Intramolecular hydrogen transfer is not the only pathway available for tautomer **e**. Cleavage of its carbon–carbon bond is equivalent to step i of reaction 6. Reaction 8 thus links two of the photoionization reactions of 2-methoxyethanol. Hydrogen transfer via a four-member ring represents an alternative pathway for molecular ion **a** and ultimately leads to loss of water to give the molecular ion of vinyl methyl ether. This step is irreversible (and is not depicted). The overall water elimination is exothermic, since the *calculated* appearance potential is below 9 eV, far lower than the ionization potential of 2-methoxyethanol. Every other decomposition observed for the molecular ion is endothermic. The kinetic preference for a six-member cyclic transition state allows reaction 8 to compete, in spite of the large thermodynamic preference for vicinal elimination.

With PIMS[34] we can examine gaseous radical ions with near-thermal energy distributions. Detailed kinetic schemes for tautomerization and decomposition of the molecular ion of 2-methoxyethanol can be drawn, and there are, in principle, enough data to solve for relative rate constants and primary isotope effects. In practice, though, the uncertainties in our experimental measurements translate into huge fluctuations in the derived values, making it currently impossible to extract meaningful quantitative conclusions. With further refinement of PIMS techniques, it will in the future become possible to obtain relative rates for decompositions and isomerizations of gaseous cations that are as reliable as the data for neutral species.

Acknowledgment. We are grateful to Professor J. N. Pitts, Jr., and Dr. G. W. Harris in whose laboratory the photoionization experiments were conducted. Support of the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 10840-AC4), and the National Science Foundation (Grant CHE 81 27133) are gratefully acknowledged.

Registry No. $CH_3OCH_2CH_2OH^{+\cdot}$, 86012-96-6; $CH_3OCH_2CH_2CH_2OH^{+\cdot}$, 86012-97-7; $\cdot CH_2OCH_2CH_2OH_2^+$, 86023-99-6; $\cdot CH_2OCH_2CH_2CH_2OH_2^+$, 86024-00-2; $DOCH_2CH_2OCH_3$, 86012-98-8; $DOCH_2CH_2OCD_3$, 86012-99-9; $HOCD_2CH_2OCH_3$, 51255-53-9; $HOCH_2CH_2CH_2OCD_3$, 86013-00-5; 2-methoxyethanol, 109-86-4; 3-methoxy-1-propanol, 1320-67-8; 1,3-propanediol, 504-63-2; iodomethane-d_3, 865-50-9.

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[34] This acronym has two meanings: Photoionization Mass Spectrometry or Primary Ion Mass Spectrometry (see Maccoll, A. *Org. Mass Spectrom.* **1982**, *17*, 1–9). In the present context, both are meant.

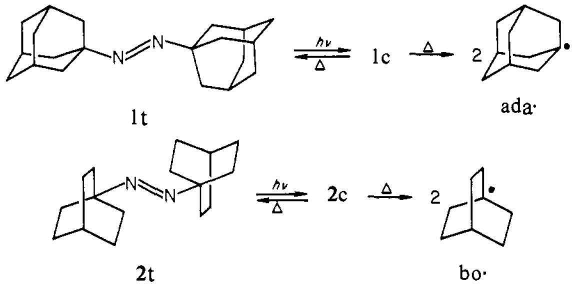
A Product Study of 1-Adamantyl and 1-Bicyclo[2.2.2]octyl Radicals in Hydrocarbon Solvents. An Unusually Large Hydrogen Isotope Effect

Paul S. Engel,*† Woo-Ki Chae,† Sharon A. Baughman,† Gregor E. Marschke,† Edward S. Lewis,† Jack W. Timberlake,‡ and Alan E. Luedtke‡

Contribution from the Departments of Chemistry, Rice University, Houston, Texas 77251, and University of New Orleans, New Orleans, Louisiana 70122. *Received February 4, 1983*

Abstract: 1-Adamantyl (ada·) and 1-bicyclo[2.2.2]octyl (bo·) radicals have been generated by photolysis of the corresponding azoalkanes in various hydrocarbon solvents. Both radicals abstract hydrogen readily from saturated hydrocarbons and they add to aromatic rings much faster than *tert*-butyl· does. Despite its reactivity, ada· is remarkably selective in hydrogen atom abstraction, preferring a benzylic hydrogen 25:1 over a cyclohexane hydrogen. The effect of solvent viscosity indicates that formation of the radical dimers biada and bibo occurs in the solvent cage. The most striking result of this work is a deuterium isotope effect of 25 for hydrogen transfer from cyclohexane to ada· at 65 °C. Steric compression in the transition state is postulated to cause an unusually large tunnel correction and hence a large k_H/k_D.

