Experimental and Calculated Activation Parameters for Ring Opening of the 1-Bicyclo[1.1.1]pentyl Radical: The Effect of Bridgehead Substituents

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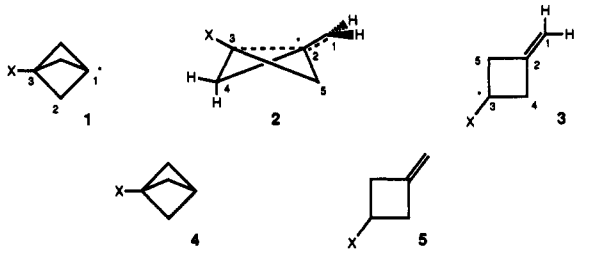
Ring opening of the 1-bicyclo[1.1.1]pentyl, 3-phenyl-1-bicyclo[1.1.1]pentyl, and 3-carbomethoxy-1-bicyclo-[1.1.1]pentyl radicals has been studied by experiment and by molecular orbital theory. Our results indicate that the parent system **1a** is extremely reluctant to ring open, with an energy barrier of at least 26 kcal mol^{-1}. The ester- and phenyl-substituted radicals rearrange somewhat more readily, with barriers of about 25 and 21 kcal mol^{-1}, respectively. This trend is also observed in the molecular orbital treatment of these processes. Previous reports that include radical rearrangements of this type must now be reconsidered in light of our new data.

Introduction

The kinetic stability of the 1-bicyclo[1.1.1]pentyl radical **1a**, in terms of its rearrangement to **3a**, is something of an enigma because of conflicting reports in the literature concerning reactions in which **1a** is—or is believed to be—an intermediate. Maillard and Walton[4] observed some years ago that the ESR spectrum of **1a** could be measured readily at temperatures up to ca. 40 °C. On the basis of the ESR experiments, the rearrangement of **1a** to **3a** was predicted to be kinetically unfavorable, with an activation barrier of at least 14.3 kcal mol^{-1}. Walton and his colleagues[5] had earlier predicted by MINDO/3 calculation that, despite the high exothermicity accompanying ring opening of the radical **1a**, the activation energy for the process would be significant (25.6 kcal mol^{-1}).

In the intervening years, an impressive array of experimental data has accumulated in the literature that supports the high activation barrier for the interconversion of **1a** to **3a**. For instance, the nature of the products derived from Barton halodecarboxylation of bicyclo-[1.1.1]pentane-1-carboxylic acid (**4d**) is consistent with the previous suggestions. Formation of the halides **4b**[6] and **4c**[7] from the acid **4d** is a radical process that involves the species **1a** and that proceeds in excellent yield without contamination by products derived from the ring-opened radical **3a**. Similarly, several research groups[8–17] have demonstrated that only 1,3-disubstituted bicyclo[1.1.1]-pentanes **6** are obtained from radical-induced opening of the propellane **7** in reactions that feature 3-substituted radicals of type **1** as intermediates.



a, X=H; **b**, X=Cl; **c**, X=Br; **d**, X=COOH; **e**, X=COOMe; **f**, X= Ph.

In contrast with the previous observations, photochemical chlorination of the parent hydrocarbon **4a** gives[18] a variety of products consisting of 1-chloro-, 2-chloro-, 1,2-dichloro-, 2,2-dichloro-, and 1,3-dichlorobicyclo[1.1.1]-pentanes (total 87%) in addition to the alkene 1-chloro-3-methylenecyclobutane **5b** (12%). The latter was suggested to arise from the rearranged species **3b**. More recently, Wiberg and Waddell[19] have shown that the reaction of [1.1.1]propellane (**7**) with electron-deficient alkenes, such as tetracyanoethylene, gives methylenecyclobutyl derivatives by what were tentatively described as radical processes.[19,20] Finally, in their study of the reaction of diphenylcarbene with **7**, Scaiano and his associates[21] have reported the formation of ring-opened products from the bicyclo[1.1.1]pentyl diradical intermediate **8**.

In an attempt to rationalize these data, we decided to evaluate the activation parameters for the process **1** → **3** by experiment and also by ab initio and semiempirical molecular orbital calculation. We now report the results of our investigations.

