38.1 (C7), 27.3 (C6), 22.9 (C5), 15.8 and 6.0 (cyclopropyl).

2'-Cyclopropylspiro[cyclopropane-3'-norbornan]-2'-ol (8). Lithium wire (sodium content 1%, 0.4 g, 57 mmol) was hammered into shiny plates and was placed into 50 mL of ether, contained in a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, an addition funnel, and a nitrogen inlet. The flask was cooled to 0 °C, and cyclopropyl bromide (2.3 g, 19 mmol, 1.2 equiv) was added dropwise to the contents at such a rate as to maintain gentle reflux. The solution was stirred at this temperature for 30 min. Compound 5 (2.2 g, 16 mmol), dissolved in 10 mL of ether, was then added dropwise and the reaction mixture was stirred for 2 h at room temperature. After quenching with 100 mL of water, it was extracted with ether (2 × 50 mL). The ether layers were washed with saturated sodium bicarbonate (50 mL) and dried ($MgSO_4$), and the solvents were rotary evaporated. Compound 8 (2.3 g, 81%) was obtained after purification of the residue by column chromatography (silica gel), eluting with 1:1 dichloromethane and ether. MS (m/z): 178 (6.9, M^+), 163 (10.5), 150 (32.3), 135 (17.8), 122 (29.0), 109 (30.1), 79 (32.9), 69 (100). ^{13}C NMR: δ 76.1 (C2), 49.1 (C1), 46.9 (C4), 38.0 (C3), 36.8 (C7), 26.7 (C6), 22.3 (C5), 18.1 (cyclopropyl α-CH), 11.9 (C8), 5.6 (C9), 0.51 and -0.74 (cyclopropyl β-CH_2).

Preparation of Carbocations. SbF_5 and FSO_3H were freshly distilled before use. The precursor alcohols dispersed in SO_2ClF were added to a solution of Magic Acid (1:1 SbF_5 and FSO_3H) in SO_2ClF, at -78 °C (dry ice/acetone bath) or at ca. -120 °C (pentane/liquid nitrogen slush), resulting in an approximately 10% solution of the ions. Efficient mixing of the solution was effected with a vortex stirrer.

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Registry No. 4, 5597-27-3; 5, 16133-64-5; 6, 61541-30-8; 7, 138260-72-7; 8, 138260-73-8; 9, 138260-74-9; 10, 138260-75-0; 11, 138260-76-1; 12, 138260-77-2; 13, 138260-78-3.

Proton, Electron, and Hydrogen Atom Transfers from Ions, Radicals, and Radical Ions Derived from Substituted Urazoles and Triazolinediones

M. J. Bausch* and B. David

Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, Carbondale, Illinois 62901-4409

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In dimethyl sulfoxide (DMSO) solution, pK_a's for the monoanion and radical derived from 4-phenylurazole have been determined to be 24.8 and 9 ± 2, respectively. The acidity constant for the 4-phenylurazolyl radical has been determined via a thermochemical cycle that incorporates proton- and electron-transfer data for ions and radicals derived from 4-phenylurazole and 4-phenyl-1,2,4-triazoline-3,5-dione. The acidity data indicate that (a) the 4-phenylurazolide monoanion is ca. 14 pK_a units less acidic than 4-phenylurazole (pK_a = 11.0) and (b) the 4-phenylurazolyl radical is slightly more acidic than 4-phenylurazole. The estimated pK_a for the 4-phenylurazolyl radical is reasonable in light of the reversible cyclic voltammetric reduction observed for 4-phenyl-1,2,4-triazoline-3,5-dione. Also in DMSO solution, the homolytic strengths of hydrazyl N-H bonds present in 4-phenylurazole, as well as for the monoanion and radical derived from 4-phenylurazole, are within 3 kcal/mol of each other. These data suggest that the 4-phenylurazolyl radical disproportionation reaction (forming 4-phenylurazole and 4-phenyl-1,2,4-triazoline-3,5-dione) is approximately thermoneutral. Similar relationships are found for ions, radicals, and radical ions derived from 4-methylurazole and 4-methyl-1,2,4-triazoline-3,5-dione.

The marriage of solution-phase proton-transfer chemistry with electrochemistry has resulted in an increased understanding of the stabilities and reactivities of several varieties of solution-phase ions, radicals, and radical ions, as well as the strengths of specific bonds contained in these species.[1] Dimethyl sulfoxide (DMSO) has proven to be a medium that is well suited for investigations of proton- and electron-transfer reactions of organic molecules.[2] The strongly basic nature of the potassium salt of the conjugate base of DMSO (the dimsyl anion) enables evaluation of proton-transfer equilibria that involve strongly basic species.[3] Kinetically stable organic dianions less basic than dimsyl can therefore be included in various thermochemical cycles provided that reliable acidity and redox data are accessible in DMSO solution.

The urazolyl[4a] moiety provides a framework that enables ready access to the equilibrium constants for proton transfers involving the neutral urazole acids, as well as the anionic and dianionic urazolide ions. A natural extension of our interest in the acidic properties of substituted urazoles and related species[5] is the investigation of the acidic nature of urazole anions in DMSO solution. The fact that the dipotassium salt of 4-phenylurazole has been dialkylated with methyl iodide, in DMSO solution, suggests

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(3) (a) The pK_a of DMSO, in DMSO, is 35.1.[3b] (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456-463.

(4) (a) The Chemical Abstracts name for urazole is 1,2,4-triazolidine-3,5-dione. (b) The Chemical Abstracts name for 4-phenyl-1,2,4-triazoline-3,5-dione is 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione.