We have recently shown that irradiation of *trans*-azo-1-adamantane (**1t**) and *trans*-azo-1-bicyclo[2.2.2]octane (**2t**) produces the cis isomers (**1c** and **2c**) which undergo competing loss of nitrogen and reversion to trans.[1] Since thermolysis of these cis isomers occurs at relatively low temperatures and produces only nitrogen as a byproduct, irradiation of **1t** and **2t** at 65 °C is a particularly clean method for generating 1-adamantyl (ada·) and 1-bicyclo[2.2.2]octyl (bo·) radicals. Unlike *tert*-butyl·, whose principal fate is disproportionation,[2] these tertiary bridgehead radicals are forced either to recombine or to react with the solvent. Most previous product studies[3-6] of bridgehead radicals were qualitative only and were confined to a limited number of solvents. These earlier studies employed peresters to generate the desired radicals, leading to additional *tert*-butoxy-containing products. Presently, we show that unlike peresters, **1t** and **2t** give the symmetrical recombination products 1,1′-biadamantyl (biada) and 1,1′-bis(bicyclo[2.2.2]octyl) (bibo) in up to 50% yield. The free ada· and bo· add more readily to the ring of benzene and toluene than does *tert*-butyl; however, the two radicals seem to exhibit comparable reactivity toward side-chain hydrogen abstraction from toluene. Finally, extremely large isotope effects are demonstrated for hydrogen abstraction by bridgehead radicals.



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† Rice University.
‡ University of New Orleans.

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Table I. Product Yields (%) from 1-Adamantyl Radicals in Aromatic Solvents

solvent	temp, °C	ada-H	biada	Ar–ada	other	total[a]
benzene	21	20	46	18		84
benzene	65	29	32	31		92
benzene	100	33	21	17		71
benzene[b]	300	42	29	2	38[c]	73
benzene-d_6	65	14	31	21		66
toluene	65	46	26	2	33[d]	76
toluene-d_1[e]	65	42	24	3	27[d]	69
toluene-d_3[e]	65	19[f]	52	21	10[d]	92
cumene	65	55	30		25[g]	86
C_6F_6	65	2	23			25

[a] Product balance calculated as in text. [b] Thermolysis. [c] Biphenyl. [d] Bibenzyl calculated like biada yield. [e] Side-chain deuterium. [f] 78% ada-D, 22% ada-H by GC/MS. [g] Bicumyl.

Table II. Product Yields (%) from 1-Adamantyl Radicals at 65 °C

solvent	ada-H	biada	total
n-pentane[a]	63	21	84
n-hexadecane	29	38	67
cyclohexane	58	33	91
cyclohexane-d_{12}	47	38	85
t-BuOD	32[b]	45	77
none[c]	0	100[d]	

[a] 12% decanes also seen by GC/MS. [b] Shown to be only ada-H. [c] Irradiation of solid *trans*-azo-1-adamantane, much of which was unreacted. [d] Only product observed.

Table III. Product Yields (%) from 1-Bicyclo[2.2.2]octyl Radicals at 65 °C

solvent	bo-H[a]	bibo[b]	other	total
n-pentane	82	17		99
cyclohexane	57	26		83
toluene-d_1	55	28	32,[c] 7[d]	90

[a] Bicyclo[2.2.2]octane. [b] 1,1-Bis(bicyclo[2.2.2]octyl). [c] Bibenzyl. [d] Bicyclo[2.2.2]octyltoluenes.

Table IV. Isotope Effects for $R\cdot + XH \rightarrow RH + X\cdot$

R·	XH	temp, °C	k_H/k_D	ref
ada·	$PhCH_2D$	65	11.4	this work
ada·	$PhCH_3 + PhCD_3$	65	9.2	this work
ada·	$c\text{-}C_6H_{12} + c\text{-}C_6D_{12}$	65	26.2	this work
ada·	$c\text{-}C_6H_{12} + c\text{-}C_6H_{11}T$	65	24.9[a]	this work
bo·	$PhCH_2D$	65	15.6	this work
bo·	$PhCH_3 + PhCD_3$	65	14.4	this work
bo·	$c\text{-}C_6H_{12} + c\text{-}C_6D_{12}$	65	32.3	this work
ada·	*t*-BuSH	25	1.9	9
$Ph_3C\cdot$	mesityl-SH	25	9.4[a]	10
Ar·	$ArC(CH_3)_3$	−30	80[b]	11
$CH_3\cdot$	$PhCH_3$	65	10.8	12
Ph·	$PhCH_3$	60	4.5	13
$CD_3\cdot$	C_2H_6	65	9.3	14
$PhC(CH_2)_2$[c]	$ArCD_3$	(25)[d]	23[b]	15
$CH_3\cdot$	CD_3CN	−163	1100	16
$(CF_3)_2NO\cdot$	$PhCH_3$	65	10.8	17

[a] Calculated from the tritium isotope effect. [b] Intramolecular hydrogen transfer. [c] 1-Phenylcyclopropyl. [d] Assumed.

