of which will be reported, along with a more detailed analysis and discussion of the mass spectrum, in future publications.

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[10] National Science Foundation Postdoctoral Fellow, 1965–1966; address correspondence to the Department of Chemistry, Columbia University, New York, N. Y. 10027.

Stephen J. Lippard[10]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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A New Approach to Conformational Analysis. Carbon-13 Nuclear Magnetic Resonance[1,2]

Sir:

Since the first report of marked conformational effects on proton chemical shifts,[3] the use of nmr spectroscopy for the investigation of stereochemistry and molecular conformation has become increasingly popular. A variety of applications has been described[4] and the use of nuclei other than protons has been illustrated, prominent among which are ^{19}F and ^{13}C studies.[2,5,6] The feature common to all of these published approaches is that the shielding or the spin coupling of the particular nucleus which is examined directly must vary with its orientation within the molecule (*e.g.*, axial *vs.* equatorial protons in cyclohexyl systems or dihedral angle for vicinal couplings). The magnitude of the variation with position governs the precision with which conformational parameters may be determined. We wish to report that in cyclohexanol derivatives the shieldings of the readily identified carbinol carbons are markedly dependent on the orientation of the oxygen functions and, consequently, these data are useful for conformational analysis. These differences are due *solely* to substituent orientation since the position of the carbon nucleus itself is unchanged relative to the other atoms in the molecule. Because these differences are relatively large, the method, when refined techniques are employed, is capable of higher precision than other nmr methods.

The ^{13}C spectra of the *cis*- and *trans*-4-*t*-butylcyclohexanols and their methyl ethers and acetates reveal that the chemical shifts of the carbinol carbons (C-1) differ substantially for each pair in this series.[7] Shielding differences of up to 5 ppm are found between carbinol carbons bearing axial and equatorial oxygen functions and, in each case, the carbon having an axial substituent absorbs at the higher field (Table I). To demonstrate that the 4-*t*-butyl group exerts a negligible effect on the chemical shift of the carbinol carbon, the *trans*-4-methyl- and 4-isopropyl-substituted derivatives were also examined. These data are included in Table I.

Table I. Carbinol Carbon Shieldings[a] of Some Cyclohexyl Systems, *cis*- and *trans*-4-R-$C_6H_{10}OR^1$

R	R^1	Orientation of OR^1 Axial[c]	Equatorial[d]	$\Delta\delta_c$,[b] ppm
t-Bu	H	126.4	121.5	4.9
	Ac	123.6	119.6	4.0
	Me	117.5	112.6	4.9
i-Pr	H		121.8	
	Ac		119.2	
	Me		112.6	
Me	H		121.4	
	Ac		119.8	
	Me		113.0	

[a] In parts per million from CS_2 (δ_c = 0 ppm). [b] Shielding difference due to substituent orientation ($\delta_c^{\text{axial}} - \delta_c^{\text{equat}}$). [c] *cis* isomer. [d] *trans* isomer.

These results establish the existence of substantial conformational effects on ^{13}C shieldings and suggest a number of possible applications in addition to their usefulness for stereochemical elucidations. One of these is the determination of conformational free energies for various substituents. For example, determination of the chemical shift of the carbinol carbon for cyclohexanol provides a measure of the relative populations of its two available chair conformations. Its carbinol absorption at δ_c = 122.8 ppm indicates that cyclohexanol is 74% equatorial on the basis of the data in Table I. This result corresponds to a conformational equilibrium constant of *ca.* 2.8 and a $-\Delta G°$ value of 0.6 kcal/mole. The latter value lies well within the range 0.4–1.2 kcal/mole found by other means.[9] In a similar manner $-\Delta G°$ values for the OMe and OAc groups on cyclohexane rings were determined and are given in Table II together with other published values.[9]

Table II. Some $-\Delta G°$ Values for OR Groups in Cyclohexyl Systems[a]

OR	Method of estimation ^{13}C	^{1}H[b]	Other[b]
OH	0.6	0.6–1.2	0.3–1.0
OAc	0.65	0.6–0.8	0.4–1.6
OMe	0.6	0.6	0.74

[a] In kcal/mole. [b] From ref 9.

