Studies in Magnetic Nonequivalence. The Conformation of Two 1-Substituted 1,2-Dibromoethanes

Maris Buza and Eugene I. Snyder[1]

Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Co., Linden, New Jersey. Received July 8, 1965

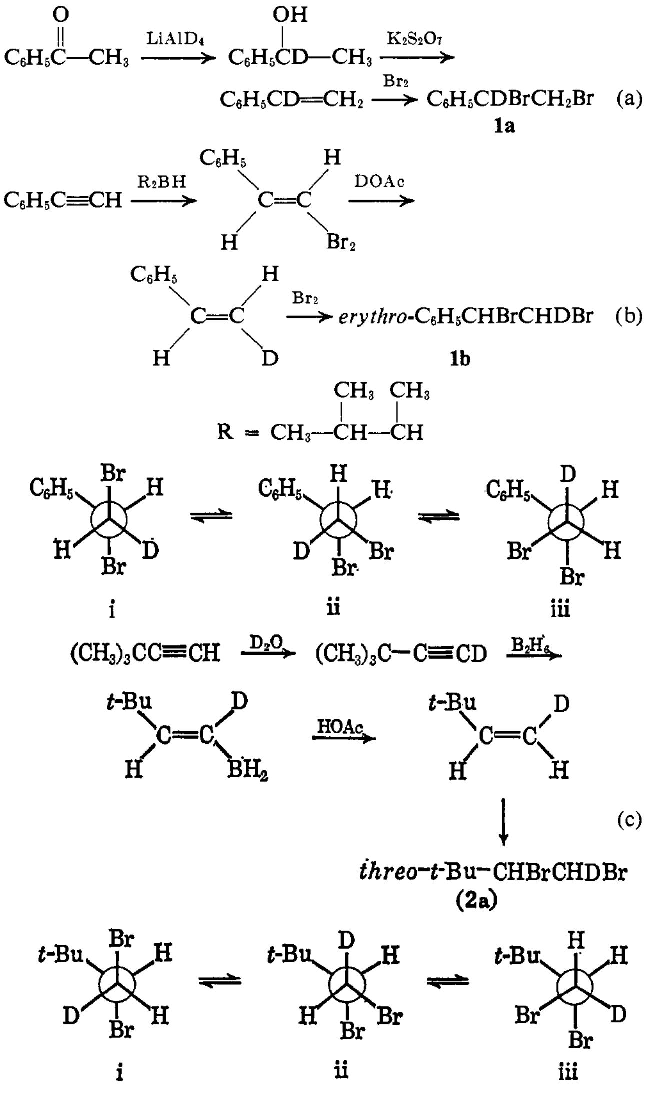
Abstract: Synthesis of *erythro*-$C_6H_5CHBrCHDBr$ and *threo*-$(CH_3)_3CHBrCHDBr$ was accomplished using known reactions of well-defined stereochemistry. Examination of the nmr spectrum of the deuterated compounds coupled with the results of spectral analysis of the undeuterated compounds permits unequivocal identification of the most stable conformer in both cases. For R = C_6H_5 the most stable conformer has *trans* bromines and phenyl *gauche* to one bromine, whereas for R = *t*-butyl the most stable conformer has *gauche* bromines and *t*-butyl *trans* to a bromine. The origins of such behavior are considered.

