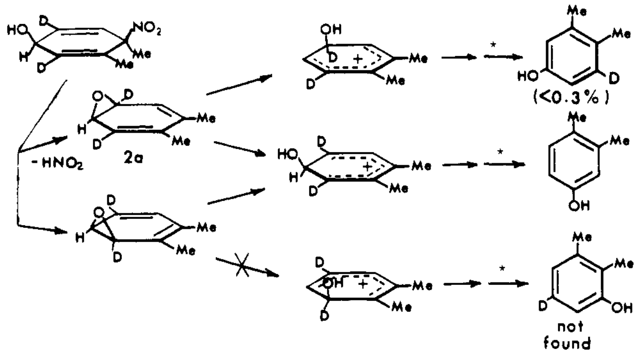
Table II. Deuterium Retention upon Solvolysis of 4-Methyl-4-nitrocyclohexadienol-*1-d*, 4-Methyl-4-nitrocyclohexadienyl-*1-d* Acetate, and Related Compounds

compd	solvent	% deuterium retention[a]
1-OH	50% EtOH, pH 2	24
	50% EtOH, pH 7	27
	50% EtOH, pH 10	28
2-OH	50% EtOH, pH 5	25
	50% EtOH, pH 7	25
	50% EtOH, pH 9	23
3-OH	50% EtOH	32
3-OD	50% EtOD	33
1-OAc	50% EtOH, pH 7	<0.2
2-OAc	50% EtOH, pH 7	<0.2
3-OAC	50% EtOH	<0.3

[a] Measured by replicate scans with use of a Finnigan 3200 GC/MS operated at an electron energy of 12 V. Measurement precision was ±1%.

Scheme II



a *, exchange.

oxidations of aromatic substrates and during solvolytic studies of appropriately labeled arene oxides.[7,8] Present interpretations of the solvolytic NIH shift of arene oxides involve a rate-limiting ring opening to yield the 1-hydroxycyclohexadienyl cation followed by an intramolecular hydrogen transfer and subsequent dienone–phenol rearrangement.[8]

Our results are not inconsistent with rate-limiting formation of the 1-hydroxycyclohexadienyl cation, but they do force consideration of a subsequent partitioning of the intermediate between two reaction paths (eq 1). The change of the hydroxyl group to an acetate apparently causes a pronounced shift in the partition ratio favoring direct proton loss to the solvent.

The possible formation of an arene oxide intermediate prior to an NIH shift has been *eliminated* by the experiment outlined in Scheme II. If 3,4-dimethylphenol were formed via the symmetrical arene oxide (**2a**) shown in Scheme II, the phenol would have to be partially deuterated at C-5. Since hydrogens acid, the experimental test is straightforward. Gas chromatographic analysis of the product of solvolysis of **2**-*2,6*-d_2 in aqueous ethanol revealed only 3,4-dimethylphenol, and mass spectral analysis of the phenol indicated <0.3% deuterium after acid-catalyzed exchange. Hence we must reject the path indicated in Scheme II.[10]

The data collected demonstrate the short lifetimes of nitrodienols that are formed by ipso nitration in aqueous acid. Even if re-formation of the ipso ion could be suppressed, the alternative path of aromatization (loss of the elements of nitrous acid) would make isolation impracticable.[2] Support for the view that 1-hydroxycyclohexadienyl cations are key intermediates in the NIH shift is provided. Consideration of $\sigma_p{}^+$ constants for the methyl (−0.31), hydroxyl (−0.92), and acetoxyl (−0.08)[9] suggests an explanation for the failure of the 1-acetoxycyclohexadienyl cation to aromatize via a NIH shift.

Reasonable extrapolations from the substituent constant data indicate that a 1,2 shift of hydrogen would be energetically "downhill" for the 1-hydroxycyclohexadienyl cation and "uphill" for the 1-acetoxycyclohexadienyl cation. The absence of a change in deuterium retention when **3**-OD is solvolyzed in EtOD/D$_2$O indicates that the proton transfer from oxygen occurs after the partition stage. With a flexible, convenient synthesis of substrates in hand, more detailed studies of these intramolecular migrations may now be projected.

