J|A|C|S
A R T I C L E S

Formation of a 1-Bicyclo[1.1.1]pentyl Anion and an Experimental Determination of the Acidity and C−H Bond Dissociation Energy of 3-*tert*-Butylbicyclo[1.1.1]pentane

Dana R. Reed,[‡] Steven R. Kass,*[,‡] Kathleen R. Mondanaro,[†,§] and
William P. Dailey[§]

Contribution from the Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455, and Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104-6323

Received September 18, 2001

Abstract: Decarboxylation of 1-bicyclo[1.1.1]pentanecarboxylate anion does not afford 1-bicyclo[1.1.1]pentyl anion as previously assumed. Instead, a ring-opening isomerization which ultimately leads to 1,4-pentadien-2-yl anion takes place. A 1-bicyclo[1.1.1]pentyl anion was prepared nevertheless via the fluoride-induced desilylation of 1-*tert*-butyl-3-(trimethylsilyl)bicyclo[1.1.1]pentane. The electron affinity of 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl radical (14.8 ± 3.2 kcal/mol) was measured by bracketing, and the acidity of 1-*tert*-butylbicyclo[1.1.1]pentane (408.5 ± 0.9) was determined by the DePuy kinetic method. These values are well-reproduced by G2 and G3 calculations and can be combined in a thermodynamic cycle to provide a bridgehead C−H bond dissociation energy (BDE) of 109.7 ± 3.3 kcal/mol for 1-*tert*-butylbicyclo[1.1.1]pentane. This bond energy is the strongest tertiary C−H bond to be measured, is much larger than the corresponding bond in isobutane (96.5 ± 0.4 kcal/mol), and is more typical of an alkene or aromatic compound. The large BDE can be explained in terms of hybridization.

Introduction

Bridgehead cations, radicals, and anions have been extensively studied, in part, because their geometry provides an attractive means for testing computational methods and probing relationships between structure and reactivity, orbital interactions, and substituent effects among others.[1−5] These reactive intermediates also are useful in the construction of a diverse range of compounds spanning from natural products to molecular Tinkertoys.[6−15]

Bicyclo[1.1.1]pentane is the smallest bridged bicyclic hydrocarbon and, perhaps, the most interesting. It has an extremely short C1−C3 nonbonded distance (1.85 Å) which leads to interesting results.[16−19] For example, the solvolysis of 1-chlorobicyclo[1.1.1]pentane takes place more readily than that of *tert*-butyl chloride despite the rate retardation generally observed at bridgehead positions.[20] In accord with this finding, computations indicate that the bridgehead cation is more stable than *tert*-butyl cation even though it is a transition state for ring opening.[16] The bridgehead radical is readily generated, has an extremely large long-range C_3−H (γ) hyperfine coupling constant, and is surprisingly stable structurally.[1,9] Likewise, the anion has been successfully used in synthetic transformations, shows no tendency to rearrange, and is predicted to be stabilized by hybridization effects resulting as a consequence of the rigid ring skeleton.[8,16] The stability of the latter two species in terms of the acidity and carbon−hydrogen bond dissociation energy (BDE) of bicyclo[1.1.1]pentane, however, is unknown. These quantities have been the subject of ab initio and density functional theory calculations,[16,21−23] and the acidity of bicyclo[1.1.1]pentane, as noted below, has been erroneously reported.[24]

---

[*] To whom correspondence should be addressed.

[†] Current address: Saint Michael's College, Department of Chemistry and Physics, One Winooski Park Box 142, Colchester, VT 05439.

[‡] University of Minnesota.

[§] University of Pennsylvania.

(1) Walton, J. C. *J. Chem. Soc. Rev.* **1992**, *21*, 105−112.
(2) Mueller, P.; Mareda, J.; Milin, D. *J. Phys. Org. Chem.* **1995**, *8*, 507−528.
(3) Della, E. W.; Schiesser, C. H. *Adv. Carbocation Chem.* **1995**, *2*, 91−122.
(4) Takeuchi, K.; Ohga, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 833−851.
(5) Eguchi, S. *Recent Res. Dev. Pure Appl. Chem.* **1998**, *2* (Pt. 2), 311−320.
(6) Kuramochi, K.; Nagata, S.; Itaya, H.; Takao, K.-I.; Kobayashi, S. *Tetrahedron Lett.* **1999**, *40*, 7371−7374.
(7) Michl, J. *Struct. Energ. React. Chem. Ser.* **1995**, *1*, 132−160.
(8) Della, E. W.; Taylor, D. K. *J. Org. Chem.* **1994**, *59*, 2986−2996.
(9) McKinley, A. J.; Ibrahim, P. N.; Balaji, V.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 10631−10637.
(10) Williams, R. M.; Sabol, M. R.; Kim, H. D.; Kwast, A. *J. Am. Chem. Soc.* **1991**, *113*, 6621−6633.
(11) Adcock, W.; Gangodawila, H. *J. Org. Chem.* **1989**, *54*, 6040−6047.
(12) Monn, J. A.; Rice, K. C. *Tetrahedron Lett.* **1989**, *30*, 911−914.
(13) Williams, R. M.; Armstrong, R. W.; Dung, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 3253−3266.
(14) Danen, W. C.; Tipton, T. J.; Saunders, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 5186−5189.
(15) Lansbury, P. T.; Sidler, J. D. *Tetrahedron Lett.* **1965**, 691−695.
(16) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820−5828.
(17) Almenningen, A.; Andersen, B.; Nyhus, B. A. *Acta Chem. Scand.* **1971**, *25*, 1217−1223.
(18) Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 1614−1617.
(19) Cox, C. W.; Harmony, M. D. *J. Mol. Spectrosc.* **1970**, *36*, 34−43.
(20) Wiberg, K. B.; Williams, V. Z., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 3373−3374.