One of the aims of this series of papers is to develop a method for determining the position of equilibrium among rotational isomers in substituted ethanes. This aim, however, is not an end unto itself, for the ultimate goal is to identify and elaborate upon those factors responsible for energy differences among the conformers. It is apparent that to satisfy this aim not only is it necessary to determine the conformational equilibrium constant, but it is also necessary to identify with reasonable certainty the proper species (*i.e.*, conformer) with a given energy. The forces responsible for determining the energetics of conformer distribution have been known, at least in part, for a reasonable time. Thus, Mizushima pointed out that available data implicate dipole–dipole repulsive forces (*trans*-1,2-dihaloethanes are more stable than *gauche* conformers, with media of higher dielectric favoring an increasing amount of the latter) and steric interaction between vicinal groups as important factors in determining conformer distribution, although the importance of other forces could not be dismissed.[2] Such qualitative notions permit one to make informed guesses regarding relative stability of various conformers, but this is certainly not without its hazards. For example, whereas it has been reported that the *gauche* form is more stable than the *trans* conformer in $ClCH_2CH_2Cl$ (methanol solution),[3a] *n*-C_3H_7Cl,[3b] and *n*-C_3H_7F,[4] it is not obvious immediately that this would be predicted on the basis of the foregoing remarks. On passing to less symmetrical systems, application of simple notions to assignment of conformer stability becomes even more tenuous.

Ideally a study as this one, which purports to treat the problem of conformational equilibrium, should have independent evidence identifying, at the very least, the most stable conformer present. Because such identification becomes increasingly difficult with increasing loss in symmetry, one must temper ideality somewhat with practicality. Of the 1,1,2-trisubstituted ethanes we have studied heretofore we have identified the most stable conformer in only two, $C_6H_5CHBrCH_2Br$ and $(CH_3)_3CCHBrCH_2Br$. Although this represents only a nominal achievement we must, for the moment, rest content with it even if we are not satisfied. This paper describes the synthesis of stereospecifically labeled $C_6H_5CHBrCHDBr$ and $(CH_3)_3CCHBrCHDBr$ and reports their nmr spectra, from which the more stable conformer can be identified unequivocally.

Complete identification of the three side-chain hydrogens in (1,2-dibromoethyl)benzene (**1**) was made by

Chart I



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[1] Author to whom inquiries should be addressed at the University of Connecticut, Storrs, Connecticut.

[2] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954.

[3] (a) A. Wada, *J. Chem. Phys.*, **22**, 198 (1954); (b) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958).

[4] E. Hirota, *ibid.*, **37**, 283 (1962).

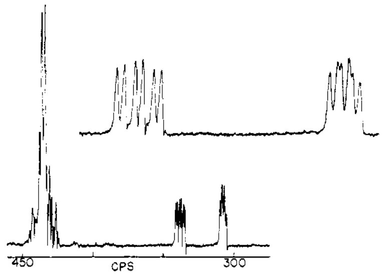


Figure 1. Spectrum of $C_6H_5CD{=}CH_2$ (CCl_4). Insert shows vinylic protons at higher resolution.

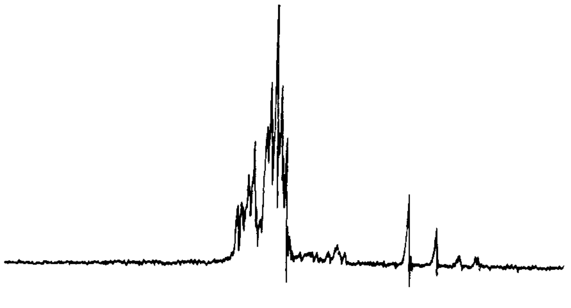


Figure 2. Spectrum of a mixture containing *trans*-$C_6H_5CH{=}CHD$, $C_6H_5CH{=}CH_2$, and $C_6H_5C{\equiv}CH$.

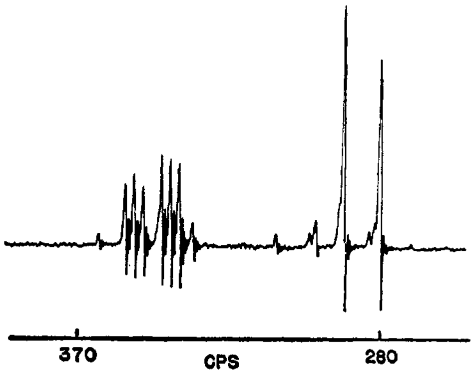


Figure 3. Spectrum of *cis*-*t*-Bu-CH=CHD (CCl_4).