Acknowledgment. We are pleased to acknowledge the helpful comments of Professors A. Fischer and K. Schofield, and we thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants supporting this work

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(2) T. Banwell, C. S. Morse, P. C. Myhre, and A. Vollmar, *J. Am. Chem. Soc.*, **99**, 3042 (1977).
(3) See particularly the reports of A. Fischer and co-workers summarized in ref 1.
(4) C. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, **100**, 975 (1978).
(5) The cis:trans ratios varied from 70:30 for **1** to 80:20 for **3**.
(6) A full account of the synthetic procedures will be published elsewhere.
(7) J. W. Daley, D. M. Jernia, and B. Witkop, *Experentia*, **28**, 1129 (1972).
(8) T. C. Bruice and P. Y. Bruice, *Acc. Chem. Res.*, **9**, 378 (1976).
(9) D. Calvert, P. B. D. de la Mare, and N. S. Isaacs, *J. Chem. Res.* (*S*), 156 (1978).
(10) Following a similar line, the results from **2**-OAc-*1-d* rule out bridging of the acetoxyl group during solvolytic eliminations.

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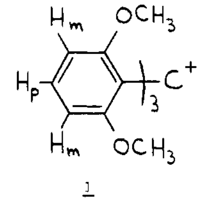
Electrophilic Aromatic Protonation of Stable π Carbocations

Sir:

We noted with interest the recent report[1] of a new type of electrophilic aromatic substitution: the reaction of H$^+$ and D$^+$ with an aromatic cyclopropenyl cation. This highly unusual reaction involves bringing together two positively charged species. We report here that the protonation of aromatic carbocations may be common and much more facile than anyone has imagined.

The NMR spectrum of the familiar trityl cation (**1**) in trifluoroacetic acid is identical with that reported by Martin[2] and is unexceptional. Quite remarkably, the spectrum in the much



1

stronger triflic acid (CF$_3$SO$_3$H)[3] is dramatically different. The doublet at δ 6.75 observed in trifluoroacetic acid and assigned to H$_m$ has completely disappeared and the triplet at 7.79, assigned to H$_p$, has collapsed to a singlet.[4] Clearly all six H$_m$ sites are exchanging more rapidly than the spectrometer can detect. Because of the nature of the medium (low nucleophilicity and high acidity[3]) and the high pK_{R^+} associated with **1** (>6.5)[2] it follows that it is **1** which is reacting with H$^+$.

Planar carbocations also undergo a similar exchange. In the lower ^{1}H NMR spectrum of Figure 1 is shown the aromatic region of carbocation **2a** in triflic acid.[5] No exchange phe-

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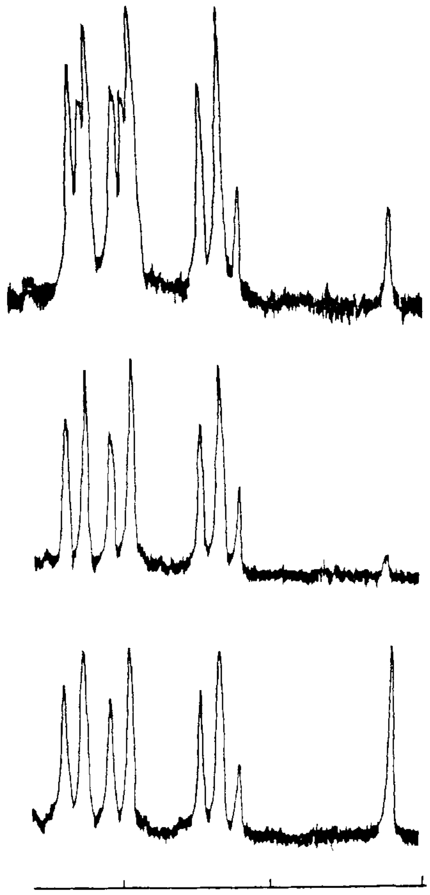
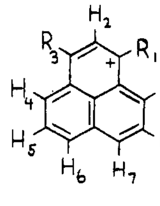


Figure 1. ^1H NMR spectrum (aromatic region) of **2a:** bottom spectrum in triflic acid; middle spectrum in triflic acid-*d* after 15 min at room temperature; top spectrum in triflic acid-*d* after heating at 100 °C for 15 h.



2

a) $R_1 = R_3 = -OCH_2CH_3$

b) $R_1 = R_3 = OH$

c) $R_1 = -OH$, $R_3 = -OCH_2CH_3$

d) $R_1 = OH$, $R_3 = -OCH_3$

e) $R_1 = OH$, $R_3 = H$

f) $R_1 = H$, $R_3 = H$

nomenon is apparent. When the tetrafluoroborate salt of **2a** is dissolved in CF_3SO_3D,[6,7] the singlet at δ 6.98 due to H_2 has virtually disappeared (within 15 min) (Figure 1, middle spectrum); the remainder of the spectrum is unchanged even after 24 h. When the sample is heated at 100 °C for 15 h, the ^1H NMR spectrum (Figure 1, top) shows a build up of a singlet between each low-field doublet ($H_4 = H_9$ and $H_6 = H_7$); again the remainder of the spectrum is unaffected. This much slower process[8] is due to the replacement of H_5/H_8 with deuterium.