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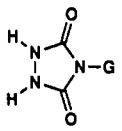
Table I. Summary of Acidity[a] and Redox[b] Data (in DMSO Solution) for Acids, Anions, and Dianions Derived from 4-G-urazoles and 4-G-1,2,4-triazoline-3,5-diones (G = Ph, Me)

exp no.	substrate	parameter	G = Ph	G = Me
i	4-G-urazole (1)	pK_a	11.0[c]	12.3[c]
ii	4-G-urazolide monoanion (1 − H^+)	pK_a	24.8	26.0
iii	4-G-urazolide monoanion (1 − H^+)	$E_{ox}/E_{1/2}$[d] (V)	0.34/0.38	0.27/0.31
iv	4-G-urazolide dianion (1 − $2H^+$)	$E_{1/2}$ (V)	−0.60	−0.74
v	4-G-1,2,4-triazolinedione (2)	$E_{1/2}$ (V)	0.38	0.31

[a] Acidity data collected as described in Experimental Section. [b] Redox potentials vs Ag/AgI; Pt working and auxiliary electrodes, 100mV/s sweep rate; potentials corrected to ferrocene/ferrocenium reversible couple at 0.875 V. E_{ox} values are anodic peak potentials, while $E_{1/2}$ values are the midpoints of well-defined anodic and cathodic reversible couples. All redox data corrected to NHE_{aq} by subtracting 0.125 from the Ag/AgI-based value.[2b] Full details in Experimental Section. [c] Reference 5a. [d] Two anodic waves were observed. See text.

that the dianion derived from 4-phenylurazole is (a) stable in DMSO and (b) reactive in an S_N2 sense toward electrophiles.[6] Additional evidence for the thermodynamic stability of urazolide dianions can be inferred from the pK_a determination of the monoanion derived from 1-phenylurazole (pK_a = 12.2 in aqueous solution).[7] We have therefore examined proton and electron transfer equilibria that involve dianions derived from 4-phenylurazole and 4-methylurazole (1 − $2H^+$, where G = Ph and Me, respectively), or, viewed from another perspective, dianions derived from 4-phenyl-1,2,4-triazoline-3,5-dione[4b] and 4-methyl-1,2,4-triazoline-3,5-dione (2 + $2e^-$, again where G = Ph and Me), since, for a given G-substituent, 1 − $2H^+$ = 2 + $2e^-$. Data from these experiments, when combined with related proton- and electron-transfer data for radicals and radical ions derived from 1 and 2, enable determinations of N–H equilibrium acidities and homolytic bond dissociation energies (BDEs) for urazole, urazolyl radicals, urazolide anions, and triazolinedione radical anions. These data are of interest in light of the wide range of published transformations involving triazolinediones (e.g., aromatic substitution,[8] ene,[9] Diels–Alder,[10] ylide formation,[11] and light-catalyzed polymerization[12]) and urazoles (e.g., synthesis of alkaline-soluble polymers[13] as well as proton,[7,14] hydrogen atom,[15] alkyl,[11] and acyl[16] transfers), many of which proceed through and/or involve radical, ionic, and radical ionic intermediates related to 1 and 2.



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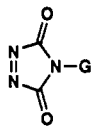

2

Table II. Reduction Potentials for 4-G-1,2,4-triazoline-3,5-diones in DMSO Solution. Acidity Constants for 4-G-urazoles in DMSO Solution

G	4-G-urazole pK_a[a]	4-G-1,2,4-triazoline-3,5-diones red. pot.[b] (V)
CH_3	12.2[c]	0.31
4-$CH_3OC_6H_4$	11.4	0.36
4-$CH_3C_6H_4$	11.3	0.37
C_6H_5	11.0	0.38
4-ClC_6H_4	10.6	0.41
3-ClC_6H_4	10.4	0.43

[a] Reference 5c unless otherwise indicated. Full details in Experimental Section. [b] The reduction potentials are true $E_{1/2}$ values and are the midpoints of anodic and cathodic reversible couples. All redox data corrected to NHE_{aq} by subtracting 0.125 from the Ag/AgI-based value.[2b] [c] Reference 5a.

Table III. Summary of Experimental and Derived Acidities, Relative Acidities, and Relative Homolytic N–H BDEs for 4-Phenyl- and 4-Methylurazole, 4-Phenyl- and 4-Methylurazolide Anions, and 4-Phenyl- and 4-Methylurazolyl Radicals

substrate (n)	pK_a[a]	ΔpK[b] (kcal/mol)	E_{ox} (n − H^+)[c] (V)	ΔE_{ox}[d] (kcal/mol)	ΔBDE[e] (kcal/mol)
4-phenylurazole	11.0	(0.0)	0.34	(0.0)	(0.0)
4-phenylurazolide monoanion	24.8[f]	18.5	−0.60	−21.7	−3
4-phenylurazolyl radical	9[f,g]	−3.2[g]	0.38	0.9	−2
4-methylurazole	12.3	(0.0)	0.27	(0.0)	(0.0)
4-methylurazolide monoanion	26.0[f]	18.4	−0.74	−23.3	−5
4-methylurazolyl radical	9[f,g]	−4.9[g]	0.31	0.9	−4

[a] Acidity data published previously,[5a] except where noted. [b] At 25 °C, 1 pK_a unit is equal to 1.37 kcal/mol. Therefore, for the 4-phenylurazole derivatives, ΔpK_a (kcal/mol) = 1.37[pK_a(n) − 11.0]; while for the 4-methylurazole derivatives, ΔpK_a (kcal/mol) = 1.37[pK_a(n) − 12.3], where 11.0 and 12.3 are the respective pK_a's for 4-phenylurazole and 4-methylurazole, in DMSO solution. Positive ΔpK_a values signify that the molecule in question is a weaker acid than the reference neutral closed-shell urazoles and are statistically corrected for the number of acidic protons present on each substrate. [c] E_{ox} values in reference to our Ag/AgI reference electrode; all values corrected to the ferrocene/ferrocenium reversible couple at 0.875 V. For a complete explanation of the DMSO-phase electrochemistry conditions, see Experimental Section. [d] At 25 °C, 1 V is equal to 23.06 kcal/mol. For the anion derived from a given substrate n, ΔE_{ox} (kcal/mol) = 23.06[$E_{ox(n-H^+)}$ − 0.34] for the 4-phenylurazole derivatives; ΔE_{ox} (kcal/mol) = 23.06[$E_{ox(n-H^+)}$ − 0.27] for the 4-methylurazole derivatives, where 0.34 and 0.27 are the respective E_{ox} values (in V) for the monoanions derived from 4-phenylurazole and 4-methylurazole. [e] The ΔBDE values in Tables I and II have been determined with the aid of eq 1. Negative ΔBDE values signify that the bond in question is weaker than the analogous bond in the reference neutral closed shell urazole. Uncertainties are about 3 kcal/mol. [f] This work. [g] Uncertainties are about 2 pK_a units (3 kcal/mol); see text.

