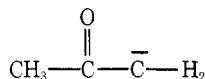


Figure 1. Comparison of gas phase deprotonation enthalpies of protonic acids in Table I, relative to cyclopentadiene, with corresponding solvation enthalpies of their anions in DMSO. Values for halide ions in water (X) estimated from enthalpies of transfer in ref 13.

dency toward solvation by ion-dipole interactions at a specific site. The differentiated solvation energies of $\text{N}\equiv\text{C}-\text{CH}_2^-$, $t\text{-Bu}-\text{C}\equiv\text{C}^-$, and



are interesting in view of the nearly equal gas phase acidities of their neutrals. The position of the acetonide anion is especially noteworthy since it links the charge-delocalized enolates with charge-localized alkoxides.

The spherical halide ions, unencumbered with organic groups, provide the normative electrostatic model for the effect of ion solvation. The difference between their behavior in aprotic DMSO and in water¹³ is attributed to differences in polarizability and hydrogen bonding. The unusually high solvation enthalpy of cyclopentadienyl anion relative to the other hydrocarbanions is consistent with Bordwell's proposal that dispersion force solvation is important here because of its unique degree of symmetrical charge delocalization over a relatively small volume.

Finally, we emphasize the striking sensitivity of alkoxide ion solvation energies to elaboration of the alkyl group. When contrasted with the other organic ions, their behavior strongly confirms our previous suggestion⁴ that steric hindrance to ion solvation is responsible for the dramatic difference between their basicity in the gas phase and that in solution. The possibilities for exploiting this phenomenon have already been noted.¹⁴

On the recommendation of a referee we wish to point out that the *accuracy* of some of the gas phase data, on which the derived solvation enthalpies depend, is questionable since they have not all been linked together by stepwise equilibration. We have therefore not reported the standard deviations of solvation enthalpies in the last column of Table I since such formal estimates of *precision* could give a misleading impression of their ultimate reliability. However, we have confidence in the basic conclusions expressed here for the following reasons: (a) Taft¹⁵ has found close agreement between Kebarle's high pressure mass spectrometry results and independent icr equilibration studies, (b) the alkoxide values were in fact based on gas phase equilibration,⁴ (c) Bordwell⁶ has noted systematic agreement between Kebarle's gas phase acidities and $\text{p}K_a$'s in DMSO for series of similar carbon acids. His results, like those in Figure 1, suggest that major inaccuracies in the gas phase acidities would probably result in vertical displacement of the

parallel lines with respect to each other rather than their slopes.

Acknowledgments. We appreciate the kindness of Professors Kebarle and Bordwell for providing us with valuable unpublished data.

