

2 h until TLC (silica, CH_2Cl_2) showed the reaction to be complete. The precipitated triphenylpyridine was filtered off, water (30 mL) added, and the whole extracted with ether (3×20 mL). The extract was washed with water (3×20 mL) and dried over anhydrous MgSO_4 , and dry HCl was passed to remove residual triphenylpyridine, which was filtered off. The filtrate was evaporated and the crude product distilled (15 mmHg) to give 2-phenylnitroethane (yield 58%), bp 125-130 °C (15 mmHg) (lit.² bp 126 °C (14 mmHg)).

Kinetic Procedure. In a typical experiment, the pyridinium salt (0.08 mmol) was dissolved in 50 mL of Me_2SO . NaH (1.3 mmol) was weighed out and dissolved in 50 mL of 1-pentanol. 2-Nitropropane (1.3 mmol) was dissolved in 50 mL of Me_2SO to give a third stock solution. All stock solutions were protected from light. Pentanolic sodium pentoxide (1 mL), 2-nitropropane in Me_2SO (1 mL), and pyridinium salt in Me_2SO (1 mL) were pipetted into Me_2SO (ca. 20 mL) in a 25-mL measuring flask, and the volume was made up to the mark rapidly with more Me_2SO . The mixture was transferred to a 1-cm quartz UV cell and placed in a SP6-500 digital display spectrophotometer. The reaction rate was followed by measuring the decrease in absorption at the required wavelength at constant temperature. The infinity reading was recorded in each experiment after change in absorbance was negligible (ca. 2 h). Table A

records a typical result (supplementary material section).

Reactions at 80-100 °C were conducted on aliquots (3 mL) of the UV-diluted reaction mixture placed in stoppered glass tubes in hot blocks. At fixed time intervals, the tubes were removed and cooled to 25 °C. The mixture was transferred to a 1-cm UV quartz cell and the absorbance noted.

Acknowledgment. We thank the Ministry of Education, Government of Pakistan, for a grant to Mr. M. A. Kashmiri.

Registry No. 1a-BF₄⁻, 66310-10-9; 1b-BF₄⁻, 71017-85-1; 1c-BF₄⁻, 72538-32-0; 1d-BF₄⁻, 71017-75-9; 1e-BF₄⁻, 83365-34-8; 1f-BF₄⁻, 2355-56-8; 1g-BF₄⁻, 66310-04-1; 1h-BF₄⁻, 73086-84-7; 1j-BF₄⁻, 81128-05-4; 2a, 25854-38-0; 2b, 25854-39-1; 2c, 24163-39-1; 7, 15519-25-2; 8, 71670-94-5; 9, 47484-87-7; 10, 83365-35-9; 11, 83365-36-0; 12-BF₄⁻, 75864-90-3; 13, 75505-94-1; sodium nitrocyclohexanide, 4702-04-9; 2,4,4-trimethyl-2-nitropentane, 5342-78-9.

Supplementary Material Available: Tables of UV data, rate constants, and equilibrium constants (5 pages). Ordering information is given on any current masthead page.

Thermochemical Relationships between Some Bicyclohexenyl and Benzenium Cations¹

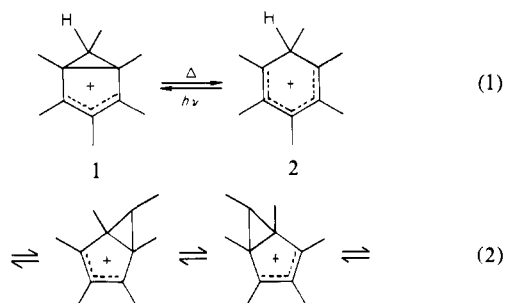
Ronald F. Childs* and D. Lindsay Mulholland

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada. Received May 26, 1982

Abstract: The heats of protonation in FSO_3H and solution in CCl_4 of penta- and hexamethylbenzene (8 and 6, respectively), hexamethyl(Dewar benzene) (3), 1,3,4,5,6-pentamethyl- and 1,3,4,5-tetramethyl-2-methylenebicyclo[3.1.0]hex-3-ene, (7 and 9, respectively), 2,3,4,4,5,6-hexamethyl-1-methylenecyclohexa-2,5-diene (10), 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one (14), and 1,3,4,5,6,6-hexamethylbicyclo[3.1.0]hex-3-en-2-one (13) were measured. The protonations were carried out at different temperatures such that different ions were formed. This enabled the relative heats of formation of the hexamethylbenzenium, 2, hexamethylbicyclo[3.1.0]hexenyl, 1, and hexamethylbicyclo[2.1.1]hexenyl cations, 4 and 5, to be obtained. The magnitude of the energy differences is discussed in terms of the resonance energies of the cations. Similar thermochemical relationships were established for the hydroxy cations 15 and 16.

