
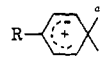


Table I. Energy Data

R			ΔE^b STO-3G	$\Delta G^{\circ b}$ Exptl (icr)	$\Delta H^{\circ b,c}$ Exptl (soln)
Me	-266.47382	-266.84917	0.0	0.0	0.0
Et ^d	-305.05333	-305.43090	1.4	0.85	-2.74
<i>n</i> -Pr ^{d,e}	-343.63299	-344.01202	2.3	1.7	
<i>i</i> -Pr ^f	-343.63067	-344.00972	2.3	2.1	-2.51
<i>n</i> -Bu ^{d,e}	-382.21248	-382.59221	2.7	2.1	
<i>t</i> -Bu ^f	-382.20297	-382.58329	3.1	2.3 ± 0.5 ^g	-3.76

^a STO-3G total energies (hartrees). ^b ΔE , ΔG°_{298} , or ΔH°_{233} of the isodesmic reaction (eq 2) (kcal/mol). ^c Reference 4a. ^d C $_{\alpha}$ -C $_{\beta}$ bond held perpendicular to ring plane. ^e All trans conformation. ^f Methyl groups symmetrically disposed about ring plane. ^g Upon protonation *tert*-butylbenzene fragments extensively, paralleling its behavior in superacid media (see ref 11a). The ΔG° of reaction quoted corresponds to an apparent proton transfer equilibrium with dimethyl ether. In the gas phase, all of the other alkyl benzenes protonated cleanly without fragmentation.

solution¹¹ that each of the monoalkyl benzenes protonates preferentially para to the substituent. It is assumed that the experimental icr data pertains to protonation at these same sites. Comparison is also made in the table between the relative basicities obtained in the gas phase and in solution, hence providing estimates of differential solvation energies.¹²

The following conclusions deserve special note.

Stabilization of protonated benzene by para positioned alkyl groups follows the sequence (Me < Et < *i*-Pr < *t*-Bu) rather than the Baker-Nathan ordering observed by Arnett and Larsen^{4a} in superacid solution. Whereas Arnett's solution measurements indicate the heat of protonation of toluene to be 3.76 kcal/mol greater than that of *tert*-butylbenzene, our data suggest the opposite ordering in the gas phase. The differential represents an increased shielding to solvation of the larger *t*-butyl group over that of methyl.¹³

The effects of *n*-propyl and isopropyl substituents in altering the proton affinity of benzene are similar (as are those of *n*-butyl and *tert*-butyl groups) suggesting, that, due to polarizability, the size of the alkyl chain is nearly as important a factor as the degree of branching. Simple carbocations behave similarly in the gas phase,^{2a} but marked attenuation of this polarizability effect is expected in solution.

STO-3G calculated π charges at C₄ (adjacent to the alkyl substituent) in the protonated benzenes show little dependence on the alkyl group, ranging from +0.38 electrons in protonated toluene to +0.39 electrons in protonated *tert*-butylbenzene. This parallels the ¹³C chemical shifts observed by Olah and coworkers^{11a} in superacid media. We note, however, that in this series of compounds charge delocalization does not parallel thermodynamic stability.

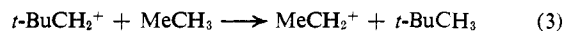
The difference between methyl and *tert*-butyl groups in stabilizing the charge delocalized benzenium cation (3.1 kcal/mol from the theoretical STO-3G calculations) is smaller than the 8.2 kcal/mol differential¹³ (7.5 kcal/

(11) (a) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972); (b) 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, Chapter 20.

(12) See also ref 1j.

(13) Experimental thermochemical data (ΔH°_{298}) from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, National Bureau of Standards, 1969.

mol using theoretical STO-3G data^{2a}) in alkyl group effectiveness when attached to the methyl cation, as measured by the energy of eq 3.



Finally the high level of agreement between experimentally determined and theoretically calculated alkyl substituent effects lends considerable force to the assertion of a classical open structure for the ground state of protonated benzene in the gas phase.

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Theoretical Approaches to Aromatic Electrophilic Substitution Processes. II. Intermediates in Electrophilic Fluorination

Sir:

The current mechanism of electrophilic aromatic substitution centers around the intervention of a stable positively charged adduct between electrophile and aromatic substrate.¹ Direct nmr spectroscopic observations in strong acid media,² and more recently gas phase ion cyclotron resonance techniques³ and theoretical *ab initio* molecular orbital calculations,^{3,4} have concluded that proton addition complexes are better represented in terms of "classical" Wheland or benzenium type structures than as "nonclassical" σ delocalized hydrogen bridged forms. These latter structures appear not to be stable forms; rather they best fit the role of low energy transition states to degenerate hydrogen scrambling.⁵

(1) Recent reviews include: (a) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971); (b) J. H. Ridd, *ibid.*, **4**, 248 (1971); (c) P. Rys, P. Skrabal, and H. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 874 (1972); (d) G. A. Olah, "Friedel-Crafts Chemistry," Interscience, New York, N. Y., 1973, Chapter 6.