Carbocations **2b–d** have exactly the same behavior in triflic acid as **2a.** Interestingly, **2e** does not exchange H_2 in CF_3SO_3D at room temperature. Upon heating the sample at 100 °C the rate of exchange of H_2 becomes measurable. Finally, the unsubstituted phenalenyl cation **2f** (in FSO_3D and D_2SO_4) does not exchange under any of these conditions.

Can one attribute these observations to the reaction of H^+ and D^+ with aromatic carbocations? Several lines of evidence indicate that this is so. The relative reactivity of the carbocations, **2a** ~ **2b** ~ **2c** ~ **2d** > **2e** > **2f,** parallels the reactivity of benzene derivatives in electrophilic aromatic substitution. The regioselectivity, where H_2 exchanges much faster than H_5 and H_8, is also consistent with the stability of the σ complex formed when H^+ and D^+ attack C_2 and C_5/C_8, respectively. Neutral molecules, formed by the reaction of **2** (or **1** for that matter) with nucleophiles in the solvent, cannot be the vehicle for the exchange. Because of the high pK_{R^+} value associated with **2a**[9] and the low nucleophilicity[12] and high acidity[3] of the medium, the concentration of this neutral molecule would be so low[13] that it could not react fast enough to account for our observed rates. The sesquixanthyl carbocation,[2] whose $pK_{R^+} = 9.05$,[2] would be even less likely to form a neutral molecule in this medium and it also exchanges protons (at H_m) in CF_3SO_3D at room temperature. Similar reasoning will also apply to the protonated ketones, **2b–e.** Furthermore, for these latter ions, one can imagine that it is the corresponding neutral ketone which exchanges. Because of the high basicity of these ketones,[14] however, the concentration of any one of them in triflic acid would be too small to account for the observed exchange rates.

One other viable mechanism[16] must be considered. If a radical in the medium underwent rapid electron exchange with **2** to yield a radical, this phenalenyl radical might exchange hydrogen with the medium. This process also can be discounted. First of all, the NMR lines are all sharp. Carbocations undergoing electron exchange yield broad NMR lines.[18] Secondly, although we detect unresolved ESR signals for some of these solutions, their presence cannot be significant because independently prepared phenalenyl radical (**2f** plus one electron) in strong acid exchanges at sites different from those observed in the present study.[19] And finally, when carbocations such as **2c** are generated in the strong oxidizing FSO_3D, where radicals are quickly oxidized, the exchange phenomenon still occurs.

In conclusion, because all alternatives are inconsistent with the data, the observed exchange phenomenon must be due to the reaction of H^+ and D^+ with carbocations. Studies in this area are continuing.[20]

Acknowledgments. We thank John Larsen for helpful comments and James Q. Chambers for allowing us to use his ESR spectrometer.

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(1) (a) R. Weiss and C. Priesner, *Angew. Chem., Int. Ed. Engl.*, **17,** 445 (1978); (b) R. Weiss, C. Priesner, and H. Wolf, *ibid.*, **17,** 446 (1978).

(2) J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **86**, 2252 (1964).

(3) $H_0 = -13$ for triflic acid. See R. D. Howells and J. D. McCown, *Chem. Rev.*, **77**, 69 (1977).

(4) If the triflic acid solution is diluted with acetonitrile, the high-field doublet (H_m) and low-field triplet (H_p) reappear.

(5) ^1H NMR of **2a** (CF_3SO_3H): δ 1.52 (t, $-CH_3$, $J = 8.0$ Hz), 2.82–3.65 (m, $-CH_2-$), 6.98 (s, H_2), 8.18 (t, H_5 and H_8, $J = 8.0$ Hz), 8.88 (d, H_4/H_9 or H_6/H_7, $J = 8.0$ Hz), and 9.23 (d, H_6/H_7 or H_4/H_9, $J = 8.0$ Hz). The spectral data for all the other ions will be reported in our full paper.

(6) All solutions were in NMR tubes sealed in vacuo after several freeze–pump–thaw cycles.

(7) CF_3SO_3D is prepared by treating triflic anhydride with D_2O followed by distillation. The acid contains no D_2O (mass spectrometry).

(8) Because the exchange of H_2 has $\tau_{1/2} < 3$ min at 20 °C and that of H_5/H_8 has $\tau_{1/2} \geq 15$ h at 100 °C, it follows that the rate of exchange of H_2 is more than 7.5×10^4 times faster than that of H_5/H_8 at 20 °C. It is also apparent that H_4/H_9 and H_6/H_7 do not exchange at all.