10.1021/ja0121890 CCC: $22.00 © 2002 American Chemical Society

Gas-phase anion studies are extremely useful for obtaining homolytic bond energies via the application of a thermodynamic cycle (eq 1).[25] In this work, we have derived the homolytic C−H

$$\mathrm{BDE(H{-}X)} = \Delta H^{\circ}_{\mathrm{acid}}(\mathrm{HX}) - \mathrm{IP}(\mathrm{H}^{\bullet}) + \mathrm{EA}(\mathrm{X}^{\bullet}) \qquad (1)$$

BDE of 1-*tert*-butylbicyclo[1.1.1]pentane at C3 by measuring its acidity via the DePuy kinetic method[26,27] and the electron affinity of the bridgehead radical by carrying out bracketing studies on 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl anion. This last species represents one of a few alkyl anions that have been generated in the gas phase.[24,28−37] The reason for this is that these ions often are difficult to prepare due to their high basicities and low or even negative electron binding energies (i.e., alkyl radicals tend to be more stable than their corresponding alkyl anions).

Originally, we planned on studying substituent effects using 3-substituted 1-bicyclo[1.1.1]pentyl anions since the corresponding 3-substituted 1-bicyclo[1.1.1]pentanecarboxylic acids can be prepared from readily available [1.1.1]propellane,[38] and 1-bicyclo[1.1.1]pentanecarboxylate anion (**1**) has previously been reported to lose carbon dioxide to afford 1-bicyclo[1.1.1]-pentyl anion (**2**, see eq 2a) upon collision-induced dissociation (CID).[24,32] Graul and Squires also measured the decarboxylation threshold for this process and used the onset energy to derive the acidity of bicyclo[1.1.1]pentane. Their structural assignment for **2**, however, was based solely on the observed threshold energy leading to an acidity which is in reasonable accord with expectation. To our surprise, upon exploring the reactivity of the decarboxylated species we rapidly discovered that 1-bicyclo-[1.1.1]pentyl anion is not formed upon CID of **1**, and thus turned our attention to this species.

Experimental Section

1-Bicyclo[1.1.1]pentanecarboxylic acid was prepared by the method of Wiberg and Waddell.[39] 2-Trimethylsilyl-1,4-pentadiene was prepared by the method of Fotidau et al.[40] 1-*tert*-Butyl-3-(trimethylsilyl)bicylo-[1.1.1]pentane (**6**) has been reported previously,[41] but the procedure is cumbersome, and an alternate one was developed. All other reagents were commercially available and used without further purification.

1-*tert*-Butyl-3-(trimethylsilyl)bicyclo[1.1.1]pentane (6). A solution of aqueous sodium thiophenoxide was prepared by adding thiophenol (4.8 g, 4.4 mL, 44 mmol) with vigorous stirring to a solution of 2.3 g of sodium hydroxide in 5−10 mL of water. This solution was stirred at room temperature for 20 min after which it was quickly added to 40 mL of an ca. 0.5 M solution of [1.1.1]propellane in diethyl ether/pentane containing methyl bromide[38] by pouring it directly into the flask. The biphasic reaction mixture was vigorously stirred at room temperature for at least 30 min after which it was transferred to a separatory funnel which had been purged with argon. The layers were separated, and the organic portion was washed with water (3 × 10 mL). The organic layer was thoroughly dried with magnesium sulfate and filtered through a glass frit to afford a solution of [1.1.1]propellane and methyl phenyl sulfide. The organic material was transferred under vacuum from a 0 °C bath to a receiving flask cooled to −196 °C. In this way a solution of [1.1.1]propellane free of methyl bromide was readily obtained. A portion of this solution of [1.1.1]propellane in diethyl ether/pentane (15 mL of ∼0.5 M) was cooled to −78 °C. *tert*-Butyllithium in ether/pentane (4.4 mL of 1.7 M in pentane, Aldrich) was added via syringe with stirring. Stirring was continued for 15 min at −78 °C, and then the reaction mixture was quenched by the addition of 0.90 mL of chlorotrimethylsilane which had been freshly distilled from calcium hydride. The reaction mixture was allowed to warm to room temperature over 2 h, and water (∼10 mL) was added. The organic layer was separated, and the aqueous layer was extracted once with pentane. The combined organic portions were washed sequentially with water, then brine. The solution was dried over magnesium sulfate, filtered, and concentrated in vacuo to afford 0.91 g of a clear colorless liquid (61% yield based on *tert*-butyllithium). The crude product was further purified by preparative GC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: −0.09 (s, 9H, $-SiCH_3$), 0.77 (s, 9H, $-CCH_3$), 1.47 (s, 6H, $-CH_2$). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 53.8, 46.2, 30.3, 25.4, 25.2, −3.4.