Results and Discussion

The Arrhenius activation parameters for the ring opening of **1** (**a**, **e**, and **f**) were estimated from determinations of the relative rate constants for rearrangement

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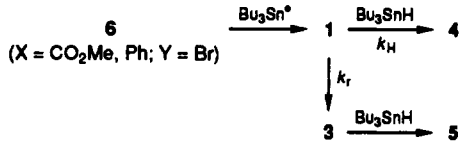
Table I. Percentage of 5f in the Total Product (4f and 5f) from the Reduction of 1-Bromo-3-phenylbicyclo[1.1.1]pentane by Tributylstannane (10^3 k_r/k_H in Parentheses)

T (°C)	$[Bu_3SnH]^a$ 0.010	0.024	0.047
140	17.5 (2.1)	8.8 (2.3)	4.1 (2.0)
150	28.2 (3.8)	12.1 (3.3)	7.6 (3.9)
160	37.6 (5.8)	19.2 (5.8)	9.8 (5.1)

[a] Pseudo-first order. Concentrations in M.

(k_r) and hydrogen abstraction (k_H) from tributylstannane at various temperatures. The rate constants were calculated from the ratios of the products 4 and 5 by employing pseudo-first-order kinetics with the standard relation (eq 1).



$$\frac{k_r}{k_H} = \frac{[5]}{[4]}[Bu_3SnH] \quad (1)$$

The ESR results of Walton,[4] together with our theoretical calculations (see later text, suggest that the activation energies for rearrangements of the type 1 → 3 would be at least 14.3 kcal mol^{-1}. Such large barriers to ring opening would necessitate the use of high reaction temperatures to drive the rearrangement, and low tributylstannane concentrations to allow a significant proportion of the intermediate radicals enough time to undergo the conversion 1 → 3 before being quenched. In practice, the determination was restricted in scope by the narrow range of suitable reaction temperatures, a consequence of the high temperature requirement. At temperatures below 130 °C, rearrangement was minimal, and at 170 °C, disappearance of the ring-opened products became apparent, presumably by reaction with tributylstannane. No further ring opening of radical 3 was observed, and in the absence of tributylstannane, the bromides 4c and 6 (X = Br; Y = Ph, COOMe) were unaffected by heating in solution at 160 °C for 10 min.

To avoid the possibility of premature reaction as the mixtures attained the required temperatures, tributylstannane solutions were thermally equilibrated for 10 min before a solution of the bromide 6 (Y = Br; 2–5 μL, ≤0.1 equiv) was injected into the Reacti-vial. Product analyses were performed using gas–liquid chromatography by direct comparison with authentic samples of 4 and 5.

Only the phenyl-substituted bicyclo[1.1.1]pentyl radical 1f underwent ring opening at sufficiently low temperatures to allow the activation parameters for the process to be determined with any reasonable degree of accuracy. The product distribution data are collated in Table I. The derived composite Arrhenius parameters (eq 2) were obtained in the usual fashion by a linear least-squares fit using the data in Table I (errors are expressed to 95% confidence) and can only be separated by using an approximation of the hydrogen-transfer parameters because the rate of reaction between 1 and tributylstannane has not, to our knowledge, been determined. Although 1 is a tertiary (bridgehead) radical, it is not clear that it would behave as such and, indeed, it may be more primary-like in nature. Fortunately, tributylstannane is relatively insensitive to the nature of the carbon-radical site.[22] The rates of hydrogen transfer between tributylstannane and primary and tertiary carbon-centered radicals, from eq 3 and 4, are approximately 1.5×10^7 and 8.0×10^6 M^{-1} s^{-1}, respectively, at 150 °C.

$$\log k_r/k_H = (6.4 \pm 1.2) - (17.1 \pm 2.3)/2.3RT \quad (2)$$

$$\log k_H = (9.1 \pm 0.3) - (3.7 \pm 0.4)/2.3RT \quad (3)$$

$$\log k_H = (8.4 \pm 0.1) - (2.9 \pm 0.2)/2.3RT \quad (4)$$

$$\log k_r = (15.5 \pm 2) - (21 \pm 3)/2.3RT \quad (5)$$

Table II. Calculated Data[a] for the Bicyclo[1.1.1]pentyl Radical 1a

	MINDO/3-RHF[b]	MINDO/3-UHF	UHF/3-21G	UHF/6-31G*
$r(C_1C_2)$	1.532	1.529	1.571	1.535
$r(C_1C_3)$	1.757	1.762	1.874	1.976
$r(C_2C_3)$	1.552	1.555	1.578	1.548
$r(C_2H)$	1.110	1.111	1.079	1.082
$r(C_3H)$	1.116	1.111	1.075	1.086
$\theta(C_1C_2H)$	120.6	120.6	116.5	117.2
ΔH_f^c	98.9	95.8		
E^d			-192.180420	-193.263781

[a] Distances in angstroms, angles in degrees. [b] From ref 5. [c] Heats of formation in kcal mol^{-1}. [d] Energies in hartrees (1 H = 627.5 kcal mol^{-1}).

