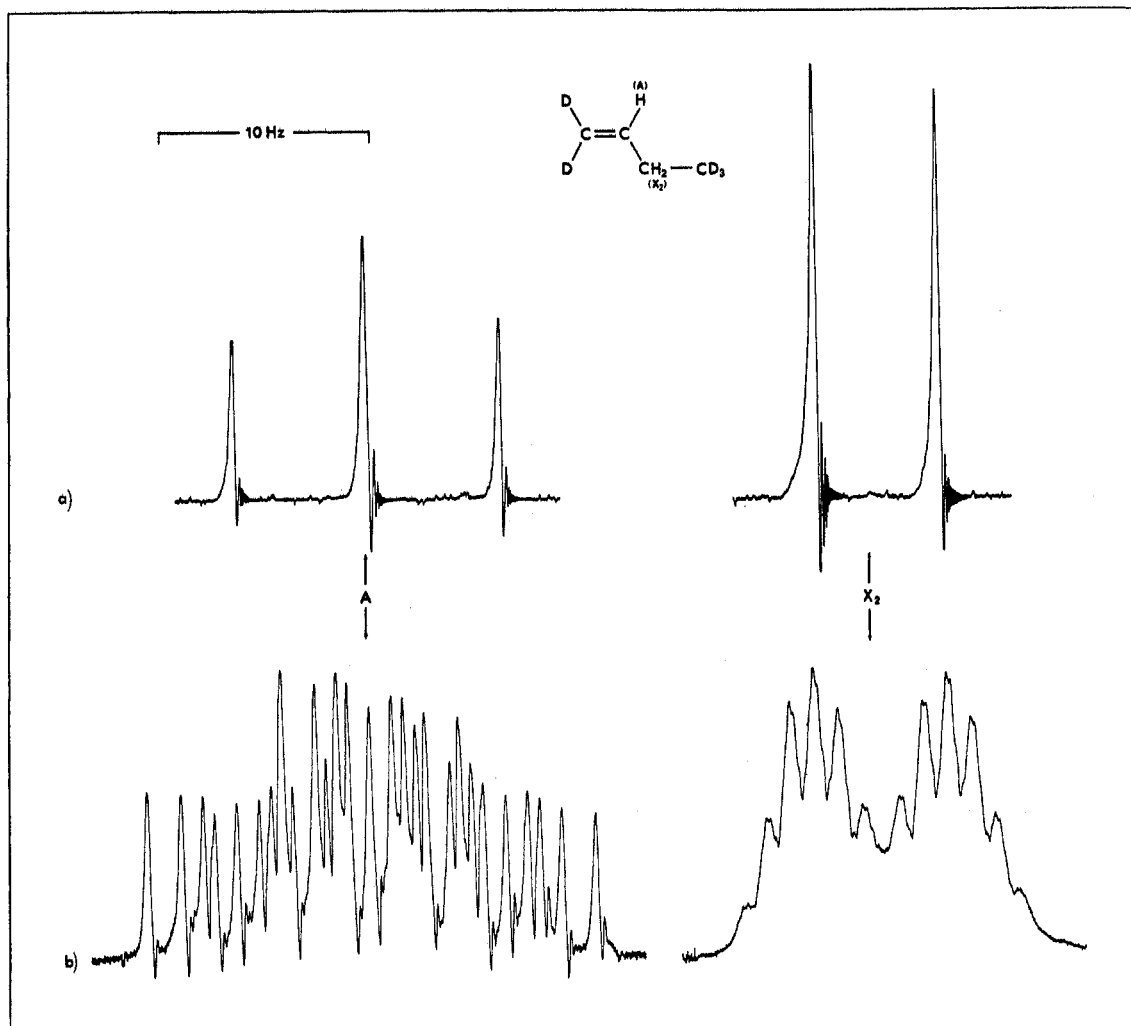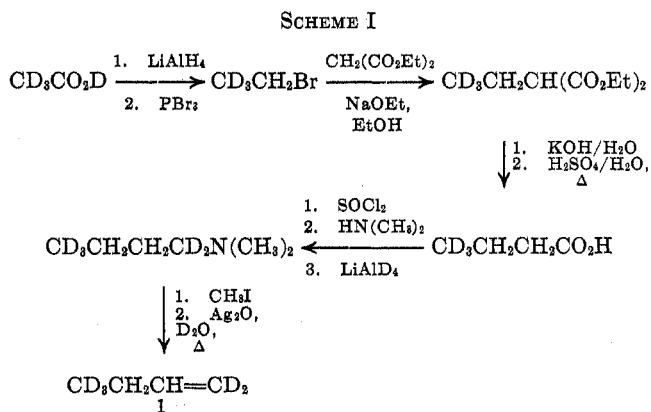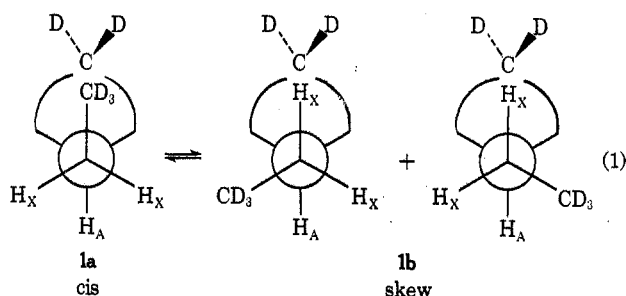
Figure 1.—The (a) deuterium-decoupled and (b) normal nmr spectra of neat 1 recorded at 45°. The vinyl, A, and allylic, X_2, portions in b were recorded at relative spectrum amplitudes of 1.0 and 0.5, respectively.