Results

Degassed 0.02 M solutions of **1t** and **2t** were irradiated in sealed tubes with 366-nm light from a filtered high-pressure mercury arc lamp until the UV spectrum showed that no azoalkane remained. GC analysis of the products employed an external rather than an internal standard because the bridgehead radicals are likely to react with virtually any organic compound. Yields were calculated as follows: yield of RH = mmol RH/(2 × mmol azoalkane), yield of RR = mmol RR/mmol azoalkane, where RH is hydrogen abstraction product and RR is biada or bibo. The yield of aryl addition products was based on twice the number of mmoles of azoalkanes as in the case of RH; thus, the product balance equals the sum of these three yields.

The results, which are summarized in Tables I–III, show product balances averaging about 80%. Formation of some nonvolatile compounds is hardly surprising and will be discussed below. The study of **2** was less comprehensive than that of **1** because only a small fraction of the photochemically produced cis isomer decomposed to free radicals.[1] Since most of the light was wasted, irradiation times became excessive. Thermolysis of **1t** was done successfully in benzene at 300 °C but several attempts to carry out this experiment with **2** led inexplicably to explosion of the sealed tubes.

Products were identified by comparison of GC retention times and mass spectra with those of the following authentic materials: adamantane, 1,1′-biadamantyl, 1-adamantylbenzene, bibenzyl, bicumyl, bicyclo[2.2.2]octane, and bis(1-bicyclo[2.2.2]octyl).[7] Friedel–Crafts alkylation[8] of toluene with 1-bromoadamantane afforded the pure para isomer. The mother liquors showed another GC peak assumed to be the meta isomer,[8c] which was also present in irradiated **1t** in toluene; however, the latter contained a third peak which was most likely 1-benzyladamantane, on the basis of previous work.[4c] This assignment is supported by the absence of the third peak in toluene-d_3 where D· abstraction is unfavorable.

The decrease of ada–H and the increase of biada in deuterated solvents (cf. Table I) suggested the existence of an isotope effect for the abstraction step. In order to quantify this effect, **1t** was irradiated in $PhCH_2D$ and the adamantane formed was analyzed for deuterium content by GC/MS. Similar experiments in 1:1 mixtures of $PhCH_3 + PhCD_3$ and $c\text{-}C_6H_{12} + c\text{-}C_6D_{12}$ led to the results shown in Table IV, which includes selected values from the literature. Since the molecular ion is the base peak for adamantane and bicyclo[2.2.2]octane, mass spectral ananlysis should be straightforward.[18] Nevertheless, known mixtures of ada–H plus ada–D were analyzed by GC/MS to ensure that the large isotope effects in Table IV were valid. As seen in the Experimental Section, the observed H/D ratios were close to the actual ones. Further confirmation of the measured isotope effects was obtained for the case of ada· plus cyclohexane by the use of tritium. A 0.15 M solution of **1t** was photolyzed to completion in tritiated cyclohexane of specific activity (*a*) 5.68 × 10^{10} dpm/mol. The adamantane was isolated by preparative GC, its activity determined, and the tritium isotope effect calculated from k_H/k_T = *a*(cyclohexane)/(12 × *a*(adamantane)). The observed value of 103 corresponds to a deuterium isotope effect of 24.9, in good agreement with the mass spectral value (cf. Table IV).

Anomalously large isotope effects would be observed if some adamantane arose from a source besides solvent hydrogen abstraction. Unlikely though it seems, disproportionation of adamantyl radicals would be such a source. This possibility was checked by irradiating **1t** to completion in 80:20 methanol–toluene, the toluene being added to dissolve **1t**. It is known that adamantene is efficiently trapped by methanol[19] but no 1-methoxy-

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[7] The authors are grateful to Professor Howard E. Zimmerman for an authentic sample of this dimer.

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Table V. Products from ada· and *tert*-Butyl· in Mol per 100 Mol of Azoalkane Decomposed

precursor	concn, M	temp, °C	solvent	RH[a]	RR[a]	RAr[a]	$Me_2C=CH_2$	$(PhCH_2)_2$	Ph-CH_2R[a]
ATB[b]	0.1	80	benzene	84	18	0.5	63		
1t	0.02	65	benzene	56	32	62			
ATB[b]	0.0203	60	toluene	111	10	0	52	20	13
1t	0.02	65	toluene	92	26	4		33	2

[a] R represents ada· or *tert*-butyl·. [b] Azo-*tert*-butane from ref 30.

