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Heats of Protonation of Unsaturated Ketones. A Thermodynamic Investigation of the Importance of Homoaromatic Stabilization[1]

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The heats of transfer from CCl_4 to FSO_3H, ΔH_{trans}, have been measured for a series of ketones. Typically it was found that ΔH_{trans} values of α,β-unsaturated ketones are about 4 kcal/mol more exothermic than those of corresponding saturated ketones. A cyclopropyl ring adjacent to a carbonyl enhances ΔH_{trans} of a ketone by a comparable amount. Values of ΔH_{trans} for cycloheptanone (**5**; −18.5 kcal/mol), cycloheptenone (**3**; −22.2 kcal/mol), 2,4-cycloheptadienone (**2**; −23.0 kcal/mol), tropone (**1**; −30.3 kcal/mol), and 2-homotropone (**6**; −25.9 kcal/mol) were obtained. The large differences in ΔH_{trans} between **2** and **1** reflect the aromatic nature of the hydroxytropylium cation. The corresponding difference between **2** and **6**, which is some 40% of that between **2** and **1**, indicates that homoaromaticity is significant but less important than aromaticity in stabilizing a cation. The importance of homoaromaticity in stabilizing homotropylium cations was reinforced by an examination of ΔH_{trans} values of a corresponding series of five-membered-ring ketones.

Although the concept of homoaromaticity was first introduced by Winstein[2] some 23 years ago, there is remarkably little definitive evidence for this type of delocalization. Many molecules and ions have been suggested to be homoaromatic,[3] but these claims have been questioned in many instances. Indeed, recently it has been suggested that homoaromaticity is only of importance for a limited number of small and medium size ring cations such as the homotropylium ion.[4,5]

Even with cations as the homotropylium ions, the experimental evidence for homoaromaticity is by no means overwhelming.[6,7] The strongest and most commonly used evidence is the ^1H NMR spectra of these ions and the apparent need to invoke an induced ring current in order to satisfactorily account for the chemical shifts of bridging methylene protons.[6a–c] This type of approach to defining aromaticity, let alone homoaromaticity, is open to serious question.[8] Other attempts to establish the stability of homotropylium ions include measurement of reduction potentials[9] and the basicity of 2,3-homotropone.[10]

To provide clear evidence for or against homoaromaticity, we planned a twofold approach to the problem. The first of these involved the determination of the structure of potentially homoaromatic ions by using X-ray crystallography.[11] The second involved calorimetry, and some of our results in this area are presented in this paper.[12]

Results and Discussion

The method used in this work was to measure the heats of protonation in FSO_3H of a series of unsaturated ketones. The protonation of ketones upon solution in FSO_3H is generally a very clean reaction, and the cationic products are stable in this strong acid. This simplifies the calorimetric measurements.

The heat of protonation of a carbonyl relates the heats of formation of the compound and its conjugate acid. Arnett et al.[13,14] have shown that the heat of protonation of a carbonyl compound is linearly related to the pK_a of its conjugate acid, the number more usually used to quantitatively relate a carbonyl with its protonated form. The heat of protonation is the more sensitive parameter, varying some 1.78 times as fast as pK_a. While a heat of protonation is an energy difference, variations in the magnitude of this term for various ketones will reflect to a large extent the stabilities of the conjugate acids of the ketones. Conjugative effects, the topic of concern in this paper, will be very much less important energetically for a neutral ketone as compared to the corresponding protonated ketone. Consequently, differences in the heats of protonation of two related ketones can be thought of as representing, to a large extent, the differences in stability of the protonated ketones. Other factors that must be borne in mind in interpreting these results are the effects of differential solvation of cations with very different structures and also major changes in structure that could occur on protonation that lead to significant changes in strain energy, etc. Some of these effects are of importance

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(1) This work was supported by grants from the Natural Science and Engineering Research Council of Canada. Synthetic assistance by M. Zeya and K. Pilon is gratefully acknowledged.

(2) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.

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(7) For theoretical approaches to the problem, see Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 890; **1974**, *96*, 5207, Haddon, R. C. *Tetrahedron Lett.* **1975**, *863*; *Ibid.* **1974**, 2797; *Aust. J. Chem.* **1977**, *30*, 1. Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 6784. Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.