The present work describes an attempt to obtain another experimental value of the enthalpy difference between **1a** and **1b** utilizing the temperature dependences of nmr spectral parameters.

Results and Discussion

1,1,1,4,4-d5-1-Butene (**1**), prepared according to Scheme I, was used in all variable-temperature nmr experiments. Figure 1 shows typical deuterium-decoupled and normal spectra of neat **1**.

The temperature dependences of the spin–spin coupling constant, J°, and the chemical shift, $\nu_x{}^\circ$, of the methylene protons are compiled in Table I. Instru-

mental difficulties[8] precluded obtaining sufficiently precise measurements of $\nu_A{}^\circ$. Both parameters exhibit a small (0.14 Hz for J° and 0.22 Hz for $\nu_x{}^\circ$) but real decrease in magnitude upon decreasing the temperature from 64 to −78°.

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(8) Phase lock instability at the audiofrequencies necessary to calibrate the spectra precluded obtaining sufficiently precise measurements of the chemical shift of the olefinic proton and reduced the number of potentially observable temperature-dependent parameters from three (ν_A, ν_X, and J_{AX}) to two (ν_A and J_{AX}).

Table I

Observed Temperature Dependences of J° and $\nu_x{}^\circ$ in Neat 1[a]

Temp,[b] °C	J°	$\nu_x{}^\circ$
64	6.257 (0.027)[c]	117.023 (0.032)[c]
61	6.254 (0.016)	117.010 (0.051)
55	6.254 (0.015)	117.029 (0.036)
46	6.263 (0.036)	117.030 (0.045)
39	6.241 (0.018)	117.029 (0.037)
38	6.252 (0.029)	117.061 (0.047)
26	6.249 (0.021)	117.013 (0.042)
21	6.233 (0.023)	117.054 (0.030)
19	6.230 (0.030)	117.035 (0.036)
16	6.226 (0.021)	117.046 (0.035)
12	6.229 (0.022)	117.040 (0.042)
0	6.222 (0.030)	117.037 (0.040)
−1	6.222 (0.027)	117.030 (0.040)
−10	6.220 (0.010)	116.995 (0.043)
−20	6.204 (0.042)	117.005 (0.045)
−29	6.203 (0.036)	116.983 (0.035)
−38	6.180 (0.011)	116.959 (0.023)
−45	6.177 (0.022)	116.981 (0.029)
−52	6.153 (0.023)	116.939 (0.029)
−59	6.145 (0.029)	116.935 (0.028)
−61	6.144 (0.026)	116.910 (0.018)
−68	6.139 (0.023)	116.879 (0.028)
−78	6.112 (0.029)	116.839 (0.030)

[a] J° is given in hertz and $\nu_x{}^\circ$ is given in hertz downfield from hexamethyldisilane (HMDS). [b] Accurate to ±1°. [c] Parenthetical values denote standard deviations.

