References and Notes

(1) Stable Carbocations. 207. Part 206. G. A. Olah, G. K. S. Prakash, and G. Liang, *J. Am. Chem. Soc.*, submitted for publication.
(2) J. D. Roberts and V. Chambers, *J. Am. Chem. Soc.*, **73**, 3176, 5034 (1951).
(3) (a) L. Radom, J. A. Pople, P. C. Hariharan, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973), and references therein; (b) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Stereochem.*, 7, 253 (1973); (c) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8193 (1973); (d) D. H. Aue, W. R. Davidson, and M. T. Bowers, *ibid.*, **98**, 6700 (1976). This reference gives the heats of formation of cyclopropyl cations in the gase phase.
(4) (a) V. Schöllkopf, K. Fellenberger, M. Potsch, P. v. R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967); (b) W. Kutzelnigg, *ibid.*, 4965 (1967); (c) V. Schöllkopf, *Angew Chem.*, Int. Ed. Engl., **7**, 588 (1968).
(5) (a) X. Creary, *J. Org. Chem.*, **40**, 3326 (1975); *J. Am. Chem. Soc.*, **98**, 6608 (1976). (b) B. D. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969). (c) D. B. Ledlie, *J. Org. Chem.*, **37**, 1439 (1972). (d) D. B. Ledlie, T. Swan, J. Pile, and L. Bowers, *ibid.*, **41**, 419 (1976). (e) P. Warner, and S. L. Lu, *J. Am. Chem. Soc.*, **98**, 6752 (1976), and previous papers in this series. (f) N. M. Weinshenker and F. D. Greene, *ibid.*, **90**, 506 (1968). (g) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 909 (1974). (h) C. B. Reese and M. R. D. Stables, *ibid.*, 4427 (1972).
(6) The tertiary bromide 3 was prepared from the corresponding dibromide and *n*-butyllithium in the presence of methyl iodide at low temperature.
(7) Above −60 °C, the ion slowly rearranged into a unidentified species which shows the following NMR spectrum: ^{1}H, δ 3.06, 2.12, 1.91, 1.82; ^{13}C, δ_{13C} 257.3 (s), 89.4, 86.5, 81.8, 45.7, 39.9, 25.0, 24.0, 22.2, 18.1. The structure of this ion is under further investigation.
(8) The possibility of complex 5 seems to be small since we were not able to observe any fluorine resonance corresponding to the structure.
(9) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **94**, 6434 (1972); **97**, 1987 (1973).
(10) (a) G. A. Olah, J. S. Staral, and G. Liang, *J. Am. Chem. Soc.*, **96**, 6233 (1974); (b) G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *ibid.*, **97**, 5489 (1975).
(11) K. Morio and S. Masamune, *Chem. Lett.*, 1251 (1974).
(12) W. J. Hehre and A. J. P. Devaquet, *J. Am. Chem. Soc.*, **98**, 4370 (1976).
(13) W. L. Jorgensen, *J. Am. Chem. Soc.*, **98**, 6784 (1976).
(14) Evidence for a distinct cyclopropyl cation has also been given by D. B. Ledlie, W. Barber, and F. Switzer, *Tetrahedron Lett.*, 607 (1977), in the solvolysis of epimeric 11-methyltricyclo[4.4.1.0^{1,6}]undecen-3-yl 11-bromides. The bent conformation for the cyclopropyl cation in the presently studied system seems to be due not only to the highly energetic ring opening but also to the stability gained by introducing the methyl substituent at C$_{11}$.^{2,3}
(15) Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007.

George A. Olah,*[15] Gao Liang

Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

David B. Ledlie,* Mark G. Costopoulos

Department of Chemistry, University of Vermont
Burlington, Vermont 05401
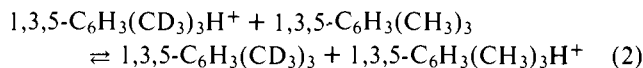*Received December 20, 1976*

Equilibrium Isotope Effects on the Proton Transfer Reactions of Methylbenzenes
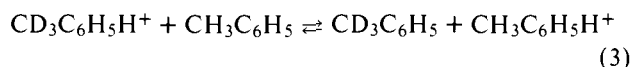
Sir:

It has recently been reported[1] that the proton transfer equilibrium between an alkylbenzene and its analogue for which the side chain is deuterated

$$C_6H_n(R_D)_{(6-n)}H^+ + C_6H_n(R_H)_{(6-n)}$$
$$\rightleftharpoons C_6H_n(R_D)_{(6-n)} + C_6H_n(R_H)_{(6-n)}H^+ \quad (1)$$
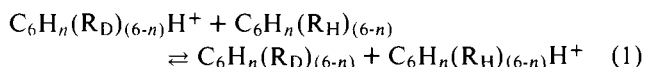
favors the formation of the nondeuterated protonated alkylbenzene. Values of $\Delta G°$ at 300 K ranging from -0.175 ± 0.053 kcal/mol for

$$1,3,5\text{-}C_6H_3(CD_3)_3H^+ + 1,3,5\text{-}C_6H_3(CH_3)_3$$
$$\rightleftharpoons 1,3,5\text{-}C_6H_3(CD_3)_3 + 1,3,5\text{-}C_6H_3(CH_3)_3H^+ \quad (2)$$

to -0.328 ± 0.040 kcal/mol for

$$CD_3C_6H_5H^+ + CH_3C_6H_5 \rightleftharpoons CD_3C_6H_5 + CH_3C_6H_5H^+ \quad (3)$$
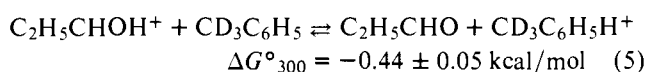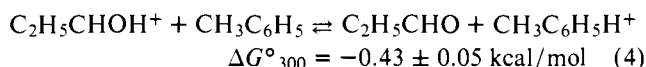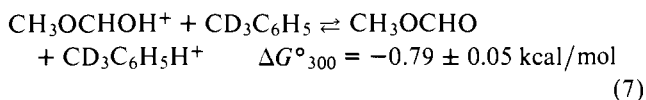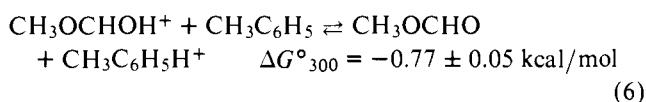
were derived from the equilibrium constants

$$-RT \ln K_{eq} = \Delta G°$$

observed in isotopic analogue mixtures of toluenes, xylenes, and mesitylene in a pulsed ion cyclotron resonance spectrometer. The existence of such large isotope effects on the heats of formation of protonated alkylbenzenes was interpreted as evidence for hyperconjugative stabilization of the protonated alkylbenzenes.[1]

In the course of an investigation in this laboratory of proton transfer equilibria, results have been obtained which indicate that, contrary to the result reported by Hehre et al.,[1] the proton affinity of $C_6H_5CD_3$ is, within experimental error, the same as that of $C_6H_5CH_3$. This conclusion was derived from experiments performed in the NBS pulsed ion cyclotron resonance spectrometer[2] in which the equilibrium constants were measured[3] for the proton transfer equilibria between propionaldehyde and the two toluenes
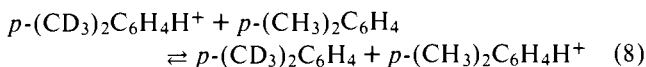
$$C_2H_5CHOH^+ + CH_3C_6H_5 \rightleftharpoons C_2H_5CHO + CH_3C_6H_5H^+$$
$$\Delta G°_{300} = -0.43 \pm 0.05 \text{ kcal/mol} \quad (4)$$

$$C_2H_5CHOH^+ + CD_3C_6H_5 \rightleftharpoons C_2H_5CHO + CD_3C_6H_5H^+$$
$$\Delta G°_{300} = -0.44 \pm 0.05 \text{ kcal/mol} \quad (5)$$

as well as the corresponding equilibria involving methyl formate

$$CH_3OCHOH^+ + CH_3C_6H_5 \rightleftharpoons CH_3OCHO$$
$$+ CH_3C_6H_5H^+ \quad \Delta G°_{300} = -0.77 \pm 0.05 \text{ kcal/mol} \quad (6)$$

$$CH_3OCHOH^+ + CD_3C_6H_5 \rightleftharpoons CH_3OCHO$$
$$+ CD_3C_6H_5H^+ \quad \Delta G°_{300} = -0.79 \pm 0.05 \text{ kcal/mol} \quad (7)$$

(where 1 kcal/mol = 4.18 kJ = 0.043 eV). These results imply that the value of $\Delta G°_{300}$ for reaction 3 is 0.00 ± 0.05 kcal/mol. (In calculating these equilibrium constants, the abundances of the two protonated toluene ions were corrected for the presence of ^{13}C-labeled parent toluene ions, but the abundance of $CD_3C_6H_5H^+$ was not corrected for the estimated 1 at. % insufficient deuteration of the $CD_3C_6H_5$.[4]) In the earlier investigation,[1] equilibrium 3 was observed in a mixture of $CD_3C_6H_5$ with $CH_3C_6H_5$ using AsH_4^+ as a proton donor in the system. This experiment could not be duplicated to give a meaningful result because the $C_7H_5D_2^+$ ion which is formed in $C_7H_5D_3$ has the same mass as $CH_3C_6H_5H^+$.