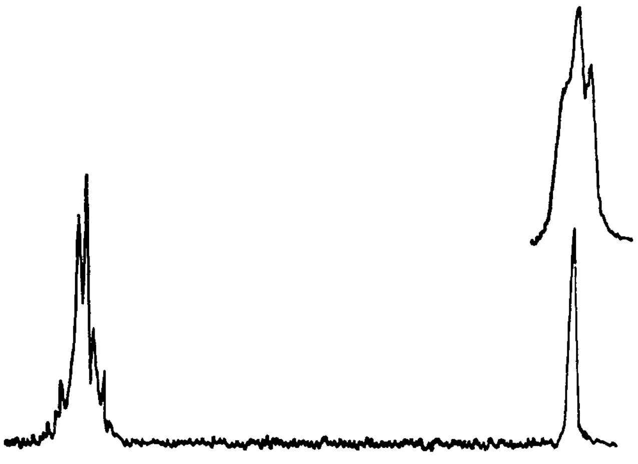
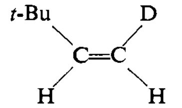


Figure 4. Spectrum of $C_6H_5CDBrCH_2Br$ in acetone. Insert shows CH_2Br group at higher resolution.

synthesis of both $C_6H_5CDBrCH_2Br$ (**1a**) and *erythro*-$C_6H_5CHBrCHDBr$ (**1b**) (Chart I, routes a and b, respectively). The nmr spectrum (Figure 1) of styrene produced by dehydration of $C_6H_5CDOHCH_3$ showed the absence of the lowest field vinyl quartet which by its chemical shift and spin coupling constants with the other vinyl hydrogens can be identified with the α hydrogen. Bromination should then lead uneventfully to **1a**.

The hydroboration–protonolysis sequence applied to phenylacetylene would be expected to produce *trans*-styrene-β-*d* in view of the established stereochemistry of these reactions.[5] Examination of the nmr spectrum of the styrene obtained (Figure 2) indicated it was *stereochemically* pure *trans*-styrene-β-*d* (to within the usual limits of nmr analysis) but only *ca.* 80% isotopically pure. Subsequent *trans* addition of bromine—to the authors' knowledge there is no substantiated example of *cis* bromination—would afford **1b**, which has the conformations indicated.

Synthesis of *threo*-$(CH_3)_3CCHBrCHDBr$ was accomplished by route c of Chart I. Base-catalyzed exchange of the acetylenic hydrogen with D_2O gave *t*-$BuC{\equiv}CD$ which was converted to



by the hydroboration–protonolysis sequence. The *cis* configuration of the olefin, 82% monodeuterated, was confirmed by nmr (see the Experimental Section and Figure 3). *trans* addition of bromine now leads to the *threo* isomer **2a**, which has the conformations indicated.

The nmr parameters for $C_6H_5CHBrCH_2Br$ and $(CH_3)_3CCHBrCH_2Br$ are repeated from the previous paper in Table I. Assignment of proton 1 to the benzylic hydrogen, reasonable *a priori* from known chemical shift behavior of benzyl *vs.* alkyl hydrogens, is unequivocally established by the absence of the low-field multiplet in spectra of **1a** (Figure 4). Lack of resolution in the high-field portions of the spectra arises because the inner two peaks of the expected AB-type quartet are further split into overlapping 1:1:1 triplets by spin–spin coupling with the vicinal deuterium and may also arise in part from quadrupole line-broadening effects. The outer members of the AB quartet were not detected because of their low intensity (calculated to be about $^1/_{20}$ that of the inner components).

The spectrum of **1b** (Figure 5; this is actually a superposition of spectra of **1b** and the 20% undeuterated dibromide present) shows the benzyl proton split into a doublet, as expected from introduction of a β-deuterium atom, whose spacing is 10.5–11.0 cps and which agrees in every case with the coupling J_{13}. Therefore the methylene proton coupled to the benzylic one in **1b** is proton 3. Because the magnitude of this vicinal coupling is well within the range of 10–17 cps, supposedly characteristic of hydrogens *trans* oriented in a freely rotating ethane,[6] the observations seem to demand that *the dominant conformer is the one with trans hydrogens, i.e., conformer i* (see Chart I).