The combination of eq 2 and 3 results in an approximate Arrhenius equation for the rearrangement of 1f (eq 5). The activation barrier of 21 ± 3 kcal mol^{-1} for the rearrangement of 1f is in excellent agreement with our calculations (see later text), and the rate constant for rearrangement of 1f (5.5×10^4 s^{-1} at 150 °C) reflects the reluctance of 1 toward rearrangement. The log A value of 15.5 ± 2 for this rearrangement, while being somewhat higher than that normally associated with intramolecular reactions in solution (12–14), overlaps with the expected range of values. In addition, there are several examples of radical rearrangements in which the preexponential term differs somewhat from expectation.[23] The ester-substituted bicyclo[1.1.1]phenyl radical 1e showed only minimal rearrangement under these forcing conditions, and the determination of the temperature dependence was not possible. With the reasonable assumption that 1e and 1f have similar preexponential terms, the small amount of rearranged product 5e produced at 170 °C (5.0%) represents an activation energy of about 25 kcal mol^{-1}, which is nearly 4 kcal mol^{-1} higher than that of 1f. The parent 1a failed to give any ring-opened products at all, indicating an even larger activation energy associated with the process 1a → 3a. Given that 3a would have been detected in quantities in excess of 1% by our GC techniques and assuming similar preexponential terms for the rearrangement of 1a and 1f, this represents a lower limit of about 26 kcal mol^{-1} for the rearrangement of the parent system 1a.

Owing to the difficulties associated with the determination of the experimental activation barriers, we felt that molecular orbital calculation would provide valuable supplementary data to those already discussed. In light of the MINDO/3 calculations reported by Walton[5] and our previous calculations on the rearrangement of the bicyclo[1.1.1]pentylium ion,[24,25] we felt that MINDO/3 (semiempirical) and ab initio molecular orbital theory would provide the most reliable theoretical data for the rearrangement of 1a. Consequently, the parent structure

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Table III. Calculated and Experimental Activation Energies[a] for the Bicyclo[1.1.1]pentyl Radicals 1a, 1e, and 1f

radical	MINDO/3 RHF	MINDO/3	3-21G	6-31G*	expt
1a	25.6[b]	21.5	22.2	25.8	>~26
1e	18.1	15.3			~25
1f	20.8	16.5			21 ± 3

[a] Energies in kcal mol^{-1}. Unless otherwise stated, all calculations are with the UHF wavefunction. [b] From ref 5.

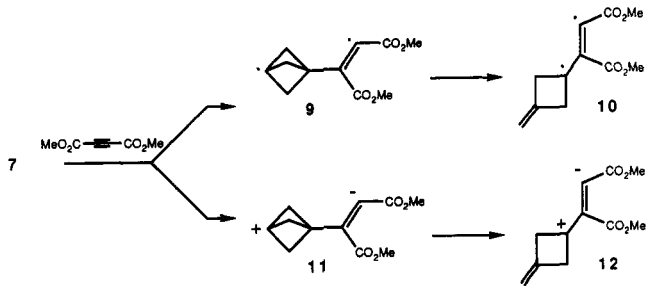
1a was located on the C_5H_7 potential energy surface using MINDO/3-UHF[26] and at 3-21G and 6-31G* (ab initio) levels of theory.

Standard semiempirical calculations were performed using the AMPAC[27] or MOPAC[28] (version 5.0) packages. Ab initio calculations were performed with the GAUSSIAN 82[29] or GAUSSIAN 90[30] program. Unless otherwise stated, the geometries of the various structures were determined at the unrestricted Hartree–Fock (UHF) level by applying gradient-optimization techniques.[31-36] All structures were proven as corresponding to minima or saddle points (transition states) on the potential energy surface by evaluation of the complete set of harmonic frequencies at each level of theory. Calculated structural data and energies are listed in Table II, together with the MINDO/3-RHF (half-electron) data of Walton.[5] The inclusion of polarization functions in the 6-31G* basis set makes this the superior method for application to highly strained systems. It is interesting to note that at this level of theory, the bridgehead–bridgehead separation in **1a** is calculated to be 1.98 Å. This is significantly larger than that calculated for the corresponding cation[25] (1.537 Å at RHF/6-31G*) and the parent hydrocarbon[37] (1.87 Å at RHF/6-31G*), suggesting that the through-space interaction in the radical is destabilizing.

The transition state **2a** for the rearrangement of **1a** to the 2-methylenecyclobutyl radical (**3a**) was located at each level of theory. The activation energy ($\Delta H^{\ddagger}$) for this reaction, as calculated at the various levels of theory, is listed in Table III, while the relevant structural data for **2a** and **3a** are displayed in Table IV. Surprisingly, MINDO/3 and 3-21G predict similar energy barriers for this rearrangement at 21.5 and 22.2 kcal mol^{-1}, respectively, while 6-31G* suggests that the barrier is 25.8 kcal mol^{-1}. It is curious to note that the MINDO/3-RHF data for Walton,[5] with a barrier of 25.6 kcal mol^{-1}, is in good agreement with the 6-31G* data.

