

The bicyclobutyl anion: an alkyl carbanion

Steven R. Kass, and Phillip K. Chou

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This reversal is consistent with the axial or pseudoaxial proton being downfield of its equatorial or pseudoequatorial counterpart in both **4** and **7(3a)**.

The above is fully reinforced by the ^1H NMR parameters for the 5-*t*-Bu analogue **3b** (major diastereomer) which evidently has the *t*-Bu (which replaces H_6) in a pseudoequatorial position.⁹ $^3J_{\text{HH}}$ and $^3J_{\text{HP}}$ values are close to those for **3a**. As we have noted previously for P(IV) 5-*tert*-butyl-2-oxo-1,3,2-oxazaphosphorinanes,^{5a-e} the combination of large J_{2P} (29.4 Hz) and J_{25} (7.3 Hz) found for **3b** can only be reconciled if the conformer populated is a boat or twist. The P(IV) systems require a group such as *tert*-butyl at C_5 in order for the steric or electronic property of a group on phosphorus to express itself in population of a twist or boat. By contrast destabilization of either chair conformation of **3a** (5 or its alternative) by the above-described steric repulsions appears to be an intrinsic property of P(V) ring systems attached apical equatorial.

Compounds **14a**¹⁰ and **14b**¹¹ were shown by X-ray crystallography to possess six-membered rings in non-chair conformations. The nitrogen lone pair of **14b** is in the equatorial plane. To our knowledge our ^1H NMR results present the first clear evidence for the population of a phosphorinane ring on P(V) in a non-chair form in solution.

The idea that boat or twist conformations for the pentacoordinate intermediates in enzymic reactions of nucleoside cyclic 3',5'-monophosphates should receive serious consideration finds support in the present NMR study and also in the X-ray results. The findings in the model systems of course do not define what actually does occur in the enzyme system.

Acknowledgment. Support of this work by Grant CA 11045 from the National Cancer Institute of the Public Health Service is gratefully acknowledged. We thank Dr. Alan E. Sopchik for obtaining the 500-MHz spectra for **3a** and **3b**.

Supplementary Material Available: Table of ^{13}C NMR data for **3a** and ^1H NMR data for **3b** (1 page). Ordering information is given on any current masthead page.

(9) Yu, J. H., unpublished results from this laboratory.

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The Bicyclobutyl Anion: An Alkyl Carbanion

Steven R. Kass* and Phillip K. Chou

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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Alkyl anions in the form of organometallic compounds are extremely important reagents and have been extensively studied in solution.¹ In the gas-phase alkyl carbanions (R^-) are exceedingly difficult or even impossible to generate for any substantial period of time. This is the result of their high reactivity and low, or in some cases even negative, electron affinities.² Despite these formidable experimental problems, acidities of a variety of alkanes have been determined by an ingenious kinetic technique which does not require the free R^- .³ More recently,

Table I. Summary of Results for Bracketing Experiments

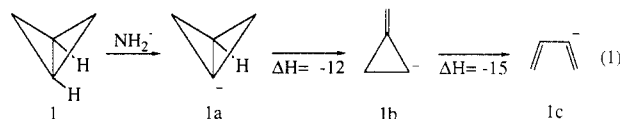
ref acid	ΔH_{acid}^a	proton transfer ^b		EA (eV)	electron transfer ^b
		ref acid	conjugate base		
NH_3	403.6	—	+		
EtNH_2	399.3	+	(slow)		
$n\text{-PrNH}_2$	398.4	+			
$i\text{-PrNH}_2$	397.3	+			
Me_2NH	396.2	+			
H_2O	390.7	+	—		
SO_2				1.10 ^c	+ ^d
O_2				0.44 ^e	— ^f

^a Acidities are in kcal mol⁻¹ and come from Lias et al. (see ref 9a).

^b A "+" indicates the occurrence and a "—" denotes the absence of the indicated reaction. The conjugate base column corresponds to reaction of **1** with the conjugate base of the reference acid. ^c Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, 90, 2574. ^d Additional products are observed at m/z 49 (HSO^-) and 117 (adduct). ^e Celotta, R. J.; Bennett, R. A.; Hall, J. L.; Siegel, M. W.; Levine, J. J. *Phys. Rev.* **1972**, A6, 631. ^f No reaction with O_2 is observed.

Squires and Graul have described the generation of a few alkyl carbanions by collision-induced dissociation of carboxylates in a flowing afterglow-triple quadrupole instrument.⁴ We now wish to report the first deprotonation of an alkane to generate the corresponding alkyl anion.