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[5] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961).

[6] See, *e. g.*, H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962). Although one can argue that the range of vicinal coupling constants between *trans* hydrogens is still open to question, there seem to be no data which would support the contention that coupling between *gauche* hydrogens is even as high as 6 cps.

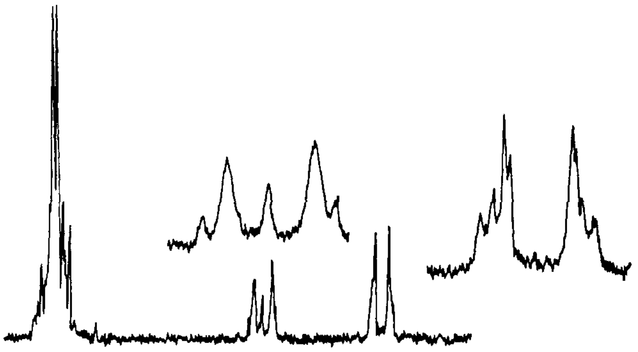


Figure 5. Spectrum of *erythro*-$C_6H_5CHBrCHDBr$ (acetone) and $C_6H_5CHBrCH_2Br$ with inserts being higher resolution sweeps.

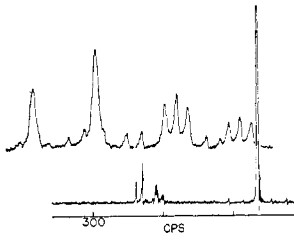
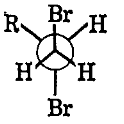


Figure 6. Spectrum of *threo*-*t*-Bu-CHBrCHDBr + *t*-Bu-CHBr-$CH_2Br(CCl_4)$ and higher resolution insert.

The spectrum of **2a** (Figure 6) also shows simplification of the low-field signals to a doublet whose spacing is 9.2–10.1 cps. Again, this identifies the sole remaining methylene proton as proton 3, and the magnitude of the vicinal coupling observed seems to require that the dominant conformation be the one with hydrogens *trans* oriented. However, because we are now dealing with the *threo* isomer, *the most stable conformer of* **2** *is ii* (see Chart I) *in contrast to what was found for* **1**.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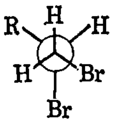
ii

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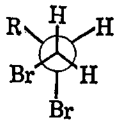
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The results described herein are independent of the model for conformational analysis introduced in the subsequent paper and seem to demonstrate unambiguously that as the "size" of the R group in RCHBr-CH_2Br increases the energetics of rotational isomerism favors ii over i. Simply stated, the conformer with bromines *trans* and the alkyl (or aryl) group *gauche* to the halogen is destabilized relative to the one with bromines *gauche* and the alkyl (or aryl) group *trans* to the halogen as the size of the alkyl (or aryl) group increases. But this sort of behavior is precisely what one would expect if steric effects were important in determining conformer stability, so that the important question is not why the change in dominant conformer occurred, but is rather the question of why i is the favored conformer of **1**. The most obvious answer is that electrostatic (dipole–dipole) repulsions between *gauche* bromines are greater than are steric repulsions between *gauche* bromine–phenyl. However, if the relatively small solvent changes in conformational distribution[7] correctly imply a correspondingly small contribution from electrostatic repulsions, then the classical arguments favoring *trans* halogens are incorrect, and the reason for the stability of conformer i of **1** remains unanswered. If one assigns steric effects as the exclusive, or predominant, factor in conformational equilibria, then one might measure the effective size of the groups by their *A* value, which is a measure of the effectiveness of a substituent in assuming the equatorial rather than the axial position in cyclohexane. The *A* value of C_6H_5 (2.6) compared to that of bromine (0.2–0.7)[8] then suggests that the most stable conformer would be the one with *trans* bromine–phenyl orientation, which is contrary to observation. This suggests that either steric effects are not the sole major contributor to conformer stability, or the *A* values are not adequate measures of steric effects in substituted ethanes.