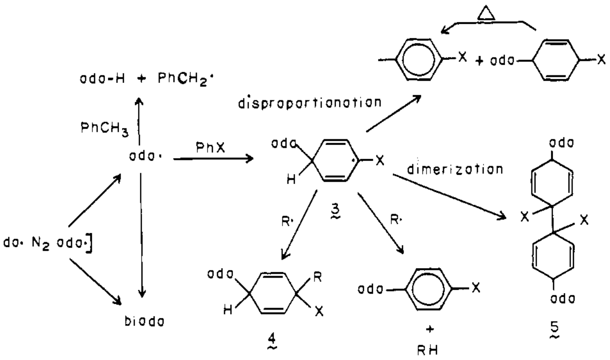
adamantane was seen by GC/MS. In a similar experiment, **1t** was photolyzed in 99% toluene-d_3 and the mass spectrum of the adamantane formed was compared with that of authentic ada–D. The ratio of m/e 136 to m/e 137 peak intensities was 0.357 in the former vs. 0.281 in the known ada–D. This difference indicates a molar ada–H/ada–D ratio in the irradiated sample of 0.079, which, after correction for the 52% biada yield, means that 6.5% of the ada· radicals might disproportionate.[20] This amount has only a small effect on our k_H/k_D values; for example, if k_H/k_D were 20, the mass spectral analysis would give 21.6. Furthermore, the 6.5% figure is a maximum since a small amount of the good hydrogen donor $PhCD_2H$ in the toluene-d_3 would give rise to an anomalously large m/e 136 peak. Thus adamantyl radicals do not disproportionate significantly under the present experimental conditions and the large isotope effects have no such unusual origin. The possibility that **1t** itself was an unexpected source of H· was discounted by the realization that at a concentration of 0.02 M, **1t** would have to be an outrageously good hydrogen donor in order to compete with the solvent. Similarly, biada is not a source of H· because the biada isolated from the tritium experiment was devoid of activity.

Discussion

The high reactivity of ada· and bo· is apparent from the observations that these radicals abstract hydrogen even from *tert*-butyl alcohol and that they readily attack the benzene ring. It seemed likely, therefore, that all of the observed dimer was formed in the solvent cage since radicals which escape would have little chance of finding one another. If this notion were valid, the yield of dimer should depend on solvent viscosity.[21-23] The measured GC yields of biada are subject to considerable uncertainty (e.g., % biada = 32 ± 6 for four determinations in benzene at 65 °C), probably because this compound is relatively insoluble and nonvolatile. Nevertheless, the results for pentane and hexadecane (Table II) are as expected for a solvent viscosity effect. bo· radicals behave similarly in that the bo-H yield is highest and the bibo yield lowest in the least viscous solvent (pentane, Table III). The decreasing yield of biada with increasing temperature in benzene (Table I) is also in accord with the known temperature dependence of the cage effect. A plot of ln ((1-biada)/biada) vs. $1/T$ gave a value for E_a(diffusion) − E_a(cage recombination) of 1.5 kcal mol^{-1}, comparable to the 1.3 kcal mol^{-1} found for cumyl radicals.[24]

To confirm that biada forms only in the solvent cage, the cage effect in toluene was determined independently by the excess scavenger technique. As detailed in the Experimental Section, the value obtained was 37% at 24 °C. This value was corrected to 65 °C by using an activation energy of 1.3 kcal mol^{-1}.[24] The resulting value of 28% agrees with the 26% biada yield in Table I. Further evidence for the validity of our interpretation is the fact that the bibo yields are close to those of biada in three solvents, despite the greater reactivity of bo· than ada·.[25] Finally, we note that if biada were formed outside the solvent cage in toluene, its yield should be lower in cumene, which is a better hydrogen donor.[26] Reference to Table I shows this not to be the case. The highest cage effect should appear in solid azoalkane; in fact, irradiation of crystalline **1t** gives only biada.

Scheme I. Possible Reactions of ada· in Aromatic Solvents[a]



[a] X represents CH_3, H, or F while R can be ada· or $PhCH_2$·. For simplicity, only para attack on the aromatic nucleus is shown.