It is interesting to note that the barrier for the rearrangement **1a** → **3a** as calculated using the MNDO,[38] AMI,[39] and (the new) PM3[40] Hamiltonians at 16.5, 9.8, and 11.0 kcal mol^{-1}, respectively, is significantly lower than the experimentally determined lower limit and the ab initio results. These data are not surprising as our previous work on the bicyclo[1.1.1]pentylium ion rearrangement[24,25] also revealed deficiencies in these NDDO-based methods. Electron correlation[31] may be expected to play an important role in these calculations. Single-point UMP2/3-21G//3-21G calculations on structures **1a** and **2a** suggest that the barrier for rearrangement could be as high as 33.0 kcal mol^{-1}.

Scheme I



The substituted radicals **1e** and **1f** proved to be too large to realistically model by ab initio theory. Nevertheless, we felt that MINDO/3 would provide, at the very least, a good qualitative picture of the details of these rearrangements. The calculated activation energies for the rearrangements of **1a**, **1e**, and **1f** are listed in Table III, together with the experimentally determined data.

The rearrangements of the substituted radicals **1e** and **1f** are predicted to be some 5–6 kcal mol^{-1} more favorable than the parent system **1a**. This is as expected on the basis of the stabilizing ability of the ester and phenyl substituents on both the transition state and product of the reaction.

It is interesting to note that the MINDO/3-RHF calculations, once again, provide the superior results, with excellent correlation between calculation and experiment for the barrier to rearrangement of **1f**. The MINDO/3-UHF calculated barriers underestimate the experiment barriers by about 5 kcal mol^{-1}. Futhermore, both methods suggest that the ester **1e** should be more prone to rearrangement than the phenyl-substituted radical **1f**. This is clearly not observed experimentally and might be the result of the MINDO/3 method overestimating the stability of ester-substituted radicals. It is known[41] that MNDO predicts a barrier substantially too high for the free rotation of the carbomethoxymethyl radical, and this may be reflected in MINDO/3.

All of the data in this study indicate the improbability of rearrangements of the kind **1** → **3** occurring in most instances and are in accord with earlier observations.[7-18] We believe that the reports cited in the literature that imply that rearrangements of this type are favorable can be accounted for by other mechanisms.

Wiberg and Waddell[19,20] consider both radical and zwitterionic mechanisms for the reaction between the propellane **7** and electron-deficient alkenes (Scheme I) and favor the former. Our data suggest that the radical mechanism is extremely unfavorable, i.e., if **9** is an intermediate, it is unlikely to undergo ring opening to give **10**. In contrast to the radical process, ring opening of the 1-bicyclo[1.1.1]pentyl cation, **11** → **12**, is expected to be especially rapid because the parent cation is predicted by

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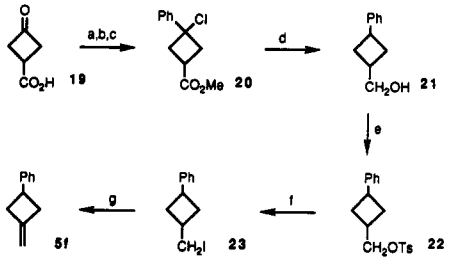
Table IV. Calculated Data[a] for the 2-Methylenecyclobut-1-yl Radical (3a) and the Rearrangement Transition State 2a

	2a			3a		
	MINDO/3	3-21G	6-31G*	MINDO/3	3-21G	6-31G*
$r(C_1C_2)$	1.421	1.468	1.452	1.329	1.312	1.316
$r(C_1C_3)$	2.034	2.072	2.062	3.428	3.429	3.408
$r(C_2C_3)$	1.808	1.949	1.905	2.098	2.117	2.092
$r(C_2C_4)$	1.532	1.561	1.532	1.527	1.543	1.527
$r(C_3C_4)$	1.517	1.562	1.530	1.485	1.531	1.514
$r(C_1H)$	1.106	1.075	1.077	1.099	1.074	1.076
$r(C_3H)$	1.110	1.075	1.084	1.093	1.068	1.073
$r(C_4H)$	1.111	1.078	1.082	1.115	1.084	1.088
$r(C_4H')$	1.111	1.081	1.086	1.115	1.084	1.088
$\theta(C_1C_2C_3)$	77.6	73.1	74.4	180.0	180.0	179.6
$\theta(C_3C_2C_4)$	53.3	51.4	51.5	45.1	46.3	46.3
$\theta(C_2C_3H)$	124.2	119.9	120.4	124.7	121.6	121.6
$\theta(C_2C_3H)$	172.5	177.7	179.0	180.0	180.0	165.2
$\theta(C_2C_4H)$	120.1	116.8	117.5	116.3	114.2	115.0
$\theta(C_2C_4H')$	118.7	115.6	115.6	116.3	114.2	114.8
$\omega(C_1C_2C_3H)$						0.0
$\omega(C_3C_1C_2C_4)$	-47.3	-45.2	-45.5			89.6
$\omega(C_3C_2C_4H)$	-115.0	-115.7	-115.5	118.7	116.4	116.9
$\omega(C_3C_2C_4H')$	114.3	110.5	111.0	-118.7	-116.4	-117.3
ΔH^b	28.1			12.4		
E^c		-192.144823	-193.222746		-192.232803	-193.312122