The possibility that an attractive force between *gauche* phenyl–bromine confers stability to conformer i of **1** cannot be dismissed on the basis of any evidence known to the authors. It is proper to note that Szasz[9] has postulated an attractive force between a methyl group and a halogen to account for the unexpectedly high percentage of *gauche* conformer in *n*-propyl and isobutyl halides.

The unambiguity in the proton assignments of **1** afforded by deuterium labeling demonstrates that whereas within the methylene group the resonance position of proton 2 is to lower field in carbon tetrachloride and chloroform, the resonance position of proton 3 is to lower field in acetone; *i.e.*, a "crossover" in chemical shift has occurred upon changing from carbon tetrachloride to acetone solution. Yet we have seen that the vicinal coupling constants vary little in these solvents, so that the spread in chemical shift is not associated with changes in conformer distribution. Such behavior in chemical shift is really no different from the behavior noted for many other systems previously described, but the "crossover" points out perhaps more poignantly the inadequacy of the chemical shift as a sole criterion of conformational mobility.

Castellano and Waugh have pointed out "that spectra of three spin systems have, in general, more than one solution."[10a] Those sets of solutions for the spectra of **1** and **2** which contain geminal and vicinal couplings of like sign give values of vicinal couplings different from the one observed in the deuterated compound. For example, a solution for **1** (CCl_4) has J_{12} = 3.96 cps, J_{13} = 11.84 cps, and J_{23} = 9.98 cps. The observed coupling in **1b** is 11.0 cps, which does not agree with J_{13} given above but does agree very well with that (10.89 cps) obtained if J_{23} is negative (*cf.* Table I). This lends confidence that the solutions of Table I are *the* correct ones,[10b] which in turn demonstrates that the vicinal and geminal couplings are of opposite sign. Hence the technique of deuterium labeling permits determination of relative signs of coupling constants by effecting a change from a tightly coupled system, where several solutions are possible, to a loosely coupled one,[11]

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(7) E. I. Snyder, accompanying papers.

(8) E. L. Eliel, "Stereochemistry of Carbon Compounds, "McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 236.

(9) G. J. Szasz, *J. Chem. Phys.*, 23, 2449 (1955).

(10) (a) S. Castellano and J. S. Waugh, *ibid.*, 34, 295 (1961). (b) To the authors' knowledge there is no case known where the two vicinal proton couplings are of unlike signs. Therefore only the two solutions mentioned need be considered.

(11) This corresponds closely to the case where spectra are obtained at higher frequencies, thereby reducing the J/δ ratio and producing first-order spectra.

Table I. Nmr Parameters at 60 Mc

Solvent	ν_1[a]	ν_2[a]	ν_3[a]	J_{12}, cps	J_{13}, cps	J_{23}, cps	J_D,[b] cps
$C_6H_5CHBrCH_2Br$							
CCl_4	8.60	72.39	76.12	5.25	10.89	−10.26	10.96
$CHCl_3$	8.60	72.63	75.89	5.58	10.60	−10.27	10.80
CH_3COCH_3	8.44	80.31	78.19	5.74	10.11	−10.47	10.46
	8.45	80.29	78.20	5.54	10.31	−10.48	
C_6H_6							10.7
CH_3CN							10.5
t-Bu-CHBrCH₂Br							
CCl_4	7.11	12.41	35.04	3.08	9.26	−11.37	9.21
CH_3COCH_3	7.22	8.95	39.51	2.64	9.91	−11.66	9.97
C_6H_6	6.90	23.87	40.76	2.76	9.63	−11.54	9.67
CH_3CN	7.11	11.22	39.59	2.42	10.07	−11.72	10.06

[a] ν_i is the resonance frequency of the *i*th proton relative to some arbitrary zero. [b] J_D is the sole vicinal coupling constant observed in $RCHBrCH_2Br$.

