(5) R. Baker, P. E. Halliday, and T. J. Mason, *Tetrahedron Lett.*, 591 (1970).

(6) M. A. Battiste and J. W. Nebzydoski, *J. Am. Chem. Soc.*, **91**, 6887 (1969).

(7) Compounds have been fully characterized by spectral means and have been determined to have the correct elemental composition.

(8) W. Herdle, unpublished work in these laboratories.

(9) A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. C*, 467 (1966).

(10) E. Vogel, F. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963). See also E. Vogel, *Pure Appl. Chem.*, **20**, 237 (1969).

(11) We thank Professor L. Paquette for informing us of this unpublished data.

(12) H. Günther, H. Schmickler, and G. Jikeli, *J. Magn. Reson.*, **11**, 344 (1973).

(13) G. C. Farrant and R. Feldmann, *Tetrahedron Lett.*, 4979 (1970).

(14) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964); J. A. Berson, W. Bauer, and M. M. Campbell, *ibid.*, **92**, 7515 (1970); K. B. Wiberg and G. J. Burgmaier, *ibid.*, **94**, 7396 (1972).

(15) H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970).

(16) An admittedly crude estimate of the nonconcerted process ($\sim$42 kcal/mol) was obtained by consideration of the energy difference between **2** and **9** ($\geq$3 kcal/mol based upon no detectable concentration of **9**) and the energy required to cleave the C-1, C-14 bond in **9** [C–C bond (84) − allylic stabilization (2 × 11)[17] − strain released in transition state (23)];[18] whereas, the observed activation energy is $\sim$32 kcal/mol. While it can be argued that a greater amount of strain exists in **9** than in norbornene (the value used in the above estimate), we are only concerned with the amount of strain that is released at the transition state and that the product is also considerably strained. The maximum release of strain energy = strain of **9** − strain of **1** and, considering the structural similarities of **9** and **1**, should be fairly approximated by the strain of norbornene.

(17) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969), and earlier references cited therein; J. A. Berson and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **90**, 4730 (1968); R. J. Field and P. I. Abell, *ibid.*, **91**, 7226 (1969); F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971); D. K. S. Sharma and J. L. Franklin, *J. Am. Chem. Soc.*, **95**, 6562 (1973); A. S. Rogers and M. C. R. Wu, *ibid.*, **95**, 6913 (1973); Z. B. Alfassi, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **5**, 155 (1973); A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1737 (1973); W. v. E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973); P. S. Engel, A. I. Dalton, and L. Shen, *J. Org. Chem.*, **39**, 384 (1974).

(18) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).

(19) J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94**, 8917 (1972); H. E. Zimmerman, *Acc. Chem. Res.*, **5**, 393 (1972).

(20) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

(21) National Institutes of Health, General Medical Sciences, Predoctoral Fellow.

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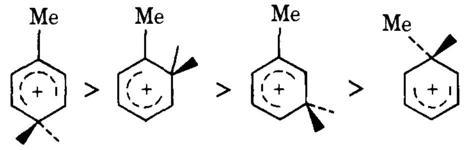
The Proton Affinities of Toluene

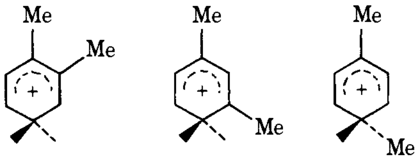
Sir:

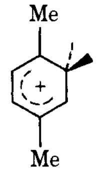
There are, at least count, four likely alternatives for the structure of protonated toluene. In addition to those geometries in which the proton has associated itself with the ring carbons ortho, meta, or para to the methyl, there is the possibility of protonation directly at the site to which the alkyl group is affixed to the ring. Protonation in the center of a carbon–carbon bond or directly above the aromatic ring seems unlikely in light of previous investigations.[2] In superacid media, toluene appears to protonate preferentially para to the methyl.[3] At temperatures below −97 °C, the NMR data are consistent with this being the only form present; as the temperature is raised the chemical shifts for the ring protons coalesce into a single line, indicative of rapid equilibration among the possible ions. The activation energy of such a process, presumably proton rather than methyl migration,[4] has been estimated by the temperature dependence of the ^{13}C spectrum to be 10 ± 1 kcal/mol.