Because of the discrepancy between the results reported by Hehre et al.[1] and those implied by the measured free energy changes for equilibria 4 through 7, a careful determination was made of the equilibrium constant for the proton transfer between *p*-xylene and *p*-xylene-d_6

$$p\text{-}(CD_3)_2C_6H_4H^+ + p\text{-}(CH_3)_2C_6H_4$$
$$\rightleftharpoons p\text{-}(CD_3)_2C_6H_4 + p\text{-}(CH_3)_2C_6H_4H^+ \quad (8)$$

where K_{eq} in the discussion which follows is defined as

$$K_{eq} = \frac{[p\text{-}(CH_3)_2C_6H_4H^+]}{[p\text{-}(CD_3)_2C_6H_4H^+]} \frac{[p\text{-}(CD_3)_2C_6H_4]}{[p\text{-}(CH_3)_2C_6H_4]}$$

In order to accurately determine this equilibrium constant, three different $p\text{-}(CD_3)_2C_6H_4\text{-}p\text{-}(CH_3)_2C_6H_4$ mixtures of

known composition were prepared on a vacuum line. During a determination, one of these mixtures was admitted to the instrument through a given inlet, while a proton-donor reagent gas was flowed into the instrument through a different inlet. Both arsine and methane were used as proton-donor gases. Possible errors due to calibration of the pressure-measuring ionization gauge for the different gases were eliminated by the use of such mixtures made up on a vacuum line.

The observed equilibrium constant for reaction 8, corrected only for the ^{13}C contribution of the $(CH_3)_2C_6H_4^+$ and $(CD_3)_2C_6H_4^+$ ions, had a value of 1.00 ± 0.06, corresponding to a value of ΔG°_{300} of 0.00 ± 0.03 kcal/mol. This value was independent of the composition of the mixture used, independent of the pressure of the mixture or of the proton-donor gas, and independent of the energy of the ionizing electrons. A value for ΔG°_{300} of -0.185 ± 0.018 kcal/mol was reported for reaction 8 in the earlier investigation.[1]

One possible source of error in the measurements would be insufficient deuteration of the p-xylene-d_6. The isotopic purity of the p-xylene-d_6 used here[4] was listed as 99 at. %. If we assume that, indeed, the $C_8H_4D_6$ sample contained 6% $C_8H_5D_5$, and correct the composition of the mixtures accordingly, the observed equilibrium constant for reaction 8 is decreased to 0.94, which corresponds to a value of ΔG°_{300} of $+0.04$ kcal/mol. Another way of estimating the possible importance of insufficient deuteration is to observe the ratios of the two parent ions, $(CD_3)_2C_6H_4^+$ and $(CH_3)_2C_6H_4^+$, and assume that these will be approximately the same as the ratios of the corresponding molecules in the mixtures. This assumption leads to a value of K_{eq} of 0.85 ± 0.04, corresponding to a value of ΔG°_{300} of $+0.099 \pm 0.03$ kcal/mol. Actually, it is certain that the latter assumption leads to a value of the equilibrium constant which is somewhat too low, and thus the value of 0.85 derived in this way may be considered as a lower limit. It is generally observed that deuterium-substituted compounds have ionization potentials higher than those of their nondeuterated analogues.[5] (For example, the ionization potential of cyclohexane-d_{12} is higher than that of cyclohexane by 0.46 kcal/mol;[3,5] the ionization potential of benzene-d_6 is higher than that of benzene by 0.03 kcal/mol.[6,7]) This expected difference will be reflected in the equilibrium constant of the charge transfer equilibrium

$$p\text{-}(CH_3)_2C_6H_4 + p\text{-}(CD_3)_2C_6H_4^+$$
$$\rightleftharpoons p\text{-}(CH_3)_2C_6H_4^+ + p\text{-}(CD_3)_2C_6H_4 \quad (9)$$
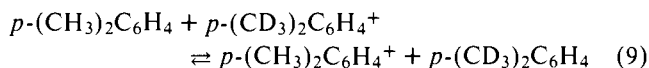
thus causing the ratio of deuterated to undeuterated parent ions to be slightly lower than the ratios of the corresponding neutral molecules in the mixture. (The results obtained here indicate that the equilibrium constant for reaction 9 is 1.11 ± 0.06, assuming 6% insufficient deuteration.)