(2) The nmr of protonated benzene has recently been reported. (a) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972), and references therein; see also (b) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 20.

(3) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 7162 (1974).

(4) (a) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 6901 (1972); for semiempirical molecular orbital studies see (b) E. Heglstand, *Acta Chem. Scand.*, **24**, 3687 (1970); **26**, 2024 (1972); (c) A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, and A. Lewis, *J. Amer. Chem. Soc.*, **92**, 6529 (1970); (d) W. Jakubetz and P. Schuster, *Angew. Chem., Int. Ed. Engl.*, **10**, 497 (1971); (e) E. L. Motell, W. H. Fink, and J. L. Dallas, *Tetrahedron*, **29**, 3503 (1973).

(5) Olah and his coworkers report that an activation energy of 10 ± 1 kcal/mol is required for hydrogen scrambling in parent protonated benzene.^{2a} *Ab initio* molecular orbital calculations suggest a larger value (20.6 kcal/mol).^{4a}

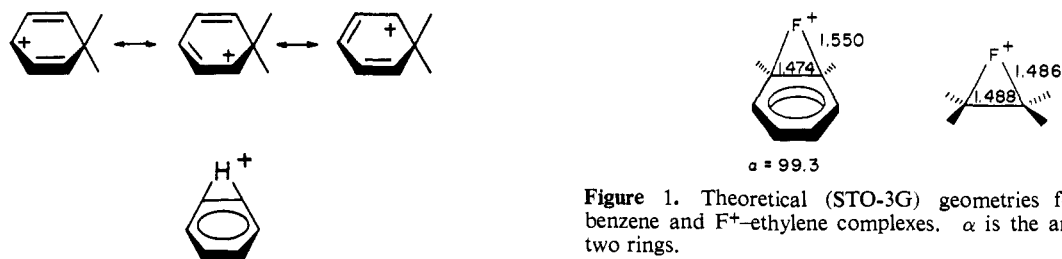


Figure 1. Theoretical (STO-3G) geometries for bridged F^+ -benzene and F^+ -ethylene complexes. α is the angle between the two rings.

Very little information is available, however, regarding structure and stability of addition complexes with other electrophiles. The heptamethylbenzenium ion is known from solution nmr studies,⁶ and from an X-ray crystallographic investigation of its tetrachloroaluminate salt,⁷ to possess an open rather than a methyl bridged structure.⁸ Similarly, the nmr spectra of addition complexes formed upon electrophilic nitration and chlorination of hexamethylbenzene and trifluoromesitylene are consistent with open benzenium-type ions.^{9,10} Degenerate rearrangement of the nitro group around the hexamethylbenzene skeleton is apparently facile (temperature-dependent nmr studies suggest an activation energy of 16.8 ± 1.5 kcal/mol⁹) but migration of chlorine in the systems studied remains unobserved.

Although bridged "benzenonium" ions have never actually been observed, there exists a considerable body of chemical evidence suggesting participation of such forms in a variety of electrophilic aromatic substitution processes,¹ particularly Friedel-Crafts alkylations, nitronium salt nitrations, and halogenations using strongly electrophilic agents. These data would seem to demand intervention of stable bridged intermediates, long lived enough to influence the direction of the reaction.

In this communication we consider the application of *ab initio* molecular orbital theory¹¹ to study of addition of F^+ to benzene as a model for electrophilic aromatic halogenation. Of prime concern will be the geometrical structure and energetic disposition of the symmetrically bridged fluorine-benzene complex. Is it adequately represented classically, or must notions of

delocalized σ bonding be invoked to account for geometrical structure? Does it represent a stable intermediate, or is the bridged complex merely one possible transition state to interconversion of open forms? The stability of the open complex will also be scrutinized. Does 1,2-hydrogen migration, leading to the 2-fluorobenzenium ion,¹⁶ proceed with a negligible barrier, or is it large enough such that any initially formed complex will be amenable to detection?