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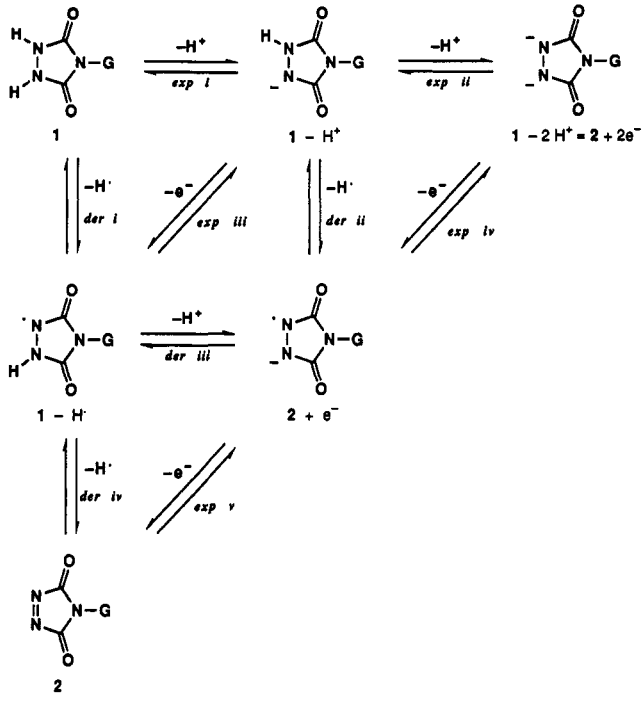
Scheme I



Results and Discussion

Ions, radicals, and radical ions derived from 1 and 2 are related via the proton, hydrogen atom, and electron-transfer reactions shown in Scheme I. Of the nine parameters, five are experimentally accessible (designated as exp i–exp v in Scheme I) with the aid of spectrophotometric and electrochemical techniques, while the other four (der i–der iv) can be derived via thermochemical cycles. The experimentally accessible data (exp i–exp v) are listed in Table I. Table II contains acidity data for six 4-G-urazoles (1, where G = 3-ClC_6H_4, 4-ClC_6H_4, H, 4-$CH_3C_6H_4$, 4-CH_3O-C_6H_4, and CH_3) along with reversible reduction potentials for six similarly substituted 4-G-1,2,4-triazoline-3,5-diones (2 where G = 3-ClC_6H_4, 4-ClC_6H_4, H, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, and CH_3). Table III contains acidity and homolytic bond dissociation energy (BDE) parameters derived from the experimental data found in Table I.

Urazole and Urazolide Anion Acidities (Table I). The magnitude of the acidities of the N–H protons present in 4-phenylurazole and 4-methylurazole (pK_a = 11.0 and 12.3, respectively, exp i in Scheme I) is due primarily to the acyl hydrazyl [i.e., —NC(=O)—] functionality adjacent to the site of deprotonation as well as to the heterocyclic nature of the urazole moiety.[5] Further inspection of Table I reveals that the pK_a's for the monoanions derived from 4-phenylurazole (1 – H^+, G = Ph) and 4-methylurazole (1 – H^+, G = CH_3) are 24.8 and 26.0, respectively (exp ii).

The equilibrium acidities for the monoanions derived from 4-phenylurazole and 4-methylurazole are therefore both within a pK_a unit of the equilibrium acidity for neutral acetamide (pK_a = 25.5[3b]). One interpretation of the similarities in the pK_a's for the urazolide monoanions and neutral acetamide is that the negative charge in the urazolide monoanion is found mainly on the oxygen that is three atoms removed from the acidic N–H proton, thus minimizing any appreciable acid-weakening effect of the imidate-like [—$^-$NC(=O)— ↔ —N=C(O^-)—] moiety. The data suggest that the acidifying effect of an adjacent [—$^-$NC(=O)— ↔ —N=C(O^-)—] group does not differ substantially from the effect of a hydrogen atom.

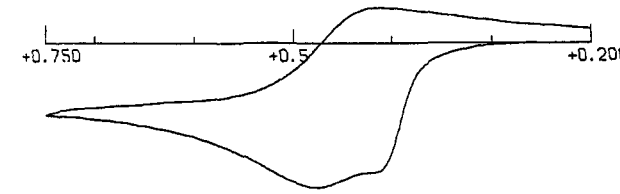


Figure 1. Anodic oxidation of monoanion derived from 4-phenylurazole (with subsequent reversible oxidation of the radical anion derived from 4-phenyl-1,2,4-triazoline-3,5-dione) utilizing platinum working and Ag/AgI reference electrodes. The peak potentials do not match those listed in Table I because the values are standardized vs ferrocene ($E_{1/2}$ = 0.875) and then corrected to $NHE_{(aq)}$, as described in the Experimental Section.

Urazole Redox Chemistry (Tables I and II). E_{ox} and $E_{1/2}$ values for 4-G-urazolide monoanions (1 – H^+, exp iii) and dianions (1 –$2H^+$, exp iv) are also listed in Table I. Careful analysis of the cyclic voltammogram that results from the 100 mV/s oxidation of the 4-phenylurazolide monoanion reveals the presence of a second wave that appears within a few mV of the initial anodic wave. Reducing the sweep rate to 25 mV/s (Figure 1) enables assignment of the peak potentials for the two anodic waves. The presence of two waves in such close proximity is highly unusual when carrying out the CV oxidation of delocalized organic anions. Hundreds of organic anions, when dissolved in DMSO as well as other inert solvents, have been oxidized at a platinum working electrode.[1,2] When subjected to identical CV conditions, the monoanion derived from 1-phenylurazole yields only one irreversible anodic wave (E_{ox} = 0.54 V), while the monoanion derived from 1,4-diphenylurazole is oxidized *reversibly* ($E_{1/2}$ = 0.71 V).[17] For reasons made apparent in the next paragraph, the second anodic wave in Figure 1 is reversible.