Table II. Some Spectral Parameters of *threo*-$(CH_3)_3CCHBrCHDBr$

Solvent	C_6H_6		CCl_4		CH_3CN		CH_3COCH_3	
	Calcd[a]	Obsd[a]	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
J_{13}	9.63	9.67	9.26	9.21	10.07	10.06	9.91	9.97
J_{D-H_3}[b]	1.77	1.68	1.75	1.63	1.80	1.70	1.79	1.76
δ_{13}[c]	33.86	34.22	27.93	28.59	32.48	32.89	32.29	32.70

[a] The calculated values are those obtained from iterative analysis of the 60-Mc nmr spectrum of $(CH_3)_3CCHBrCH_2Br$; the observed values are those measured in *threo*-$(CH_3)_3CCHBrCHDBr$. [b] J_{D-H_3} is the geminal proton–deuteron coupling on the methylene group of **1a**. J_{D-H_3}(calcd) = $0.1535J_{23}$(calcd). [c] δ_{13} is the chemical shift (in cps) between protons 1 and 3.

where the absolute magnitude of one or more parameters can be measured readily. The spectra of **2** affords an even better example by being more complete. The solution of **2** (benzene) with all couplings of like sign gives J_{12} = 1.87 cps, J_{13} = 10.32 cps, and J_{23} = 11.43 cps. In the spectrum of **2a** one can measure $|J_{13}|$, $|J_{D-H_3}| = 1/6.514\ |J_{23}|$, and $\delta_{13} = |\nu_3 - \nu_1|$. The value of J_{13} observed, 9.57 cps, is not in good agreement with that given above, but is in excellent agreement with that obtained in the solution where J_{23} is negative. The favorable comparisons afforded by the other parameters (Table II) lend further support that the solutions for **2** with J_{23} negative are *the* correct ones. Interestingly δ_{13} in the deuterated dibromine is systematically higher by 0.4–0.6 cps than that calculated for undeuterated material. This suggests a difference in the deuterium isotope effect on the chemical shift of geminally and vicinally situated protons, opposed to what has been observed in olefinic systems.[12]

Experimental Section

Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer system under operating procedures identical with those described in the previous paper.

1-Phenylethanol-1-*d*. To a stirred slurry of 2 g of $LiAlD_4$ (Metal Hydrides, Inc.) in ether was slowly added an ethereal solution containing 23.0 g of acetophenone. Stirring was continued for 15 min after addition was complete. The ether phase obtained by filtration after alkaline treatment[13] of the reaction mixture was combined with the ether washings of the inorganic salts. Residue obtained upon concentration of the solution was distilled through a short Vigreux column, bp 60–80° (1 mm), 22.0 g. Analysis by glpc (polypropylene glycol on diatomaceous earth, 154°) indicated a mixture containing 89% alcohol, 9% acetophenone, and 2% styrene.

Styrene-α-*d*. The procedure was patterned after that described by Overberger and Saunders.[14] Deuterated phenylethanol (22 g) prepared as described above was added to 2.5 g of potassium pyrosulfate, containing *ca.* 0.1 g of *t*-butylcatechol, at 225° (100 mm). The rate of addition, critical to maximization of yield, was such that the vapors which distilled were at 60–80°. When addition of alcohol was complete the pressure was lowered to 20 mm to distil the remaining liquid. A pentane solution of the distillate was dried ($MgSO_4$), pentane was distilled at ambient pressure, and styrene was distilled from *t*-butylcatechol through a small Vigreux column, bp 76–78° (75 mm), 10.0 g. Examination by glpc on a silicone oil column at 107° showed only one peak. The infrared spectrum (10% CCl_4 solution) of deuterated material showed a band at 830 cm^{-1}, replacing one at 990 cm^{-1} in undeuterated olefin, and one at 2460 cm^{-1} in addition to other bands found in styrene. Mass spectral examination indicated the material was monodeuteriostyrene "on the 100% level." Examination of the nmr spectrum showed the complete disappearance (to within the limitations of the technique) of the α-proton signal.