The major aspects of the calculated geometrical structure of the fluorine bridged complex II are presented in Figure 1 along with data on the ethylene fluoronium ion. We have previously commented¹⁷ that the geometry of this latter ion corresponds closely to that of the isoelectronic three-membered ring oxirane, that is to say it appears to be well described in terms of a formally divalent and positively charged fluorine. The alternative picture of a loose complex between ethylene and fluorine was suggested to be inappropriate. The distinction between the two alternative descriptions in the case of the bridged fluorine-benzene system is not as clearly demarked. Although one benzene ring bond lengthens considerably as a consequence of fluorine bridging (from 1.390 Å in benzene to 1.474 Å in II), the overall effect is not nearly as great as is observed for the corresponding ethylenic system, where the double bond is stretched on the order of 0.2 Å from its (STO-3G) equilibrium value of 1.305 Å. In addition, whereas the carbon-fluorine bond length in the ethylene bridged ion (1.486 Å) corresponds almost exactly to those found in analogous acyclic systems in which three-center delocalized σ bonding is not easily realized (e.g., 1.487 Å in protonated fluoromethane¹⁸), that linking the halogen to benzene is markedly longer (1.550 Å *vs.* 1.457 Å in protonated fluorobenzene). Also noteworthy is the fact that the fluorine does not lie directly over a ring bond. Rather, the angle between the fused benzene and three-membered rings is 99.3°. A similar but somewhat smaller effect was seen in the hydrogen bridged form of protonated benzene.^{4a}

The STO-3G basis suggests the fluorine bridged complex to be stable with respect to distortion in the direction of an open ion, but this result is not supported by our limited explorations with the extended 4-31G functions.¹⁹ Here the fluorine bridged ion is found to be an

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(7) N. C. Baenziger and A. D. Nelson, *J. Amer. Chem. Soc.*, **90**, 6602 (1968).

(8) Energy required for 1,2-methyl shift in heptamethylbenzenium ion 18.2 ± 0.6 kcal/mol: V. A. Koptyug, V. G. Shubin, A. I. Resvukhin, D. V. Korchagina, V. P. Tretyakov, and E. S. Rudakov, *Dokl. Akad. Nauk SSSR*, **171**, 1109 (1966). Similar activation energies have been reported for methyl migrations in related ions. For a review see ref 2b.

(9) G. A. Olah, H. C. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

(10) For a discussion of the possibility of bridged addition complexes in electrophilic nitration, see paper I of this series: F. Bernardi and W. J. Hehre, *J. Amer. Chem. Soc.*, **95**, 3078 (1973), and references therein.

(11) The minimal STO-3G basis functions¹² are employed to calculate equilibrium and transition state geometries alike, the detailed procedures for which have already been discussed.¹³ Computations at interesting points are then performed using the 4-31G extended basis set.¹⁴ All calculations have been carried out using the GAUSSIAN 70 series of computer programs.¹⁵

(12) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(13) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(14) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(15) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

(16) Protonation of fluorobenzene occurs detectably only in the 4-position. (G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967)), and although the 2-fluorobenzenium ion remains to be characterized experimentally, our calculations indicate the two to be of nearly equal stability.

(17) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **96**, 2665 (1974).

(18) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, **11**, 175 (1974).

(19) This is not surprising in view of the tendency of the minimal basis to favor small ring molecules over their acyclic isomers; *c.f.* W. A. Lathan, L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971); L. Radom, W. A. Lathan, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Fortschr. Chem. Forsch.*, **40**, 1 (1973).

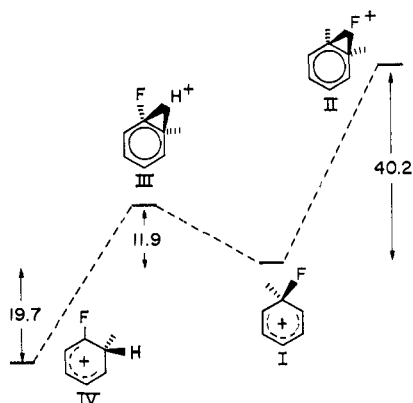


Figure 2. Stability of F^+ addition complexes (kcal/mol). 4-31G total energies: I, -329.36504 ; II, -329.30095 ; III, -329.34611 ; IV, -329.39641 . Geometries for III and IV based on optimum STO-3G structures for bridged and open forms of protonated benzene.^{4a} The fluorine in each case is attached with the same bond angles as the hydrogen replaced but with optimized (STO-3G) connecting bond lengths (1.346 and 1.324 Å, respectively).

energy maximum, some 40 kcal/mol above the open electrophilic adduct (I) (Figure 2). Although this latter ion rests in a potential well and is, in principle, a detectable intermediate, the calculations suggest 1,2-hydrogen migration— $I \rightarrow III \rightarrow IV$ —to be a facile process, in line with experimental determination in related fluorine substituted benzenium ions.²⁰

Finally we find fluorination at the ring face to be very unfavorable, in line with the high energy reported for the corresponding face protonated form of benzene.^{4a}