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[1] Part VII in the series on ^{13}C nmr studies.

[2] Part VI: D. H. Marr and J. B. Stothers, *Can. J. Chem.*, **43**, 596 (1965).

[3] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957).

[4] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, Chapter 9; N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 6; N. C. Franklin and H. Feltkamp, *Angew. Chem. Intern. Ed. Engl.*, **4**, 774 (1965).

[5] J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3710 (1963); **87**, 3884 (1965); D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, **87**, 2862 (1965).

[6] (a) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964); (b) W. R. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966); (c) K. S. Dhami and J. B. Stothers, *Tetrahedron Letters*, **No. 12**, 631 (1964); *Can. J. Chem.*, **43**, 479, 498 (1965).

[7] The spectra were determined at 15.1 Mcps using rapid-passage, dispersion mode conditions with double irradiation at 60 Mcps to remove proton coupling effects.[6c] All samples contained ^{13}C in natural abundance and were examined as neat liquids or concentrated solutions in CS_2. A spherical sample cell having a spherical reference cavity[8] was employed to eliminate the need for bulk susceptibility correction.

[8] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

[9] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 7.

These conformational effects are by no means restricted to cyclohexyl derivatives. We have found that the relative orientation of hydroxyl groups in bicyclic systems is reflected by the chemical shift of the carbinol carbon. The results for borneol and isoborneol show that the carbon bearing an *endo*-OH (borneol) is shielded by *ca.* 4 ppm relative to that in the *exo* epimer and a similar difference is found for the *exo-* and *endo*-norborneols. Comparable differences can be expected in pyranose ring systems and an investigation of the ^{13}C shieldings of some monosaccharides is in hand to establish the utility of this technique for problems in carbohydrate chemistry. To overcome the limited precision inherent in the method[10] employed to obtain the results reported in this communication, it would be desirable to use the greater sensitivity and resolution of the absorption mode conditions as described by Paul and Grant[11] in future work with natural abundance materials. If ^{13}C-enriched material were used, normal high-resolution techniques could be employed to study concentration effects at very low dilutions.

At present, however, it is clear that ^{13}C spectroscopy constitutes an alternative approach to the study of molecular conformations and gains new strength as a tool for stereochemical elucidations. A wide variety of potential applications of this technique remains to be investigated.

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[10] The precision of these chemical shift measurements is estimated to be ±0.3 ppm.[8]

[11] E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **86**, 2977 (1964).

[12] Holder of an Ontario Graduate Fellowship, 1965–1966.

G. W. Buchanan,[12] D. A. Ross, J. B. Stothers
Department of Chemistry, University of Western Ontario
London, Ontario, Canada

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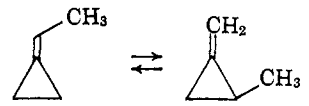
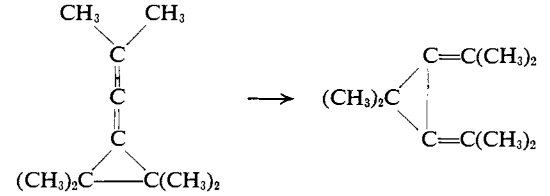
The Pyrolysis of Alkenylidenecyclopropanes. A Convenient Synthesis of Dimethylenecyclopropanes

Sir:

We wish to record a simple and efficient new synthetic method for the preparation of dimethylenecyclopropanes that makes this interesting class of highly unsaturated small-ring compounds readily available for the first time.[1,2] Consideration of the thermal rearrangements common to methylenecyclopropanes,[3] as illustrated below for a simple example (**1** ⇄ **2**), suggested that a similar rearrangement might obtain in the case of alkenylidenecyclopropanes. In that event, pyrolysis of the fully methylated derivative **3**[4] in a flow system at 360° and 0.25 mm resulted in an almost quantitative conversion to **4**. The structure of **4** is deduced from its spectroscopic properties which agree in every detail with those reported by Bleiholder and Shechter[1] for this same compound obtained in another manner. A similar efficient conversion of **5** is instructive in that the three isomeric dimethylenecyclopropanes **6**, **7**, and **8** are produced. The ratio of these products varies with temperature, being about 10:2:3 at 360° and 2:3:6 at 410°. Furthermore, pyrolysis of pure samples of either **6** or **7** at 380° yields a mixture of the three isomeric compounds whereas **8** is recovered essentially unchanged from this treatment. Raising the temperature to 460°, however, causes a transformation of **8** to **6** and **7**.[5] Gas chromatographic separation provided pure samples for spectroscopic examination. Compound **6** exhibits infrared absorption at 5.56 and 6.06 μ and ultraviolet absorption (hexane) at 245 mμ (ε 20,000) and 253 mμ (ε 17,500), and its nmr spectrum shows a six-proton singlet at τ 8.84, singlets at τ 8.19 and 8.09 overlapping a doublet in the same region (nine protons), and a one-proton quartet at τ 4.60 ($J = 7$ cps). Compound **7** has infrared absorption at 5.56 and 6.03 μ, ultraviolet maxima (hexane) at 244 mμ (ε 18,700) and 254 mμ (ε 15,700), and resonances at τ 8.78 (six-proton singlet), 8.2 (nine-proton multiplet), and 4.42 (a one-proton quartet, $J = 7$ cps). Compound **8** is uniquely defined by its absorption in the infrared at 5.53 and 6.05 μ, in the ultraviolet (hexane) at 251 mμ (ε 19,700) and 262 mμ (ε 18,560), and in the nmr at τ 8.89 (three-proton distorted doublet, $J \sim 6$ cps) and ~8.1 (a thirteen-proton grouping). A rigorous distinction between **6** and **7** is not easy to make but the assignments given are based on the expectation that the olefinic proton in **7** should absorb at lower fields than the corresponding proton in **6** due to its position in the deshielding zone of the other double bond.[6] Each of the compounds gives a strong molecular ion at m/e 136 in its mass spectrum,[7] and an accurate mass determination on **8** confirmed its molecular formula (calcd for $C_{10}H_{16}$, 136.125; found, 136.123).[8]



1 **2**



3 **4**

The mechanistic details of these thermal interconversions are very likely analogous to those of methylenecyclopropanes themselves. The rearrangements of the

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[1] R. F. Bleiholder and H. Shechter, *J. Am. Chem. Soc.*, **86**, 5032 (1964).

[2] Trimethylenecyclopropanes have also been reported recently. See E. A. Dorko, *ibid.*, **87**, 5518 (1965); P. A. Waitkus L. I. Peterson, and G. W. Griffin *ibid.*, **88**, 181 (1966); G. Kobrich and H. Heinemann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965).

[3] J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 2720 (1963); E. F. Ullman, *ibid.*, **81**, 5386 (1959); **82**, 505 (1960); E. F. Ullman and W. S. Fanshaw, *ibid.*, **83**, 2379 (1961).

[4] H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

[5] A small-scale pyrolysis of **8** showed major amounts of an additional product by gas chromatography. However, repeated attempts to duplicate this result on a preparative scale gave only minor amounts of a fourth component having the same retention time as **5**.

[6] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 88–89.

[7] Mass spectra were obtained using an AEI MS-9 spectrometer.

[8] The carbon and hydrogen microanalytical values for **6**, **7**, and **8** consistently totaled less than 100% in a nonreproducible fashion, possibly due to reaction of these dienes with atmospheric oxygen. However, the carbon-to-hydrogen ratios were proper and there were no peaks other than isotopic ones at m/e greater than 136.