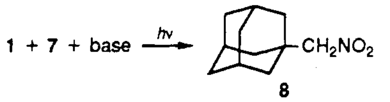
which suggests that it should be able to do so with bridgehead radicals.

As potassium *tert*-butoxide was shown to be a good electron donor in DMSO under photostimulation, we performed the photostimulated reaction of **1** with **7** in the presence of an excess of this base. We found a 30% yield of iodide ion, a small amount of **3** and a 27% yield of the substitution product 1-adamantylnitromethane (**8**)[15] (eq 8, base = t-BuO$^-$) (expt 12, Table I). These results suggest that even though **7** is unable to initiate the photostimulated $S_{RN}1$ reaction, it does propagate very efficiently the chain reactions.



8

(8)

In order to augment the photostimulated initiation step, we carried out the same experiment, but in the presence of **5a** together with 18-crown-6 (eq 8, base = $PhCOCH_2^-$). Under these reaction conditions we obtained a 64% yield of iodide ion, 58% yield of the substitution product **8** and a complete absence of the substitution product **6a** (expt 13, Table I). When the reaction was performed in the presence of **2** (eq 8, base = $CH_3COCH_2^-$), once again we obtained a high yield of iodide ion (93%) and the substitution product **8** (87% yield), with only a 2% yield of adamantane, and no substitution product **4** (expt 14, Table I). When the photostimulated reaction was carried out in the presence of p-dinitrobenzene, inhibition occurred (expt 15, Table I).

Based on the results herein obtained, we conclude that substrate **1** is able to react with carbanionic nucleophiles by the $S_{RN}1$ mechanism under irradiation in DMSO, thus opening an interesting synthetic route to build a new C–C bond in a bridgehead position.

Other features related to these reactions imply that the stronger the base used, the more it catalyzes the photostimulated initiation step (the pK_a's in DMSO are: acetone, 26.5; acetophenone, 24.7; and nitromethane, 17.2).[16] Furthermore, 1-adamantyl radicals are quite selective with these carbanionic nucleophiles; the apparent reactivity decreases in the order **7** > **6a** > **2** (inverse order of the respective pK_a's in DMSO). Further study on both the scope and limitations of this novel radical nucleophilic substitution at the bridgehead position with different carbanionic nucleophiles and different bridgehead halides is planned.

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[15] 1-Adamantylnitromethane was isolated by column chromatography (silica gel) eluted with petroleum ether–diethyl ether, 95:5: ^1H NMR (δ, relative to TMS) 1.70–2.50 (15 H, m), 4.30 (2 H, s); mass spectrum, m/e (relative intensity) 195 (0.29), 179 (0.48), 163 (8), 149 (100), 135 (13), 121 (17), 119 (23), 107 (26), 105 (23), 93 (53), 91 (28), 81 (61), 79 (61), 67 (75), 55 (38), 43 (27), 41 (33); high-resolution mass spectrum,[14] m/e 195.1249 (M$^+$, calcd 195.1259).

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Acidities of Arenium Ions in Acetonitrile[1]

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Summary: The pK_a's of benzenium, 1-naphthalenium, and 9-anthracenium in acetonitrile have been estimated to be −24.0, −19.7, and −9.1, respectively, by using a thermochemical cycle.

Carbocations derived by protonation of aromatic hydrocarbons—*arenium ions*—are important intermediates in organic chemistry. These species exist only as short-lived intermediates except in strongly acidic solutions. Consequently, all of the available thermochemical[3] and spectroscopic[4] measurements have been made in solvent systems such as superacids or liquid HF. Clearly, these data may not necessarily apply to polar organic solvents.

Table I. Oxidation and Reduction Potentials of Dihydroaromatic Derived Radicals[a]

radical	V vs SCE $E_{1/2}^{ox}$	 $E_{1/2}^{red}$
1a	−0.04	−1.78
1b	0.30	−1.70
2a	0.03	−1.69
2b	0.3[b]	*c*
3a	0.18	−1.40
3b	0.20	−1.36

[a] Measured by modulation voltammetry in acetonitrile/di-*tert*-butyl peroxide (9:1) containing 0.1 M tetrabutylammonium perchlorate using 53-Hz modulation and detection of the out-of-phase component. The potentials have an uncertainty of ±50 mV. [b] Reference 9, ±100 mV. [c] Reduction wave not observed due to high background current.

While it is not possible to make direct thermochemical determinations of the pK_a's of these intermediates in organic solvents, the values can be derived by using a thermochemical cycle (eqs 1–4).[5-8] In this work we report

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[3] (a) Mackor, E. L.; Hofstra, A.; van der Waals, J. H. *Trans. Faraday Soc.* **1957**, *54*, 66. (b) Mackor, E. L.; Hofstra, A.; van der Waals, J. H. *Trans. Faraday Soc.* **1957**, *54*, 186. (c) Perkampus, H.-H. *Adv. Phys. Org. Chem.* **1966**, *4*, 195 and references cited therein. (d) Arnett, E. M.; Larsen, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 792. (e) Arnett, E. M.; Larsen, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 1438.

[4] For example, see: (a) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299. (b) Buchanan, A. C., III; Dworkin, A. S.; Byrnestad, J.; Gilpatrick, L. O.; Poutsma, M. L.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5430. (c) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *J. Am. Chem. Soc.* **1980**, *102*, 5262. (d) Farcasiu, D. *Acc. Chem. Res.* **1982**, *15*, 46. (e) Farcasiu, D. *Adv. Chem. Ser.* **1987**, 285. (f) Farcasiu, D.; Marino, G.; Miller, G.; Kastrup, R. V. *J. Am. Chem. Soc.* **1989**, *111*, 7210.