(1,2-Dibromoethyl-1-d_1)benzene (1a). Bromine was added to a CS_2 solution of α-deuteriostyrene at 0° until the bromine color persisted. Solid obtained upon evaporation of solvent was treated with charcoal in hot methanol, then twice recrystallized from methanol to give pure II, mp 73–74°.

***trans*-Styrene-β-d_1.** Hydroboration was performed according to the procedure of Brown and Zweifel.[5] Disiamylborane was prepared by passing diborane, generated externally from addition of 7.0 g (0.19 mole) of $NaBH_4$ in 200 ml of diglyme to 34 g (0.5 mole) of BF_3 etherate, into a solution of 35 g (0.5 mole) of 2-methylbutene-2 dissolved in 50 ml of tetrahydrofuran, cooled by an external ice bath. Phenylacetylene (20 g, 0.2 mole) was added to the disiamylborane at 0°. After 1 hr the mixture was subjected to protonolysis by adding CH_3CO_2D prepared from 30 g of acetic anhydride and 6 g of D_2O. This solution remained at ambient temperature for 18 hr, when it was poured into ice and extracted with pentane. Acid was removed from the pentane solution by repeated base washing. Because much boron-containing organic material was present in the residue obtained upon concentration of the dried ($MgSO_4$) pentane solution the residue was dissolved in 150 ml of THF and treated with a mixture of 51 ml of 3 *N* NaOH and 51 ml of 30% peroxide for 2 hr. This solution was diluted with water and extracted with pentane, the pentane was washed thoroughly with

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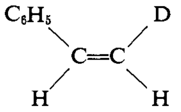
(12) G. S. Reddy and J. A. Goldstein, *J. Mol. Spectry.*, **8**, 475 (1962); *cf.* E. I. Snyder, *J. Phys. Chem.*, **67**, 2873 (1963).

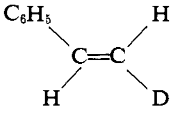
(13) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1990 (1953).

(14) G. C. Overberger and J. H. Saunders, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 204.

water and bisulfite and dried ($MgSO_4$), and pentane again was removed at ambient pressure. The residue had a styrene:phenylacetylene ratio of 1:2 (glpc). Attempted distillation led to extensive polymerization. Preparative glpc separation on 10.3 g of product, half of which consisted of material other than styrene and phenylacetylene, led to a mixture of 2.25 g of the latter in the ratio of 1:2.40 (glpc). The ratio of the highest field vinyl signals to the middle group of vinyl signals in the nmr spectrum (Figure 2) indicates that the styrene is *ca.* 80% monodeuterated. The presence of



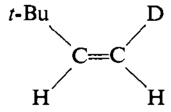
would transform the remaining methylene hydrogen signal at highest field from a doublet of doublets into a doublet by removing the small splitting resulting from the geminal coupling constant. That this is not observed indicates stereochemical purity (>95%) of the styrene as



***erythro*-(1,2-Dibromoethyl-2-*d*)Benzene (1b).** The styrene-phenylacetylene mixture described above was brominated in CS_2 solution. A methanol solution of the material obtained upon removal of CS_2 was cooled to −40°, and solid which separated was collected. Charcoal treatment followed by two recrystallizations from methanol gave 0.808 g of pure dibromide, mp 73°.