In this communication, we apply experimental pulsed ion cyclotron resonance (ICR) spectroscopy[5] and ab initio molecular orbital theory[6] in an attempt to assign which of these four (most likely) structures is closest to the true ground state geometry of protonated toluene in the gas phase, and, in addition, to provide estimates of the relative stabilities of the remaining (unobserved) positional isomers. Assuming, as we shall demonstrate, that methyl substituent effects are approximately additive, such a tabulation should enable us to calculate the proton affinities of more highly alkylated benzenes. The ICR experiment alone, of course, provides no indication whatsoever as to the geometrical structure of an ion under investigation. Only its mass is subject to characterization. Furthermore it is not even possible to ascertain whether the spectrum observed in an ICR spectrometer is due to a single ion or to an equilibrium collection of two or more positional isomers. In actual practice, if the relative energies of such isomers are separated by more than a few kilocalories per mole, only the most stable ion will be present after several hundred milliseconds in a large enough concentration to be detectable.

We shall start by assuming the following ordering of stabilities for the four isomers of ring protonated toluene. This is as suggested by quantitative ab initio molecular orbital calculations at the minimal basis STO-3G level. Actual theoretical values for the four toluene proton affinities (relative to that in benzene) as well as the single experimental energy[10] (assumed to correspond to protonation para to the methyl) are presented in Table I. Using theoretical values for all four toluene affinities, and assuming that the effects of methyl substituents on the protonation energy of benzene are additive, it is possible to assign least energy structures to the protonated xylenes.[12] The same set of structures are also predicted by direct calculation (Table I) although for para xylene the sole alternative form appears to be of approximately equal stability. It should be emphasized that the numerical values of the xylene proton affinities arrived at by the simple additivity relationship are nearly identical with those obtained by direct calculation.





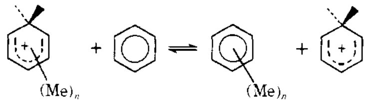


Relative proton affinities for the isomeric xylenes have also been determined by ICR spectroscopy and are also presented in Table I. Again assuming additivity of methyl substituent effects, these data enable us to arrive at approximate experimental values for the energies of protonation of toluene, ortho, meta, and ipso to the alkyl group. Thus, subtracting the relative proton affinity of toluene from that of *m*-xylene leads to an experimental estimate of 6.0 kcal/mol for the effect of an ortho methyl substituent on the proton affinity of benzene. Such a value is in reasonable agreement with the calculated relative affinity of 6.5 kcal/mol. Correspondingly, the difference in proton affinities between *o*-xylene and toluene (2.4 kcal/mol) is a measure of the far smaller energetic effect of a methyl group meta to the site

Table I. Proton Affinities of Toluene, the Xylenes, Mesitylene, and Hexamethylbenzene, Relative to the Proton Affinity of Benzene

Molecule	Position of protonation	Exptl (kcal/mol)[a] ΔG°	ΔH°	STO-3G (kcal/mol)[a] ΔE
Toluene	1	...	$(\leqslant 1.2)^b$	0.3
	2	...	$(6.0)^c$	6.5
	3	...	$(2.4)^d$	2.0
	4	6.1	7.2	8.5
o-Xylene	4	8.9	9.6	$10.4\ (10.5)^e$
m-Xylene	4	12.5	13.2	$14.9\ (15.0)^e$
p-Xylene	1	{8.2}	8.4	$8.5\ (8.8)^e$
	2		8.4	$8.5\ (8.5)^e$
Mesitylene	2	16.6	$17.0\ (19.2)^f$	$19.5\ (21.5)^e$
Hexamethylbenzene	1	23.2	$22.8\ (24.3)^f$	$...\ (25.8)^e$

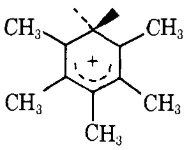
[a] ΔG°, ΔH°, or ΔE for the reaction.