These data subsequently were used in an attempt to obtain a qualitative estimate of ΔH for eq 1 by solving eq 2 for P_{aj}, P_{bj}, and ΔH using an iterative least-squares approach that has been described in detail elsewhere.[9,10a] In eq 2, P_{aj} and P_{bj} are the jth of l

$$\ln\left(\frac{P_{aj} - P^\circ{}_{ij}}{P^\circ{}_{ij} - P_{bj}}\right) = \frac{-\Delta H}{RT_{ij}} + \frac{\Delta S}{R} \qquad (2)$$

intensive parameters of conformers **1a** and **1b**, respectively, and $P^\circ{}_{ij}$ is the jth of l observed parameters at the ith of k temperatures, T_{ij}.

Whereas there are several criteria for the applicability of eq 2 to equilibrium systems,[10a,b,11] the most critical criterion for conformational equilibria is that P_{aj} and P_{bj} be temperature independent. It is understood that P_{aj} and P_{bj}, in principle, may exhibit temperature dependences that arise from temperature dependences of vibrational state populations.[11a,b] Examples, possibly, of such temperature dependences have been noted for heteroatom-substituted hydrocarbons,[11e,12] but not for simple hydrocarbons. The proton–proton couplings

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in cyclohexane[13a] and in cyclohexene[13b] have been found to be temperature independent within experimental uncertainty over temperature changes of 141 and 102°, respectively.

Because of this impending uncertainty of the applicability of eq 2 to problems concerning conformational equilibria, we have set for ourselves an operational standard for applicability. This standard is that, if solutions of eq 2 using chemical shift and coupling constant temperature dependences separately provide comparable solution values of ΔH at common set values of ΔS, then P_{aj} and P_{bj} may be taken as being temperature independent and the temperature dependence of $P^\circ{}_{ij}$ is considered to be dominated by the changes in conformer populations with temperature. The basis for this standard for applicability of eq 2 presumes that the contribution to the temperature dependences of $P^\circ{}_{ij}$ that arise from effects of vibrational state population changes will be different for nuclear spin couplings than for nuclear resonance frequencies and will weight the solutions of eq 2 for ΔH, P_{aj}, and P_{bj} differently.

This operational standard for the applicability of eq 2 has been met for 11 saturated and unsaturated hydrocarbons[9,10a,13b,14] and we have yet to encounter or learn of a hydrocarbon for which this standard is not realized.

As $|P_{aj} - P_{bj}| \to 0$ or as $\Delta H \to \infty$ or $\Delta H \to 0$, unique solutions of eq 2 for all of the unknowns become increasingly problematical.[10a] This is understandable, because, at the indicated limits, $P^\circ{}_{ij}$ will be temperature independent. Extensive calculations have shown that unique solutions of eq 2 for all unknowns and for ΔH (between 200 and 2000 cal/mol), P_{aj}, and P_{bj} (ΔS held constant) may be expected only when the standard deviations, σ, in $P^\circ{}_{ij}$ are $<0.4|P_{aj} - P_{bj}|$ (10^{-3}) and $<2|P_{aj} - P_{bj}|$ (10^{-3}), respectively.[9a] The average standard deviations in J° and $\nu_x{}^\circ$ are 0.025 and 0.036, respectively. Unique solutions of eq 2 for ΔH, P_{aj}, and P_{bj} would require that $|J_a - J_b|$ and $|\nu_{x,a} - \nu_{x,b}|$ be of the magnitudes 13 and 18 Hz, respectively. As it is unlikely (see later) that $|J_a - J_b| \simeq 13$ Hz, we were disappointed but not surprised that the iterative least-squares processing of J° and $\nu_x{}^\circ$ separately and collectively did not lead to a unique (convergent) solution of eq 2.[10a]