Also found in Table I are the $E_{1/2}$ values for the reversible reductions of 4-G-1,2,4-triazoline-3,5-dione (2, where G = Ph and CH_3, exp v). Of significance is that the $E_{1/2}$ values for the reductions of 2 (for both G = Ph and CH_3) are *equal* to the $E_{1/2}$ values for the second (reversible) anodic waves observed when the 4-G urazolide monoanions (1 – H^+, again where G = Ph and CH_3) were oxidized. On the basis of these observations, we propose that the product of the anodic oxidation of a given 4-G-urazolide monoanion (exp iii) is transformed into the radical anion derived from 4-G-1,2,4-triazoline-3,5-dione (2 + e^-). The newly formed 2 + e^- radical anion is then oxidized to 2. On the reverse CV sweep, the electrochemically formed 2 is reduced, forming 2 + e^-, a transformation that accounts for the reversible nature of the second set of waves observed when 1 – H^+ is oxidized.

The experimental reproducibility in the $E_{1/2}$ and E_{ox} values listed in Table I is ≤25 mV (0.5 kcal/mol). The reversible character of the 4-G-urazolide dianion (1 – $2H^+$) oxidations and the 4-G-1,2,4-triazoline-3,5-dione (2) reductions allows ready inclusion of these data into thermochemical cycles. The observed irreversibility of the 4-G-urazolide monoanion (1 – H^+) oxidations is problematic in that the observed E_{ox} values can only serve as estimates for the truly thermodynamic $E_{1/2}$ values. Fortunately, there are numerous literature precedents suggesting that anodic peak potentials (e.g., E_{ox} values) obtained for irreversible CV oxidations of delocalized organic anions are reasonable estimates for the $E_{1/2}$ values for the reactions at hand.[1,2] In many of these studies, the incor-

(17) David, B. MS Thesis, Southern Illinois University at Carbondale, Carbondale, IL, 1989.

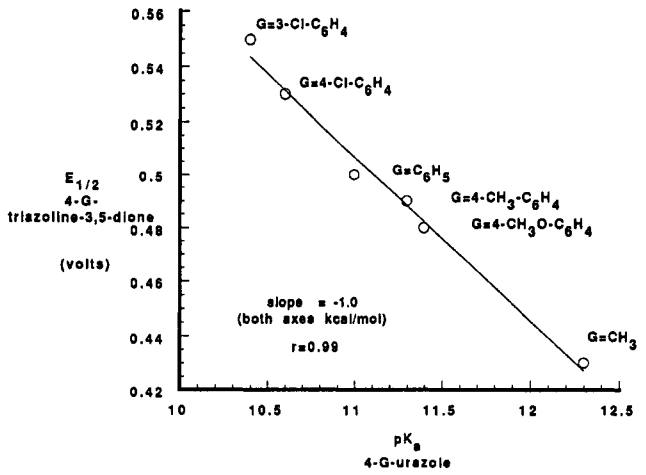
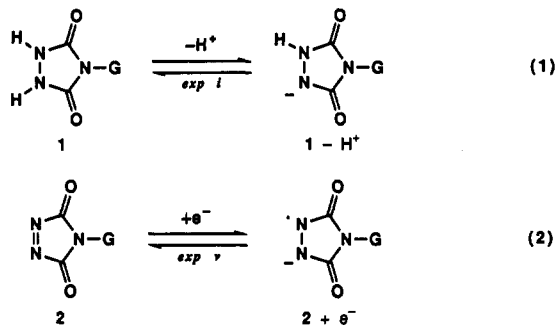


Figure 2. Reduction potentials for six 4-G-1,2,4-triazoline-3,5-diones plotted as a function of the pK_a's for six analogously substituted 4-G-urazoles. The slope of the least-squares line is −0.0613 V/pK_a unit (−1.0 when both axes converted to kcal/mol).

poration of irreversible E_{ox} values into various thermochemical cycles has resulted in important new solution-phase data that correlate nicely with gas- and solution-phase data. It is therefore likely that the irreversible E_{ox} values listed in Table I are accurate to ≤100 mV (±2.3 kcal/mol).

Listed in Table II are two sets of data, all of which were collected in DMSO: (a) pK_a's for six analogously substituted 4-G-urazoles (1, where G = 3-ClC_6H_4, 4-ClC_6H_4, C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, and CH_3) and (b) reduction potentials for six different 4-G-1,2,4-triazoline-3,5-diones (2, where G = 3-ClC_6H_4, 4-ClC_6H_4, C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, and CH_3). Inspection of the data in Table II reveals that effects of 4-G substituents on these parameters are small but regular in that a given 4-substituent that acidifies 1 also results in a cathodic shift in the reduction potential of 2. For example, while 4-(chlorophenyl)-1,2,4-triazoline-3,5-dione is about 0.1 V (2.3 kcal/mol) easier to reduce than 4-methyl-1,2,4-triazoline-3,5-dione, 4-(chlorophenyl)urazole is about 1.6 pK_a units (2.2 kcal/mol) easier to deprotonate than 4-methylurazole.

The data listed in Table II are plotted in Figure 2, where the reduction potentials for the 4-G-1,2,4-triazoline-3,5-diones (exp v and eq 1) are plotted as a function of the



(1)

(2)

pK_a's for the analogously substituted 4-G-urazoles (exp i and eq 2). In analyzing the effects of substituents on equilibria such as those in eqs 1 and 2, it is generally assumed that the magnitudes of the perturbations that result from the presence of substituents are larger on the charged species (i.e., 1 − H^+ and 2 + e^- in eqs 1 and 2). To a first approximation, it is reasonable to assume that 4-substituents affect the stabilities of 1 and 2 in a nearly equal fashion. It follows from the linearity (r = 0.99) and unit slope (when both axes are converted to kcal/mol) evident in Figure 2 that 4-substituents affect the stabilities of urazolide monoanions (1 − H^+) and triazolinedione radical anions (2 + e^-) nearly equally. It is likely that this relationship results from the fact that 4-substituents are not able to interact with the unpaired and/or negative charge density present in 1 − H^+ and 2 + e^- via resonance. Additional evidence for this proposition (i.e., that 4-substituents have comparable effects on the stabilities of 1 − H^+ and 2 + e^-) is presented in the discussion on homolytic bond dissociation energies for urazoles and radicals and ions derived from urazoles.