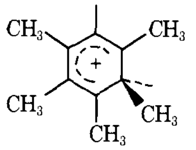


ΔH° is obtained from ΔG° by correcting for changes in the ratio of rotational symmetry numbers of the base and its conjugate acid. [b] The upper bound of 1.2 kcal/mol is obtained as a difference in the relative proton affinities of *p*-xylene (assuming ipso protonation) and toluene. [c] Obtained as a difference of the relative proton affinities of *m*-xylene and toluene. [d] Obtained as a difference of the relative proton affinities of *o*-xylene and toluene. [e] Values arrived at by assuming additivity of theoretical toluene proton affinities. [f] Values arrived at by assuming additivity of "experimental" toluene proton affinities and the theoretical value of 0.3 kcal/mol for an ipso methyl substituent.

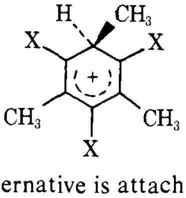
of protonation. Again agreement with the theoretically determined affinity (2.0 kcal/mol) is good.

In superacid media *p*-xylene appears to protonate exclusively at the 2 position, rather than at the site of attachment of one of the methyl groups.[13] In fact, except for hexamethylbenzene in which there is no alternative, in no case has ipso protonation of a polymethylated benzene been established. In the extreme this includes pentamethylbenzene, where ipso protonation, encouraged by a statistical factor of two over protonation at the one unalkylated site, would result in the loss of the effect of but a single meta methyl substituent.





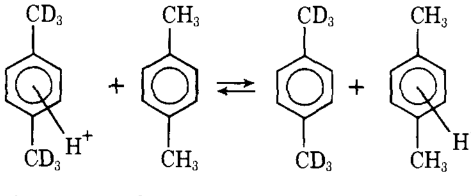
Protonation at the site of a methyl group to the aromatic ring has, however, been established in such systems as where the alternative is attachment to a halogen substituted center.



X = F, Cl, Br

As mentioned previously, the STO-3G calculations suggest that protonation of *p*-xylene may occur with approximately equal facility on any of the six ring positions. Thus, it is not immediately apparent whether we should represent the enhancement of the proton affinity of *p*-xylene relative to benzene as due to the stabilizing effects of combined ortho and meta, or of ipso and para methyl substituents. In the former instance, the observed relative *p*-xylene proton affinity (8.4 kcal/mol) agrees precisely with what would be expected by addition of our previously determined *o*- and *m*-toluene affinities (6.0 and 2.4 kcal/mol, respectively). On the other hand, ipso protonation would lead to an assignment of 1.2 kcal/mol (obtained by differencing the relative para xylene and toluene proton affinities) for the stabilization to the ion resulting from a methyl group attached directly to the reaction site. Such a value appears to be somewhat too large in view of the theoretical estimate of 0.3 kcal/mol for the stabilization imparted by an ipso methyl group. Lacking direct experimental evidence as to the site of protonation in *p*-xylene, the best we can do at assigning the relative ipso proton affinity of toluene is to set the value at less than or equal to 1.2 kcal/mol.

The determination of the equilibrium isotope effect for the proton transfer reaction involving *p*-xylene and *p*-xylene-α-d_6 may be of use as an indicator of the site on which protonation actually occurs.



Thus, once the magnitudes of the isotope effects on the proton transfer reactions involving toluene and *o*- and *m*-xylene have been established, it should be possible to spot any anomalies due to ipso protonation.[14]

Finally we have tabulated relative proton affinities for mesitylene and hexamethylbenzene both directly measured and calculated (mesitylene only), and as obtained by addition of the appropriate experimental and theoretical toluene affinities. It can be seen that the assumption we have made regarding the additivity of substituent effects holds reasonably well even in the extreme case of hexamethylbenzene.

