

We are currently studying the formation of other hetero analogues of carbapenems through the C₃-N coupling route.

Acknowledgment. This work was supported by NIH Grants GM-07874 and GM-13854. The support of the NSF/NMR Northeast Regional Facility at Yale University (Grant CHE-7916210) is acknowledged.

Supplementary Material Available: ¹H NMR, infrared, mass spectral, and elemental analytical data, physical constants, and purification procedures for key intermediates (9 pages). Ordering information is given on any current masthead page.

Dynamic NMR and Molecular Mechanics Study of the Rotation of a 1-Adamantyl, a 1-Bicyclooctyl, a 1-Norbornyl, and a *tert*-Butyl Group. The Relative Size of an Adamantyl Group. The Dilemma of Calculated Barriers to Rotation

J. E. Anderson,* H. Pearson, and D. I. Rawson

Chemistry Department, University College
London WC1E 6BT, U.K.

Received May 7, 1984

The particularities of the bridgehead position in bicyclic molecules have long interested organic chemists. Some unusual property of a substituent attached to the bridgehead is usually related to differences between the bridgehead and a *tert*-butyl quaternary carbon, the obvious acyclic analogue. As the geometry around the bridgehead changes, both the character of the bond attaching the substituent and the steric interactions experienced by the substituent change.

We now report an investigation that concentrates on the steric interactions. We have introduced a suitably large group C(Me)₂Cl at the bridgehead in a series of compounds and have measured the barrier to its rotation by dynamic NMR spectroscopy. The results^{1,2} in these compounds and in other compounds of interest^{4,5} are shown in Chart I.

The barrier to rotation in the *tert*-butyl compound **4** is higher than for any of the bridged compound **1-3**, so in that sense the bicyclic compounds appear smaller to a bridgehead substituent than does a *tert*-butyl group.

Interestingly high rotational barriers are found in the more flexible molecules, the *tert*-butyl **4**, and the bicyclooctyl **2**.⁶ This suggests that flexibility in attaining a stable rotational ground state may be as important as any transition state effects in determining the relative magnitudes of barriers.

The bicycloheptane system has smaller endocyclic bond angles⁷ at the bridgehead. In a sense, the bridges are pinned back more, and so interactions during rotation are less. The low barrier agrees

Chart I. Barriers to Rotation (kcal/mol)

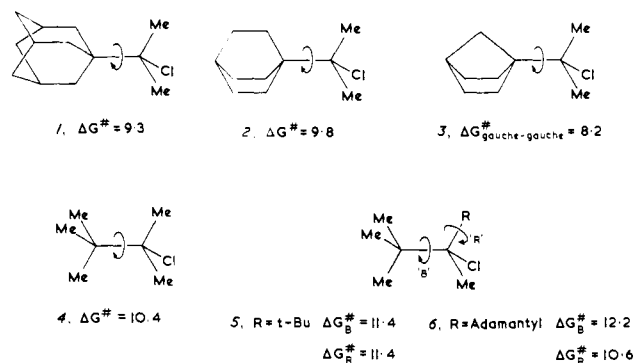
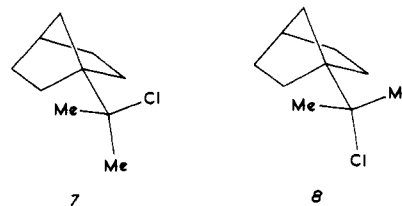


Table I. Calculations and Experimental Barriers (kcal/mol) for R-C(Me)₂Cl

R	ΔH*		exptl ΔG*
	MM2	MM2OS	
4 , <i>tert</i> -butyl	7.1	10.2	10.4
1 , 1-adamantyl	7.3	10.5	9.3
2 , 1-bicyclooctyl	8.2	10.7	9.8
3 , 1-bicycloheptyl gauche-gauche	6.4	9.6	8.2
gauche-anti	6.5	9.7	

with this. The barrier corresponds here to interconversion of gauche conformations, i.e., **7**, with its enantiomer **7'**. Such a



conformation is more stable than the anti one **8**, by at least 0.7 kcal/mol, since no signals are seen for the latter conformation when rotation **7** ⇌ **7'** is slow on the NMR timescale.²

The adamantyl rotational barrier is about 1 kcal/mol lower than the *tert*-butyl barrier, both in **1** vs. **4** and in **6R** vs. **5R**.⁸ In contrast to this, when these groups are acting only as substituents on an ethane bond (see **5B** and **6B**) rather than forming one end of it (as in **1** and **4**), the adamantyl group hinders rotation more than the *tert*-butyl group. Thus the relative "size" of *tert*-butyl and adamantyl groups depends on the context.