The bicyclohexenyl cations are an important group of carbenium ions that are isomeric with the well-established benzenium ions. The bicyclo[3.1.0]hexenyl ions are related to the corresponding benzenium ions by a ground state forbidden, photochemically allowed, disrotatory electrocyclic reaction, eq 1.²⁻⁵ While the thermally induced conversion of a bicyclo[3.1.0]hexenyl cation to a benzenium ion is a relatively difficult process, these bicyclic ions exhibit facile, highly stereoselective circumambulatory rearrangements, eq 2.

There are few reports of the preparation of stable bicyclo[2.1.1]hexenyl cations. The two hexamethyl-substituted ions shown in eq 3 have been prepared by protonation of hexamethyl(Dewar benzene).^{6,7} These two ions rapidly interconvert



at low temperatures, while at higher temperatures they undergo a slow, irreversible isomerization to the hexamethylbenzenium ion. The bicyclo[3.1.0]- and -[2.1.1]hexenyl cations are related to each other by 1,2 or 1,3 shifts of the bridging carbon, eq 4.

The photochemical and thermal interconversions of these ions have been studied extensively; however, there is a dearth of information on their thermochemistry. Sorensen and Rauk⁸ have suggested the energy difference between the unsubstituted bicyclo[3.1.0]hexenyl and benzenium ions might be as high as 40 kcal/mol. Calculations at the 4-31G level indicate an energy difference of 34 kcal/mol.⁹ No experimental information seems

(1) This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

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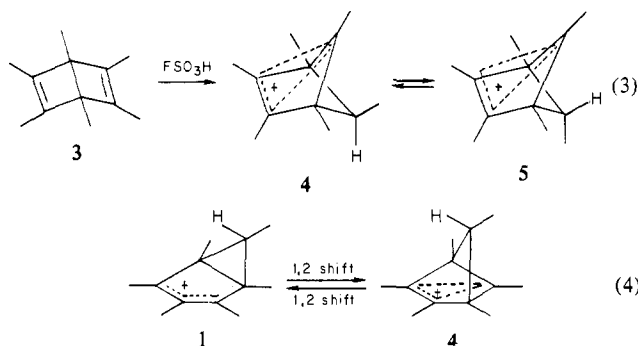
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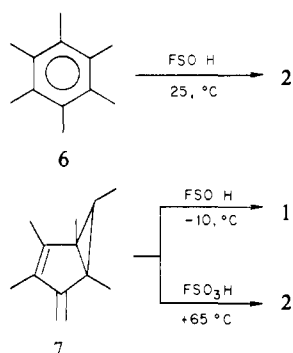


to be available, and consequently we have examined the relative heats of formation of several of these ions.

Results

The precursors of the various hexamethyl-substituted ions shown in eq 1-3 are hydrocarbons **6**, **7**, and **3**. The enthalpy difference between **6** and **3** has been reported to be 59.5 kcal/mol.¹⁰ No information is available on the relative heat of formation of **7**.

The heats of protonation of these hydrocarbons in FSO₃H ($\Delta H_{\text{FSO}_3\text{H}}$) were measured with a similar type of calorimeter as that described by Arnett and Petro.¹¹ At 25 °C, **6** dissolves in the FSO₃H to produce **2**, while **3** gives an equilibrium mixture of the cations **4** and **5**. The measured heats of protonation for these two processes are given in Table I. The cleanliness of each of these protonations was confirmed by examining the ¹H NMR spectra of solutions prepared under comparable conditions to those used in the calorimetric experiments.



In the case of the homofulvene **7**, the protonation had to be carried out at low temperatures in order for the bicyclic ion **1** to be kinetically stable.^{2,5} Calculation of the expected half-life of **1** on the basis of the known free energy of activation at 20 °C indicated that at -20 °C the half-life of **1** would be over 30 h. ¹H NMR experiments confirmed that **1** was cleanly produced on protonation of **7** at -20 °C and this temperature was used to measure the heat of protonation.