(8) For example, compare the recent structural evidence reported by the following: Stam, C. H.; Counotte-Potman, A. D. van der Plas, H. C. *J. Org. Chem.* **1982**, *47*, 2856. Hoskin, D. H.; Wooden, G. P.; Olofson, R. A. *Ibid.* **1982**, *47*, 2858, with earlier ^1H NMR based claims cited therein.

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(10) Holmes, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 2531.

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(12) For an earlier paper on calorimetry of the bicyclo[3.1.0]hexenyl cations, see Childs, R. F.; Mulholland, D. L. *J. Am. Chem. Soc.*, **1983**, *105*, 96.

(13) Arnett, E. M.; Quirk, R. P.; Larsen, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 3977.

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Table I. Calorimetric Data

ketone	temp, °C	ΔH_{FSO_3H},[o] kcal/mol	ΔH_{CCl_4},[o] kcal/mol	ΔH_{trans},[o] kcal/mol this work	ΔH_{trans},[o] kcal/mol lit.	^{1}H NMR ref
1	30	−28.5 ± 0.2	1.8 ± 0.1	−30.3 ± 0.3		*a*
2	30	−22.0 ± 0.3	1.0 ± 0.5	−23.0 ± 0.8		*b*
3	30	−21.9 ± 0.9	0.31 ± 0.01	−22.2 ± 0.9		*c*
4	25	−21.5 ± 0.3	0.50 ± 0.02	−22.0 ± 0.3		*b*
5	25	−18.5 ± 1.3	0.0 ± 0.04	−18.5 ± 1.3	−18.2 ± 0.2[n]	*d*
6	25	−25.1 ± 0.8	0.77 ± 0.06	−25.9 ± 0.9		*e*
7	−20	−25.4 ± 0.8	−2.4 ± 0.1	−23.0 ± 0.9		*e*
8	26	*p*	*p*	−20.2 ± 0.4		*e*
9	25	−23.4 ± 0.7	0.76 ± 0.04	−24.2 ± 0.7		*f*
10	25	−19.3 ± 0.2	0.32 ± 0.03	−19.6 ± 0.2		*g*
11	26	−18.2 ± 0.8	0.24 ± 0.03	−18.4 ± 0.8	−17.6 ± 0.1[n]	*d*
12	26	−22.2 ± 0.2	1.1 ± 0.2	−23.3 ± 0.4		*h*
13	26	−22.3 ± 0.6	0.8 ± 0.2	−23.1 ± 0.8		*i*
14	25	−23.3 ± 0.2	0.0 ± 0.1	−23.3 ± 0.3		*j*
15	26	−23.4 ± 0.4	1.04 ± 0.3	−24.4 ± 0.4		*k*
16	−20				−22.3[l]	
17	25	−21.49 ± 0.08	0.8 ± 0.1	−22.3 ± 0.2		*m*
18					−18.8 ± 0.2[n]	
19	25	−21.9 ± 0.5	0.64 ± 0.04	−22.5 ± 0.5		*m, h*
20	25	−19.3 ± 0.8	0.85 ± 0.1	−20.2 ± 0.9		*h*
21					−23.9 ± 0.3[n]	
22	25	−21.4 ± 0.4	0.6 ± 0.2	−22.0 ± 0.6		*h*
23					−18.2 ± 0.1[n]	