In conclusion, the results obtained here show that the equilibrium constant for the proton transfer equilibrium in p-xylene and p-xylene-d_6 is in the range 0.85–1.00. Uncertainties in the equilibrium constant measurement result from uncertainties in the degree of insufficient deuteration; if the correction for insufficient deuteration is ignored, the importance of the proton transfer to the undeuterated species will be overestimated. The isotope effect on the proton transfer reaction, if it exists, is small (~ 0.05 kcal/mol).

References and Notes

(1) J. F. Wolf, J. L. Devlin, D. J. DeFrees, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 5097 (1976).
(2) S. G. Lias, J. R. Eyler, and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **19**, 219 (1976).
(3) Experimental and computational details of such determinations in this instrument have been described: S. G. Lias, P. Ausloos, and Z. Horvath, *Int. J. Chem. Kinet.*, **8**, 725 (1976).
(4) Both the toluene-α-d_3 and the p-xylene-α,α'-d_6 were obtained from Merck & Co., Inc. Both had listed isotopic purities of 99 at. %. The p-xylene was an A.P.I. standard reference material, 99.96 ± 0.02% pure.
(5) P. Ausloos and S. G. Lias, *Rad. Res. Rev.*, **1**, 75 (1968).
(6) R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, *J. Chem. Phys.*, **45**, 1298 (1966).
(7) S. G. Lias and P. Ausloos, unpublished work.

P. Ausloos,* S. G. Lias

Institute for Materials Research
*National Bureau of Standards*
Washington, D.C. 20234

Synthesis of Azulenes by the [6 + 4] Cycloadditions of 6-Aminofulvenes to Thiophene S,S-Dioxides†

Sir:

Azulenes have been synthesized by a variety of methods,[1] of which the Ziegler-Hafner synthesis[2] has proven to be the most versatile. Recently, we reported an intermolecular version of this synthesis,[3] exploiting the propensity of very electron-rich dienes to add in a [6 + 4] fashion to fulvenes.[4] Reversing the

Scheme I
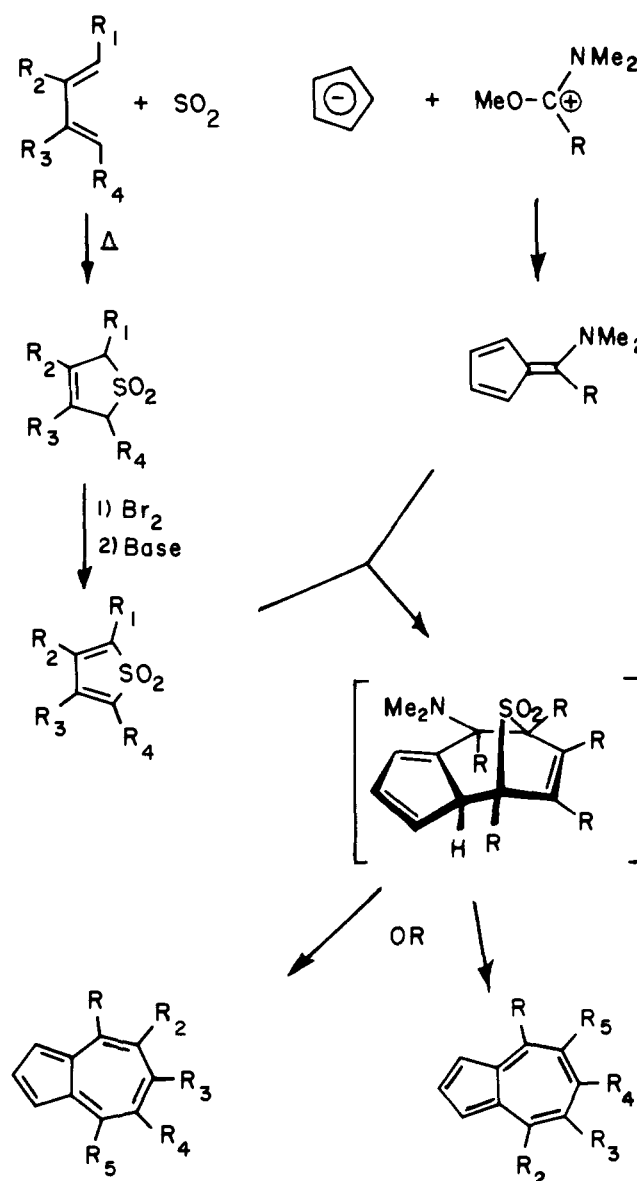
† This article and the "Woodward blue" 5,6-dichloroazulene are dedicated to Professor R. B. Woodward on the occasion of his sixtieth birthday.