the presence of only one compound. Upon distillation of the residue [105° (25 mm)], 5.0 g (95% yield) of 1,3-diacetoxybenzene (**2**) was isolated. The product was identified by comparison of its ir and nmr spectra with authentic sample prepared by acetylation of **3** with Ac_2O.

1,4-Cyclohexanedione (5.0 g, 0.045 mol) was aromatized as in the above case with concentrated H_2SO_4 (4.27 g, 0.045 mol) in 50 mol of Ac_2O and 50 ml of AcOH. After work-up and distillation of the residue, 8.1 g (93% yield) of 1,4-diacetyoxybenzene was isolated.

Aromatization of 1,2-cyclohexanedione (5.0 g, 0.045 mol) with 4.27 g (0.045 mol) of H_2SO_4 in Ac_2O–AcOH solvent afforded after distillation 7.8 g (90% yield) of 1,2-diacetoxybenzene.

Isolation of Intermediates in the Aromatization of 1,3-Cyclohexanedione. The aromatization was done as before except that only 0.13 g (1.3 mmol) of concentrated H_2SO_4 were used. After work-up, a glc analysis indicated the presence of only one compound. It was identified as the monoenol acetate of 1,3-cyclohexanedione (**12**): ir (neat) 5.65 (-OAc), 6.1 (C=C), 5.95 μ (C=O); nmr ($CDCl_3$) δ 5.59 (s, 1 H, >C=CH–), 2.21 [s, 3 H, CH_3-C(=O)O].

When the aromatization was done as in the previous example except that the reaction mixture was quenched at reflux, about 10–15% of **2** was isolated along with 85–90% of **12**.

Aromatization of 1,2-Cyclohexanedione in Ac_2O. The aromatization of the title compound was done as before except that 100 ml of Ac_2O was used as solvnet instead of Ac_2O–AcOH. After work-up, a glc analysis indicated the presence of two compounds. The first (70%) was identified as 1,2-dihydroxybenzene diacetate by comparison of its ir and nmr spectra with an authentic sample prepared by acetylation of catechol with Ac_2O. The second compound (25%) is tentatively identified as 1,2,3-trihydroxybenzene triacetate. Further identification of this material and the type of aromatization will be fully discussed in a separate paper.

Aromatization of 5,5-Dimethyl-1,3-cyclohexanedione. The title compound (9.0 g, 0.065 mol) was aromatized with 7.0 g (0.072 mol) of concentrated H_2SO_4 in 100 ml of Ac_2O as in the above example. After work-up and distillation of the residue [115–125° (0.3 mm)], 11.4 g (80% yield) of 4,5-dimethyl-1,3-diacetoxybenzene was isolated. Hydrolysis of the product afforded **11** as identified by ir and nmr and comparison with known material.[2]

Sublimation and recrystallization from benzene gave pure **11**, mp 135–135.5° (reported 135.5–136°[2] and 133–134.5°, 134–135°[11]).

Preparation and Aromatization of 2-Methylcyclohexane-1,3-dione. Into a 1-l. flask equipped with a condenser, drying tube, dropping funnel, and thermometer were charged 300 ml of absolute methanol and 21.6 g (0.94 mol) of sodium metal in small pieces, followed by 112.0 g (1.0 mol) of **1**. The solution was then cooled to 15°, and 162.0 g (1.14 mol) of methyl iodide in 50 ml of methanol was added slowly through the dropping funnel over a period of 0.5 hr. The solution was then refluxed for 3.5 hr followed by evaporation of the solvent. Water (400 ml) was then added and the residue and solids thus formed were filtered (62.0 g, 50% yield), mp 199–204°. Recrystallization from benzene gave pure **8**, mp 205–206° (reported[12] 205–207°).

Aromatization of **8** (3.0 g, 0.024 mol) with 2.34 g (0.024 mol) of concentrated H_2SO_4 in 50 ml of Ac_2O, as in the previous cases, afforded after hydrolysis 2.5 g (85% yield) of **9**, mp 97–98°, 106–107.5° when molten compound was seeded with authentic sample (reported[4a] 96–97°, 106–108°, and 106–108°[13]).

Registry No.—**1**, 504-02-9; **2**, 108-58-7; **4**, 637-88-7; **6**, 765-87-7; **8**, 1193-55-1; **10**, 126-81-8; **11**, 527-55-9; **11** diacetate, 35236-36-3; **12**, 50557-37-4.