All gas-phase experiments were carried out using a model 2001 Finnigan FTMS equipped with a dual cell and a 3 T superconducting magnet.[42] Fluoride ion was produced in the source cell by dissociative electron attachment of carbon tetrafluoride, which was introduced via a pulsed valve up to a maximum pressure of 10^{-5} Torr. Deprotonation of a small static pressure of 1-bicyclo[1.1.1]pentanecarboxylic acid (10^{-8} Torr) with F^- afforded its conjugate base. All of the resulting anions were transferred into the second (analyzer) cell by grounding the conductance limit for 20−70 μs, and the desired carboxylate ion at *m*/*z* 121 was isolated using a series of chirp and SWIFT excitation pulses.[43,44] Argon was subsequently pulsed into the cell up to a pressure of $\sim 10^{-5}$ Torr, and collision-induced dissociation (CID) was carried out using either sustained off-resonance irradiation (SORI) or direct on-resonance excitation.[45] The reactivity of the decarboxylated species was examined by allowing it to react with a static pressure of a series of probe reagents. Reaction delays and neutral pressures ranged from 100 ms to 120 s and 1×10^{-8} to 5×10^{-7} Torr, respectively. In a similar fashion, 1,4-pentadien-2-yl anion was formed in the source cell via the fluoride-induced desilylation of 2-trimethylsilyl-1,4-pentadiene. All of the ions were transferred to the analyzer cell where the M − TMS anion (*m*/*z* 67) was isolated, collisionally cooled with argon, and allowed to react with a variety of reagents.

3-*tert*-Butyl-1-bicyclo[1.1.1]pentyl anion was generated by reacting fluoride ion with 3-*tert*-butyl-1-(trimethylsilyl)bicyclo[1.1.1]pentane, but this transformation is very inefficient. To improve the signal-to-noise ratio of the M − TMS anion (*m*/*z* 123), F^- was kinetically excited

---

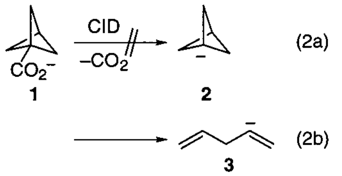
(21) Sauers, R. R. *Tetrahedron* **1999**, *55*, 10013−10026.
(22) Alkorta, I.; Elguero, J. *Tetrahedron* **1997**, *53*, 9741−9748.
(23) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133−4139.
(24) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517−2529.
(25) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765.
(26) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968−1973.
(27) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051−4053.
(28) Broadus, K. M.; Kass, S. R.; Osswald, T.; Prinzbach, H. *J. Am. Chem. Soc.* **2000**, *122*, 10964−10968.
(29) Hare, M.; Emrick, T.; Eaton, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 237−238.
(30) Lee, H. S.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1996**, *118*, 5068−5073.
(31) Gunion, R. F.; Karney, W.; Wenthold, P. G.; Borden, W. T.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 5074−5082.
(32) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2506−2516.
(33) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 892−899.
(34) Kass, S. R.; Chou, P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899−7900.
(35) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607−608.
(36) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2853−2862.
(37) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556−2558.
(38) Lynch, K. M.; Dailey, W. P. *Org. Synth.* **1997**, *75*, 98−105.
(39) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194−2216.
(40) Fotidau, F.; Cros, P.; Faure, B.; Buono, G. *Tetrahedron Lett.* **1990**, *31*, 77−80.
(41) Della, E. W.; Taylor, D. K.; Tsanaktsidis, J. *Tetrahedron Lett.* **1990**, *36*, 5219−5220.
(42) Reed, D. R.; Hare, M.; Kass, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 10689−10696.
(43) Marshall, A. G.; Roe, D. C. *J. Chem. Phys.* **1980**, *73*, 1581−1590.
(44) Wang, T. C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1986**, *58*, 2935−2938.
(45) Gauthier, J. W.; Trautamn, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211−225.

via SORI. The energy and duration of the excitation pulse were optimized to maximize the intensity of the desired ion. It was subsequently isolated via a series of chirp and SWIFT excitation pulses, but it was not transferred to the analyzer cell because of the low signal intensity. Fortunately, the neutral trimethylsilane precursor was not particularly reactive and did not interfere with the subsequent reactivity studies.