Results from the solution of eq 2 for P_{aj} and P_{bj} holding ΔH constant at values between 50 and 250 cal/mol and ΔS constant at 1.376 eu, and using the temperature dependences of $\nu_x{}^\circ$ and J° separately, are collected in Table II. The statistical fit of the data (see RMS in Table II) is seen to be identical for all values of ΔH between 50 and 250 cal/mol. Clearly, a unique solution of eq 2 does not exist. Figure 2 also graphically illustrates this point. There, it is seen that the calculated temperature dependence of J° (solid line) is identical for $\Delta H = 100$, 150, and 200 cal/mol.

If we make the reasonable assumption, based on our previous experiences[9,10a,13b,14] (see earlier discussion), that the temperature dependence of J° in 1 is dominated by conformer population changes, the sign of

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TABLE II
SOLUTION RESULTS OF EQUATION 2 USING THE TEMPERATURE DEPENDENCES OF $J°$ AND $\nu_z°$ AT FIXED ΔH AND ΔS^a

ΔH^b (fixed)	RMS^c	$J_a{}^d$	$J_b{}^d$	$\nu_{z,a}{}^d$	$\nu_{z,b}{}^d$
50	0.0068	-1.28 ± 0.18	10.33 ± 0.10		
100	0.0068	2.69 ± 0.08	8.34 ± 0.05		
150	0.0068	3.99 ± 0.05	7.68 ± 0.03		
200	0.0068	4.64 ± 0.04	7.36 ± 0.03		
250	0.0068	5.02 ± 0.03	7.17 ± 0.02		
50	0.0250			108.03 ± 0.64	121.93 ± 0.35
150	0.0249			114.34 ± 0.19	118.76 ± 0.13
250	0.0249			115.57 ± 0.10	118.15 ± 0.08

^{a} ΔS fixed at 1.376 eu. ^{b} In cal/mol. ^{c} Standard deviation (in hertz) of the observed and calculated parameters $P_{ij}°$ and $P_{ij}{}^{calcd}$, respectively. ^{d} In hertz. Subscripts a and b denote nmr property parameters calculated for the cis and skew conformers, respectively.
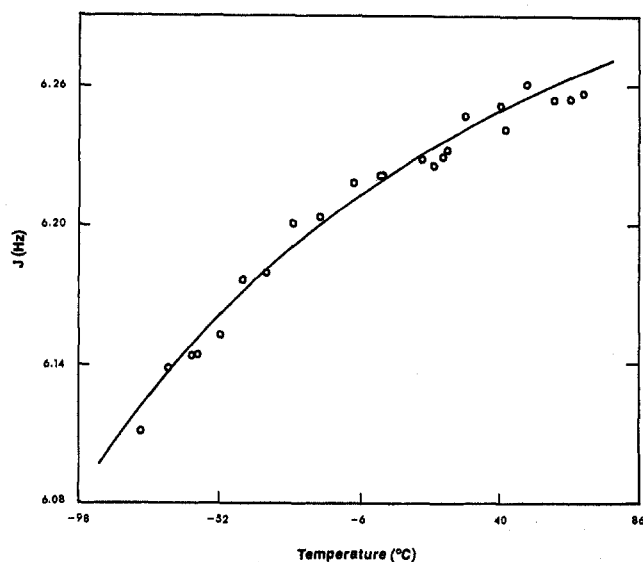

Figure 2.—Observed temperature dependence of $J°$ in neat 1. The solid line through the experimental points is the calculated temperature dependence of $J°$ using the solution parameters J_a and J_b corresponding to ΔH = 100, 150, and 200 cal/mol and ΔS = 1.376 eu.

and an estimate of the magnitude of ΔH may be made. As $J°$ is observed to increase with increasing temperature, the most stable conformer in eq 1 must have the smaller magnitude of J. As J_a in 1a will be smaller than J_b in 1b, 1a is established as being more stable than 1b, and ΔH for eq 1 is positive.