References and Notes

- (1) This work was generously supported by N.S.F. Grant G.P. 6550-X.
- (2) (a) M. Szwarc, "Ions and Ion Pairs on Organic Reactions", Vol. 2, Wiley, New York, N.Y., 1974; (b) "Carbanions, Living Polymers and Electron Transfer Processes", Wiley, New York, N.Y., 1968; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965; (d) R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1973; (e) A. Streitwieser, Jr., *Prog. Phys. Org. Chem.*, **3**, (1965); (f) O. A. Reutov, K. P. Butin, and I. P. Beletskaya, *Russ. Chem. Rev.*, **43**(1) (1974); (g) J. R. Jones, "Ionization of Carbon Acids", Academic Press, New York, N.Y., 1973.
- (3) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 6561 (1968).
- (4) E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974).
- (5) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 5940 (1974).
- (6) F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin, and W. S. Matthews, *J. Am. Chem. Soc.*, **97**, 3226 (1975).
- (7) (a) E. M. Arnett, T. C. Moriarty, L. E. Small, J. P. Rudolph, and R. P. Quirk, *J. Am. Chem. Soc.*, **95**, 1492 (1973); (b) E. M. Arnett and T. C. Moriarty, *ibid.*, **93**, 4908 (1971).
- (8) Extensive subsequent research in collaboration with Bordwell's group confirms and improves the original correlation. Our joint efforts will be presented in detail in a full report.
- (9) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972.
- (10) Corresponding free energies and entropies of solvation would be interesting but the necessary Henry's law constants for these compounds over DMSO are not available. In view of the remarkably good correlation of our ΔH_s^0 (DMSO) values with Bordwell's $\text{p}K_a$'s^{7a,b} we doubt if relative free energies of solvation in DMSO for this series will differ drastically from their relative heats of solvation.
- (11) Evidence that ion-pairing energies between these anions and the potassium counterion are negligible is found in (a) the close correlation of our data with Bordwell's^{7a,b} although his anion concentration is a hundred-fold^{7a} less than ours and (b) the insensitivity of our ΔH_s^0 (DMSO) values for acetylacetone, phenylacetonitrile, and cyclopentadiene to the addition of di-benzo-18-crown-6 ether—a strong complexing agent for potassium ion.^{7b}
- (12) J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71**, 3063 (1967), have previously noted a close correlation between the electron affinities of polycyclic aromatic hydrocarbons in THF and in the gas phase.
- (13) B. G. Cox, *Annu. Rep. Prog. Chem.*, **70**, (Section A) (1973).
- (14) (a) C. A. Brown, *J. Org. Chem.*, **39**, 1324 (1974); (b) *ibid.*, **39**, 3913 (1974); (c) *J. Am. Chem. Soc.*, **95**, 982 (1973).
- (15) R. W. Taft in "Proton Transfer Reactions", Chapman and Hall, London, 1975.

Edward M. Arnett,* Dale E. Johnston, Leonard E. Small

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received April 28, 1975

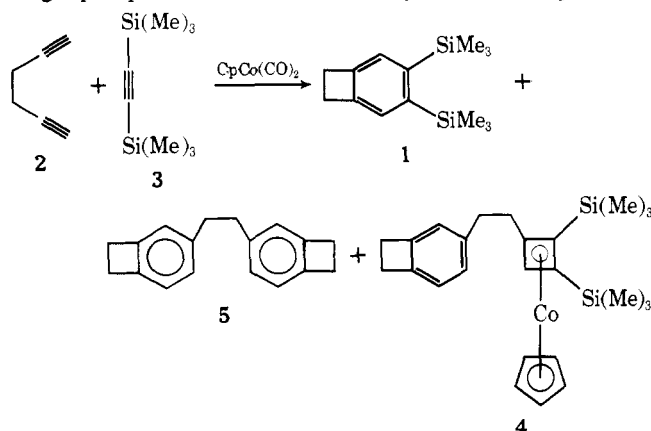
Transition Metal Catalyzed Acetylene Cyclizations. 4,5-Bis(trimethylsilyl)benzocyclobutene, a Highly Strained, Versatile Synthetic Intermediate

Sir:

Benzocyclobutenes, valuable precursors to theoretically interesting molecules,¹ are now gaining increasing importance as intermediates toward the synthesis of natural products.^{2,3} For this purpose complete control of substitution in the aromatic ring of benzocyclobutene is highly desirable and has been the source of considerable synthetic difficulty.⁴ We have recently developed a general synthesis of benzocyclobutenes via the co-oligomerization⁵ of 1,5-hexadiynes and substituted acetylenes using a cobalt catalyst.⁶ Yields, however, were only moderate (ca. 15%) for functionalized systems, and benzocyclobutenes substituted by electrophilic moieties (halogen, acetyl, etc.) were inaccessible due to the instability of the corresponding acetylenic precursors and/or catalyst under the reaction conditions.⁷

We now wish to report a solution to both of these problems by the synthesis and chemistry of the most strained⁸ simple benzocyclobutene hitherto synthesized, 4,5-bis(trimethylsilyl)benzocyclobutene (**1**).