G2 and G3 calculations[46,47] were carried out using Gaussian 94 or 98 on IBM and SGI workstations as described in the literature.[48] All of the resulting energies were corrected to 298 K using the HF/6-31G-(d) frequencies and a scaling factor of 0.8929.[49]

Results/Discussion

Deprotonation of 1-bicyclo[1.1.1]pentanecarboxylic acid by fluoride ion in the gas phase affords 1-bicyclo[1.1.1]pentanecarboxylate anion (**1**, *m*/*z* 121), which loses carbon dioxide upon on- or off-resonance collision-induced dissociation (eq 2). To establish the identity of the decarboxylated anion ($C_5H_7^-$, *m*/*z* 67), reactions with a variety of probe reagents were carried out.[50] Protonation occurs with methanol ($\Delta H^\circ_{\mathrm{acid}} = 381.8 \pm 1.0$ kcal/mol), but not with weaker acids such as water ($\Delta H^\circ_{\mathrm{acid}} = 390.7 \pm 0.1$ kcal/mol) and ammonia ($\Delta H^\circ_{\mathrm{acid}} = 404.3 \pm 0.3$ kcal/mol).[51] When deuterated reagents are used, one hydrogen–deuterium exchange is observed with ND_3 and D_2O, whereas deuteron transfer and up to five H/D exchanges are observed with CH_3OD. The isotopic label in the d_1 species cannot be washed out with H_2O or CH_3OH, and it does not deprotonate methanol, ethanol ($\Delta H^\circ_{\mathrm{acid}} = 378.3 \pm 1.0$ kcal/mol), or *tert*-butyl alcohol ($\Delta H^\circ_{\mathrm{acid}} = 374.6 \pm 1.6$ kcal/mol). These results are inconsistent with Graul and Squires' reported proton affinity of 411 ± 3.5 kcal/mol for 1-bicyclo[1.1.1]pentyl anion (**2**)[24] and our G3 predicted energy of 409.7 kcal/mol for this species.[52] They also indicate that the $C_5H_7^-$ ion undergoes an acid-catalyzed isomerization to a more stable and less basic species. This ion, consequently, cannot be **2**.



Scheme 1

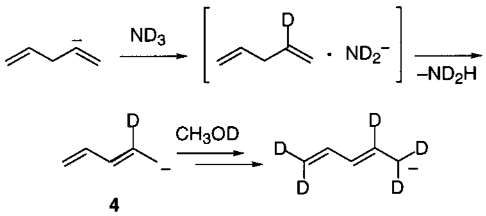
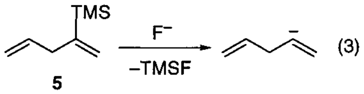


Table 1. Reaction Products of **3** with Different Probe Reagents

reagent	observed products
ND_3	1 H/D exchange, no ND_2^-
D_2O	1 H/D exchange, no OD^-
CH_3OD	5 H/D exchanges + CH_3O^-
N_2O	HNO_2^- (47%) + $C_5H_5^-$ (16%) + $CH_2{=}CHCH_2C(O^-){=}CH_2$ (37%)
COS	HS^- (22%) + $CH_2{=}CHCH_2C(S^-){=}CH_2$ (78%)
CS_2	$CH_2{=}CHCH_2C(S^-){=}CH_2$

As for the structure of the $C_5H_7^-$ ion, it is 1,4-pentadien-2-yl anion (**3**, eq 2b). This vinyl ion should be (and is) basic enough to react with weak acids such as ND_3 and D_2O to undergo acid-catalyzed isomerization to pentadienyl anion **4** (Scheme 1). Four additional H/D exchanges are observed when **4** is allowed to react with methanol-OD, which is in accord with previous observations by DePuy et al. on unlabeled pentadienyl anion.[53] Scheme 1 accounts for why the isotopic label cannot be washed out from the d_1 ion, and given that $\Delta H^\circ_{\mathrm{acid}}$(1,3-pentadiene) = 369.2 ± 1.2 kcal/mol, it also explains why **4** does not deprotonate methanol, ethanol, or *tert*-butyl alcohol (i.e., the ion is not basic enough).

To further establish the structure of **3**, it was independently prepared by the fluoride-induced desilylation of 2-trimethylsilyl-1,4-pentadiene (**5**, eq 3). The ion produced by this method displayed identical reactivity to the one formed by the decarboxylation of **1** with a variety of reagents. A summary of the results is given in Table 1.[54]



An alternative method for generating negative ions is the DePuy reaction in which a substituted trimethylsilane ($RSi(CH_3)_3$) is reacted with fluoride ion to afford R^-.[55,56] This approach has been used successfully to prepare alkyl anions even in a case where collision-induced dissociation of a carboxylate ion (RCO_2^-, R = cubyl) failed.[29,57,58] Consequently, 1-(trimethylsilyl)bicyclo[1.1.1]pentane was synthesized, but it turned out to be difficult to purify.[59] Since a remote alkyl substituent at C3 should have little impact on the properties of

---

(46) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221–7230.