Bicyclobutane (**1**) is a well-known, thermally stable but highly strained hydrocarbon.⁵ Its rigid ring structure results in the bridgehead carbon-hydrogen bonds having a high degree of s-character (40% s).⁶ This is reflected in the unusually large ^{13}C - ^1H coupling constant, 202 Hz, and leads to enhanced acidity in solution.⁵ The gas-phase behavior was examined in a flowing afterglow device,⁷ where it was found that NH_2^- reacts with **1** by proton abstraction to readily afford a (P-1)⁻ ion (m/z 53). Simple deprotonation would lead to the bicyclobutyl anion (**1a**), but ring opened structures (**1b** and **1c**) are thermodynamically favored and could arise from an allowed electrocyclic process (eq 1).^{8,9}



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(5) Wiberg, K. B. *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G., Eds.; Academic Press: New York, 1968; Vol. 2, pp 185-205.

(6) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, 85, 2022.

(7) All experiments were carried out with He buffer gas at 298 ± 2 K and at pressures of 0.35-0.40 T. The technique has previously been described and has recently been reviewed. See: (a) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopt, A. *Adv. At. Mol. Phys.* **1969**, 5, 1. (b) Smith, D.; Adams, N. C. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 1. (c) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, 14, 146. (d) Graul, S. T.; Squires, R. R. *Mass Spect. Rev.* **1988**, 7, 263. Our particular apparatus will be fully reported on in a subsequent publication.

(8) For a general discussion on electrocyclic ring openings of cyclopropyl anions, see: (a) Staley, S. W. *Organic Chemistry. Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, pp 199-264. (b) le Noble, W. J. *Reactive Intermediates*; Jones, M., Jr., Moss, R., Eds.; John Wiley and Sons: New York, 1978; Vol. 1, pp 27-67. (c) Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* **1982**, 47, 2614 and references therein. Examples of cyclopropyl anions which do not undergo ring opening in the gas phase are given in the following: (d) Andrist, A. H.; DePuy, C. H.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, 106, 845. (e) Dawson, J. H. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, 334, 3.

(9) Heats of reaction given in eq 1 come from the heats of formation of the anions which are given by $\Delta H_f(\text{A}^-) = \Delta H_{\text{acid}}(\text{AH}) - \Delta H_f(\text{H}^+) + \Delta H_f(\text{AH})$. The quantities used (in kcal mol⁻¹) are $\Delta H_f(\text{H}^+) = 365.7$ (ref a), $\Delta H_f(\text{1}) = 51.90$ (ref b), $\Delta H_{\text{acid}}(\text{methylene-cyclopropane}) = 390 \pm 3$ (ref c), $\Delta H_f(\text{methylene-cyclopropane}) = 47.92$ (ref b), $\Delta H_{\text{acid}}(\text{1,3-butadiene}) = 397 \pm 6$ (ref d), and $\Delta H_f(\text{1,3-butadiene}) = 26.11$ (ref b). (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, 17, Supplement 1. (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. (c) Kass, S. R.; DePuy, C. H., unpublished data. (d) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, 105, 2565.

(1) See: March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons: New York, 1985; pp 151-162, and references therein.

(2) (a) Schleyer, P. v. R.; Spitznagel, G. W.; Chandrasekhar, J. *Tetrahedron Lett.* **1986**, 27, 4411. (b) Leroy, G.; Wilante, C.; Peeters, D.; Uyewa, M. M. *J. Mol. Struct.: Thechem* **1985**, 124, 107. For experimental evidence see ref 3 and 4.

(3) DePuy, C. H.; Bierbaum, V. M.; Damrau, R. *J. Am. Chem. Soc.* **1984**, 106, 4051. For an alternative view, see: Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, 110, 2714 and references therein.

The structure of the (P-1)⁻ ion obtained from bicyclobutane was shown to be **1a** based on its reactivity and hydrogen/deuterium exchange behavior.¹⁰ Deuterium oxide is a sufficiently strong Brønsted acid to react with the ion by deuterium transfer to afford OD⁻. In contrast, addition of ND₃, which is less acidic, to the (P-1)⁻ results in one exchange of hydrogen for deuterium. This is consistent only with the proposed structure **1a**. Ions **1b** and **1c**, independently produced by proton abstraction from methylenecyclopropane or 1-methylcyclopropene^{9c,11} and 1,3-butadiene, undergo up to 5 H/D exchanges with D₂O and ND₃, respectively. Therefore, neither **1b** or **1c** can be the ion produced by proton abstraction from bicyclobutane.¹²

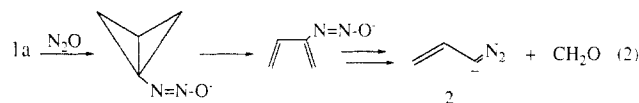
The acidity of **1** was measured with the bracketing technique. This is the simplest method for measuring acidities and involves adding progressively stronger and stronger bases to an acid until proton transfer occurs. The reliability of the process is greatly enhanced if the other direction is also examined by adding successively potent acids to the conjugate base of interest. Both directions were studied, and the results, summarized in Table I, allow us to assign $\Delta H_{\text{acid}} = 398 \pm 2 \text{ kcal mol}^{-1}$ to bicyclobutane. This is in excellent agreement with a calculated value of 400 kcal mol⁻¹ using AM1¹⁴ and a linear correction, which is required to reliably reproduce hydrocarbon acidities.¹⁵