The calorimetric procedure used in these experiments involved adding the hydrocarbon at room temperature to the acid. Thus the heat of protonation measured at -20 °C also includes a heat-capacity term for the hydrocarbon. This was corrected for by measuring the heat of solution of **7** in CCl₄ (ΔH_{CCl_4}) at both 25 and -20 °C, Table I. In this particular case the heat of solution of **7** in CCl₄ at 25 °C is 0 ± 0.2 kcal/mol and this means that the corrected heat of protonation equals the heat of transfer (ΔH_{trans}) as defined by Arnett and Larsen.¹³

The protonation of **7** was examined at high temperatures in order to obtain the difference in energy between **1** and **2**. At 65 °C the half-life of **1** is expected to be less than 1 s. Such a rate

Table I. Calorimetric Results

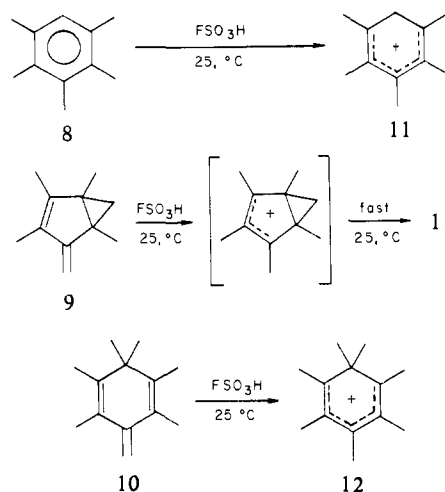
compd no.	ion	temp, °C	ΔH_{CCl_4} , kcal/mol	$\Delta H_{\text{FSO}_3\text{H}}^a$, kcal/mol	ΔH_{trans} , kcal/mol
7	1	-20	-2.4 ± 0.4	-37.9 ± 0.3	-35.5 ± 0.7
7		25	0 ± 0.2		
7	2	65	+3.0 ± 0.2 ^{a,b}	-41.4 ± 0.6	-44.4 ± 0.8
6	2	25	+4.8 ± 0.1	-1.66 ± 0.02	-6.5 ± 0.1
3	4/5	25	+0 ± 0.1	-44.5 ± 0.2	-45.5 ± 0.3
8	11	25	+3.3 ± 0.1	-3.02 ± 0.07	-6.7 ± 0.2
9	11	25	0 ± 0.1	-39.3 ± 0.5	-39.3 ± 0.6
10	12	25	+2.81 ± 0.03	-48.4 ± 0.5	-51.2 ± 0.5
14	16	-20	-3.4 ± 0.5	-28.9 ± 1.3	-25.5 ± 1.8
14		25	-0.2 ± 0.5		
14	16	50	+1.6 ± 0.2	-23.7 ± 0.5	-25.3 ± 0.7
13	15	-20	<i>c</i>	<i>c</i>	-22.3 ± 0.4
13	16	50	<i>c</i>	<i>c</i>	-34.0 ± 1.6
CCl ₄		25		-1.73 ± 0.05	

^a Value also contains a heat-capacity term when temperature differs from 25 °C. ^b Heat of solution measured in CH₂ClCH₂Cl.

^c **13** was dissolved in CCl₄ prior to protonation.

of isomerization is sufficiently rapid to allow measurement of the heat of protonation of **7** and its isomerization to **2**. Cation **2** was the only ion that could be detected by NMR when the protonation of **7** was carried out at 65 °C.

The heats of protonation of pentamethylbenzene (**8**), the fulvene **9**, and methylenecyclohexadiene **10** were also measured. In the case of **9** the cation formed was the benzenium ion **11**. The isomerization of the pentamethylbicyclo[3.1.0]hexenyl ion to **11** is much more rapid than that of **1** to **2**,³ and the temperature limits of the calorimeter used did not permit the measurement of the heat of protonation of **9** without isomerization.



The protonation of the related ketones **13** and **14** was also examined calorimetrically.^{2,14} A similar approach employing different temperatures was used in order to get the differences in heats of formation of the two ions. The reactions measured are summarized in eq 5, 6, and 7. Ketone **13** is a relatively low melting solid and difficulty was experienced in quantitatively adding it to the acid in its solid form. Instead, concentrated solutions of **13** in CCl₄ were used and corrections made for the heat of solution of CCl₄ in FSO₃H.