A qualitative estimate of the magnitude of the coupling constant expected between the vinyl and allylic protons in the cis conformer is calculated from semiempirical relationships[15] to be 3.6 Hz. By setting upper and lower limits of 4.0 and 0.0 Hz, respectively, on the allowed values of J_a, and from the data in Table II, the enthalpy change for eq 1 can be estimated to be 100 ± 50 cal/mol.

The positive value of ΔH for eq 1 is at variance with the microwave study by Kondo,[6] et al., which proposes that the methyl–vinyl hydrogen interactions in 1a led to 1b being the most stable conformer, but by only 150 ± 150 cal/mol. A similar result is predicted by Johnson and Malhotra's[16] concept of $A^{(1,3)}$ strain.

From the results reported herein and those reported by Kondo,[6] et al., it can be concluded with some confidence that there is little enthalpy difference between the cis and skew conformers of 1-butene.

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Experimental Section

Diethyl *3,3,3-d₃*-Propane-1,1-dicarboxylate.—This compound was prepared from diethyl malonate (83.0 g, 0.52 mol) and 1-bromo-*2,2,2-d₃*-ethane[17] (55.3 g, 0.49 mol) in the presence of sodium ethoxide.[18] Distillation of the crude product gave 83.0 g of material, bp 176–179° (8–9 mm). The nmr spectrum of the distillate indicated it to be a mixture of diethyl malonate (8–10%) and the desired deuterium-labeled alkylation product (90–92%). The material was used without further purification.

***4,4,4-d₃*-Butyric Acid.**—An 83-g sample of the mixture of diesters obtained above was hydrolyzed and decarboxylated in the usual manner.[19] After the decarboxylation was complete, 100 ml of aqueous liquid was distilled, saturated with sodium chloride, and extracted with 50 ml of ether. A 100-ml portion of water was returned to the distillation flask and a second 100 ml of distillate was collected and extracted with ether. This procedure was repeated until about 1.5 l. of liquid had been distilled. The extracts were combined and the ether was removed by distillation. The crude product was dried by the addition of 100 ml of benzene and distilling the mixture. After 80 ml of distillate had been collected the residual liquid was fractionated at atmospheric pressure to afford 30.0 g (0.33 mol) of *4,4,4-d₃*-butyric acid, bp 163°.

***N,N*-Dimethyl-*4,4,4-d₃*-butyramide.**—A 30-g (0.33 mol) sample of *4,4,4-d₃*-butyric acid was treated with thionyl chloride (50.0 g, 0.42 mol) according to a general procedure.[20] The crude acid chloride, 40.0 g, which was obtained upon distillation (bp 91–102°) of the reaction mixture at atmosphere pressure, was diluted with 200 ml of anhydrous benzene and slowly added to a stirred solution of 45 g (1.0 mol) of anhydrous dimethylamine in 200 ml of dry benzene which was cooled in an ice bath. The crude amide obtained after work-up[21] was fractionated under reduced pressure, giving a 90% yield of *N,N*-dimethyl-*4,4,4-d₃*-butyramide, bp 97–98° (35 mm) [lit.[22] bp 70° (10 mm)], based on the starting carboxylic acid. The nmr spectrum (CCl₄) of the pure product exhibits the following characteristics: τ 8.47 (broad t, $J \cong$ 7.0 Hz, 2 H), 7.79 (t, $J \cong$ 7.0 Hz, 2 H), 7.15 (s, 3 H), and 7.02 (s, 3 H).