References and Notes

(1) For the previous paper see M. S. Kablaoui, *J. Org. Chem.*, **39**, 2126 (1974).

(2) W. von E. Doering and F. M. Beringer, *J. Amer. Chem. Soc.*, **71**, 2221 (1949).

(3) Project Kreole, Contact DA-18-108-405-CML-29 U.S. Army Chemical Center, Procurement Agency, Army Chemical Center, Md.

(4) (a) R. S. Marmor, *J. Org. Chem.*, **37**, 2901 (1972). (b) R. Valters and O. Neilands, *Latv. PSR Zinat. Akad. Vestis. Chem. Ser.*, **6**, 710 (1968); F. Korte and H. Sieper, *Justus Liebigs Ann. Chem.*, **630**, 71 (1960); R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 311 (1945).

(5) N. Schamp, R. Verhe, and L. DeBuyck, *Tetrahedron*, **29**, 3857 (1973).

(6) E. A. Jeffery and D. P. N. Satchell, *J. Chem. Soc.*, 1913 (1962).

(7) T. V. Mal'kova, *Zh. Obshch. Khim.*, **30**, 2113 (1960).

(8) J. F. King, P. DeMayo, E. Morkred, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963); B. Helferich and W. Klebert, *Justus Liebigs Ann. Chem.*, **657**, 79 (1962); A. Mustafa, *Chem. Rev.*, **54**, 195 (1954).

(9) M. S. Kablaoui, U.S. Patents 3,624,134 (1971).

(10) M. Beringer and I. Kuntz, *J. Amer. Chem. Soc.*, **73**, 364 (1951).

(11) H. J. Backer and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **62**, 66 (1943); P. Karrer and E. Schick, *Helv. Chim. Acta*, **26**, 800 (1943).

(12) D. A. Sutton, *J. Chem. Soc.*, 10 (1946).

(13) R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 311 (1945).

Carbon-13 Nuclear Magnetic Resonance Characteristics of 3-Methylcyclohexane-1,2-diols

H. Ziffer* and J. I. Seeman

National Institute of Arthritis, Metabolism and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20014

R. J. Highet and E. A. Sokoloski

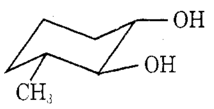
National Heart and Lung Institute, National Institutes of Health, Bethesda, Maryland 20014

Received April 12, 1974

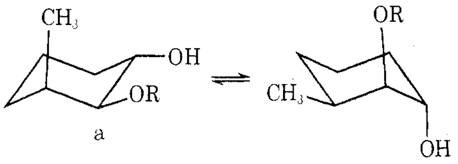
The proton nmr parameters which establish the stereochemistry and conformation of the diols **1–4** are described. The relation between the ^{13}C chemical shifts of the carbon atoms and the stereochemistry of the diols is analyzed with regard to substituent effects and vicinal interactions.

In a recent investigation of the metabolism of toluene[1] we had occasion to prepare a series of 3-methylcyclohexane-1,2-diols to confirm the stereochemistry assigned to a reduction product of the metabolite encountered. We describe here the proton nmr spectra which establish the configuration of these materials, and an investigation of the relation of the ^{13}C chemical shifts of the series to the configurations.

Klein and Dunkelblum[2] have recently described the preparation and characterization of three 3-methylcyclohexane-1,2-diols. The all-trans equatorial configuration **1** was assigned to the diol obtained by the hydroboration of 3-methyl-2-cyclohexenone. The assignment was anticipated from the mode of preparation and supported by the appearance of H-2 as a triplet at 2.80 ppm, J = 9 Hz. The trans,cis diol, configuration **2**, was obtained from the reaction of 3-methylcyclohexene with hydrogen peroxide and formic acid. The nmr spectrum defied analysis, but the authors inferred from its complexity that the isomer exists in rapid equilibrium between the conformations **2a** and **2b**. The cis,trans isomer **4** was obtained from the reaction of 3-methylcyclohexene with either potassium permanganate or



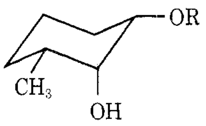
1



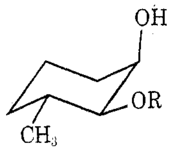
a

b

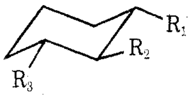
2, R = H
9, R = COPh



3, R = H
10, R = COPh



4, R = H
11, R = COPh



5, R_1 = OH; R_2 = H; R_3 = CH_3
6, R_1 = R_2 = OH; R_3 = H
7, R_1 = OH; R_2 = CH_3; R_3 = H
8, R_1 = OCOPh; R_2 = H; R = CH_3

wet silver acetate and iodine. The assignment was based on the appearance of H-2 as a doublet of doublets, J = 3 and 9 Hz. This isomer possessed an infrared spectrum consonant with an intramolecular hydrogen bond between the *cis*-hydroxyl groups.