Discussion

The heats of protonation of several methyl-substituted benzenes in super acid media have been reported previously.¹⁵ Their magnitude has been shown to depend on acid strength and the values obtained here for the protonation of **6** and **8** in FSO₃H cannot be compared directly with earlier results obtained with

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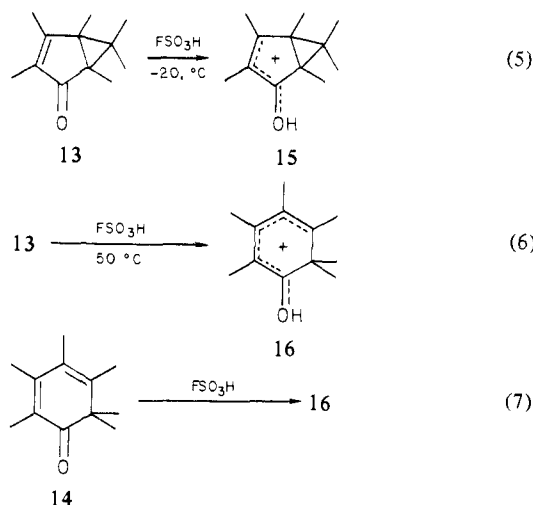
(11) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402.

(12) The entropy of activation associated with the isomerization of **1** to **2** is expected to be small, and it was neglected in this estimate.

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different media. The small size of ΔH_{trans} for **6** and **8**, however, is in line with the values found in similar acids. The small values reflect the stability of the benzenoid materials rather than the instability of benzenonium ions **2** and **11**. This is particularly evident by the very large ΔH_{trans} found for the protonation of **10**. The triene **10** is one of the most basic simple hydrocarbons known.¹⁶

The approach used here to interrelate the relative heats of formation of ions **1** and **2** and **15** and **16** assumes that the heats of protonation of the various precursors are independent of temperature. Arnett et al.^{11,17} have shown this to be the case in their work on the heats of formation of the *tert*-butyl cation in a variety of solvents. In this work we examined the protonation of **14** at both -20 and 50 °C, and within the limits of error we could detect no difference in the heats of protonation. At the higher temperatures we noted that some compounds charred and that irreproducible results were obtained. For example, the protonation of **3** at 65 °C should lead to the formation of **2**,⁵ and indeed by NMR this ion is observed. The acid solution, however, was somewhat dark in color, suggesting that charring had occurred, and very scattered calorimetric results were obtained.

From the results given in Table I and the known differences in the heat of formation of **6** and **3**, it is possible to interrelate the relative energies of hydrocarbons **3**, **6**, and **7** and cations **1**, **2**, **4**, and **5**. This information is summarized in Figure 1.

As can be seen from Figure 1, the homofulvene **7** is some 42.7 kcal/mol less stable than hexamethylbenzene (**6**). The heat of formation of the latter compound (ΔH_f) is -25.26 kcal/mol,¹⁸ which means the heat of formation of **7** is $+17.4$ kcal/mol. A complete analysis of the pentamethyl-substituted system is not possible owing to the very rapid isomerization of the bicyclic ion, although the energy difference between **8** and **9** can be obtained. This energy difference is found to be 36.3 kcal/mol, which is somewhat less than that found between **6** and **7**. When the known ΔH_f of **8** (-17.79 kcal/mol) is used,¹⁸ the heat of formation of **9** is $+18.5$ kcal/mol.

In contrast to the substantial energy difference between **7** and **6**, the difference between cations **1** and **2** is very much smaller. The 8.9-kcal/mol difference observed, Figure 1, is much smaller than that suggested by Sorensen and Rauk⁸ (40 kcal/mol) or calculated by Hehre⁹ (34 kcal/mol) for the unsubstituted ions. There are some obvious reasons why the observed energy difference should be less. The methyl substituents on **1** and **2** are expected to exhibit an attenuating effect. Further, the experimental determination was carried out in a condensed phase, FSO_3H , where the ions will be solvated, while the calculations refer to the gas phase.¹⁹ Despite these attenuating factors, the energy difference