Empirical force field calculations have been used with much success in predicting the structures of bicyclic and suchlike molecules.⁹⁻¹¹ They predict rotational barriers less satisfactorily, giving values markedly lower than experiment, particularly in more crowded molecules. Osawa¹² has recently proposed new values for some of the parameters¹³ for MM2, chosen to produce calculated rotational barriers that are more consonant with those determined experimentally. Table I compares experimental barriers for **1** to **4** with ones calculated by using MM2 and also by using Osawa's modification (MM2OS).

Both parameter sets put the bicyclic compounds in the correct order of increasing barrier, but MM2OS predicts values greater than

(8) We have observed a similar effect in one other pair of compounds with heteroatom substituents.

(9) Burkaert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982; Adv. Chem. Ser. Ab. 177.

(10) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8129. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1977**, *13*, 395. (c) The calculated barriers reported here are the difference in the value of the "steric energy" of the MM2 program for the ground and transition states.

(11) Osawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1.

(12) Jaime, C.; Osawa, E. *Tetrahedron* **1983**, *39*, 2769.

(13) The changes affect the calculated torsional interactions principally.

(1) Barriers were determined from a full line-shape analysis of changes in the NMR spectrum around the coalescence temperature, and free energies of activation quoted in the scheme are for these temperatures (see supplementary material).

(2) Our search for anti conformations of **3** was based on the assumption that a signal 5% or more of such a conformation would be detected at around -125 °C, when limiting low temperatures are observed. No such signals were located, but there is evidence for some very small amount of an anti conformation (<5%) in that the C-H and C-Cl signals broaden around -100 °C and then sharpen at lower temperatures, compared with the C-quat and CH₂-7 signals. None of these four signals should be affected by the observed gauche-gauche interconversion. Application of the Anet and Basus equations³ to these observations is not possible in the absence of reasonable chemical shift values.

(3) Anet, F. A. L.; Basus, J. J. *Magn. Reson.* **1978**, *32*, 334-337.

(4) Anderson, J. E.; Pearson, H. *J. Chem. Soc. B* **1971**, 1209.

(5) Anderson, J. E.; Pearson, H. *J. Am. Chem. Soc.* **1975**, *97*, 964.

(6) In the bicyclooctyl case, the three -CH₂-CH₂- bridges can easily alter their degree of zigzagging, and, interestingly, calculations (vide infra) suggest that this does change during rotation by 7-10°.

(7) Chiang, J. F.; Wilcox, C. F.; Bauer, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 3149.

experiment while as expected MM2 produces values less than experiment but agreeing almost as well. All calculations for $^{1-3}$ are at least 0.8 kcal/mol different from experiment, but as always, caution should be exercised in comparing enthalpies of activation calculated for rotation in the gas phase and free energies of activation measured in solution.

The entropies of activation necessary to reconcile the MM2 calculated values and the DNMR experimental values range from -8 to -17 eu, rather greater in size than is normally considered likely for an internal rotation, but we have determined⁵ a value of -7.2 eu for the compound **4**. This value is significantly in the correct sense, and it is unfortunate that the quality of the changes in the low-temperature carbon-13 spectra of **1-3** do not allow the determination of entropies of activation for these molecules. To reconcile the MM2OS calculated enthalpies and the experimental free energies would require unprecedented *positive* entropies of activation for these bridged compounds.

Neither set of force field parameters predicts that the *tert*-butyl compound **4** has a greater rotational barrier than the bridged compounds. A consideration of entropies of activation may also help to remove this discrepancy. In the *tert*-butyl compound **4**, the entropy¹⁴ of the more congested transition state can be quite different from that of the unconstrained ground state. For the bridged compounds **1-3**, constraints are present in both the ground and transition states, so there is less scope for entropy change.¹⁴ The more negative entropy of activation for the *tert*-butyl compound that results would lead to the higher free energy of activation, which is experimentally observed.

Acknowledgment. We are grateful to two referees for encouraging us to discuss the entropy of activation explicitly and for helpful comments thereon.

Registry No. **1**, 33932-93-3; **2**, 94859-65-1; **3**, 10498-92-7; **4**, 918-07-0.

Supplementary Material Available: Relevant NMR spectral details and spectral changes with temperature (2 pages). Ordering information is given on any current masthead page.

(14) The important entropy term is that associated with rotation of individual methyl groups. There are five of these for the *tert*-butyl compound and only two for the bridged compounds.

Isolation and Characterization of Iron Methylene (FeCH₂) via FTIR Matrix Isolation

Sou-Chan Chang, Zakya H. Kafafi,* Robert H. Hauge, W. Edward Billups, and John L. Margrave

Rice Quantum Institute and Department of Chemistry
Rice University, Houston, Texas 77251

Received December 4, 1984

Since the early work of Fischer,¹ a number of simple alkylidene and methylene complexes have been reported.² The isolation and characterization of these complexes is of importance since they are now recognized as major intermediates in catalytic processes such as olefin metathesis³ and alkane activation.⁴ We report here the matrix isolation and characterization of the simple unligated species FeCH₂.