Although these authors mention the cis,cis isomer, its mode of preparation was identical with that given for the cis,trans isomer, and no nmr data were reported for the compound. The preparation of an incompletely characterized isomer of the series by hydrogenation of 3-methylcyclohexane-1,2-dione has been described.[3] In our hands hydrogenation of 3-methylcyclohexane-1,2-dione over platinum produced a mixture rich in a new diol. This material was purified *via* its monobenzoate, the proton nmr spectrum of which indicated the cis,cis stereochemistry. Saponification of the monobenzoate provided a pure sample of the parent diol.

It was now possible to examine the proton nmr spectra of the four isomers at 220 MHz, at which higher frequency the chemical shifts and coupling constants of H-1 and H-2 could be clearly distinguished. These appear in Table I. The data on the trans,trans isomer 1 and the cis,trans isomer 4 are in substantial agreement with those reported by the earlier authors.[2] The coupling constants of 4 were confirmed by decoupling experiments. It is clear that the earlier difficulty in the interpretation of the spectrum of the trans,cis isomer 2 resulted from the small difference of the chemical shifts of H-1 and H-2. At higher fields, the coupling constants were readily determined. The data on the new diol 3 fit the anticipated cis,cis stereochemistry.

The data listed in Table I for **1**, **3**, and **4** correspond well to the generalizations which have been developed for protons on cyclohexane rings in the chair conformation:[4] diaxial couplings are large, *ca.* 9 Hz; axial–equatorial couplings are smaller, approximately 3 Hz. The two equatorial protons (H-2 in 3 and H-1 in 4) occur *ca.* 0.6 ppm at lower field than the axial protons. It is known that the presence of a vicinal equatorial substituent shifts an axial proton further upfield.[5] In the case of H-2 of 1 the presence of two vicinal equatorial substituents results in the remarkable shift of 2.84 ppm. Thus, although it might well be anticipated that the presence of three vicinal substituents might force the system into unusual conformations, the proton data demonstrate that the properties of these three materials can be examined within the framework of normal chair forms, with alternative conformations contributing only a minor proportion of the equilibrium population. However, the diol 2 evidently exists as a mixture of two conformations of similar importance, for observed chemical shifts are intermediate between the typical values for axial and equatorial protons, and the coupling constants observed do not conform to the generalization[6] that the ratio of trans to cis couplings must be greater than 2.0. The earlier speculation on this material must be valid.[7]

Table I
Pmr Parameters

	1	2	3	4
H-1	3.32 ppm	3.64 ppm	3.25 ppm	3.98 ppm
H-2	2.84 ppm	3.45 ppm	3.81 ppm	3.20 ppm
J_{12}	9.6 Hz	8.8 Hz	2.8 Hz	3.0 Hz
J_{23}	9.6 Hz	4.8 Hz	2.8 Hz	9.0 Hz
J_{16}	10.4 Hz	10.0 Hz	4.9 Hz	[a]
	4.6 Hz	4.4 Hz	12.9 Hz	[a]

[a] Coupling constants could not be determined.

Table II
^{13}C Chemical Shifts[a] (in ppm)

	1	2	3	4
C-1	75.1	70.4	73.9	69.8
C-2	81.1	76.9	72.7	77.5
C-3	37.8	33.6	35.6	33.2
C-4	33.6	30.3	28.1	32.7
C-5	23.6	19.3	23.6	19.3
C-6	33.3	32.4	26.7	31.4
CH_3	18.4	12.8	18.1	18.4

[a] Chemical shifts of C-4 and C-6 may be interchanged.