***N,N*-Dimethyl-*1,1,4,4,4-d₅-n*-butylamine.**—Lithium aluminum deuteride (6.3 g, 0.15 mol) reduction of the above amide (17.7 g, 0.15 mol) in refluxing ether according to a general method[23] gave 9.54 g (60%) of *N,N*-dimethyl-*1,1,4,4,4-d₅-n*-butylamine, bp 92–93° (lit.[24] bp 94°). No attempt was made to isolate the small amount of amine which codistilled with ether during work-up. Analysis of the ether distillate by glpc indicated that the loss was not substantial (<5%).

***1,1,4,4,4-d₅-n*-Butyltrimethylammonium Iodide.**—To a solution of 5.30 g (0.05 mol) of the deuterium-labeled tertiary amine in 10 ml of absolute methanol was added dropwise 10.65 g (0.075

(17) Lithium aluminum hydride reduction of acetic acid-*d₄* in ether afforded *2,2,2-d₃*-ethanol (50% yield), which was converted to the corresponding alkyl bromide in 66% yield by treatment with phosphorus tribromide at −10°. See V. J. Shiner, *J. Amer. Chem. Soc.* **75**, 2925 (1953).
(18) C. S. Marvel, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 495.
(19) E. B. Vliet, C. S. Marvel, and C. M. Hsueh, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 416.
(20) B. Helferich and W. Schaeffer, "Organic Syntheses," Collect. Vol. I, Wiley New York, N. Y., 1941 p 147.
(21) A. C. Cope and E. Ciganek, *Org. Syn.*, **39**, 19 (1959).
(22) P. G. Gassman and B. L. Fox, *J. Org. Chem.*, **31**, 982 (1966).
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mol) of methyl iodide at such a rate that gentle refluxing was observed. A small amount of the quaternary salt separated during the addition and the remainder was precipitated upon dilution with 50 ml of ethyl acetate and cooling. After being collected and dried at room temperature, the product, mp 229–230° (lit.[24] mp 231–232°), amounted to 11.75 g (94%).

1,1,4,4,4-d₅-1-Butene (1).—A solution of 3.72 g (0.015 mol) of the deuterium-labeled quaternary ammonium iodide in 35 ml of deuterium oxide and 5 ml of methanol-O-d was stirred for 1 hr with freshly precipitated silver oxide. The mixture was rapidly filtered through Celite and lyophilized. The solid material was dissolved in 25 ml of deuterium oxide and the lyophilization procedure was repeated. The viscous, colorless residue was dissolved in 40 ml of deuterium oxide and pyrolyzed according to a known procedure.[24] The olefin was condensed in a trap immersed in liquid nitrogen during the pyrolysis and later allowed to distil into a constricted 5-mm nmr tube containing hexamethyldisilane (HMDS) and immersed in a Dry Ice–acetone slush. The nmr tube was subsequently degassed and sealed at atmospheric pressure at −68°. From a typical run it was possible to obtain two samples of 1 suitable for analysis by nmr spectroscopy.

The isotopic purity of 1 prepared in this manner was 97% in the methyl group and 93% at C-1 as determined by nmr. When the pyrolysis was conducted in water ca. 15% of the terminal olefinic deuteriums were exchanged.

The silver oxide used in the above synthesis was prepared by treatment of a hot (85°) solution of 5.1 g (0.03 mol) of silver nitrate in 51 ml of water with an equally warm solution of 1.2 g of sodium hydroxide in 12 ml of water. The precipitated material was washed by decantation with five 20-ml portions of hot deuterium oxide.

Nmr Spectral Determinations.—All spectra were recorded on a Varian A-60 spectrometer equipped with an NMR Specialities HD-60A heteronuclear spin decoupler, a V-6058A homonuclear decoupler, and a V-6040 temperature controller. Conditions of deuterium decoupling were maintained on phase lock mode of the homonuclear decoupler for all spectral determinations. Spectra were calibrated by interpolation between audio-modulation sidebands of internal hexamethyldisilane (HMDS) produced using a Hewlett-Packard Model 3300A function generator monitored by a Hewlett-Packard Model 3734A frequency counter.