[a] Distances in angstroms, angles in degrees. [b] Heats of formation in kcal mol^{-1}. [c] Energies in hartrees (1 H = 627.5 kcal mol^{-1}). Calculations at the UHF level.

Scheme II[a]

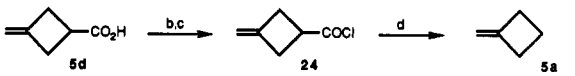


[a] Reagents: (a) PhMgBr; (b) MeOH/H$^+$; (c) HCl; (d) $LiAlH_4$; (e) TsCl/py; (f) NaI/DME; (g) ^{t}BuOK.

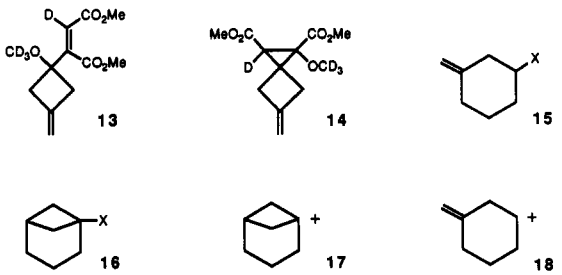
calculation[24] and has been found experimentally[7,42] to rearrange with little activation. Indeed, the formation of **13** and **14** when deuteriomethanol is used as solvent, is also strongly suggestive of a zwitterionic pathway, inasmuch as the parent carbocation cannot be trapped but gives ring-opened products exclusively in protic media.[7,42] On the other hand, the sluggish rate of rearrangement of the corresponding radical **9** (ca. 0.4 s^{-1} at 25 °C) would allow ample time for it to be trapped, even by a poor hydrogen atom donor such as methanol.[43]

Wiberg and Williams[18] identified **5b** among the products obtained from photoinduced chlorination of bicyclo[1.1.1]pentane (**4a**). It is clear from the results of the present study that **5b** cannot have arisen from the radical intermediate **3a** produced by ring opening of the bicyclic isomer **1a**. We suggest that the chloride **5b** represents an artifact, most likely being derived from rearrangement of 1-chlorobicyclo[1.1.1]pentane (**4b**) by an ionic mechanism. We have observed similar contamination by the alkenyl halides **15** (X = Br, Cl) in the corresponding samples of 1-bromo- and 1-chlorobicyclo[3.1.1]heptane (**16**; X = Br, Cl) upon prolonged standing or if subjected to column chromatography on silica gel. This has been attributed to rearrangement of the cation **17** (to **18**) produced by heterolysis of the carbon–halogen bond under these conditions. 1-Chlorobicyclo[1.1.1]pentane (**4b**),[42] like 1-bromobicyclo[3.1.1]heptane (**16**; X = Br),[44] is very susceptible to ionization; indeed, the rate of solvolysis of each of these bicyclic halides is faster than that of the *tert*-butyl halide.

Scheme III[a]



[a] Reagents: (b) NaH/THF; (c) $(COCl)_2$; (d) Na$^+$ $^-$O—NCH=CHCH=CHC=S/DMAP/Bu_3SnH.



The observation by Scaiano and co-workers[21] that the species **8** ring opens readily is not unexpected because **8** is a cyclobutylmethyl radical and such radicals have been reported[5,45-47] to rearrange readily. Indeed, we have recently observed that the bicyclo[1.1.1]pentylmethyl radical itself is prone to rapid rearrangement at subambient temperatures.