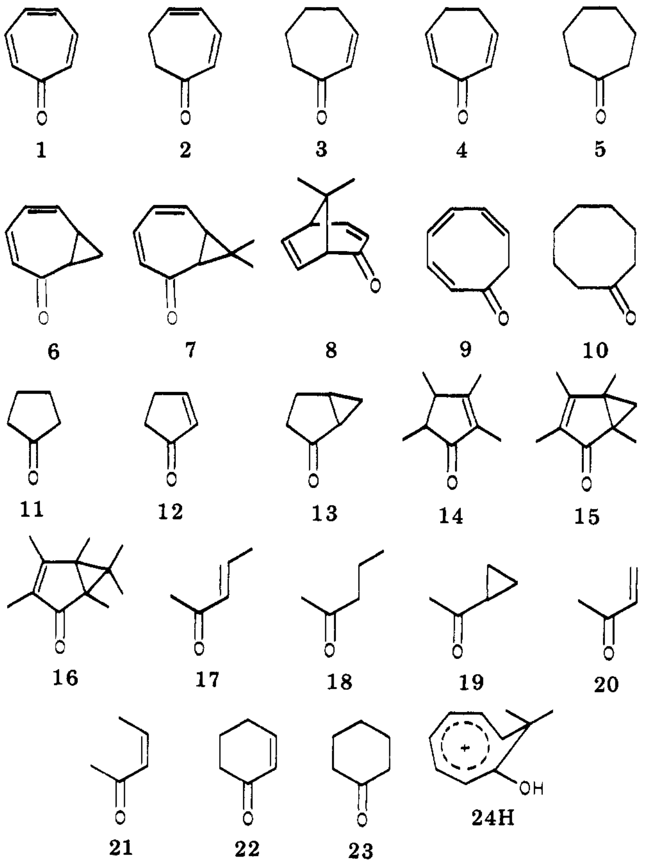
[a] Dauben, H. J., Jr.; Gresham, W. R. quoted by Harmon, K. M. *Carbonium Ions* **1973**, *4*, 1579. [b] Reference 29. [c] Hine, K. E.; Childs, R. F. *Can. J. Chem.* **1976**, *54*, 12. [d] Brookhart, M.; Levy, G. C.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1735. [e] Reference 33. [f] Reference 25. [g] Resonances at δ 1.3 (m, 2), 1.66 (quint, 4), 2.26 (quint, 4), 3.16 (t, 4). [h] Olah, G. A.; Halpern, Y.; Mo, Y. K.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 3554. [i] Resonances occur as multiplet δ 2.3–3.7. [j] Resonances at δ 1.37 and 1.52 (d, 3 H, J = 5 Hz), 1.98 and 2.52 (s, 3 H), 2.87 (m, 2 H). [k] Childs, R. F.; Shaw, G. S.; Varadarajan, A. *Synthesis* **1982**, 198. [l] Reference 12. [m] Reference 37. [n] Reference 13. [o] Errors quoted are standard deviation of measurements from mean value. [p] **8** is a solid and it was dissolved in CCl_4 prior to protonation.

in this work and will be discussed later.

The heats of protonation in FSO_3H (ΔH_{FSO_3H}) of various ketones were measured with a scaled-down calorimeter of similar design to that described by Arnett and Petro.[15] The ketones were introduced directly into the rapidly stirred acid with a microliter syringe. Control experiments were run in each case to ensure that the protonations were quantitative and the resulting protonated carbonyl compounds were kinetically stable under the conditions used. These control experiments involved an identical protonation of the carbonyl compound in FSO_3H at somewhat higher concentration and examination of the ^1H NMR spectrum of the resulting solution. In each case studied, clean oxygen protonation was observed and the ^1H NMR spectrum obtained corresponded either to that reported previously or that expected for the cation. Except for **7**, all heats of protonation were measured at temperatures close to room temperature. Cation **7H** undergoes thermal isomerization at room temperature[16] and the heat of protonation had to be measured at −20 °C. The ketones used in this work are shown in Scheme I and the various ΔH_{FSO_3H} values are given in Table I.

As measured by the technique outlined above, the heats of protonation (ΔH_{FSO_3H}) include a small heat capacity term for the neutral ketone, resulting from the temperature difference between the calorimeter and ambient temperature, and a term corresponding to the heat of sublimation or vaporization of the ketone. Both of these terms were corrected for by measuring the heat of solution of the ketones in CCl_4 (ΔH_{CCl4}) and subtraction of this term from ΔH_{FSO_3H} to give ΔH_{trans}. This term corresponds to the heat of protonation of the ketones from the gas phase.[17] Data are given in Table I.

Scheme I[a]



[a] Corresponding oxygen protonated ketones denoted by 1H, 2H, etc.

In two cases, compounds **5** and **11**, we obtained similar values to those previously reported.[13] Thus for **5**, ΔH_{trans}

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(15) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402.
(16) Childs, R. F.; Rogerson, C. V. *J. Am. Chem. Soc.* **1980**, *102*, 4159.
(17) Arnett, E. M.; Larsen, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 1438.

found here is −18.5 ∓ 1.3 kcal/mol, as compared to −18.2 ∓ 0.2 kcal/mol. For **11**, ΔH_{trans} is −18.5 ∓ 0.8 kcal/mol as compared to −17.6 ∓ 0.1 kcal/mol. (The value obtained in this work is the average of some 22 determinations carried out at different times over a period of several months.) It is gratifying to see, as was suggested by Arnett and co-workers,[13] that measurement of the heat of protonation of a ketone is seemingly more reliable than the determination of the pK_a of their conjugate acid.