(47) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Oritz, J. V.; Stefanov, B. B.; Lui, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Ketih, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(49) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345–350.

(50) The results are the same over a wide variety of CID conditions (i.e., on- or off-resonance irradiation, argon pressures from 10^{-8}–10^{-5} Torr, and nominal kinetic energies from ~0–100 eV).

(51) All acidities, EA, and heats of formation, unless otherwise noted, come from: Bartmess, J. E. In *Secondary NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899, 2001 (http://webbook.nist.gov).

(52) The acidity using G2 theory is 408.7 kcal/mol. Similar values have been computed at other levels of theory. See refs 16, 21, and 22.

(53) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921–2922.

(54) The reactivity of **3** is similar to other vinyl anions, see: Anderson, K. K.; Kass, S. R. *Tetrahedron Lett.* **1989**, *30*, 3045–3048.

(55) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 6443.

(56) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K. *J. Am. Chem. Soc.* **1980**, *102*, 5012–5015.

(57) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 4357–4359.

(58) Decarboxylation of cubanecarboxylate via collision-induced dissociation does not afford cubyl anion. Reed, D. R.; Kass, S. R., unpublished data.

(59) Mondanaro, K. R.; Dailey, W. P., unpublished data.

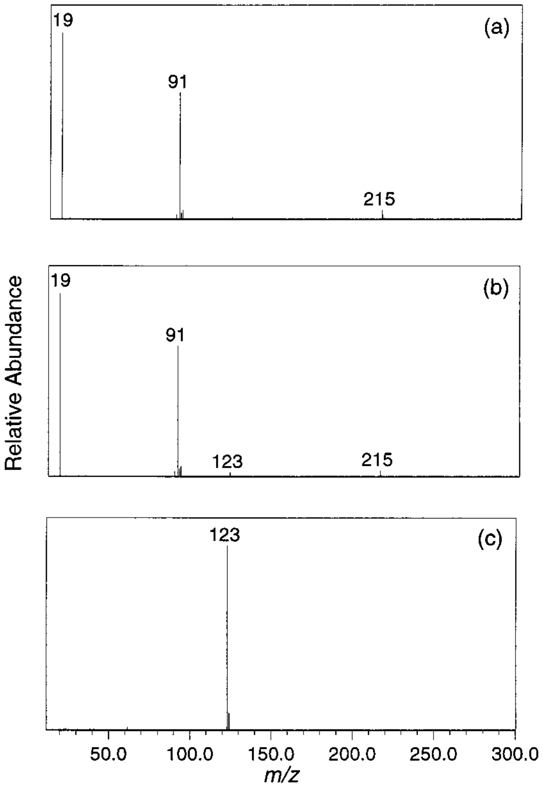
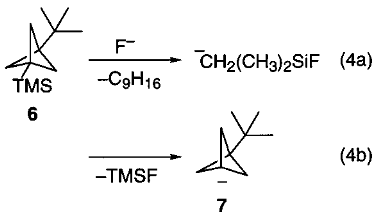


Figure 1. (a) Reaction of **6** with F^- at room temperature; the ions at *m/z* 19, 91, and 215 correspond to F^-, $^-CH_2(CH_3)_2SiF$, and $(\mathbf{6} + F)^-$. (b) Reaction of **6** with kinetically exicted F^- via sustained off-resonance irradiation; the ion at *m/z* 123 is $(\mathbf{6} - TMS)^-$ and has a signal-to-noise ratio of 14.2 (eight scans). (c) Improved signal-to-noise ratio (530:1, eight scans) for **7** obtained by using very large amounts of F^-, and subsequent isolation via a combination of chirp and SWIFT ejections of unwanted species.

1-bicyclo[1.1.1]pentyl anion, and a clean sample of 3-*tert*-butyl-1-(trimethylsilyl)bicyclo[1.1.1]pentane (**6**) can be prepared readily, this compound was examined.[60] Fluoride ion reacts with **6** to give the conjugate base of fluorotrimethylsilane (*m/z* 91) as the dominant product ion (>99%) along with a trace (<1%) of 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl anion (**7**, *m/z* 123) (eq 4). The relative yield of the desired ion was increased to 3% by giving fluoride ion excess kinetic energy via sustained off-resonance irradiation (Figure 1). A further improvement in the signal-to-noise ratio of **7** was achieved by using very large (saturated) signals of F^- (Figure 1c). As a result of these improvements, it was much easier to explore the reactions of 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl anion.