Addition of a solution of 1,5-hexadiyne (**2**) in *n*-octane to a refluxing solution of a fivefold excess of bis(trimethylsilyl)acetylene (**3**)⁹ and catalytic amounts of η^5 -cyclopentadienylcobalt dicarbonyl in *n*-octane during 72 hr using a syringe pump¹⁰ leads to colorless crystals of compound **1**

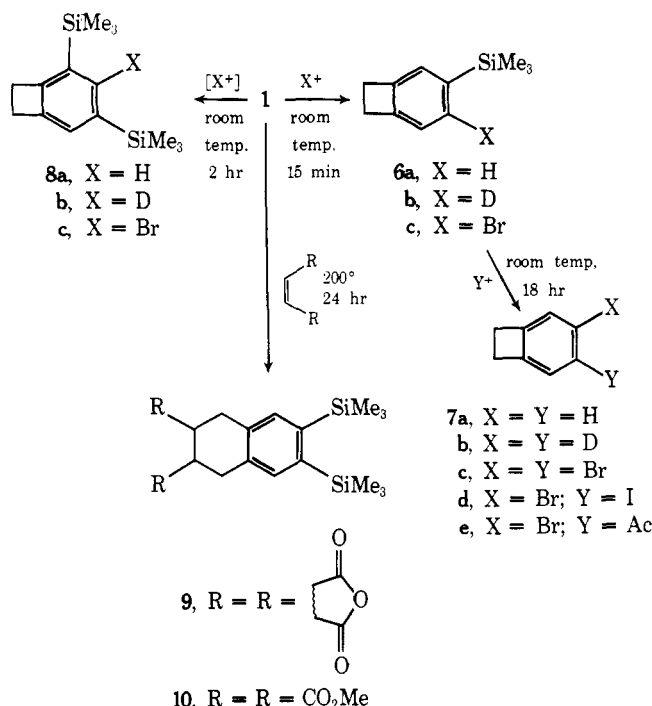


(>60%; mp 43–44°),^{12,15} 30% of trimer **5**,⁵ and 3% of the cyclobutadiene complex **4**¹² (ca. 40% based on initial catalyst), as a yellow oil and the only isolable cobalt containing molecule.

The high-yield formation of **1** is remarkable considering the strenuous conditions employed and the fact that **3** was thought to be unable to participate in acetylene cyclotrimerization reactions.^{11b} The inevitable presence of Co^{III} ions in the reaction mixture (via traces of air) does not seem to lead to rearrangement of the bulky substituents as observed in *o*-di-*tert*-butylbenzenes.¹³ The spectral data reveal that, not unexpectedly,¹⁴ the benzene ring retains its aromatic character. The ¹³C NMR spectrum¹⁵ shows an upfield shift (ca. 4–7 ppm) for the proton-bearing aromatic carbons when compared with 1,2,3,4-tetrahydro-6,7-bis(trimethylsilyl)naphthalene⁷ and other model systems,¹⁶ a strong indication of increased strain in the system.

Further confirmation of this finding is found in the chemical behavior of **1**. Deuteriodesilylation of **1** in CD₃COOD–CCl₄ (1:1.5:3 by volume) exhibits pseudo-first-order kinetics and a reactivity of the first trimethylsilyl group 33 times higher than the second. Thus, in comparison with *o*-bis(trimethylsilyl)benzene¹⁷ (protodesilylation rate ratio 17:1) fusion of the four-membered ring does not appear to increase the double bond character of the C₄–C₅ bond,^{18,24} significantly. The reaction proceeds cleanly via monosilyl compound **6a** to benzocyclobutene (**7a**) (>90%). Of all the recent syntheses of benzocyclobutene,²⁰ we regard this one to be the simplest and most straightforward. Deuterated acid leads to the deuterated derivatives **6b** and **7b**.¹² On the other hand, dilute acid (5–10%) rearranges²² **1** to **8a** (mp 20–25°)¹² and **8b** (>75% deuterium incorporation), respectively. Thus, starting from **1** and its 3,6-dideuterio analog⁷ various concentrations of deuterated or protic acid enable the formation of a large variety of deuterated benzocyclobutenes, of great utility in mechanistic and labeling studies on derived systems.^{16,21}