3,3-Dimethylbutyne-1-*d*. A mixture of 20 g of 3,3-dimethylbutyne, 50 ml of pyridine (dried over BaO, stored over CaH_2), 50 ml of D_2O, and 0.658 g of sodium methoxide was shaken in a sealed tube for 4 days. The acetylene was isolated by simple distillation. Examination of the infrared spectrum showed the appearance of a new band at 2580 cm^{-1} and a decrease in intensity of the old one at 3320 cm^{-1}, with a ratio of intensities of 8.71:2.02. (This leads to an approximate value of 81% t-Bu-C$\equiv$CD.) A broad band centered at 960 cm^{-1} is absent in undeuterated material. From the cracking pattern of the acetylene, comparison of the mass 67–66 pair in t-Bu-C$\equiv$CH and the 68–67 pair in the above samples shows that the sample is 82.4% t-Bu-C$\equiv$CD.

3,3-Dimethyl-*cis*-1-*d*-butene-1. A solution of BF_3 in diglyme was prepared by mixing 350 ml of BF_3–Et_2O with 500 ml of diglyme and pumping on the stirred mixture at 0° for 2 hr. Diborane, generated by addition of $NaBH_4$ to the diglyme solution of BF_3, was bubbled into a solution of 14.5 g of t-Bu-C$\equiv$CD in 145 ml of THF until all the acetylene was reacted (as evidenced by vpc examination of the reaction mixture). Acetic acid (70 ml) was added and the solution was permitted to remain overnight. After addition of water the mixture was extracted several times with $CHCl_3$. The organic extract was washed with 5% Na_2CO_3 and water and dried overnight. This material then was distilled slowly through a Heli-Pak column to give a dilute chloroform solution of olefin.[15] A sample of pure olefin was obtained by preparative vapor phase chromatography (20-ft silicone oil column at 53°) and its nmr spectrum was examined. The observed proton–proton coupling constant of 10.6 cps and deuteron–proton coupling of 2.59 cps, corresponding to a proton–proton coupling of 16.9 cps, establish the configuration of the olefin as



Integration of the vinyl proton area *vs.* the t-butyl proton signal in the deuterated compound and comparison of this ratio with that observed in undeuterated olefin showed the olefin was 78.5–85.9% monodeuterated and that 98.3–103.1% of the deuteriums were in the terminal methylene position.

***threo*-1,2-Dibromo-3,3-dimethyl-1-*d*-butane (2a).** The olefin-chloroform distillate was treated with bromine at −60° until the bromine color persisted. The solution was shaken with 5% bisulfite, washed with water, and dried ($MgSO_4$). After evaporation of chloroform the residue was distilled through a short column to afford 4.28 g of dibromide, bp 58–60° (5 mm). Examination by vpc indicated a purity of 92%, with four other materials comprising the remaining 8%.

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[15] Evidently protonolysis of the organoborane is not complete at room temperature. Addition of acetic acid to the pot when olefin was barely detectable in the distillate was followed almost immediately by a tenfold increase of olefin concentration in distillate.

Studies in Magnetic Nonequivalence. A Model for Conformational Analysis of Acyclics from Spin-Coupling Constants

Eugene I. Snyder

Contribution from the Central Basic Research Laboratories, Esso Research and Engineering Co., Linden, New Jersey, and the Department of Chemistry, University of Connecticut, Storrs, Connecticut. *Received July 8, 1965*

Abstract: A much simplified model is presented to account for conformational (rotational) isomerism in acyclic molecules. The model assumes (1) a $\cos^2 \phi$ dependence of the vicinal coupling constant, (2) an equilibrium dihedral angle near 65°, (3) that conformers with a bulky group *gauche* to two other such groups are energetically highly unfavorable. One can then develop equations relating the conformational equilibrium constant to the two vicinal coupling constants in 1,2-disubstituted and 1,1,2-trisubstituted ethanes. Several tests for our model are mentioned; results of conformational analysis of several systems are presented and discussed.

In the previous two papers we have qualitatively related the results of spectral analysis of several compounds of the type XCH_2CHYZ to rotational isomerism in these molecules and have also presented evidence which, we feel, establishes with reasonable certainty the most stable conformer in two such molecules. In this paper we shall present a model which we use in conformational analysis of acyclics using nmr data, we shall attempt to critically examine it, and we shall discuss the results of our conformational analyses