The ^{13}C spectra of these materials were now determined (Table II). The peaks resulting from complete proton decoupling were readily differentiated by off-resonance decoupling, allowing the immediate identification of the methyl carbons as the only quartets, and the 3-carbons as the only doublets at high field. In each spectrum, the triplet at highest field could reasonably be assigned to C-5, as the 3-methyl and 1-hydroxyl groups must shift C-4 and C-6 downfield. Of the remaining two triplets, which did not differ by more than 1.4 ppm, a tentative assignment was made to conform with the expectation that benzoylation would not affect the chemical shift of the carbon atom most distant. When this criterion was not available, the carbon atom at lower field was assigned to C-4, consistent with earlier observations of the effect of substituting methyl or hydroxyl groups.[8]

To aid in the assignment of the ^{13}C chemical shifts the monobenzoates **8**, **9**, **10**, and **11** were prepared from the corresponding diols or alcohol (Table III). Benzoylation shifted the proton resonances sufficiently to allow very ready differentiation of C-1 and C-2 in the diols by single proton decoupling. The chemical shifts of the remaining three carbon atoms in the diols could now be assigned by comparison with the effects produced by the benzoylation of 3-methylcyclohexanol (*cf.* Table IV).

The assignment of the chemical shifts now allowed the examination of the substituent effects in known conforma-

Table III
Chemical Shifts[a] of Benzoates (in ppm)

	8	9	10	11
C-1	73.8	67.3	76.5	67.8
C-2	40.6	77.8	71.7	80.7
C-3	31.6	30.6	35.6	30.9
C-4	34.1	30.0	26.7	32.7
C-5	24.0	19.2	23.5	19.1
C-6	31.3	29.5	24.6	31.3
CH_3	22.3	16.0	18.0	18.1

[a] Chemical shifts of C-4 and C-6 may be interchanged.

Table IV
^{13}C Shifts (in ppm) of Model Compounds[a]

	5	6	7
C-1	70.5	75.7	76.4
C-2	44.6	75.7	40.3
C-3	31.5	33.0	33.8
C-4	35.3	24.5	25.8
C-5	24.3	24.5	25.3
C-6	34.2	33.0	35.6
CH_3	22.4		18.7

[a] Assignments are those of previous workers. The shifts here determined differed only slightly from the previous values.

Table V
Substituent Effects

	1–5[a]	1–6[b]	1–7[c]	3–5[d]	4–7[e]
C-1	4.6	−0.6	39.5	3.4	34.2
C-2	36.5	5.4	4.7	28.4	1.1
C-3	6.3	4.8	−2.5	4.1	−7.1
C-4	−1.7	9.3	−0.2	−7.2	−1.1
C-5	−0.7	−0.9	−2.2	−0.7	−6.5
C-6	−0.9	0.3	8.0	−7.5	6.1
CH_3	−4.4		−0.3	−4.3	−0.3

[a] The addition of an equatorial hydroxyl at C-2. [b] The addition of an equatorial methyl at C-3. [c] The addition of an equatorial hydroxyl at C-1. C-1 of 7 is taken to correspond to C-2 of 1. [d] The addition of an axial hydroxyl at C-2. [e] The addition of an axial hydroxyl at C-1.

Table VI
Effect of Configurational Changes

	3–1[a]	4–1[b]
C-1	−1.2 (β_e)[c]	
C-2		−3.6 (βe)
C-3	−2.2 (β_e)	−4.6 (γe)
C-4	−5.5 (γ(H))	−0.9 (δ(H))
C-5	0.0	−4.3 (γ(H))
C-6	−5.6 (γ(H))	−1.9 (β(H))

[a] Effect of changing C-2 hydroxyl from equatorial to axial. [b] Effect of changing C-1 hydroxyl from equatorial to axial. [c] The values reported earlier, with the signs reversed to correspond to the different reference, are βe = −1.7 ± 0.3 and γ_e = −2.8 ± 0.3 ppm (13).

tions. Previous workers have studied such effects within cyclohexyl systems.[8] It is quite generally observed in the simple systems that carbon atoms bearing axial substituents are more shielded by approximately 6 ppm than those with equatorial substituents, and that such an axial substituent produces a similar upfield shift in atoms in a gauche relation to it. The present study allows the examination of the effect of stereochemical relations upon the chemical shifts of hydroxyl-bearing carbons.

Such comparisons are not readily made for the diol **2**, because it exists as a mixture of similar proportions of the two conformers **2a** and **2b**. However, comparison of the observed chemical shifts with those of the all-equatorial isomer 1 shows the effect of the contribution of forms bearing the axial substituents. Of these, the most obvious effect is upon the methyl group, of which the chemical shift is some 6 ppm to higher field than those of the other isomers. In **2b**, each ring carbon either bears an axial substituent, or exists with an axial substituent three bonds away. In **2a**, this is true of C-1, -3, and -5. As a consequence, the chemical shifts of all of the ring carbons occur to higher field than those of 1.