The probe temperatures were measured before and after each experiment by means of a copper–constantan thermocouple inserted into an empty stationary nmr tube positioned in the probe. The temperatures generally agreed within 0.5°. The average of the two temperatures was used as the temperature of

(24) P. A. S. Smith and S. Frank, J. Amer. Chem. Soc., 74, 509 (1952).

the experiment and is believed to be accurate to ±1°. For each experiment, the probe and sample were allowed to thermally equilibrate 4–5 hr before commencing spectral determinations.

Spectra were determined using neat samples containing ca. 15% v/v HMDS as internal standard and prepared as described above. In general, 24 HMDS side-band calibrated spectra were recorded for the allylic protons at each temperature by alternately sweeping up-field and downfield. A FORTRAN IV computer program was written and used to facilitate data refinement. The program calculated the frequency of each observed transition of each spectrum from the center at half-height using the frequencies of the sidebands and the corresponding calibration factor. The calculated frequencies for a given transition were averaged over all spectra and those frequencies whose deviations were greater than or equal to twice the standard deviation were discarded. The calculation was repeated for each transition in the spectrum until all deviations from the average were less than twice the corresponding standard deviations. This procedure led to an average of 18 spectra at each temperature and afforded standard deviations of the transition frequencies of less than 0.06 Hz with the majority in the range 0.02–0.04 Hz.

The deuterium-decoupled nmr spectrum of neat 1 consists of a triplet and a doublet for the vinyl (A) and allylic (X_2) protons, respectively. The frequency difference between transitions composing the doublet was taken as J_{AX} and the chemical shift, ν_x, of the allylic protons was taken as the mean frequency of the doublet transitions. All transitions at each temperature had widths at half-height comparable to that of HMDS (0.3–0.6 Hz).

Phase lock instability at the audiofrequencies necessary to calibrate spectra between 340 and 380 Hz by interpolation resulted in intolerably large (0.08–0.12 Hz) standard deviations in the transition frequencies of the triplet. In normal mode of operation, field fluctuations precluded obtaining optimum deuterium decoupling. Other spectrum calibrated techniques[9] led to an improvement in precision, but not to the degree that the standard deviations in ν_A were less than the change of ν_A over the temperature range adopted. Consequently, ν_A could not be used in the conformational analysis of 1.

Conformational Inversion of 9,10-Dihydro-9,10-o-xylyleneanthracenes[1a]

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2,7-Dimethyl-9,10-dihydro-9,10-o-xylyleneanthracene (2), synthesized from the reaction of 2,7-dimethylanthracene with o-xylylene, was used for a variable-temperature nmr study of the conformational inversion proposed earlier for the parent hydrocarbon (1). The signal for the six methyl hydrogens of 2 remained a sharp singlet in a variety of solvents down to −120°, the lowest attainable temperature. The Diels–Alder adduct (8) from 2,7-dimethylanthracene and benzocyclobutadiene, prepared as a model of 2 "locked" in its preferred conformation, showed two sharp singlets separated by 13.5 Hz for the two methyl groups. Use of this value as a minimum $\Delta\nu_{max}$ for 2 and −120° as a maximum temperature of coalescence of the methyl signals in 2 leads to a ΔG_{max}^* of 7.7 kcal/mol for conformational inversion in 2. This value is compared with values reported for related systems.

Several years ago, Sisido and coworkers[2–4] reported the preparation of 9,10-dihydro-9,10-o-xylylenean-

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(4) K. Sisido, R. Noyori, N. Kozaki, and H. Nozaki, Tetrahedron, 19, 1185 (1963).

thracene (1) from the reaction of anthracene with o-xylylene. They noted that molecular models of the symmetrical conformer 1b can only be constructed with substantial expansion of the tetrahedral angles about the methylene carbon atoms whereas conformers 1a and 1a', although being fully eclipsed, are devoid of angle distortion. This, along with the observation that in the room temperature nmr spectrum of 1