Iron atoms were codeposited with a mixture of argon and diazomethane onto a rhodium-plated copper mirror at 14 K. The infrared spectra, measured with an IBM IR98 Fourier Transform spectrometer, showed new peaks at 2995.0, 2941.6, 1122.4, 700.3, and 623.6 cm⁻¹ (Figure 1). These absorptions retained the same

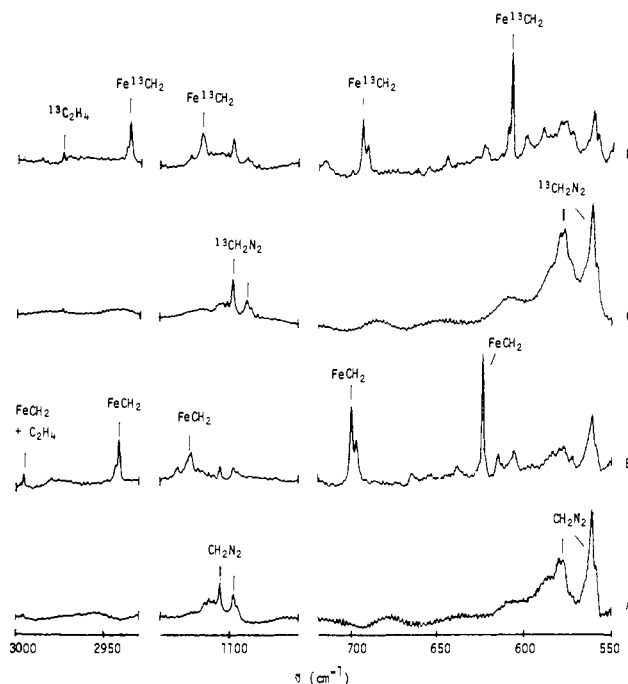


Figure 1. FTIR spectra of matrix-isolated diazomethane and diazomethane iron in solid argon. Molar ratios: (A) CH₂N₂:Ar = 9.8:1000; (B) Fe:CH₂N₂:Ar = 9.5:9.8:1000; (C) ¹³CH₂N₂:Ar = 11.6:1000; (D) Fe:¹³CH₂N₂:Ar = 7.7:11.6:1000. The strongest peak at 623.6 cm⁻¹ in B has an absorbance of 0.092.

Table I. Iron-Carbon Stretching Frequencies (cm⁻¹) for Some Selected Matrix-Isolated Organoiron Compounds

Fe=CH ₂	623.6	present study
HFe-CH ₃	522	ref 5
HFe-CHCH ₂	507	ref 7
H ₃ CFe-CHCH ₂	538	ref 8

relative intensities at different iron and diazomethane concentrations and remained in the spectrum even under the most dilute conditions (Fe:CH₂N₂:Ar = 0.07:1.0:100).

Preliminary isotopic studies using carbon-13 enriched diazomethane showed that the peak at 623.6 cm⁻¹ is shifted by 15.9 cm⁻¹. The same band showed an iron-54 isotopic shift of 2.3 cm⁻¹. Thus both isotopic studies indicated that the 623.6-cm⁻¹ peak is due to an iron-carbon stretching mode and that the species contains only one iron atom and one carbon atom. By comparing the measured iron-carbon stretching frequency of this species to those known for iron-carbon single bonds (Table I), one concludes that this Fe-C bond must involve some double-bond character. Other bands related to this species were observed at 2995.0, 2941.6, 1122.4, and 700.3 cm⁻¹ and were assigned to the asymmetric and symmetric stretching, bending, and rocking or wagging modes of a CH₂ group. Thus the species responsible for these absorptions as well as the Fe=C stretching frequency has been identified as iron methylene, Fe=CH₂. Additional studies on the reactions of iron and ¹³CH₂N₂, CD₂N₂, and CHDN₂ are in progress.

Diiron was also found to react with diazomethane in solid argon to yield (N₂)Fe₂CH₂. This diiron compound probably has a bridging methylene although additional isotopic work will be required to fully elucidate its structure. The presence of nitrogen can be inferred from the strong nitrogen-nitrogen stretching frequency which appears at 1812 cm⁻¹.

When hydrogen was added to the Fe/CH₂N₂ system in argon, CH₃FeH was produced⁵ along with methane. At higher diazomethane concentrations, absorptions due to ethylene were observed (Figure 1). The dimerization of methylene appears to be favored

(1) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651.
 (2) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; p 171.
 (3) Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.
 (4) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97; *Kinet. Katal.* **1977**, *18*, 1129.

(5) (a) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393. (b) Kafafi, Z. H.; Hauge, R. H.; Fredin, L.; Billups, W. E.; Margrave, J. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1230.