(9) 1-Hydroxyphenalene has $pK_{R^+} = 0$–2.[10] Each ethoxy group should increase this value by ~2 units.[11] Thus, the pK_{R^+} value associated with **2a** is likely to be ~4–6. This, of course, is an "averaged" value because **2a** is unsymmetrical.

(10) D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 57 (1958).

(11) D. Bethel and V. Gold, "Carbonium Ions, An Introduction", Academic Press, New York, 1967, Chapter 4.

(12) In addition to **2a**, the only species present are BF_4^- and $CF_3SO_3H(D)$; no water is present.[7]

(13) One can estimate crudely the concentration of a neutral molecule (N) formed by the reaction of **2a** with water by the following: $H_0 = pK_{R^+} + \log [N]/[\mathbf{2a}]$. For **2a,** $pK_{R^+} \approx 5$[9] and $[\mathbf{2a}] = 1$. If one assumes that $H_0 = -13$[3] it follows that $[N] = 10^{-18}$. Remember, however, that no water is present[7] and that nucleophiles poorer than water are in the medium.

(14) Carbocation **2e** has $pK_a = -1.4$.[15] Carbocations **2b–d** should be even less acidic because of the presence of an electron-releasing group.

(15) G. Culbertson and R. Pettit, *J. Am. Chem. Soc.*, **85,** 741 (1963).

(16) The loss of H^+ from C_2 of **2** to form a highly strained allene or carbene followed by addition of D^+ seems highly unlikely. Loss of H_4, H_6, H_7, and/or H_9 to form a carbene would appear more likely. The experiments, of course,

indicate that these sites do not exchange. Other mechanisms[17] require the presence of good nucleophiles and they are not present.

(17) A. A. El-Anani, C. C. Greig, and C. D. Johnson, *Chem. Commun.*, 1024 (1970).

(18) For example, carbocation **2f** in the presence of the phenalenyl radical (**2f** + 1 electron) shows no ^{1}H NMR signals.

(19) R. M. Pagni, P. Easley, and R. Smith, unpublished results.

(20) This work was supported by the University of Tennessee.

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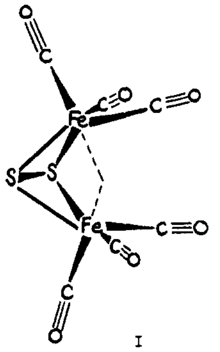
Novel Bridging Sulfide Anion Complexes of the Hexacarbonyldiiron Unit: a New Route to Alkylthio Complexes of Iron

Sir:

The interesting iron–sulfur cluster complex, μ-dithio-bis(tricarbonyliron), I, has been known for 20 years since its first preparation by Hieber and Gruber,[1] and its structure, as indicated in I, was determined by Wei and Dahl.[2] Although new procedures for the preparation of I have been developed recently by Russian workers,[3] only little work has been reported concerning the chemical transformations of this complex. Of some interest is the reaction of $S_2Fe_2(CO)_6$ with $GeCl_2$ precursors, which resulted, it was claimed, in the insertion of $GeCl_2$ into the Fe–Fe bond.[4]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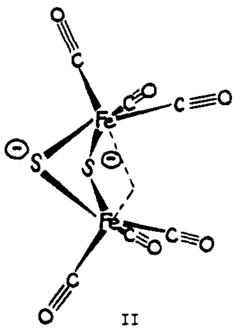
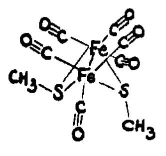
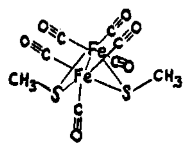

II

In an extension of our interest and activity in the area of heteroatom-containing transition metal carbonyl cluster complexes,[5] we have begun an investigation of the chemistry of $S_2Fe_2(CO)_6$. We report here some initial results.