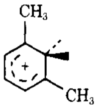
Acknowledgment. This research was supported in part by grants from the National Science Foundation and from the Research Corporation.

References and Notes

(1) Alfred P. Sloan Fellow, 1974–1976.
(2) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 6901 (1972).
(3) (a) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Am. Chem. Soc.*, **94**, 2034 (1972). A recent gas phase ICR study of the reaction of D_2O with toluene indicates that, under the experimental conditions, all five ring protons exchange: (b) B. S. Freiser, R. L. Woodin, and J. L. Beauchamp, *ibid.*, **97**, 6893 (1975).
(4) See D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 837.
(5) Trapped ion cyclotron resonance spectroscopy: method (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971); representative applications (d) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971); (e) R. T. McIver, Jr., and J. R. Eyler, *ibid.*, **93**, 6334 (1971); (f) R. T. McIver, Jr., and J. H. Silvers, *ibid.*, **95**, 8462 (1973); (g) R. T. McIver, Jr., and J. S. Miller, *ibid.*, **96**, 4323 (1974); (h) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *ibid.*, **96**, 7162 (1974); (i) J. F. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *ibid.*, **97**, 2902 (1975).
(6) We employ the STO-3G minimal basis set.[7] Geometries for the neutral alkyl benzenes are as specified by the standard model;[8] those for protonated species are based on the standard model structure for protonated benzene[5h] with standard methyl groups (tetrahedral, r_{CH} = 1.09 Å) attached at bond lengths of 1.52 Å (ortho, meta, and para) and 1.54 Å (ipso). All calculations have been performed using the GAUSSIAN 70 series of computer programs.[9]
(7) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(8) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(9) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(10) The proton affinities of toluene, the three xylenes, mesitylene, and hexamethylbenzene have all been linked to that of benzene by use of the recently developed proton affinity scale: J. F. Wolf, I. Koppel, R. W. Taft, R. T. McIver, Jr., R. H. Staley, and J. L. Beauchamp, to be submitted for publication. The values for *o*- and *p*-xylene relative to that of toluene (ref. 5h) and for hexamethylbenzene (ref. 11) have already been reported.

(11) J. F. Wolf, P. G. Harch, and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 2904 (1975).

(12) It should be commented that Beauchamp and co-workers (ref. 3b) observe the exchange of only a single ring proton upon reaction of *m*-xylene with D_2O under ICR conditions. This would seem to imply that the



ion is the true ground state form of a protonated aromatic, an observation which is at odds with the results of the STO-3G calculations, which suggests the energy of such a structure to be 2.0 kcal/mol above the ion proposed here. We can think of no explanation for this discrepancy.

(13) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, **84**, 1564 (1965).

(14) (a) J. F. Wolf, J. L. Devlin, III, D. J. DeFrees, R. W. Taft and W. J. Hehre, *J. Am. Chem. Soc.*, in press. For the initial account of our application of ion cyclotron resonance spectroscopy to the determination of equilibrium isotope effect, see (b) J. F. Wolf, J. L. Devlin, III, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *ibid.*, **98**, 287 (1976).

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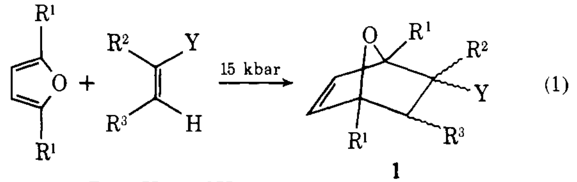
Organic Reactions at High Pressure. Cycloadditions with Furans[1]

Sir:

The 7-oxabicyclo[2.2.1]heptyl system has been employed in synthetic[2] and mechanistic[3] organic chemistry as well as applied chemistry.[4] The most straightforward approach to the construction of the 7-oxabicyclo[2.2.1]hept-5-ene framework (**1**) takes advantage of the Diels–Alder reaction between furan and a suitable dienophile.[5] Unfortunately, due to the aromatic character of furan[6] and the strain of the bicyclo[2.2.1]heptane system,[7] the cycloadducts are rather sensitive thermally toward reversal to starting materials. Consequently, only with the use of very reactive dienophiles (such as maleic anhydride and dimethyl acetylenedicarboxylate) can respectable yields of product be attained. In this communication we report the successful utilization of monoactivated dienophiles when the reactions are conducted at ~15 000 atm pressure[8] (15 kbar) and room temperature (eq 1).