Although the molecules dealt with here are too large to be considered at *ab initio* basis set levels beyond 4-31G, it is interesting to speculate on the possible consequences of such improvements. Hariharan, Lathan, and Pople²¹ have noted that allowance for polarization-type functions on all centers contests the prediction of the 4-31G basis of a "classical" open equilibrium structure for the ethyl cation (with a barrier to proton migration of 7.3 kcal/mol) and suggests instead that the hydrogen bridged complex is the lower energy form (by 0.9 kcal/mol). The full brunt of the correction (8.2 kcal/mol) brings our value for the energy of proton migration in protonated benzene much closer to Olah's solution phase determination^{2a} (12.4 kcal/mol *vs.* 10 ± 1 kcal/mol experimentally) and places further doubt on the stable existence of the open fluorine-benzene adduct (I), which now appears to be able to rearrange to the 2-fluorobenzenium ion (IV) with negligible barrier. It is more difficult to assess the effects of improved basis set description on the relative energies of the open and bridged fluorine benzene complexes (I and II, respectively). Comparison might be made with the recent study of Hariharan, Radom, Pople, and Schleyer on the $C_3H_7^+$ system.²² Here the addition of polarization functions did little to alter the energy separation between symmetrically bridged (corner protonated cyclopropane) and open (1-propyl cation) structures.

(20) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 9241 (1972), and references therein.

(21) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).

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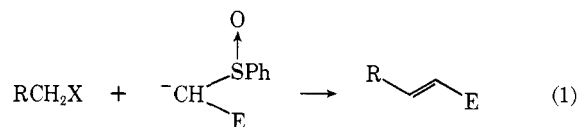
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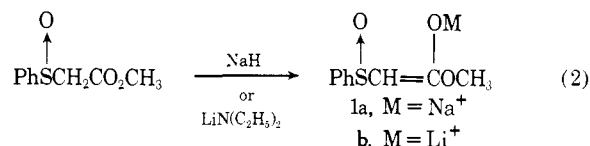
New Synthetic Reactions. Alkylative Elimination

Sir:

The facile elimination of α -sulfinyl carbonyl compounds to their α,β -unsaturated derivatives (with complete absence of β,γ -isomers) suggested a new one-pot olefin synthesis of rather broad scope (see eq 1).^{1,2}



While any sulfoxide anion in principle may be used, the high temperatures required for thermal eliminations of simple sulfoxides decrease their practicality. On the other hand, the facilitation of the elimination (as well as anion generation) by an α electronegative substituent makes this reaction an attractive approach. We wish to report the realization of this approach for the synthesis of α,β -unsaturated esters utilizing the anion of methyl 2-phenylsulfinylacetate³⁻⁵ (see eq 2).



While anion formation proceeds well in many solvents (THF, DME, DMSO, or HMPA), alkylation with alkyl halides proceeds well only in dipolar aprotic solvents of which HMPA appears best. Carbon-carbon bond formation occurs at room temperature after which

(1) B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, **95**, 6840 (1973).

(2) For the first example of this net process see B. M. Trost and T. J. Fullerton, *J. Amer. Chem. Soc.*, **95**, 292 (1973). A two pot process utilizing selenium derivatives has appeared: K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Amer. Chem. Soc.*, **95**, 6137 (1973). This method requires alkylation of the α -phenylselenyl ester and subsequent oxidation-elimination.

(3) Available by condensation of methyl bromoacetate with thiophenol [R. G. Hiskey and F. I. Carroll, *J. Amer. Chem. Soc.*, **83**, 4647 (1961)] followed by oxidation with sodium metaperiodate (methanol, room temperature, 18 hr) to give colorless solid, mp 46–48°; Cf. G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 659 (1968).

(4) For alkylations of anions of β -ketosulfoxides see P. G. Gassman and G. D. Richmond, *J. Org. Chem.*, **31**, 2355 (1966); O. P. Vig, K. L. Matta, J. M. Sehgal, and S. D. Sharma, *J. Indian Chem. Soc.*, **47**, 894 (1970).

(5) In addition to aldol and Perkin and related condensations, other methods include Reformatsky reaction [M. Gaudemar, *Organometal. Chem. Rev. A*, **8**, 183 (1972); M. W. Rathke and D. F. Sullivan, *J. Amer. Chem. Soc.*, **95**, 3050 (1973)], phosphorus ylide [A. Maercker, *Org. React.*, **14**, 270 (1965)], phosphonate anion [J. Boutagy and R. Thomas, *Chem. Rev.*, **74**, 87 (1974)], and anions of α -silyl esters [K. Shimoi, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **96**, 1620 (1974); S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, *Tetrahedron Lett.*, 1403 (1974)].