In contrast to the reactivity of **3** and **4**, but as expected for **7**, 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl anion undergoes deuteron transfer and no H/D exchange with ND_3, D_2O, and CH_3OD. Reactions with additional reagents also were examined, and the results are summarized in Table 2. Electron transfer is observed with *p*-cyanotrifluoromethylbenzene (EA = 0.759 ± 0.087 eV) and sulfur dioxide (EA = 1.107 ± 0.008 eV) but not carbonyl sulfide, carbon disulfide, and hexafluorobenzene (EA = 0.46 ± 0.20, 0.51 ± 0.10, and 0.52 ± 0.11 eV, respectively).[51] These results suggest that the electron affinity of the 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl radical is between 0.52 ± 0.11 and 0.759 ± 0.087 eV, or 0.64 ± 0.14 eV (14.8 ± 3.2 kcal/mol). In good accord with this assignment, the G3 computed value for the parent species is 11.2 kcal/mol.[61]

Table 2. Reactivity Summary of 3-*tert*-Butyl-1-bicyclo[1.1.1]pentyl Anion (**7**) with Probe Reagents

reagent	ΔH°_{acid} or EA[a]	observed products
ND_3	404.3 ± 0.30	ND_2^-, no H/D exchange
D_2O	393.0 ± 0.20	OD^-, no H/D exchange
CH_3OD	381.8 ± 1.0	CH_3O^-, no H/D exchange
N_2O	0.22 ± 0.10	none
COS	0.46 ± 0.20	HS^- (65%) + $C_9H_{15}S^-$ (35%)
CS_2	0.51 ± 0.10	$C_9H_{15}S^-$
C_6F_6	0.52 ± 0.11	F^-
$CF_3C_6H_4CN$	0.759 ± 0.087	$CF_3C_6H_3CN^-$ (80%) + $CF_3C_6H_4CN^{\bullet -}$ (20%)
SO_2	1.107 ± 0.008	$SO_2^{\bullet -}$

[a] Acidities are in kcal/mol, and electron affinities are in eV.

A lower limit of 404 kcal/mol for the acidity of 1-*tert*-butylbicyclo[1.1.1]pentane at C3 can be assigned given that **7** reacts with ammonia-d_3 via deuteron transfer. To more accurately determine this value, the DePuy kinetic method was used.[26,27] In this approach, a series of substituted trimethylsilanes (RTMS) in which RH has known acidities is selected and allowed to react with hydroxide ion. A plot of the natural logarithm of the statistically corrected $(CH_3)_3SiO^-/R(CH_3)_2SiO^-$ product ratios (*s*) versus ΔH°_{acid} (RH) affords a calibration line which can be used to obtain the acidity of compounds with unknown values. Five reference compounds were employed in this case (R = cyclopropyl, ethyl, methyl, phenyl, and vinyl), and a linear least-squares analysis of the data gave the following equation: $\Delta H^\circ_{acid}(RH) = -4.45 \times \ln(s) + 416.4$ kcal/mol, $r^2 = 0.983$.[62] Observed product ratios of 8.05 ± 0.34 and 2.01 ± 0.07 for **5** and **6**, respectively, were obtained and give acidities of 402.3 ± 1.0 kcal/mol (1,4-pentadiene at C2) and 408.5 ± 0.9 (1-*tert*-butylbicyclo[1.1.1]pentane at C3).[63] These values are in excellent accord with computed G3 acidities at 298 K of 402.0 and 409.7 kcal/mol for 1,4-pentadiene and bicyclo[1.1.1]pentane, respectively.[52]

A linear correlation between the gas-phase acidity (ΔH°_{acid}) and the s-character of a carbon−hydrogen bond as reflected by the heteronuclear $^{13}C-^1H$ coupling constant has been reported.[34] This simple empirical relationship is only applicable to localized

---

(60) To probe the effect of the *tert*-butyl group at C3, MP2(full)/6-31G(d) optimizations and MP2(full)/GTlarge single point energies were carried out on 1-*tert*-butylbicyclo[1.1.1]pentane, 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl anion, and 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl radical. As expected, substitution of hydrogen by *tert*-butyl has little effect on the C1−C3 distances in all three species (<0.006 Å); the *tert*-butyl derivatives also have the larger separation in contrast to what one would expect if hyperconjugation were important. Likewise, the *tert*-butyl group only has a small effect on the C3−H bond dissociation energy and acidity (0.03 and 2.1 kcal/mol, respectively).

(61) The EA using G2 theory is 12.3 kcal/mol. A similar value is obtained via DFT calculations; see ref 21.

(62) For additional details about the calibration see: Reed, D. R. K. S. R. *J. Mass Spectrom.* **2000**, *35*, 534−539.

(63) The cited uncertainty comes from an error analysis of the kinetic data, as has become common practice. Systematic errors, which are always a possibility in kinetic determinations, could lead to a larger uncertainty in the final result. There is no apparent reason to suspect a problem in this case, however, as there is excellent agreement between experiment and theory.