In attempts to relate ^{13}C chemical shifts to structure and stereochemistry, Grant, *et al.*,[9] and Roberts, *et al.*,[11] have been concerned with the additivity of substituent effects in substituted cyclohexanes. In the case of alkylcyclohexanols, Roberts, *et al.*, have shown that introduction of an axial methyl or hydroxyl group results in different α, β, and γ shifts than does introduction of an equatorial methyl or hydroxyl group. We were interested in learning if the parameters established for alkylcyclohexanols could be transferred to these diols. In order to establish the effect of introducing an axial or equatorial methyl and/or hydroxyl group we determined the ^{13}C spectra of *cis*-3-methylcyclohexanol (**5**), *trans*-1,2-cyclohexanediol (**6**), and *trans*-2-methylcyclohexanol (**7**) (see Table IV). The effect of adding an equatorial methyl at C-3 can then be determined from a comparison of the spectra of 1 and **6**. A comparison of the spectra of **5** and **7** with 1 yields the parameters associated with introducing an equatorial hydroxyl group. The observed differences are tabulated in Table V and are quite similar to those previously observed,[11] when the addition of the substituent does not involve the formation of an additional gauche interaction with a vicinal substituent. In such cases (*e.g.*, the effect upon C-2 of the addition of the hydroxyl at C-1), the downfield shifts are reduced by approximately 3 ppm. Similarly, comparison of **3** with **5** and **4** with **7** shows the effect of adding the axial hydroxyl group at C-2 and C-1, respectively. Earlier observations of this effect give α, 37.8, β, 5.5 and γ, −7.2 ppm.[10,12] The effects of adding the axial hydroxyl to form **3** and **4** are similar at the γ-carbon atom but are again diminished for α and β in situations in which new gauche interactions with vicinal groups result.

In the course of examining the ^{13}C spectra of inositols and sugars Roberts, *et al.*, have developed some parameters to describe the effect on the β and γ carbon atoms of changing the stereochemistry of a hydroxyl group from equatorial to axial.[13,14] "β_e" is the change produced by altering a hydroxyl group from equatorial to axial observed in the chemical shift of a carbon β to the site of the alteration and bearing an equatorial hydroxyl. Values for β_e, γ_e, and δ_e can be obtained from a comparison of **3** with 1 and **4** with **1**. These values are given in Table VI along with Roberts' values. The agreement is poor and suggests that Roberts' parameters apply rather specifically to the sugars.

This study has demonstrated that the chemical shifts of the ring carbons for this series of diols can be correlated with the stereochemistry of the substituents. As the number of substituents on the parent system increases, steric factors, changes in geometry, and vicinal effects partly vitiate the use of parameters previously developed for substituent effects in establishing the stereochemistry of highly substituted systems.

Experimental

The proton nmr spectra were determined on a Varian HR 220-MHz spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. The chemical shifts are accurate to ±0.02 ppm. The ^{13}C spectra were obtained on a Varian XL-100 spectrometer equipped with a Digilab Fourier transform accessory, using the same solvent and reference. Chemical shifts are accurate to ±0.05 ppm.

Preparation of the Diols. Compound **1** was prepared by hydroboration of 3-methylcyclohexenone as described by Klein and Dunkelblum, mp 39–40° (reported[2] mp 39–40°).

The trans,cis diol **2** was prepared by oxidation of 3-methylcyclohexene with 30% hydrogen peroxide–90% formic acid as described for *trans*-1,2-cyclohexandiol.[17] The crude diol was crystallized from hexane and recrystallized from isooctane, mp 94–95° (reported[2] mp 91–92°). The cis,trans diol **4** was prepared by OsO_4–H_2O_2–*tert*-butyl alcohol oxidation of 3-methylcyclohexene as well as from the solvolysis of the dibromide (prepared by brominating the olefin in carbon tetrachloride at 0°) with silver acetate in acetic acid–water. The diol crystallized from hexane–ethyl acetate, mp 81–82° (reported[15] mp 81–82°).

The monobenzoate **9** and **11** were obtained by reaction of equimolar quantities of **2** or **4** and benzoyl chloride in pyridine. The monobenzoate was purified by chromatography on silica gel, yielding an oil whose proton and ^{13}C nmr spectra were consistent with the structure assigned.

The benzoate **8** was prepared from *cis*-3-methylcyclohexanol as described for **9**: ^{1}H nmr δ 5.00 (q, J = 3.5, 6.5 Hz), 4.00 (m), 0.98 (J = 7 hz).