The remarkable reactivity of the first trimethylsilyl group toward electrophiles makes compound **1** an excellent synthetic intermediate. Stepwise reaction with a first electrophile (X⁺) followed by a second (Y⁺) leads to functionalized compounds **6c** (mp 55–56°) and **7c** (mp 72–73°), **7d** (mp 49–51°), and **7e** (bp 100° (0.05 mm), microstill) in excellent yields.¹² The rearrangement pathway to **8** can be ef-



fectively suppressed by using excess X⁺ or adding base (for example pyridine in the synthesis of **6c**) to speed up silyl abstraction.

Moreover, the two trimethylsilyl groups do not impair the ability of **1** to function as an *o*-xylylene synthon as exemplified by the essentially quantitative conversion to cycloadducts **9** and **10**, respectively.¹² Protodesilylation gives the known tetraline analogs.²³ Thus, using the *o*-bis(trimethylsilyl) unit in conjunction with the benzocyclobutene nucleus provides a most general synthetic entry with extensive control of substitution into systems containing the *o*-xylylene moiety. This should significantly improve the present scope of the use of benzocyclobutenes in synthesis.

Finally, we note with interest the exclusive formation of cobalt complex **4** in the synthesis of **1**. Also, no other trimethylsilyl containing oligomers nor a dimer of **2** could be isolated. Although **4** catalyzes the transformation of **2** to **5**, the rate of this process is very slow and no **1** is obtained, ruling out its role as the effective catalyst in the synthesis of **1**. Presumably **1** and **4/5** are formed via independent pathways.

Mechanistic details are under investigation.

Acknowledgments. We are grateful to Professors R. G. Bergman, M. S. Gibson, F. R. Jensen, and D. S. Noyce for helpful discussions and the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the National Institutes of Health (Biomedical Sciences Support Grant RR-7006) for financial support.

References and Notes

- (1) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967.
- (2) (a) W. Oppolzer, *J. Am. Chem. Soc.*, **93**, 3833 (1971); (b) W. Oppolzer and K. Keller, *ibid.*, **93**, 3836 (1971); (c) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **11**, 1031 (1972); (d) R. Hug, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 10 (1972); (e) B. J. Arnold and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 30 (1972); (f) W. Oppolzer, *Tetrahedron Lett.*, 1001 (1974).
- (3) (a) T. Kametani, K. Ogasawara, and T. Takahashi, *J. Chem. Soc., Chem. Commun.*, 675 (1972); (b) T. Kametani, T. Takahashi, and K. Ogasawara, *J. Chem. Soc., Perkin Trans. 1*, 1464 (1973); (c) T. Kametani, T. Takahashi, T. Honda, K. Ogasawara, and K. Fukumoto, *J. Org. Chem.*, **39**, 447 (1974); (d) K. Kametani, *Heterocycles*, **2**, 9 (1974).
- (4) (a) C. Eaborn, A. A. Najam, and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 1*, 2481 (1972); (b) for a review, see I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970); (c) G. Kaupp, *Chimia*, **25**, 230 (1971).