The linearity observed in Figure 2 is reminiscent of the linearity (r = 0.99, over a range of 25 kcal/mol) observed in a plot of reduction potentials vs equilibrium acidities for 10-substituted 9-methylanthracenes.[2d] Both relationships indicate that remote substituents have proportional effects on the stabilities of radical anions and anions derived from urazoles, triazolinediones, and anthracenes. These observations are not unique in light of the dozens of studies that have shown that the reduction potentials for a given family of molecules plot linearly with Hammett σ constants.[18] Since the present studies utilize pK_a and redox parameters obtained from structurally similar substrates, in the same solvent (DMSO), more meaningful comparisons of the substituent effects are possible.

Urazolyl Radical Acidities (Table III). Depicted in Scheme I as der iii, the position of the equilibrium for the transfer of a proton between 4-G-urazolyl radicals (1 − H•) and 4-G-1,2,4-triazoline-3,5-dione radical anions (2 + e^-) can be determined with the knowledge of three experimental parameters: the pK_a for the 4-G-urazolide monoanion (1 − H^+); the E_{ox} for the 4-G-urazolide monoanion (1 − H^+); and the $E_{1/2}$ for the 4-G-urazolide dianion (1 − 2H^+).[19] These parameters are described as exps ii–iv in Scheme I and Table I. The derived pK_a values (der iii in Scheme I) for the 4-G-urazolyl radicals (1 − H•) are determined as shown in eq 3, where 16.8 is a constant that

$$pK_a\,(1 - H^\bullet) = pK_a\,(1 - H^+) - 16.8\,[E_{ox}(1 - H^+) - E_{1/2}(1 - 2H^+)] \quad (3)$$

enables conversion (at 25 °C) of volts into pK_a units [16.8 = (23.06 kcals/volt)(1 pK_a unit/1.37 kcal)]. The uncertainties in the derived pK_a's determined via eq 3 are about 3 kcal/mol (2 pK_a units), since the uncertainties in the exps ii–iv data are ±0.3 (±0.2 pK_a units), ±2.3 (±100 mV), and ±0.6 kcal/mol (±25 mV), respectively.

Inspection of the 4-phenylurazolyl and 4-methylurazolyl radical acidity data in Table III reveals pK_a values of 9 ± 2 for both species. Acidity constants of this magnitude for urazolyl radicals are sensible in light of the observation that the radical anion derived from 4-phenyl-1,2,4-triazoline-3,5-dione (2 + e^- where G = Ph) is protonated in acetic acid solution.[10b]

It is instructive to compare the pK_a's for 4-phenylurazole, the 4-phenylurazolide monoanion, and the 4-phenylurazolyl radical (11.0, 24.8, and 9 ± 2, respectively). While deprotonation of 4-phenylurazole deacidifies the urazole framework by 13.5 pK_a units, hydrogen atom removal from 4-phenylurazole slightly acidifies the urazolyl framework. The data suggest that the presence of an unpaired electron located primarily in the –NC(O)– linkage adjacent to the site of deprotonation (as in 1 − H•) slightly weakens the N–H bond (in 1) in a heterolytic sense, while

(18) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

(19) (a) Parker has devised a similar cycle to determine solution-phase dihydroanthryl radical acidities, a cycle that includes a calculated gas-phase equilibrium constant for the addition of H_2 to anthracene, forming 9,10-dihydroanthracene.[19b] (b) Parker, V. D.; Tilset, M.; Hammerich, O. *J. Am. Chem. Soc.* **1987**, *109*, 7905–7906.

the presence of an adjacent *pair* of electrons in the same –NC(O)– linkage (as in 1 – H$^+$) strengthens the analogous N–H bond.

We are not aware of any published research that describes investigations of the thermodynamic acidities of organic radicals that, upon treatment with a suitable base, are deprotonated at nitrogen. There have been several investigations of the aqueous-phase acidities of ketyl radicals that enable comparison with the pK_a's with their hydrogenated closed-shell analogues. For example, the pK_a's of methanol (CH_3OH) and the hydroxymethyl radical ($\cdot CH_2OH$) are 15.5 and 10.7,[20] respectively. The enhanced acidity of $\cdot CH_2OH$ (relative to CH_3OH) is thought to be related to the resonance stabilization present in its conjugate base, the ketyl radical anion $\cdot CH_2O^-$. On the other hand, aqueous phase acidity data for acetic acid (CH_3CO_2H) and its corresponding radical ($\cdot CH_2CO_2H$) (pK_a's = 4.76 and 4.9,[21] respectively) indicate that the presence of an unpaired electron that resides on an atom once removed from (and not in resonance with) the site of deprotonation has little effect on the equilibrium acidity of acetic acid.

Any argument that attempts to rationalize the slightly greater acidity of 4-phenylurazole (compared to the 4-phenylurazolyl radical) must include comparisons of the stabilities of two quite different pairs of acid–base partners: 4-phenylurazole and its conjugate base (the 4-phenylurazolide anion), along with the 4-phenylurazolyl radical and its conjugate base (the radical anion derived from 4-phenyl-1,2,4-triazoline-3,5-dione). Because the acidity constants for 4-phenylurazole (pK_a = 11.0) and the 4-phenylurazolyl radical (pK_a = 9 ± 2) differ by only 2 ± 2 pK_a units, detailed hypotheses that attempt to explain *why* the 4-phenylurazolyl radical is more acidic than 4-phenylurazole are probably unwarranted. It is therefore most appropriate to attempt to rationalize the high degree of acidity possessed by the 4-phenylurazolyl radical. Further discussion of this point can be found later in this article.

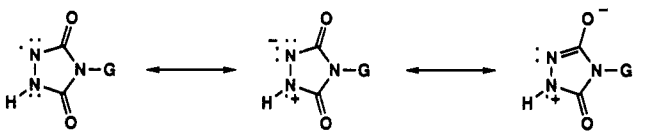
The present determination of the pK_a of the 4-phenylurazolyl radical is also relevant in rationalizing the "unusual" CV waves observed during the CV oxidation of the 4-phenylurazolide monoanion. It is likely that the anodically generated 4-phenylurazolyl radical is deprotonated by the 4-phenylurazolide monoanion present in solution, since the former is slightly more acidic than the conjugate acid of the latter. The deprotonation of the 4-phenylurazolyl radical (der iii in Scheme I) results in the formation of the radical anion derived from 4-phenyl-1,2,4-triazoline-3,5-dione, a species whose redox chemistry accounts for the second set of reversible waves noted previously in the CV oxidation of the 4-phenylurazolide monoanion. Similar conclusions are in order when analyzing the CV oxidation of the 4-methylurazolide monoanion, since the pK_a's for 4-methylurazole, the 4-methylurazolide monoanion, and the 4-methylurazolyl radical are 12.3, 26.0, and 9, respectively.