Syntheses. Access to the bicyclo[1.1.1]pentyl system was accomplished most conveniently using Michl's procedure[13] with [1.1.1]propellane (**7**) as precursor. The phenyl-substituted bicyclo[1.1.1]pentyl compounds **6** (X = Br; Y = Ph) and **4f** were synthesized from 3-oxocyclobutanecarboxylic acid (**19**)[48] following Applequist's me-

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(47) Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1987**, 231.
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thod,[49] which also provides access to the cyclobutyl derivative **5f**, an expected product of the radical ring opening reaction under investigation (Scheme II). The rearranged product **5f** was obtained from the chloride **20** by treatment with lithium aluminum hydride followed by conversion of the alcohol **21** into the tosylate **22** under standard conditions. Reaction of **22** with sodium iodide afforded the iodide **23**, which underwent elimination when treated with potassium *tert*-butoxide in 1,4-dioxane. This extra step is worthwhile because attempted elimination of the tosylate gives predominantly the substitution product.[50] A sample of methylenecyclobutane (**5a**) was prepared by reduction of the acid chloride **24**, which was itself derived from the reaction of oxalyl chloride with the sodium salt of 3-methylenecyclobutanecarboxylic acid (**5d**; Scheme III). We resorted to this method of generating the acid chloride **24** in preference to the conventional thionyl chloride mediated procedure because the latter was found to give a complex mixture of products.

Experimental Section

Semiempirical molecular orbital calculations were carried out on a PRIME 9955, SUN4/260, or Solbourne 5/602 computer. Ab initio calculations were performed on a CRAY-1S/2200 or SUN SparcStation 1+ computer. Melting points and boiling points are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 237 grating spectrometer. Routine ^1H NMR spectra were obtained on a Varian EM-360A spectrometer. ^{13}C and some ^1H NMR data were collected on a JEOL FX90Q instrument. All IR and NMR measurements were determined in CCl_4 solution unless otherwise stated, and chemical shifts relative to TMS are reported in ppm (δ). Mass spectra and high-resolution mass spectra (HRMS) were recorded on a Kratos MS25RF spectrometer, chemical ionization mass spectra (CIMS) were obtained using NH_3, and gas chromatographic samples were introduced via a Carlo Erba GC 6000 chromatograph equipped with an Alltech Associates RSL-150 (0.32 mm × 25 m) fused silica column. Analytical GC were performed on a Perkin-Elmer 8410 chromatograph using an Alltech Associates RSL-300 (0.53 mm × 30 m) fused silica column. Elemental analyses were carried out by the Australian Microanalytical Service.

1-Bromobicyclo[1.1.1]pentane (**4c**),[7] 1-bromo-3-phenylbicyclo[1.1.1]pentane (**6**; X = Br, Y = Ph),[51] methyl 3-bromobicyclo[1.1.1]pentane-1-carboxylate (**6**; X = Br, Y = COOMe),[49] bicyclo[1.1.1]pentane (**4a**),[18] and methyl bicyclo[1.1.1]pentane-1-carboxylate (**4e**)[52] were prepared by literature procedures as noted. Methyl 3-methylenecyclobutanecarboxylate (**5e**) was available from earlier work.

Methylenecyclobutane (5a). 3-Methylenecyclobutanecarboxylic acid (**5d**; 3.0 g, 26.8 mmol) was added dropwise to a stirred suspension of oil-free sodium hydride (1 equiv) in anhydrous tetrahydrofuran over 10 min under a nitrogen atmosphere. Removal of the tetrahydrofuran afforded the sodium carboxylate as a white solid to which *tert*-butylbenzene (5 mL) was added, followed by oxalyl chloride (3.3. g, 26 mmol). When the evolution of gas had ceased, the solution of the acid chloride **24** in *tert*-butylbenzene was added in a dropwise manner to a stirred mixture of the sodium salt of *N*-hydroxypyridine-2-thione (1.2 equiv), 4-(dimethylamino)pyridine (several mg), and tributylstannane (1.5 equiv) and the mixture heated to 65 °C and irradiated with light from a 300-W tungsten lamp. The flask was swept with nitrogen throughout the reaction, and after 2 h, the product that collected in a trap cooled in liquid nitrogen was analyzed (^1H and ^{13}C NMR) and shown to be **5a** by comparison of its spectral properties with those reported.[53] A solution of **5a** in *tert*-butylbenzene was prepared for use as a GC standard.

1-(Hydroxymethyl)-3-phenylcyclobutane (21). Methyl 3-chloro-3-phenylcyclobutanecarboxylate (**20**;[48] 1.5 g, 6.67 mmol) in THF (3 mL) was added to lithium aluminum hydride (0.9 g, 23.7 mmol) in tetrahydrofuran (8 mL) and the mixture stirred at reflux overnight. Normal workup followed by distillation (Kugelrohr, 100 °C (1.0 mm)) afforded **21** (74%) as a mixture of cis and trans isomers (10:90), whose ^1H NMR data were in accord with those reported by Escale *et al.*:[54] ^{13}C NMR δ 146.16 (C_{ipso}), 128.29 (C_m), 126.33 (C_o), 125.79 (C_p), 66.69 (CH_2O), 36.62 (C_1), 32.94 (C_3), 30.88 ($C_{2,4}$) for the trans isomer and 67.23 (CH_2O), 36.03 (C_3), 32.18 ($C_{2,4}$) for the cis isomer. The aromatic carbon resonances for the cis isomer were masked by those of the trans isomer.