- (5) K. P. C. Vollhardt and R. G. Bergman, *J. Am. Chem. Soc.*, **96**, 4996 (1974).
- (6) K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Am. Chem. Soc.*, **96**, 4998 (1974).
- (7) R. L. Hillard III, and K. P. C. Vollhardt, unpublished observations.
- (8) The strain inherent in **1** is possibly equivalent to the strain encountered in 1,2,4,5-dicyclobutabenzene, a tricyclic benzenoid system: M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **82**, 2524 (1960).
- (9) K. C. Frisch and R. B. Young, *J. Am. Chem. Soc.*, **74**, 4853 (1952); Aldrich Chemical Co.
- (10) Compound **3** does not trimerize under the reaction conditions.^{11a} Considerably lower yields of **1** are obtained when equimolar amounts of **2** and **3** are employed⁵ (3%) or **2** is added to excess **3** in one portion (8%).
- (11) (a) H. Sakurai and J. Hayashi, *J. Organomet. Chem.*, **70**, 85 (1974); (b) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, **12**, 323 (1974).
- (12) All new compounds reported gave satisfactory analytical and/or spectral data.
- (13) U. Krüerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).
- (14) Aromatic rings can significantly distort from planarity without losing aromatic character: H. Wynberg, W. C. Nieuport, and H. T. Jonkman, *Tetrahedron Lett.*, 4823 (1973).
- (15) ¹H NMR (CCl₄) τ 2.86 (s, 2 H), 6.86 (s, 4 H), 9.67 (s, 18 H); ¹³C NMR (CDCl₃) ppm 2.41 (SiMe₃), 30.2 (C_{1,2}), 129.1 (C_{3,6}), 144.3 (C_{4,5}), 145.9 (C_{7,8}); uv $\lambda_{\text{max}}^{\text{EtOH}}$ large end absorption, 226 sh (ϵ 10,200), 248 sh (11,000), 266 (620), 272.5 (815), 280.5 nm (645).
- (16) (a) A. J. Jones, P. J. Garratt, and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **12**, 241 (1973); (b) W. Adcock, B. D. Jupta, T. C. Khor, D. Doddrell, D. Jordan, and W. Kitching, *J. Am. Chem. Soc.*, **96**, 1595 (1974); (c) J. B. Stothers, "Carbon-13 N.M.R. Spectroscopy", Academic Press, New York, N.Y., 1972.
- (17) C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Chem. Soc. B*, 15 (1969).
- (18) (a) C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27**, 701 (1971); (b) G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, *J. Phys. Chem.*, **72**, 668 (1968).
- (19) A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc. B*, 12 (1969).
- (20) See R. P. Thummel, *J. Chem. Soc., Chem. Commun.*, 899 (1974), and the references therein.
- (21) See, for instance, H. P. Figeys, *Top. Carbocyclic Chem.*, **1**, 269 (1969).
- (22) Similar observations were made in the case of *o*-bis(trimethylsilyl)benzene, but prolonged exposure to high temperatures and acidic catalyst were necessary to effect isomerization: D. Seyferth and D. L. White, *J. Am. Chem. Soc.*, **94**, 3132 (1972).
- (23) (a) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.*, 15 (1962); (b) R. D. Haworth and F. H. Slinger, *J. Chem. Soc.*, 1321 (1940).
- (24) A structural determination of **1** is in progress.

W. G. L. Aalbersberg, A. J. Barkovich, R. L. Funk
R. L. Hillard III, K. P. C. Vollhardt*
Department of Chemistry, University of California
Berkeley, California 94720
Received May 5, 1975

Stereochemical Course of the Reaction of Iron Carbonyl with Diastereomeric Vinyloxiranes

Sir:

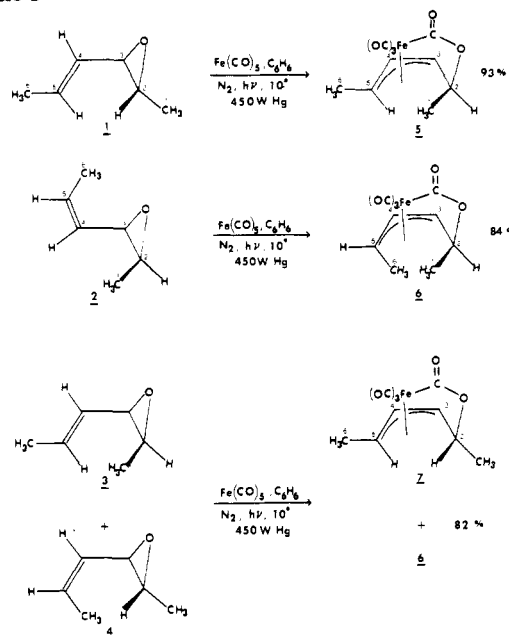
The reaction of the vinylcyclopropyl system with iron carbonyl has been investigated extensively.¹ Recently the analogous reaction with vinyloxiranes has been reported.² This latter system appeared amenable to a detailed stereochemical analysis, and we report results of the reaction using diastereomeric vinyloxiranes.