Trends in ΔH_{trans}. Before examining the question of homoaromaticity, it is useful to note some trends in the ΔH_{trans} values of the ketones given in Table I. First, in going from a saturated to an α,β-unsaturated ketone, there is a large increase in the ΔH_{trans} values observed. Thus for the closely related ketones $\Delta\Delta H_{\text{trans}}$ = 3.7 kcal/mol for **3** and **5**, 3.9 kcal/mol between **22** and **23**, 3.5 kcal/mol between **18** and **17**, and 4.9 kcal/mol between **12** and **11**. Overall the difference is of the order of 4 kcal/mol, and in terms of pK_a, this difference would correspond to about 2.3 units[13,14], which is considerably less than the difference between the reported pK_a values of the closely related protonated ketones. For example, the difference in pK_a of **22H** and **23H** is 3.5 pK_a units and that between **12H** and **11H** 4.45 units.[18,19] This considerable discrepancy probably results from the different acidity scales used in obtaining the pK_a values of the conjugate acids of unsaturated ketones vs. saturated ones.[18-20] Such difficulties do not arise in the calorimetric approach and the differences of about 4 kcal/mol observed here give a better idea of the difference in basicity of corresponding saturated and unsaturated ketones.[21]

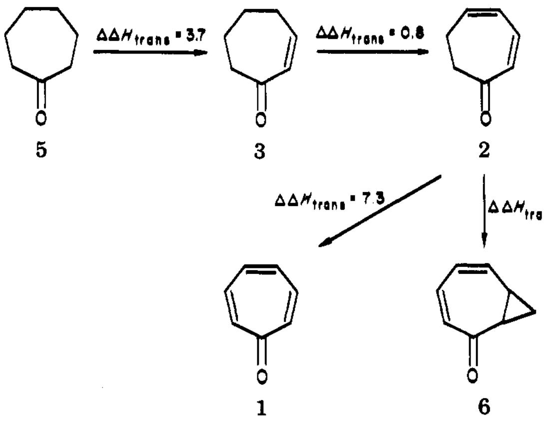
A second point to note is that a cyclopropyl ring is about as effective as a double bond in enhancing the stability of a protonated ketone. Thus the difference in ΔH_{trans} of **18** and **19** is 3.7 kcal/mol and that between **11** and **13** 4.7 kcal/mol. These differences correspond in magnitude with those mentioned above for the effect of a conjugating double bond.[22]

The additive effect of β-methyl substitution on the basicity of α,β-unsaturated ketones is also shown in ΔH_{trans} values.[18,20,23] This can be clearly seen in the series **20** to **17** to **21**, where increments of 2.1 and 1.6 kcal/mol are observed. A similar effect is not observed between **12** and **14**, although this may be due to a steric hindrance to solvation.

Effect of Cyclic Conjugation. While the introduction of the first double bond adjacent to a carbonyl makes a considerable difference to its basicity, the effect of a further double bond is small. This can be seen comparing the ΔH_{trans} values of cycloheptadienones **2** and **4** with that of **3**. Within experimental error the values observed are not significantly different and certainly well below the approximately 4 kcal/mol difference seen earlier for the introduction of the first double bond. Zalewski and Dunn have also noted that the effect of the second double bond is small in their measurements of pK_a values of steroidal ketones.[23]

The minor effect of a second double bond stands in marked contrast to the introduction of a third double bond or a cyclopropyl group to a cycloheptadienone. thus tropone (**1**; ΔH_{trans} = −30.3 kcal/mol) is by far the most basic ketone of the series shown in Scheme II. The very large jump in the ΔH_{trans} values observed in going from **2** to **1** in this series can be taken to reflect the aromatic character of the hydroxytropylium cation.

Scheme II[a]



[a] All values in kilocalories/mole.

Similarly, 2-homotropone (**6**) also exhibits a large ΔH_{trans} value. As is illustrated in Scheme II, the difference in ΔH_{trans} in going from **2** to **6** is substantial. As has already been pointed out, a cyclopropyl group in conjugation to a carbonyl function has a very similar effect on ΔH_{trans} to that of a double bond. In comparing ΔH_{trans} of **2** and **6**, it must be remembered that there are already two double bonds in conjugation with the ketone function and the effect of the introduction of a cyclopropyl substituent would be expected to be small in the absence of any special cyclic delocalization. The differences in ΔH_{trans} values observed in this series of ketones fully supports the view that **6H** is an homoaromatic ion.[3,10,16] It is interesting that the magnitude of $\Delta\Delta H_{\text{trans}}$ between **2** and **6** (2.9 kcal/mol) is some 40% as large as the difference between **2** and **1**. Clearly homoaromatic delocalization is not as effective as conventional aromatic delocalization in stabilizing a seven-membered-ring cation.