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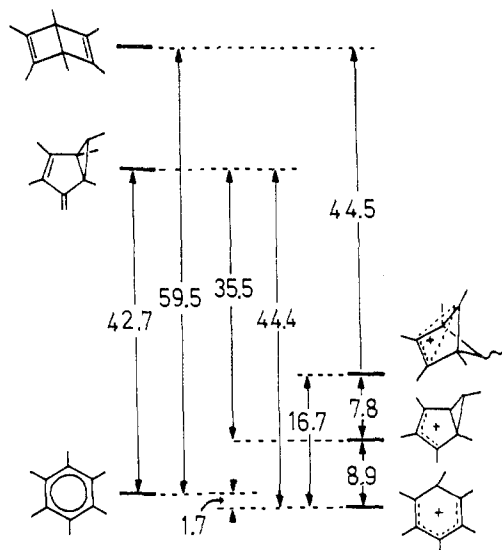


Figure 1. Relative heats of formation (kcal/mol) of $\text{C}_6(\text{CH}_3)_6$ hydrocarbons and $\text{C}_6(\text{CH}_3)_6\text{H}^+$ cations.

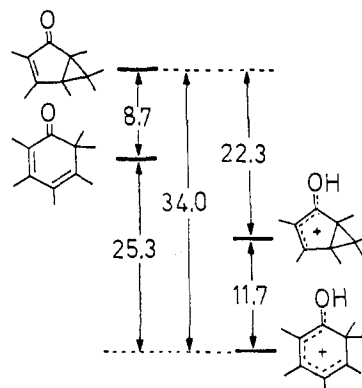


Figure 2. Relative heats of formation (kcal/mol) of ketones **13** and **14** and hydroxy cations **15** and **16**.

observed between **1** and **2** seems to be small and it is instructive to try and dissect the various contributions to this 8.9-kcal/mol difference and estimate the resonance energies of the two ions.

In addition to the difference in resonance energy of **1** and **2**, the strain energy and the different number of σ and π bonds in the two cations has to be taken into account. Some measure of the magnitude of the latter two terms can be obtained from considering the observed energy difference between **6** and **7**. In this case the major contribution to the observed 42.7-kcal/mol difference will be the resonance energy associated with the aromatic stabilization of **6**. The magnitude of the difference in resonance energies of **6** and **7** is expected to be about 33 kcal/mol. This estimate, on the basis of the usually quoted resonance energies of a benzene vs. a 1,3-diene,²⁰ means that the combined strain-/bond-energy difference between these two compounds is of the order of 8 kcal/mol.

Support for such an estimate is found in the difference in the relative heats of formation found for ketones **13** and **14**. When the thermochemical cycle shown in Figure 2 is used, this difference is found to be 8.7 kcal/mol.²¹ In this case the difference in the resonance stabilization of the two ketones can be considered to

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(20) Wheland, G. W. "Resonance in Organic Chemistry"; Wiley, New York, **1955**; p 75.

(21) Estimates²² of ΔH_f of 2,4-cyclohexadienone (-8.45 kcal/mol) and bicyclo[3.1.0]hex-3-en-2-one ($+1.16$ kcal/mol) and ΔH_f between the two of 9.6 kcal/mol are in good agreement with the values obtained here for the hexamethyl-substituted systems.

(22) Eigenmann, H. K.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 1687 and cited references.

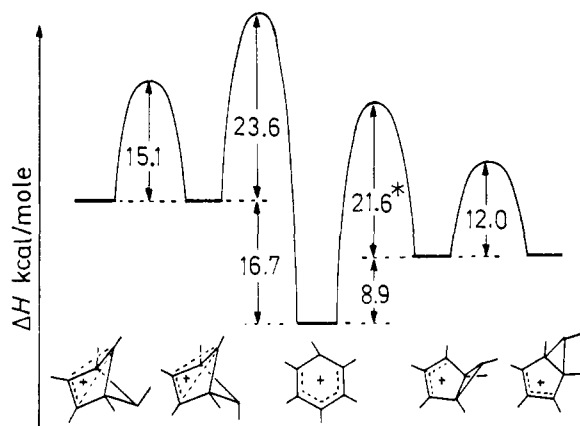


Figure 3. Energy surface for cations 1, 2, 4, and 5. (Value marked with an asterisk is ΔG^\ddagger .)

be small and the 8.7-kcal/mol difference observed can largely be attributed to ring strain- and bond-energy differences. The difference in the relative heats of formation of the protonated ketones **15** and **16** is 11.7 kcal/mol, Figure 2. This is some 3 kcal/mol more than that found for the neutral ketones. Typically we have found the heats of protonation (ΔH_{trans}) of dienones in FSO_3H to be about 1 kcal/mol greater than that of structurally related enones.²³ Thus the combined strain-/bond-energy difference between cations **15** and **16** must be comparable to that of ketones **13** and **14**.