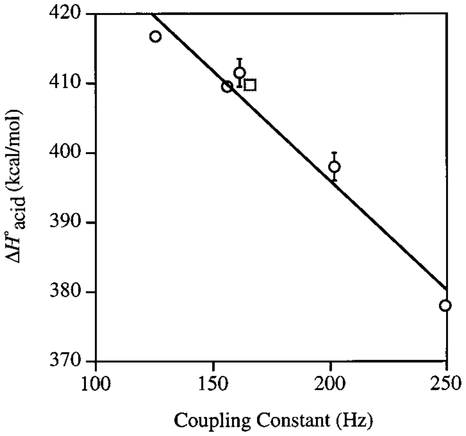
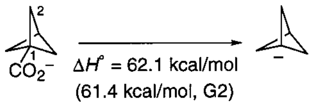


Figure 2. Acidity vs ^{13}C−H coupling constant. Compounds represented by circles are methane (416.7 ± 0.7 kcal/mol, 125 Hz), cyclopropane (411.5 ± 2.0 kcal/mol, 161 Hz), ethylene (409.4 ± 0.6 kcal/mol, 156 Hz), bicyclo[1.1.0]butane (398.0 ± 2.0 kcal/mol, 202 Hz), and acetylene (377.8 ± 0.6 kcal/mol, 249 Hz), and were used in linear least-squares analysis to obtain $\Delta H^\circ_{acid} = -0.317 \times J + 459.4$, $r^2 = 0.965$. Bicyclo[1.1.1]pentane (409.7 kcal/mol (G3), 166 Hz) is represented by a square.

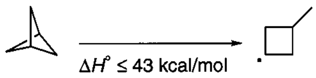
carbanions derived from small hydrocarbons since resonance, polarization, and inductive effects will result in its break-down. Bicyclo[1.1.1]pentane is a suitable substrate and has a ^{13}C−^{1}H NMR coupling constant of ∼166 Hz.[64] This value and the correlation shown in Figure 2 lead to a predicted acidity of 406.8 kcal/mol, which is in good agreement with the G2, G3, and measured deprotonation energy of 1-*tert*-butylbicyclo[1.1.1]-pentane (408.7, 409.7, and 408.5 kcal/mol, respectively). The high degree of s-character in the bridgehead C−H bond, which results from the additional p-character needed to form the strained C−C bonds, is responsible for the enhanced acidity of bicyclo[1.1.1]pentane.

The electron affinity of 3-*tert*-butyl-1-bicyclo[1.1.1]pentyl radical (X$^\bullet$) can be combined with the acidity of 1-*tert*-butylbicyclo[1.1.1]pentane (HX) and the known ionization potential of hydrogen atom (313.6 kcal/mol) in a thermodynamic cycle (eq 1) to derive the bridgehead C−H bond dissociation energy for 1-*tert*-butylbicyclo[1.1.1]pentane. A bond energy of 109.7 ± 3.3 kcal/mol is obtained, which is in good accord with the computed G3 value of 107.1 kcal/mol.[65] It also is larger than the tertiary C−H bond in isobutane (96.5 ± 0.4 kcal/mol)[25] and any other tertiary C−H bond that has been measured. In fact, this bond strength is typical of aromatic and alkene C−H bonds, which is not surprising given that all of these compounds have sp^2 hybridization.

Why the decarboxylation of 1-bicyclo[1.1.1]pentanecarboxylate (**1**) affords 1,4-pentadien-2-yl anion (**3**) instead of 1-bicyclo-[1.1.1]pentyl anion (**2**) can now be addressed. By using experimental data, Benson's group additivity scheme,[66] and a G3 computed heat of formation for bicyclo[1.1.1]pentane (48.9 kcal/mol),[67] the decarboxylation energy for the formation of 1-bicyclo[1.1.1]pentyl anion from **1** is estimated to be 62.1 kcal/mol (eq 5).[68] A similar value of 61.4 kcal/mol is obtained using G2 theory. In contrast, the carbon−carbon bond dissociation energy for bicyclo[1.1.1]pentane is predicted to be ≤43 kcal/mol (eq 6); this value was obtained by using the C−H BDEs of cyclobutane and ethane, and assuming that the second C−H BDE for methylcyclobutane is unperturbed by the radical center formed when the first C−H bond is broken.[69] Srinivasan has measured the activation energy for the thermal decomposition of bicyclo[1.1.1]pentane (E_a = 49.0 kcal/mol), and his value is 6 kcal/mol larger than our estimate for the bond energy.[70] Regardless, it is apparent that the ring cleavage of **1** and subsequent isomerization to 1,4-pentadiene-2-carboxylate (**8**) is energetically favored over the decarboxylation to **2**. This is especially so when one considers that the C1−C2 ring bond in **1** should be weaker than in the parent compound given that BDE (CH$_3$−H) − BDE ($^-$O$_2$CCH$_2$−H) = 10 kcal/mol. Consequently, it is not surprising that **3** is formed in preference to **2** upon collision-induced dissociation of **1**.