Supporting evidence for the relative thermodynamic stabilization of the conjugate bases derived from the 4-phenylurazolyl and 4-methylurazolyl radicals (2 + e$^-$, where G = Ph and CH_3, respectively) is obtained by noting the positive $E_{1/2}$ values (+0.38 and +0.31 V vs NHE_{aq}) obtained for the reduction potentials of 4-phenyl-1,2,4-triazoline-3,5-dione and 4-methyl-1,2,4-triazoline-3,5-dione (Table III). In addition, the CV reductions of 4-phenyl-1,2,4-triazoline-3,5-dione and 4-methyl-1,2,4-triazoline-3,5-dione are reversible. That the radical anions derived from 4-phenyl-1,2,4-triazoline-3,5-dione and 4-methyl-1,2,4-triazoline-3,5-dione are stable (in reference to protonation by DMSO) is further understood if one considers that the rather acidic nature of the 4-phenylurazolyl and 4-methylurazolyl radicals suggests that the respective conjugate bases derived from these species (i.e., the radical anions derived from 4-phenyl-1,2,4-triazoline-3,5-dione and 4-methyl-1,2,4-triazoline-3,5-dione) are highly stabilized entities.

Homolytic Bond Dissociation Energies (Table III). An accurate assessment of the *relative* homolytic strengths of labile N–H bonds present in organic molecules (ders i, ii, and iv in Scheme I) can be obtained by comparing (a) the N–H equilibrium acidities for the species at hand (exps i, ii, and der iii in Scheme I) and (b) the E_{ox} values for the conjugate bases derived from the species at hand (exps iii–v in Scheme I), as shown in eq 4 (all parameters in kcal/mol).[2a,2e] It has been demonstrated that relative BDEs obtained in this fashion can be converted into "absolute" BDEs that agree with gas-phase BDEs via the addition of a constant (ca. 56 kcal/mol) to the right side of eq 1.[1b,2c] N–H BDEs for 4-phenylurazole and 4-methylurazole (79 kcal/mol each), determined in this way, are indicative of substantial radical stabilizing effects that result from the presence of the heterocyclic acyl hdyrazyl [i.e., –NC(O)–] moiety adjacent to the site of odd electron density, since the DMSO-phase N–H BDE for acetamide is 107 kcal/mol.[22]

$$\Delta BDE\ (N\text{–}H) = \Delta pK_a(N\text{–}H) + \Delta E_{ox}(N^-) \qquad (4)$$

EPR spectra indicate that urazolyl radicals are ground-state π radicals.[15] Furthermore, since the a_{N-1}/a_{N-2} ratios for urazolyl radicals are similar to that for DPPH, it is likely that significant unpaired electron density is present on the trivalent hydrazyl nitrogen atom in urazolyl radicals, as shown in canonical forms 1 – H•**b** and 1 – H•**c**.[15]



A major reason, therefore, for the 28 kcal/mol difference in the homolytic strengths of N–H bonds found in acetamide and 4-phenylurazole is the delocalization of the unpaired electron to the (adjacent) trivalent nitrogen.

The ΔBDE data in Table III were obtained using eq 4 and data from Table I. The fact that N–H homolytic BDEs for the 4-phenylurazolide monoanion and 4-phenylurazolyl radical are within 3 kcal/mol of the N–H BDE for 4-phenylurazole itself is remarkable, in light of the varying nature of the three hydrogen-donating species (i.e., 1, 1 – H$^+$, and 1 – H$^\cdot$; all where G = Ph) and their respective dehydrogenated analogues (1 – H$^\cdot$, 2 + e$^-$, and 2). These data are the first of their kind, since to our knowledge there are no published gas-phase or solution-phase BDE data for the homolytic cleavage of N–H bonds present in neutral species possessing unpaired electron density.

Earlier in this article it was proposed that 4-substituents affect the stabilities of urazolide monoanions (1 – H$^+$) and

(20) (a) Using pulse radiolysis techniques: Asmus, K. D.; Henglein, A.; Wigger, A.; Beck, G. *Ber. Bunsenges Phys. Chem.* **1966**, *70*, 756–758. (b) Using ESR techniques: Laroff, G. P.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 1283–1288.

(21) Hoffman, M. Z.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 990–996.

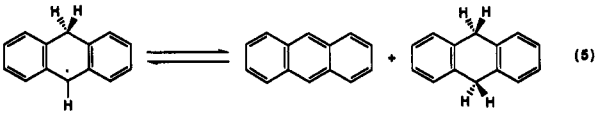
(22) Bordwell, F. G.; Algrim, D. J.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5903–5904.

triazolinedione radical anions (2 + e⁻) similarly, since a plot of the reduction potentials for the 4-G-1,2,4-triazoline-3,5-diones (2) vs the pK_a's for the analogously substituted 4-G-urazoles 1 is linear with unit slope (Figure 2). This supposition can be independently corroborated by comparing the N–H homolytic BDEs for 1 – H⁺, when G = CH_3 and Ph, since 1 – H⁺ and 2 + e⁻ (for a given G) differ only by a hydrogen atom. The ΔBDEs are determined via eq 4, using the pK_a values for 1 – H⁺ and the E_{ox} values for 1 – 2H⁺ (all data from Table III). The ΔBDE data indicate that the N–H bond in 1 – H⁺ is ca. 2 kcal/mol weaker (in a homolytic sense) when G = CH_3, compared to when G = Ph. An effect of this magnitude is supportive of the contention that 4-substituents affect the stabilities of urazolide monoanions (1 – H⁺) and triazolinedione radical anions (2 + e⁻) nearly equally. As stated previously, G-substituents in both 1 – H⁺ and 2 + e⁻ are not able to interact with the unpaired and/or negative electron density present in either species via resonance. This is a likely reason for the observed effects of 4-methyl and 4-phenyl substituents on the stabilities of 1 – H⁺ and 2 + e⁻.