Starting with the three pure dienes (*E,E*)-2,4; (*Z,Z*)-2,4; and (*Z,E*)-2,4-hexadienes, monoepoxidation yielded the vinyloxiranes **1**, **2**, **3** + **4**, respectively.³ Both thermally and photochemically these compounds reacted with iron carbonyl to yield ferrelactone complexes. The thermal reaction yielded mixtures of diastereomers⁵ but the photochemical reaction⁶ proceeded *completely stereospecifically* (Scheme I).

The starting point for unraveling the stereochemical structures of complexes **5**, **6**, and **7** was an X-ray crystallographic determination on **7**. With this established, NMR studies enabled elucidation of the structures of **5** and **6**.

Ferrelactone **7** crystallized in the centrosymmetric orthorhombic space group *Pbca*. The cell dimensions were *a* =

Scheme I



12.0732 (16) Å, *c* = 12.2010 (15) Å, and $\rho_{\text{calcd}} = 1.575$ g/cm³ for **Z** = 8. X-Ray diffraction data ($2\theta_{\text{max}} = 50^\circ$, Mo K α radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved via Patterson, Fourier, and least-squares refinement methods. The final discrepancy indices were $R_F = 3.21\%$, $R_{wF} = 3.06\%$ for 2377 independent reflections. The molecular structure, with selected bond distances, is shown in Figure 1.

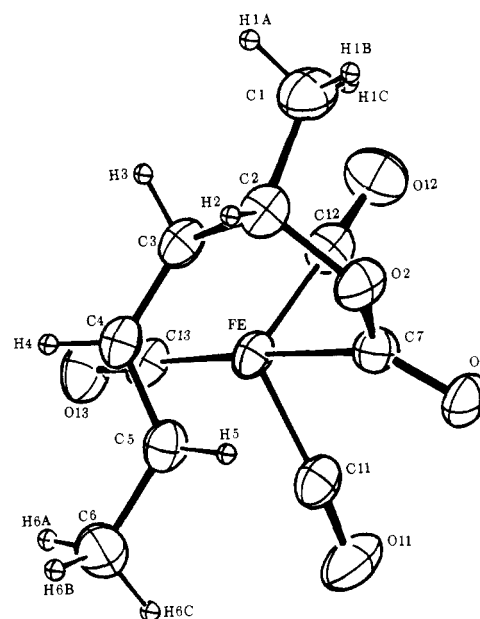


Figure 1. Molecular geometry of ferrelactone **7**. Important intraligand bond distances (in Å) are: C(1)–C(2) = 1.503 (5), C(2)–C(3) = 1.510 (4), C(3)–C(4) = 1.406 (3), C(4)–C(5) = 1.389 (4), C(5)–C(6) = 1.498 (4); C(2)–O(2) = 1.438 (3), O(2)–C(7) = 1.364 (3), C(7)–O(7) = 1.211 (3). Iron-carbon bond distances are: Fe...C(3) = 2.090 (2), Fe...C(4) = 2.077 (3), Fe...C(5) = 2.209 (3), and Fe–C(7) = 1.985 (2).

Using the ¹H NMR spectrum of **7** as a reference the relative stereochemistries of **5** and **6** were determined by analysis of coupling constants and induced chemical shifts (Table I). First, comparing **5** and **7** the only difference in coupling constant is the vicinal coupling ³J_{2,3} of 4.0 Hz in **5**