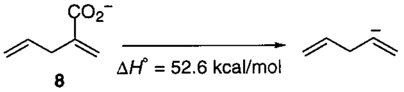


(5)



(6)

As for Graul and Squires energy-resolved threshold data,[24] it is now apparent that it should not be used to derive the acidity of bicyclo[1.1.1]pentane since 1-bicyclo[1.1.1]pentyl anion is not the decarboxylation product of **1**. The process that actually was measured is not immediately obvious, but one possibility is the decarboxylation of **8** (eq 7) as this step represents the largest barrier in the conversion of **1** to **3**.[71] If this is the case, then one can derive an upper limit for the acidity of 1,4-pentadiene at C2 of 412 ± 5 kcal/mol, which is 10 kcal/mol too large.[71,72] Regardless, this example shows that using threshold data alone to derive thermodynamic information can be a risky proposition and that reactivity studies are invaluable in determining ion structure.



8

(7)

Conclusions

Collision-induced dissociation of 1-bicyclo[1.1.1]pentanecarboxylate (**1**) does not afford 1-bicyclo[1.1.1]pentyl anion (**2**)

---

(64) This value is the average of the coupling constants (164 and 168 Hz) given in references a and b. (a) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820−5828. (b) Rhodes, C. J.; Walton, J. C.; Della, E. W. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2125−2128.

(65) The BDE is computed to be 107.2 kcal/mol using G2 theory. See refs 16 and 23 for other computations of this quantity.

(66) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419−2438.

(67) This quantity was computed from the atomization energy and the experimental values for the heats of formation of the atoms. In the same way, G2 theory predicts a heat of formation of 48.8 kcal/mol.

(68) This reaction enthalpy was calculated using the following quantities: $\Delta H^\circ_f = -94.05$ (CO$_2$), 92.9 (**2**), −63.2 (**8**), and −40.5 kcal/mol (**1**, see ref 66); ΔH°_{acid} = 409.7 (bicyclo[1.1.1]pentane, G3) and 343 kcal/mol (**1**).

(69) The bond energy was estimated using the following quantities: BDE = 97 (cyclobutyl-H) and 100 kcal/mol (ethyl-H), see ref a; $\Delta H^\circ_f = -3.8$ kcal/mol (methylcyclobutane), where this was derived from the known heat of formation in the liquid phase (−10.64 kcal/mol) and an estimated heat of vaporization (6.86 kcal/mol, the same value as for cyclopentane), see ref b. (a) Lide, D., Ed. *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL, 1996. (b) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman Hall: New York, 1986.

(70) Srinivasan, R. *J. Am. Chem. Soc.* **1968**, *90*, 2752−2754.

(71) This reaction enthalpy was calculated using the following quantities: ΔH°_f = 61.5 (**3**), −85.1 (**9**), 25.2 (1,4-pentadiene, see ref 69b), and −62.4 kcal/mol (1,4-pentadiene-2-carboxylic acid, see ref 66); ΔH°_{acid} = 402.0 (1,4-pentadiene, G3) and 343 ± 3 kcal/mol (1,4-pentadiene-2-carboxylic acid, estimated to be the same value as for **1**).

contrary to a previous claim. Instead, a charge-remote fragmentation takes place which ultimately leads to 1,4-pentadien-2-yl anion (**3**); the structure of **3** was confirmed by reactivity studies and independent synthesis via the DePuy reaction. This rearrangement takes place because the homolytic cleavage of a ring C−C bond in **1** is easier than the heterolytic scission of the $C-CO_2^-$ bond. The fluoride-induced desilylation of 3-*tert*-butyl-1-(trimethylsilyl)bicyclo[1.1.1]pentane (**6**), on the other hand, does afford a bicyclo[1.1.1]pentyl anion (**7**). Thermochemical properties of this ion were measured and found to be in good accord with high-level G2 and G3 calculations. Most notably, the bridgehead C−H bond dissociation energy (109.7 ± 3.3 kcal/mol) is much greater than a typical tertiary C−H bond (∼96 kcal/mol) and more typical of an aromatic or alkene C−H bond. This is the result of the $C_{sp^2}-H$ hybridization in bicyclo[1.1.1]pentane, which arises from the need for additional p-character in the C−C ring bonds.

Acknowledgment. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute is gratefully acknowledged.

JA0121890

---

(72) Unlike ref 24 where the uncertainty for ΔH°_{acid} was taken as the maximum uncertainty of several terms that need to be summed or subtracted together, we have propagated the error in the usual way (i.e., the square root of the sum of the squares). The following energetic quantities in kcal/mol were used: $\Delta H^\circ_f = 25.2 \pm 0.2$ (1,4-pentadiene, see ref 69b), -62.4 ± 2.0 (conjugate acid of **8**, see ref 66; error estimated).