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[6] A similar approach has been used to estimate the pK_a's of radical cations[7] and dications.[8]

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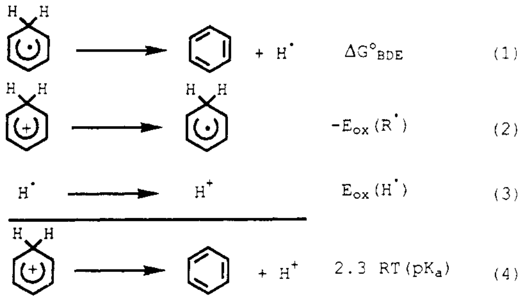
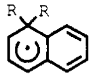


the pK_a's of three arenium ions in acetonitrile. The data allow us to assess the relevance of the thermodynamic data measured in strongly acidic media to reactions in organic solvents.

Using a technique that is described elsewhere,[9] we have determined half-wave potentials for the electrochemical oxidation and reduction of three dihydroarenyl radicals (**1**–**3a**) as well as those for the respective *gem*-dimethyl-substituted derivatives (**1**–**3b**) (Table I).[10] Combining these data with values for eqs 1[11] and 3[5] gives an estimate of the acidities (eq 4) of the arenium ions in acetonitrile.


1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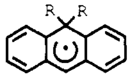
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(a) R = H
(b) R = Me

A relatively large cathodic shift was observed in the oxidation potentials of the radicals **1a** (340 mV) and **2a** (270 mV) as compared to the respective *gem*-dimethylated derivatives (**1b** and **2b**). There was essentially no effect on the oxidation of **3a** compared to **3b** nor on the reductions of **1**–**3a** versus the respective *gem*-dimethyl analogues. The cathodic shifts on the oxidations of **1** and **2** (undoubtedly a kinetic effect associated with the rapid loss of a proton from the carbocation generated at the electrode) preclude the use of these data for eq 2 since they will not have thermodynamic significance (i.e. $E_{1/2} \neq E°$).

Table II. Acidities of Carbocations at 300 K[a]

carbocation	$\Delta G°_4$ (kcal mol^{-1})	pK_a(MeCN)[b]	pK_a(HF)[c]
$1a^+$	-33.0	-24.0	-9.3
$2a^+$	-27	-19.7[d]	-4.2
$3a^+$	-12.6	-9.1	3.2

[a] Calculated from eqs 1–4. [b] $pK_a = \Delta G°_4/2.303RT$; the uncertainty in these values is ±2. [c] Measured in liquid HF, corrected for symmetry, ref 2a,b. [d] The uncertainty in this value is ±3.

The ^{13}C NMR spectra of $1\text{-}3a^+$ at low temperature in SO_2ClF[4a] suggest that benzannelation of $1a^+$ does not significantly increase the delocalization of the charge (in fact, it tends to localize the positive charge). The similarity of the oxidation potentials of **1**–**3b** is consistent with this conclusion and we have, therefore, used these potentials in the thermochemical calculations.

The pK_a's derived using eqs 1–4 are given in Table II. The loss of a proton from $1a^+$ or $2a^+$ is much more exoergonic than proton loss from $3a^+$, a result that is consistent with the magnitude of the observed cathodic shifts. Our ΔpK_a data also agree surprisingly well with the ΔpK_a's measured in liquid HF[3a,b] (Table II), suggesting that the relative thermodynamic data obtained in the strongly acidic media correctly describe thermodynamic differences in organic solvents.

The absence of a solvent effect on the relative pK_a's is remarkable since it implies that the there is a constant difference between the Gibbs solvation energies of the ions in the two media. A similar effect has been observed for the formation of cumyl and diarylmethyl carbocations in a number of solvents.[13,14] The small effects may simply be related to the relatively small Gibbs solvation energy of the delocalized ions (ca. -40 kcal mol^{-1})[9] compared to the proton (-258 kcal mol^{-1}).[5] In the present case, the change in solvation properties of the proton may account for much of the constant difference between the two sets of data.

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(9) Basically, this technique uses modulated photolysis for the generation of radicals with phase-sensitive electrochemical detection. Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(10) Radicals were generated by hydrogen atom abstraction from the appropriate dihydroaromatic compound using *tert*-butoxyl radical. 1,4-Cyclohexadiene and 9,10-dihydronaphthalene were commercially available. All other compounds were prepared by literature procedures. Radical **3b** was generated by hydrogen atom abstraction with *tert*-butoxyl radical from 1,1-dimethyl-1,2-dihdyronaphthalene. In this case two anodic waves were observed, at $E_{1/2} = 0.3$ V and at $E_{1/2} = 0.8$ V. We have assumed that these waves correspond to the oxidation of the abstraction product and addition product, respectively.

(11) Gibbs bond energies for **1**–**3a** are 17.1 ± 2, 23.0 ± 3, and 35.2 ± 2 kcal mol^{-1}, respectively. These values were derived from literature data[5,12] and by assuming that the entropy of the hydrocarbon and radical cancel ($T\Delta S = 8$ kcal mol^{-1}). The value for **2a** was based on an estimate of $\Delta H°_f$ (**2a**) using the MMX force field. This approach gave Gibbs bond energy values for **1a** and **3a** that were within 1 kcal mol^{-1} of the experimental values.

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Synthesis of Dihydro-1*H*-indenes via a Formal 3 + 2 Cycloaddition of *p*-Quinone Methides and Styrenes

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Summary: The synthesis of dihydro-1*H*-indenes via the formal 3 + 2 cycloaddition of an electron-rich alkene and a *p*-quinone methide is reported.

During the course of studies on the chemistry of *p*-quinone methides we have discovered a facile synthesis of dihydro-1*H*-indenes via a formal 3 + 2 cycloaddition.[1]

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