The differences in ΔH_{trans} of ketones **1**, **5**, and **6** found here correspond closely to 1.78 times the differences in pK_a values of the conjugate acids of these ketones.[19,10,24] The reported pK_a values of **1**, **5**, and **6** are all based on the H_0 acidity scale.

In comparison to the substantial differences in ΔH_{trans} between **5** and **6** (7.4 kcal/mol), the difference between **10** and **9** is considerably smaller ($\Delta\Delta H_{\text{trans}}$ = 4.6 kcal/mol) At first glance this is suprising as the protonation of **9** gives **9H**, which has been regarded as a further example of a homoaromatic cation.[3,25] Indeed, the difference in ΔH_{trans} of **9** and **10** is about the same as that between **5** and **2** (4.5 kcal/mol) and is what might have been expected if **9H** were regarded as a protonated linear trienone.

Care must be taken in assessing the relative importance of homoaromaticity in 9H and 6H , for it is necessary to take into account the different starting points for these ions. As was shown by the structural work on **6H**, the homoaromatic bond distance between C_1 and C_7 is 1.626 (8) Å, which is somewhat larger but not too far removed from that normally encountered for a cyclopropane. On the other hand, trienone **9** does not possess a cyclopropane grouping and some considerable geometric change can be envisaged in the conversion of **9** to **9H**. This change is

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(18) Zalewski, R. I., Dunn, G. E. *Can. J. Chem.* **1969**, *47*, 2263.

(19) Campbell, H. J.; Edward, J. T. *Can. J. Chem.* **1960**, *38*, 2109. Values corrected to H_0 scale of Jorgensen, M. J.; Hartter, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 878.

(20) Jensen, J. L.; Thibeault, A. T. *J. Org. Chem.* **1977**, *42*, 2168.

(21) Arnett, E. M.; Scorrano, G. *Adv. Phys. Org. Chem.* **1976**, *13*, 83.

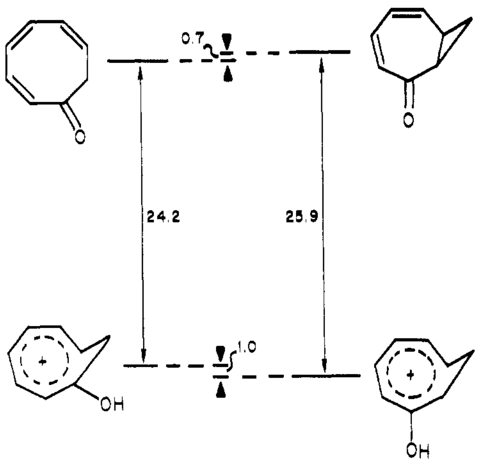
(22) Levy, G. C.; Cargioli, J. D.; Racela, W. *J. Am. Chem. Soc.* **1970**, *92*, 6238. McClelland, R. A.; Reynolds, W. F. *Can. J. Chem.* **1976**, *54*, 718.

(23) Zalewski, R. I., Dunn, G. E. *Can. J. Chem.* **1970**, *48*, 2538.

(24) Kende, A. *Adv. Chem. Phys.* **1965**, *8*, 136.

(25) Brookhart, M.; Ogliaruso, M.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1965.

Scheme III[a]



[a] All energies in kilocalories/mole.

likely to be accompanied by an increase in strain energy, which will be reflected in $\Delta H_{\mathrm{trans}}$ for this ketone.

In earlier work on the acid-catalyzed rearrangements of 7 it was shown that the free energy difference between **7H** and **24H** was of the order of 1 kcal/mol.[26] Assuming that **7H** and **24H** are good models for the unsubstituted ions and that entropy differences are small, then in terms of enthalpy **6H** would be expected to be more stable than **9H** by about the same amount. Combining this with the heats of protonation of **6** and **9**, this means that **6** shold be less stable than **9** by about 0.7 kcal/mol (Scheme III). Estimates of the heats of formation of these two ketones using Benson's additivity relationships[27] indicates that **6** is less stable than **9** by about 3 kcal/mol. Bearing in mind the errors associated with the measurements and some question about ring correction factors in the enthalpy estimates, this is good agreement and indicates that the results are thermodynamically consistent.