1

R^1 = H or CH_3
R^2 = H or CH_3
R^3 = H, CH_3, or CO_2R
Y = CN, CO_2R, CHO, or $COCH_3$

We have previously described the results of our investigation of cycloadditions of enamines and dienamines which demonstrated the advantages of 8–20 kbar pressure, particularly in those cases where the application of heat to promote a sluggish reaction caused the destruction of the reactants.[9] Prior studies[10-12] indicated that cycloadditions between furans and ethylenes activated by only one electron withdrawing substituent take place slowly and with poor to mediocre yields when carried out at ambient pressure. We have reexamined several of these reactions at 15 kbar pressure and found that, except in those instances where both steric and electronic effects operate to retard reactivity, good yields of cycloadducts are realized. Our results are summarized in Table I.

Inspection of the data in Table I reveals that satisfactory yields (about 55%) of [4 + 2] adducts were obtained after only 4 h with acrylic dienophiles and furan (entries 1–4); in each instance approximately 1:1 ratios of exo/endo isomers were produced. Compared to thermally induced processes, the implimentation of these extremely high pressures provides substantial improvement for the conversion of reactants to products. Thus, it was reported that *5 weeks* are required to obtain a 39% yield of 2-cyano-7-oxabicyclo-[2.2.1]hept-5-ene from furan and acrylonitrile.[10] Likewise, the cycloadduct from furan and methyl acrylate is produced in less than 20% yield after a month or more.[11] And in the cases of acrolein or methyl vinyl ketone and furan, only ring

Table I. Products[a] Obtained from Ultrahigh Pressure Cycloadditions[b]

Entry	R^1	R^2	R^3	Y	Hours	% yield[c,d]
1	H	H	H	CN	4	55
2	H	H	H	CO_2CH_3	4	62
3	H	H	H	CHO	4	53
4	H	H	H	$COCH_3$	4	48
5	H	H	CH_3	CN	14	0
6	H	H	CH_3	CO_2CH_3	14	6
7	H	H	CH_3	CHO	8	24
8	H	H	CH_3	$COCH_3$	8	20
9	H	CH_3	H	CO_2CH_3	8	8
10	H	CH_3	H	CHO	8	7[e]
11	H	H	CO_2CH_3[f]	CO_2CH_3	8	94[g]
12	H	H	$CO_2C_2H_5$	$CO_2C_2H_5$	8	92[g]
13	CH_3	H	H	CN	4	65
14	CH_3	H	H	CO_2CH_3	4	66
15	CH_3	H	H	CHO	4	42
16	CH_3	H	H	$COCH_3$	4	36

[a] See formula **1** for structure of product. Unless indicated otherwise, all products were composed of approximately 1:1 ratios of exo/endo isomers. [b] All reactions were carried out at 15 kbar and room temp; the concentrations of the reactants were nominally 3 M in methylene chloride. [c] Yields are based on distilled materials unless indicated otherwise. Reaction conditions have not been optimized; in addition to product, only starting materials were present at the conclusion of the reaction. [d] Satisfactory analytical and spectral data were obtained for each product. [e] A substantial amount of polymeric material was also produced. [f] In this case R^3 is cis to Y in dienophile (eq 1). [g] Crude yield; NMR spectrum indicated material to be of very high purity. Product reversed to starting materials during attempted distillation. See text for stereochemistry of adduct.