The cis,cis isomer **3** was prepared using a procedure similar to that of Garanti and Marchesini[3] in which 3-methylcyclohexane-1,2-dione[16] was hydrogenated in ethanol over PtO_2. Nmr spectra of the crude diol showed it to be a mixture of cis,cis and cis,trans diols. The diol mixture, 3.783 g (2.9 mmol), was treated with benzoyl chloride, 4.51 g (3.2 mmol), in 25 ml of pyridine overnight at room temperature. The reaction mixture was poured into dilute HCl, extracted into ether, washed with aqueous $NaHCO_3$, dried, and concentrated to yield 6.569 g (97%). The monobenzoate **10** was crystallized from methanol–water to yield 4.05 g (62%): mp 82–83°; ^{1}H nmr δ 4.92 (m, J = 11.4, 4.8, 2.6 Hz), 3.92 (t, J = 2 Hz). *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.61.

The monobenzoate (6.9 g) was hydrolyzed by refluxing in 50 ml of methanol, 2.5 g of KOH, and 10 ml of H_2O followed by extracting into ethyl acetate. The diol was crystallized from hexane–ethyl acetate, mp 64–65°. *Anal.* Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.37; H, 10.91.

Registry No.—**1**, 15806-70-9; **2**, 19700-12-0; **3**, 52730-58-2; **4**, 19700-14-2; **5**, 5454-79-5; **6**, 1460-57-7; **7**, 7443-52-9; **8**, 52699-45-3; **9**, 52748-17-1; **10**, 52759-91-8; **11**, 52759-90-7.

References and Notes

(1) H. Ziffer, D. M. Jerina, D. T. Gibson, and V. M. Kobal, *J. Amer. Chem. Soc.*, **95**, 4048 (1973).
(2) J. Klein and E. Dunkelblum, *Tetrahedron*, **24**, 5701 (1968).
(3) L. Garanti and G. Marchesini, *Ann. Chim. (Rome)*, **53**, 1619 (1963).
(4) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, Pergamon Press, New York, N.Y., 1969, p 238.
(5) H. Booth, *Tetrahedron*, **22**, 615 (1966); E. L. Eliel, M. H. Gianni, and T. H. William, *Tetrahedron Lett.*, 741 (1962).
(6) J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971).
(7) Calculation of the energies of interactions of the axial groups involved suggests that the two conformers are of similar energy. *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N.Y. 1965, p 356.
(8) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N.Y., 1972, pp 163–170.
(9) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **94**, 5318 (1972).
(10) The values quoted are those for the introduction of the hydroxyl to form *trans-4-tert*-butylcyclohexanol. *Cf.* ref 8 and 11.
(11) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).
(12) The values quoted are those for the introduction of the hydroxyl to form *cis-4-tert*-butylcyclohexanol. *Cf.* ref 11.
(13) D. E. Dorman and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 1355 (1970).
(14) D. E. Dorman, S. J. Angyal, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 1351 (1970).
(15) M. Mousseron and G. Manon, *Bull. Soc. Chim. Fr.*, 392 (1949).
(16) O. Wallach, *Justus Liebigs Ann. Chem.*, **414**, 296 (1917).
(17) "Organic Syntheses," Collect. Vol. III, Wiley, New York, N.Y., 1955, p 217.

Proton Magnetic Resonance and Stereochemical Assignments of Polycyclic Ketones and Olefins. Relative Double Bond Shielding Strengths

Edward Weissberger

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457

Received April 16, 1974

The proton magnetic resonance assignments of a series of related polycyclic cyclopentanones and their precursor olefins are compared. Stereochemical assignments are based upon observed coupling constants between bridgehead and cyclopentanone protons with iron pentacarbonyl induced coupling leading to exo-trans-exo products. The strengths of the shielding cones of ketonic and olefinic linkages are compared.

Recently, reports[1,2] of iron carbonyl coupling of olefins leading to cyclopentanone derivatives of the type illustrated in reactions 1, 2, and 3 have appeared and the mechanism[3] of this reaction considered. A particularly important aspect of the reaction, both synthetically and as it relates to mechanistic considerations, is product stereochemistry. Olefin reactivity and product stereochemistry are sensitive to the presence of bulky groups[1a] and complexing groups[2a] at the 7 position of 1 with significant stereochemical changes being observed when 7,7-dimethoxybenzonor-