Urazolyl Radical Acidities: A Rationalization. Outlining reasons for the highly acidic nature of the 4-phenylurazolyl radical (pK_a = 9 ± 2) is a challenging task. Inspection of the canonical forms 1 – H•**b** and 1 – H•**c** reveals that the 4-phenylurazolyl radical can be thought of as a nitrogen-centered radical cation. Aqueous pK_a's for the radical cations derived from phenothiazine (4–5[23a]), dimethylamine (6.5–7.5[23b]), and aniline (7[23c]) and the DMSO pK_a for the radical cation derived from phenothiazine (4.3[24]) suggest that nitrogen-centered radical cations are often quite acidic species.

The acidic properties of the 4-phenylurazolyl radical are therefore ascribed to a combination of (a) the radical cation-like nature of its 2N atom (the nitrogen that bears the acidic proton) and (b) the relatively large degree of thermodynamic stability possessed by its respective conjugate base, the radical anion derived from 4-phenyl-1,2,4-triazoline-3,5-dione [as indicated by the 0.38 V (vs NHE_{aq}) reduction potential for 4-phenyl-1,2,4-triazoline-3,5-dione].

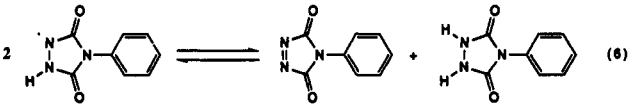
Disproportionations. A BDE of 45 kcal/mol has been suggested for the homolytic cleavage of the sp^3C–H bond found in the 9,10-dihydroanthryl radical,[25] a value some 30 kcal/mol smaller in magnitude than the 75 kcal/mol BDE determined for the sp^3C–H bond in 9,10-dihydroanthracene itself.[26] It follows that the disproportionation reaction of the 9,10-dihydroanthryl radical (as written in eq 5) is downhill (in an enthalpic sense) by about 30



(5)

kcal/mol. This result is not suprising in light of the expected thermodynamic driving force associated with the formation of anthracene.

As described earlier in this article, the N–H homolytic BDEs for 4-phenylurazole and the 4-phenylurazolyl radical are within ca. 2 kcal/mol of each other. A consequence of the near-equality of the BDEs for 4-phenylurazole and the 4-phenylurazolyl radical is that the disproportionation reaction shown in eq 6 is approximately thermoneutral.



(6)

It is therefore likely that the disproportionation mechanism invoked to rationalize the 4-phenylurazole induced acceleration of the deazadimerization reaction of 4-phenyl-1,2,4-triazoline-3,5-dione is in fact a reasonable explanation of the observed chemistry.[10c]

Summary

Data, facts, and relationships that have resulted from this research include the following: (a) experimentally determined equilibrium acidity constants (in DMSO solution) for 4-phenylurazolide and 4-methylurazolide monoanions (pK_a = 24.8 and 26.0, respectively); (b) derived equilibrium acidity constants for 4-phenylurazolyl and 4-methylurazolyl radicals (again in DMSO solution, pK_a = 9 and 9, respectively); (c) a linear relationship (with unit slope) between the reduction potentials for six 4-substituted triazolinediones and the equilibrium acidities of similarly substituted urazoles; and (d) homolytic N–H BDEs for 4-phenylurazole, the 4-phenylurazolyl radical, and the 4-phenylurazolide anion that are within 3 kcal/mol of each other.

We rationalize a–c as follows. Since the pK_a's for the urazolide anions are nearly equal to the equilibrium acidity constant for acetamide (pK_a = 25.5), it is likely that the negative charge in the urazolide anions is present on the oxygen atom three atoms removed from the acidic N–H proton. The fact that the 4-phenylurazolyl radical is slightly more acidic than its closed shell analogue 4-phenylurazole is rationalized by suggesting that substantial unpaired electron density is located on the trivalent (hydrazyl) nitrogen atom that undergoes deprotonation. The acidic nature of the urazolyl radical is therefore associated with its radical cation-like nature. The acidity of the 4-methylurazolyl radical is explained similarly.

The linear relationship depicted in Figure 2 is not unreasonable if the 4-substituents in the urazolide anions (1 – H⁺) and triazolinedione radical anions (2 + e⁻) do not interact with the unpaired and/or negative charge densities via resonance.

Finally, a consequence of the fact that the homolytic N–H BDEs for 4-phenylurazole and the 4-phenylurazolyl radical differ by only 2 kcal/mol is that the disproportionation reaction of the 4-phenylurazolyl radical is approximately thermoneutral.

Experimental Section

Materials. Dimethyl sulfoxide was purified, and potassium dimsylate was synthesized as described by Matthews and Bordwell.[27] $Et_4N^+BF_4^-$ was recrystallized from acetone and allowed to dry at 110 °C under vacuum before dissolution in DMSO. The syntheses of the 4-arylurazoles (1, where G = 3-ClC_6H_4, 4-ClC_6H_4, H, 4-$CH_3C_6H_4$, and 4-$CH_3OC_6H_4$) have been described previously,[28] while 4-methylurazole and 4-methyl-1,2,4-triazoline-3,5-dione were gifts from Prof. J. H. Hall. 4-(4-Methylphenyl)-

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1,2,4-triazoline-3,5-dione and 4-(3-chlorophenyl)-1,2,4-triazoline-3,5-dione appear to be new compounds.