1-[(Tosyloxy)methyl]-3-phenylcyclobutane (22). The alcohol **21** (0.6 g, 3.7 mmol) in dichloromethane (5 mL) and pyridine (1.5 mL) was cooled to 5 °C and then treated with *p*-toluenesulfonyl chloride (1.0 g, 5.2 mmol) in the usual manner to yield **22** (1.1 g, 94%) as a white solid: IR and ^1H NMR data were in accord with those reported by Escale:[54] trans isomer ^{13}C NMR δ 144.70 (C_{ipso}), 129.86 (C_o), 128.34 ($C_{m'}$), 127.91 (C_m), 126.23 ($C_{o'}$), 125.96 ($C_{p'}$), 73.57 (CH_2O), 36.13 (C_1), 30.61 ($C_{2,4}$), 29.96 (C_3), 21.62 (CH_3); the ipso carbon resonances for the tosyl group were not observed.

1-(Iodomethyl)-3-phenylcyclobutane (23). The tosylate **22** (0.8 g, 2.53 mmol) in 1,2-dimethoxyethane (6 mL) was heated with sodium iodide (4 equiv) at 65 °C for 4 h. After another 16 h at room temperature, the mixture was diluted with hexane (100 mL), washed with water (75 mL), and then dried ($MgSO_4$) and the solvent evaporated. Distillation (Kugelrohr, 86 °C (0.2 mm)) furnished a mixture of *cis*- and *trans*-**23** (10:90) as a colorless liquid (0.46 g, 65%): IR (neat) 3035, 2970, 2940, 2855, 1605, 1175, 750, 705 cm^{-1}; ^1H NMR (trans) δ 7.14 (br s, 5 H), 3.6–2.0 (m, 8 H); ^{13}C NMR (trans) δ 145.24 (C_{ipso}), 128.29 (C_m), 126.28 (C_o), 125.79 (C_p), 34.89 ($C_{2,4}$), 34.62 (C_3), 34.51 (C_1), 14.14 (CH_2I); mass spectrum *m/z* (relative intensity) 272 (7), 145 (100), 131 (37); HRMS calcd for $C_{11}H_{13}I$ 272.0061, found 272.0047.

1-Methylene-3-phenylcyclobutane (5f). *tert*-Butyl alcohol (1.5 mL) was added to a stirred suspension of oil-free potassium hydride (250 mg) in 1,2-dimethoxyethane (100 mL), under nitrogen, after which the iodide **23** (0.4 g, 1.47 mmol) was added. The mixture was warmed at 40 °C for 2 h and then diluted with hexane and washed thrice with brine before being dried ($MgSO_4$). The solution was concentrated and the residue distilled (Kugelrohr, 105 °C (108 mm)) (lit.[55] bp 90–95 °C (16 mm)) to deliver the exocyclic alkene **5f** (0.18 g, 85%): IR (neat) 3080, 3045, 2960, 2935, 1685, 1605 cm^{-1}; ^1H NMR δ 7.27 (br s, 5 H) 4.83 (quintet, J = 2.4 Hz, 2 H), 3.69–3.20 (m, 1 H), 3.15–2.68 (m, 4 H); ^{13}C NMR δ 146.00 (C_{ipso}), 128.34 (C_m), 126.44 (C_o), 125.96 (C_p), 105.69 (= CH_2), 145.62 (C_1), 39.71 ($C_{2,4}$), 34.89 (C_3); mass spectrum *m/z* (relative intensity) 144 (7), 129 (55), 105 (88), 104 (100), 91 (35), 77 (52); HRMS calcd for $C_{11}H_{12}$ 144.0934, found 144.0943.

1-Phenylbicyclo[1.1.1]pentane (4f). The bromide **6**[51] (X = Br, Y = Ph) (0.70 g, 3.14 mmol) and a catalytic amount of AIBN were dissolved in tributylstannane (2 equiv) and irradiated with UV light (450-W Hanovia mercury lamp at 15-cm separation) for 5 min. Excess tributylstannane was quenched with methyl iodide and the mixture distilled (Kugelrohr, 150 °C (30 mm)) to provide **4f** (0.34 g, 73%) as a colorless liquid: ^1H NMR ($CFCl_3$) δ 7.12 (s, 5 H), 2.50 (s, 1 H), 2.04 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 141.67 (C_{ipso}), 128.07 (C_o), 126.25 (C_m), 125.90 (C_p), 52.12 ($C_{2,4,5}$), 47.16 (C_1), 26.63 (C_3); CIMS *m/z* (relative intensity) 144 (13), 143 (38), 129 (46), 103 (39), 91 (12), 77 (20), 57 (100); HRMS calcd for $C_{11}H_{12}$ 144.0934, found 144.0934. Anal. Calcd for $C_{11}H_{12}$: C, 93.6; H, 6.4. Found: C, 93.6; H, 6.4.