In the liquid phase it has been observed that there is a linear correlation between acidity, pK_a , and ¹³C-¹H coupling constants.¹⁶ We have found this relationship to be equally true for gas-phase acidities of small hydrocarbons.¹⁷ It will break down for compounds whose conjugate bases are resonance stabilized and for larger molecules where polarization effects are important. Nevertheless, this relationship may be of value in predicting acidities and finding accessible alkyl anions.

The electron affinity (EA) of **1a** was bracketed and found to be $0.77 \pm 0.33 \text{ eV}$ ($17.8 \pm 7.6 \text{ kcal mol}^{-1}$, see Table I). Even with the relatively large uncertainty, this is the largest EA reported to date for an alkyl anion. When combined with the acidity, a bridgehead C-H bond dissociation energy of $\sim 102 \text{ kcal mol}^{-1}$ is obtained.¹⁸ The C-H bond energy in cyclopropane¹⁹ is 106 kcal mol⁻¹ so the $\sim 10 \text{ kcal mol}^{-1}$ difference in electron affinities³ can be attributed to the enhanced acidity of bicyclobutane.

The reactivity of **1a** with nitrous oxide, carbon disulfide, and isoamyl nitrite has been briefly explored. All three reactions occur quite readily. Addition of N₂O to **1a** produces two ionic products of m/z 67 and 97, which correspond to the vinyl diazomethane

anion (**2**) and an adduct, in approximately a 9:1 ratio (eq 2). The



mechanism is presumably the same, after isomerization of the initial adduct, as in the known reaction between the (P-1)⁻ of 1,3-butadiene and N₂O.²⁰ Carbon disulfide and isoamyl nitrite both react in a manner that is consistent with what has previously been described.^{21,22} The major product with the former compound is an ion of m/z 85 which corresponds to sulfur atom transfer. The latter reagent reacts with **1a** to afford NO₂⁻ (m/z 46) and an ion which corresponds to C₄H₄NO⁻ (m/z 82) as the major products. Smaller amounts of CN⁻ (m/z 26), 3-methyl-1-butoxide (m/z 87), and an ion of m/z 42 are also produced.

Further investigations into the chemistry of the bicyclobutyl anion and other small ring anions are in progress and will be presented in due course.

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Evidence for Free Monomeric Thiometaphosphate Anion in Aqueous Solution

J. Burgess, N. Blundell, P. M. Cullis,* C. D. Hubbard, and R. Misra

Department of Chemistry
The University, Leicester, LE1 7RH, UK

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Phosphoryl- and thiophosphoryl-transfer reactions have been extensively studied, particularly in relation to enzyme-catalyzed processes.¹ Despite this close scrutiny the mechanisms of these reactions have still not been unambiguously established. Of particular interest has been the series of studies pertinent to the "freeness" of monomeric metaphosphate in reactions of phosphate monoesters.² We have recently made a comparative study of model phosphoryl- and thiophosphoryl-transfer reactions with principally stereochemical methods.³ On the basis of these studies we believe that there are significant differences between the phosphoryl- and thiophosphoryl-transfer reactions in aqueous

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(12) Ions **1b** and **1c** can also be ruled out based on their reactivity with N₂O and O₂. The former ion reacts with N₂O to afford CN⁻ as the major product,¹³ while **1c** and O₂ undergo a rapid reaction to afford a variety of products. Another isomer which was considered is the vinyl anion obtained by proton abstraction from cyclobutene. This ion undergoes 1 H/D exchange with ND₃¹³ but reacts readily with O₂ to afford O₂⁻ and with N₂O to produce both the vinyl diazomethane anion (**2**, m/z 67) and cyclobutanone enolate or the enolate of methyl vinyl ketone (m/z 69).^{9c}

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(17) A plot of gas-phase acidities versus ¹³C-¹H coupling constants is linear: $y = -0.296x + 455.3$, $r = 0.98$. The data points are CH₄ (416.6, 125), C₂H₄ (406, 156), c-C₃H₆ (412, 161), **1** (398, 202), and C₂H₂ (379.6, 249) where the acidities (ref 9a) and coupling constants (Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *32*, 767 and 1471 and ref 5), in that order, are given in the brackets.

(18) BDE (A-H) = $\Delta H_{\text{acid}}(\text{AH}) - \text{IP}(\text{H}^+) + \text{EA}(\text{A})$ where $\text{IP}(\text{H}^+) = 313.6 \text{ kcal mol}^{-1}$ (see ref 9a).

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