The five different 4-aryl-1,2,4-triazoline-3,5-diones (2 where G = 3-ClC_6H_4, 4-ClC_6H_4, H, 4-$CH_3C_6H_4$, and 4-$CH_3OC_6H_4$) were synthesized via the following general procedure.[29] *N*-Bromosuccinimide (20 mmol) was added to an ice-cold suspension of urazoles (10 mmol) in 150 mL of CH_2Cl_2. After being stirred for 20 min, the resulting red solution was extracted five times with water. The CH_2Cl_2 layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting solution was chilled to -10 °C (freezer) overnight and gave pink to dark red crystals of the various triazolinediones. The yield (%), melting point, ^1H NMR, and elemental analyses are as follows: (a) **4-phenyl-1,2,4-triazoline-3,5-dione**, red solid, (82%); mp 169-180 °C (dec at lower temperature) (lit.[28b] mp 165-175 °C); ^1H NMR ($CDCl_3$) δ 7.41-7.60 (m, 5 H, aryl protons); (b) **4-(4-methoxyphenyl)-1,2,4-triazoline-3,5-dione**, brick red solid, (80%); mp 130-131 °C dec (lit.[30] mp 130-131 °C); ^1H NMR ($CDCl_3$) δ 3.85 (s, 3 H, CH_3), 7.0 (d, 2 H, *m*-H), 7.35 (d, 2 H, *o*-H); (c) **4-(4-chlorophenyl)-1,2,4-triazoline-3,5-dione**, cherry red crystals, (60%); mp 131-133 °C (expanded) (lit.[29] mp 130-132 °C); ^1H NMR ($CDCl_3$) δ 7.4 (d, 2 H, m-H), 7.55 (d, 2 H, m-H); (d) **4-(4-methylphenyl)-1,2,4-triazoline-3,4-dione**, deep purple crystals, (82%); mp 160-168 °C (dec before melting); ^1H NMR ($CDCl_3$) δ 2.4 (s, 3 H, CH_3), 7.3 (m, 4 H, aryl protons). Anal. Calcd for $C_9H_7N_3O_2$: C, 57.14; H, 3.70; N, 22.22. Found: C, 57.20; H, 3.75; N, 22.29;[31] (e) **4-(3-chlorophenyl)-1,2,4-triazoline-3,5-dione**, red crystals (70%); mp 109-110 °C (with dec); ^1H NMR ($CDCl_3$) δ 7.4-7.55 (m, 4 H, aryl protons). Anal. Calcd for $C_8H_4N_3O_2Cl$: C, 45.93; H, 1.91; N, 20.10; Cl, 16.75. Found: C, 45.91; H, 1.92; N, 19.96; Cl, 16.97.[31]

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(31) Elemental analyses performed by Atlantic Microlab, Inc.

Acidity Determinations. An overlapping indicator method identical to that described previously[3b] was utilized to acquire the acidity data listed in Table I. The acidity constants for the neutral urazoles have been published previously; these pK_a's are thought to be accurate to less than 0.1 pK_a unit (0.1 kcal/mol).[5] The 4-phenylurazole monoanion was equilibrated against 9-[*p*-(methylsulfonyl)phenyl]xanthene, 1,1,3-triphenylpropene, 9-*tert*-butylfluorene, and iminostilbene (pK_{H-A}'s for these indicators are 24.4, 25.6, 24.3, and 26.1, respectively),[3b] while the 4-methylurazole monoanion was equilibrated against 1,1,3-triphenylpropene, 9-(*m*-chlorophenyl)xanthene, and iminostilbene (pK_{H-A}'s for these indicators are 25.6, 26.6, and 26.1, respectively).[3b] The internal agreement for the data collected when measuring pK_a's for the 4-phenylurazole monoanion and 4-methylurazole monoanion is such that the uncertainties in the pK_a's for these species are ca. 0.2 pK_a units (0.3 kcal/mol).

Redox Determinations. Dimethyl sulfoxide electrochemistry: 0.1 M $Et_4N^+BF_4^-$ electrolyte; Pt working and Ag/AgI reference electrodes (ferrocene/ferrocenium = +0.875 V as internal standard, values corrected to NHE_{aq} by subtracting 0.125 V). In the argonated electrochemical cell, the substrates were present in 1-2 mmol concentrations. The E_{ox} values in Table I are the anodic peak potentials as reported by a BAS 100A electrochemical analyzer, are the averages of several runs for each compound, and are reproducible to ≤25 mV (ca. 0.5 kcal/mol). The $E_{1/2}$ values in Table I are the midpoints between the anodic and cathodic CV waves for the reversible redox reactions in question. Cyclic voltammetry sweep rate: 0.1 V/s, except where indicated.

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Fluorinated Tertiary Alcohols and Alkoxides from Nucleophilic Trifluoromethylation of Carbonyl Compounds

Stefan P. Kotun, John D. O. Anderson, and Darryl D. DesMarteau*

Department of Chemistry, H. L. Hunter Laboratory, Clemson University, Clemson, South Carolina 29634-1905

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$(CH_3)_3SiCF_3$ reacts with fluoro ketones in the presence of excess KF in CH_3CN to produce alkoxides derived from formal addition of CF_3^- to the carbonyl carbon. These alkoxides may be isolated as such or acidified to the corresponding alcohols. Ketones to which this technique was applied include $(CF_3)_2C{=}O$, $CF_3C(O)CF_2Cl$, $CF_3C(O)CF_2H$, and $[(CF_3)_2CF]_2C{=}O$. The last compound reacts with replacement of one of its perfluoroisopropyl groups by CF_3. With 2 equiv of TMS-CF_3, the acid fluorides RC(O)F (R = CF_3CF_2, *n*-C_3F_7, *n*-C_7F_{15}) yield products of the form $RC(CF_3)_2OX$ (X = K, H) due to both substitution and addition of CF_3 at the carbonyl. Similarly, $F_2C{=}O$ with 3 equiv of TMS-CF_3 provides a novel and high-yield synthesis of the perfluoro-*tert*-butoxide group. Phosgene does not appear to react directly with the TMS-CF_3/KF system, but is converted first to $F_2C{=}O$. The intermediate ketone $CF_3CF_2C(O)CF_3$ is observed in reactions of equimolar amounts of $CF_3CF_2C(O)F$ and TMS-CF_3.

Introduction

During an investigation into the chemistry of fluorine-containing hypohalites, we developed a need for highly-fluorinated tertiary alcohols and their alkoxides, especially $(CF_3)_3COH$ and $(CF_3)_3COM$. Perfluoro-*tert*-butyl alcohol is very expensive even when it can be found and is subject to severe availability problems. While we had developed a method for the preparation of certain longer-chain alcohols via ring-opening of fluorinated oxetanes with HF/SbF_5,[1] this and related superacid reactions[2] proved to be of limited generality. $(CF_3)_3COH$ can in fact be obtained using such a ring-opening approach,[3,4] but the cyclic precursor in this case is the epoxide of the extremely toxic[5,6] perfluoroisobutene, $(CF_3)_2C{=}CF_2$. Other known

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