The observations among these seven-membered-ring cations stand in marked contrast to the effects seen in the five-membered-ring series. Here the instability of cyclopentadienones and the parent bicyclo[3.1.0]hexenone limited extension of the measurements to a complete series as in the case of the seven-membered-ring ketones above. However, while the normal large increment in $\Delta H_{\mathrm{trans}}$ is observed on going from **11** to **12** or **13**, the difference between **14** and **15** is now only 1.1 kcal/mol, barely outside of experimental error. Cyclopropyl involvement in ions such as **15** is thought to involve the external cyclopropane bonds rather than the internal one, and the ion can be regarded as being nonaromatic.[28,12] The introduction of a cyclopropyl stabilizes rather than destabilizes **15H** as compared to **14H**. There is no evidence for any "antihomoaromatic" destabilization of **15H**. These results support the conclusions reached on measurement of the heat of isomerization bicyclo[3.1.0]hexenyl cations to benzenium ions.[12]

It can be seen from the data in Table I that the presence of two geminal methyl groups on a cyclopropyl ring has a considerable effect on the heat of protonation of a ketone. Thus, $\Delta H_{\mathrm{trans}}$ of **7** is some 2 kcal/mol less than that measured for **6**. A similar reduction is seen for **16** as compared to **15**. This effect probably results from steric hindrance to solvation in the acid medium.[29] A similar effect is probably in operation with **8** and the low value of $\Delta H_{\mathrm{trans}}$ should not be taken to infer destabilization relative to a cyclohexenone resulting from "bishomoantiaromaticity" in **8H**.

In conclusion, the results we have obtained here for the heats of transfer of 2.3-homotropone and related cyclic ketones provide a measure of the importance of homoaromaticity in homotropylium ions. These results, when taken together with the structure of the 2-hydroxyhomotropylium ion as determined by X-ray crystallography,[11] establish that homoaromaticity is significant in determining the ground-state properties of the homotropylium ions.

Experimental Section

General Procedures. Details of the calorimeter and procedures used have been given in earlier papers.[12,30] The enthalpies quoted are the arithmetic mean of at least six measurements carried out in a minimum of two independent runs. The errors quoted are the standard deviation of the measurements from the mean. The FSO_3H was purified by double distillation and purging with dry nitrogen.[30] The ketones used were either commerically available or prepared by literature methods: **1**,[31] **2**,[32] **3**,[33] **4**,[33] **6**,[34] **7**,[35] **8**,[16] **9**,[36] **13**,[37] **14**,[38] **15**,[39] **16**.[40] In each case the ketones were dried over molecular sieves and distilled, and their purity was checked by ^1H NMR and gas chromatography before use.

Enthalpy Calculations. These were carried out by use of Benson's group additivity tables.[27] For **9**: $C_d(C)(H)$ 8.59, $C_d(C_d)(H)$ 4 × 6.78, $C_d(CO)(H)$ 5.0, $C(C_d)(H)_2(CO)$ −3.8, $CO(C_d)(C)$ −31.4, ring correction (1,3,5-cyclooctatriene) 8.9, giving $\Delta H_f° = 14.4$ kcal/mol. For **6**: $C_d(H)(C_d)$ 2 × 6.78, $C_d(C)(H)$ 8.59, $C_d(CO)(H)$ 5.0, $C(CO)(C)_2(H)$ −1.7, $C(C_d)(C)_2$ −1.48, $C(C)_2(H)_2$ −4.95, $C(C_d)(C)$ −31.4, ring correction (bicyclo[5.1.0]octane) 29.6, giving $\Delta H_f° = 17.2$ kcal/mol.

Registry No. **1**, 539-80-0; **2**, 1901-34-4; **3**, 1121-66-0; **4**, 1192-93-4; **5**, 502-42-1; **6**, 3818-97-1; **7**, 56568-74-2; **8**, 66053-98-3; **9**, 4011-22-7; **10**, 502-49-8; **11**, 120-92-3; **12**, 930-30-3; **13**, 4160-49-0; **14**, 54458-61-6; **15**, 81722-03-4; **16**, 2206-69-1; **17**, 625-33-2; **18**, 107-87-9; **19**, 765-43-5; **20**, 78-94-4; **21**, 141-79-7; **22**, 930-68-7; **23**, 108-94-1.

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