Typical Kinetic Experiment. A septum-sealed Pyrex vial was purged with N_2 and charged with a measured quantity (0.2–0.5 mL) of a deoxygenated standard solution of tributylstannane, in benzene for substrates **6** (X = Br, Y = COOMe) and **6** (X = Br, Y = Ph) and *tert*-butylbenzene for the parent bromide **4c**. The vial was thermally equilibrated in a constant-temperature bath for 10 min before a solution of the substrate (<0.1 equiv) and AIBN in benzene (or *tert*-butylbenzene) was injected into the vial.

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The injected volumn was typically 2 μL and did not significantly change the total volume of the solution. The reaction times were between 10 and 40 min. Excess tributylstannane in the cooled mixture was quenched by the addition of methyl iodide. The samples were then analyzed by GC.

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Electrochemistry of Anilines. 6.[1] Reactions of Electrogenerated Biphenylylnitrenium Ions

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3,5-Di-*tert*-butyl-substituted biphenyl-4-ylnitrenium ions are generated by anodic oxidation of the corresponding biphenylylamines in acetonitrile in the presence of a base. The reactions of these species with several nucleophiles are studied. The principal reaction sites are identified as the positions ortho and para to the =NH moiety. No reactions at the iminium nitrogen and in the second ring of the biphenyl system are observed. Products are characterized by spectroscopic techniques. Some common spectroscopic features of the iminoquinolide reaction products are discussed.

Introduction

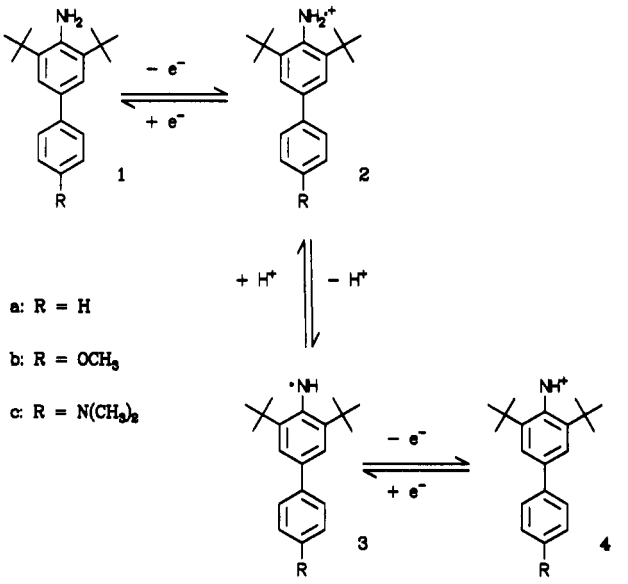
Investigations into the anodic oxidation of anilines 1 have shown[2] that *nitrenium ions* 4 are among the key intermediates of this reaction. Genies and Lapkowski have found spectroelectrochemical evidence for the involvement of a nitrenium ion in the electropolymerization of unsubstituted aniline.[3] A persistent ion **4c** has been characterized by spectroscopic and electrochemical methods.[4] The hypothesis has been formulated that the ions[5] are formed by an overall two-electron transfer via radical cations 2[6] and most likely the nitryl radicals 3 (Scheme I).

The proton-transfer equilibrium lies far to the radical cation side in acetonitrile,[6] but may be shifted to the neutral radical side in the presence of a base. The pathway from 1 to 4 corresponds to the ECE mechanism or one of its nuances.[7,8] Voltammetric evidence for this mechanism has recently been presented[9] in the case of 1-naphthylamine oxidation in DMSO.

Although the intermediate occurrence of secondary[10-14] and primary[3,15-17] nitrenium ions in the anodic oxidation of several anilines has been formulated, no systematic study of the reactions undergone by electrogenerated electrophiles of this type with nucleophiles has appeared to our knowledge.

In this paper, we report on chemical reactions of three electrogenerated biphenylylnitrenium ions **4a-c** with various nucleophiles.

Scheme I



Results and Discussion

Cyclic Voltammetry. Cyclic voltammograms of the anilines **1a-c** in acetonitrile in the presence of 2,6-lutidine (lu) were obtained (Figure 1). The anodic peaks increase to approximately twice their height in neutral solvent,

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