Using the estimate of 8 kcal/mol for the combined strain-/bond-energy difference between **6** and **7** and making the assumption that this does not change much on going to cations **1** and **2**, we found the difference in delocalization energies of the two cations to be about 1 kcal/mol. This is somewhat less than that estimated above for the protonated ketones **14** and **15**. The question arises as to whether such a difference is that expected for an allyl vs. a pentadienyl cation?

The resonance energy of an allyl cation has been defined as the difference in energy between the planar and perpendicular forms.²¹ The latter species corresponds in structure to the transition state for the rotation of one of the bonds of the allyl cation. Using the same type of definition for the resonance energy of a pentadienyl cation, the calculated difference in resonance energy between the unsubstituted allyl and pentadienyl cations is of the order of 13 kcal/mol.²⁴ This would be attenuated somewhat in solution owing to solvation and a value of some 9 kcal/mol might be expected.¹⁹ Thus the difference in resonance energy of the parent bicyclo[3.1.0]hexenyl and benzenium ions would be expected to be about 9 kcal/mol if they could be viewed simply as being allyl and pentadienyl cations with no involvement of the cyclopropyl ring. While the methyl substituents on ions **1** and **2** will have an attenuating effect, the 1-kcal/mol estimated dif-

ference in resonance energy of these ions is considerably smaller than the 9-kcal/mol estimate for the resonance-energy difference between the allyl and pentadienyl cations. This suggests that the cyclopropane in **1** acts to stabilize this ion, presumably by a conjugative interaction involving the external cyclopropane bonds. While this analysis is only approximate, there is no evidence for any destabilization of **1** due to an "antihomoaromatic" interaction.²⁵

Cations **4** and **5** can be thought of as being bishomoaromatic with a delocalization similar to that observed in the 7-norbornenyl cations.²⁵ It is noteworthy that this factor is not sufficient to make cations **4** and **5** more stable than **1**.

It is possible to combine the relative heats of formation of ions **1**, **2**, **4**, and **5** together with the activation barriers associated with their interconversions. This allows an energy surface to be constructed for these systems as is shown in Figure 3. The pathways for the conversion of **4** and **5** to **2** have been discussed in a previous paper and will not be reiterated here.²

In conclusion, it is worth noting that the methyl-substituted benzene/homofulvene interconversion has been suggested as a potential photochemical/latent heat storage system for solar energy.²⁶ The large energy differences observed here between these systems make them attractive candidates for solar-energy storage.

Experimental Section

General ^1H NMR spectra were obtained with a Varian EM-390 spectrometer.

Most compounds used were commercially available. Compounds **9**,²⁷ **10**,²⁸ **13**,²⁹ and **14**²⁹ were made by following literature procedures. The purity of all compounds was checked by ^1H NMR spectra and GLC.

Trial protonations of all materials were conducted by rapidly injecting the compound from a 25- μL syringe directly into stirred FSO_3H . The temperature of the acid was kept at the same temperature as used in the calorimetry. The protonations were examined by ^1H NMR spectroscopy to ensure the identity of the ion produced. The calorimeter used was a modification of the design described by Arnett and Petro.¹¹ The modifications made have been described previously.³⁰ The operation of the calorimeter was checked by measuring the heat of protonation of water in FSO_3H and the heats of solution of a variety of Lewis bases in $\text{SbCl}_5/\text{CH}_2\text{Cl}_2$.

The samples were introduced into the calorimeter with a weighed 25- μL syringe. The needle of the syringe was arranged to be ca. 0.5 cm above the level of the liquid in the calorimeter. The syringe was reweighed after the sample was introduced. Typically a compound was protonated some four to five times (with 10–20-mg samples) in a given calorimetric run. At least two independent calorimetric runs were made for each compound.

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