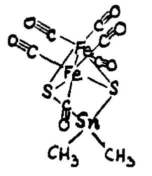
The reaction of $S_2Fe_2(CO)_6$ with suitable reducing agents results in cleavage of the sulfur–sulfur bond, giving a dianion, presumably II, which has bridging sulfide anion ligands. Although structural studies have not been carried out as yet, the reactions of II suggest the assigned structure since reactions with alkyl iodides give products with bridging mercapto ligands. In a typical reaction, addition of 2.74 mmol of ruby-red crystals of $S_2Fe_2(CO)_6$ in THF to a suspension of 6.9 mmol of potassium hydride in THF (all operations under nitrogen in a drybox or using Schlenk apparatus) gave a dark red solution and caused gas evolution. Starting material was consumed (by TLC) within 4 h at room temperature. Filtration was followed by addition of 14.4 mmol of iodomethane to the red filtrate. After a reaction period of 12 h at room temperature, the solvent was removed and the residue was chromatographed (silicic acid–pentane) to give the known[6,7] isomers of $(CH_3S)_2Fe_2(CO)_6$ in 53% combined yield. This isomer mixture could be resolved by column chromatography into pure III, mp 65–67 °C (lit.[6] mp 65–67.5 °C), and IV, mp 101.5–102.5 °C (lit.[6] mp 101.5–103.5 °C). Isomers III and IV, whose structures had been assigned on the basis of considerations of the structure of $(C_2H_5S)_2Fe_2(CO)_6$ as determined by X-ray diffraction,[7] were formed in 2.7:1 ratio.

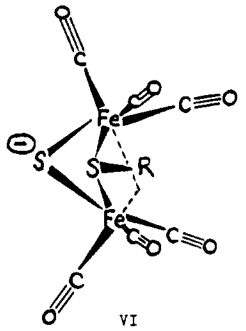

III


IV

Dianion II also could be formed by the reaction of $S_2Fe_2(CO)_6$ with sodium sand[8] or commercial sodium dispersion. Alkylation of II thus produced with iodomethane gave $(CH_3S)_2Fe_2(CO)_6$ (a mixture of III and IV in each case) in yields of 34 and 31%, respectively. Alkylation of II prepared by the sodium dispersion route with iodoethane resulted in formation of the known[7,9] $(C_2H_5S)_2Fe_2(CO)_6$ in 29% yield. The product, a dark red, air-stable solid, had mp 73–75 °C (lit.[9] mp 75.5 °C). The potassium hydride procedure gave this complex in 46% yield.

While complexes of type $(RS)_2Fe_2(CO)_6$ are more easily and directly prepared by reactions of thiols, sulfides, and disulfides with iron carbonyls,[10,11] dianion II nevertheless can have interesting and useful preparative applications. One example, its reaction with dimethyltin dichloride to give $(Me_2SnS_2)Fe_2(CO)_6$, a black-purple solid which is fairly air stable, mp 95 °C dec, presumably with structure V, serves to illustrate this. The ^{1}H NMR spectrum of V (in acetone-d_6) shows the CH_3 resonance as a singlet with ^{117}Sn and ^{119}Sn satellites (J = 30 and 32 Hz). The molecular ion was observed in the mass spectrum. Also observed were fragment ions due to successive loss of the six carbonyl ligands and the two methyl groups, giving finally the cluster ion $[Fe_2SnS_2]^+$.


V


VI

A monoanion derived from I (VI) also may be generated by reaction of $S_2Fe_2(CO)_6$ with an alkyllithium reagent, and in these homogeneous reactions much better product yields are obtained. For instance, the reaction of $S_2Fe_2(CO)_6$ in THF with an equimolar quantity of $CH_3Li/LiBr$ in diethyl ether (Alfa Inorganics) at −78 °C under nitrogen gave a green solution at the equivalence point. Addition of iodomethane, followed by a 12-h reaction time at room temperature, resulted in the formation of the two isomers of $(CH_3S)_2Fe_2(CO)_6$ in 82% yield (III/IV ratio, 3.1). A similar reaction in which anion VI (R = CH_3) was allowed to react with iodoethane gave $(CH_3S)(C_2H_5S)Fe_2(CO)_6$, an air-sensitive, dark red oil, bp 50 °C (0.2 Torr) (short-path still), in 77% yield. In another experiment, a THF solution of $S_2Fe_2(CO)_6$ at −78 °C was treated with n-butyllithium in hexane to give anion VI (R = n-C_4H_9). Reaction of the latter with CH_3I produced $(CH_3S)(n\text{-}C_4H_9S)Fe_2(CO)_6$, an air-sensitive red oil, which also could be distilled, in 70% yield.

μ-Dithio-bis(tricarbonyliron) thus has been shown to be a source of interesting sulfur-centered mono- and dianions. The monoanion provides a useful reagent for the preparation of unsymmetrical bis(alkylthio)hexacarbonyldiiron complexes, μ-(RS)-μ-(R'S)$Fe_2(CO)_6$, and the dianion should show interesting applications in the synthesis of acyclic and cyclic metal-sulfur-iron complexes. These applications, as well as further development of the chemistry of $S_2Fe_2(CO)_6$, are receiving our attention.

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