According to Table I, adamantylbenzene is a major product but adamantyltoluene is unimportant unless the toluene side chain is fully deuterated. This observation is explained by Scheme I, which shows the possible reactions of ada· in aromatic solvents. Although side-chain hydrogen abstraction dominates in toluene, removing the methyl group or decreasing its reactivity by deuteration allows attack upon the aromatic nucleus. The fate of adduct radical **3** is well-known from studies of homolytic arylation of benzenes.[27-29] Perfluorobenzene exhibited a very low product balance and TLC of the reaction mixture showed that in contrast to the other cases, much material remained at the origin. These results are reasonable in light of Scheme I because the adduct radical **3** (X, H = F) can only recombine to form non-volatile products like **4** and **5**. Similar considerations apply in the case of C_6D_6, whose adamantyl adduct is less likely to disproportionate than is the adduct of C_6H_6. In toluene, benzyl radicals react with **3** (X = CH_3) to give **4**, which would not be detected in the present GC analysis. It is likely that all adamantane formed in toluene arises by side-chain and not ring attack. Support for this statement comes from the low yield of adamantyltoluenes in $PhCH_3$ and $PhCH_2D$ coupled with the fact that the amount of adamantane derived from ring attack cannot exceed the yield of adamantyltoluene. Moreover, the adamantane formed in $C_6H_5CD_3$ is 78% deuterated despite the large isotope effect of side-chain hydrogen abstraction (Table IV).

It is interesting to compare the behavior of ada· with that of *tert*-butyl·, for which product data are available in benzene and toluene.[18,23,30] As seen from the results in Table V, attack upon the benzene ring is much more prominent for ada·. Further evidence for the unreactivity of *tert*-butyl· toward benzene is the

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(20) Let k_1 be the rate constant for disproportionation of adamantyl radical pairs, k_2 that for solvent D abstraction, and k_3 that for ada· recombination. The 52% yield of biada in toluene-d_3 can be assumed to equal that in toluene-d_8 so that $k_3/(k_1 + k_2 + k_3) = 0.52$. The observed molar ada-H/ada-D ratio suggests that $k_1/(2k_2) = 0.079$. It follows that $k_1/(k_1 + k_2 + k_3) = 0.065$.

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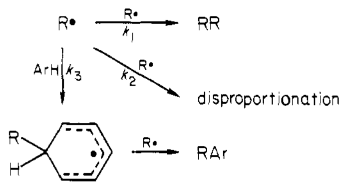
Scheme II



absence of an ESR signal due to cyclohexadienyl radicals.[28] The difference in behavior between ada· and *tert*-butyl· can be attributed either to ada· attacking the aromatic ring with a larger rate constant than *tert*-butyl· does or to slower self reaction of ada· than *tert*-butyl·. Of course, *tert*-butyl· disproportionates 4.6 times as often as it recombines[2] while ada· does not disproportionate (see above). If the recombination rate constant were the same for the two radicals, one would expect about five times as much ring attack by ada·. Instead, the data in Table V show more than a 100-fold increase in alkylbenzene yield, implying that ada· radicals recombine more slowly or attack benzene faster than *tert*-butyl· radicals do. Although the front strain of ada· is calculated to be about 7% greater than *tert*-butyl·,[31] 1,1′-biadamantane thermolyzes at the same rate and possesses the same strain energy as hexamethylethane.[32] The recombination rate constant of the two radicals is therefore not likely to differ much; hence, the proposal that ada· attacks benzene much faster than does *tert*-butyl· is the more likely explanation. In fact, Tiecco and co-workers[4] have nicely demonstrated the high propensity of bridgehead radicals for homolytic aromatic substitution.

A simplified scheme in which alkyl radicals react either with themselves or with benzene allows an estimate of the relative rate constants (cf. Scheme II). Because the product balance is very high in benzene (cf. Table V), the yield of RAr is $k_3[\mathrm{ArH}]/(k_1[\mathrm{R}\cdot] + k_2[\mathrm{R}\cdot] + k_3[\mathrm{ArH}])$. For R· = *tert*-butyl·, $k_2 = 4.6k_1$ and the RAr yield is 0.25%, while for R· = ada·, $k_2 = 0$ and the RAr yield is 32%. With the assumption of the same k_1 for both radicals, one calculates that k_3 is 33 times larger for ada·. Pryor[30] has stated that more electrophilic radicals attack the benzene nucleus more readily, suggesting that ada· is more electrophilic than *tert*-butyl·. Good evidence exists that *tert*-butyl· is more nucleophilic than ada·,[4] and that ada$^+$ is more electrophilic than *tert*-butyl$^+$.[34] Since a σ-type radical[35] such as ada· contains the odd electron in an orbital with greater s character than does a π-type radical like *tert*-butyl·,[36] it is entirely reasonable that ada· is more electrophilic than *tert*-butyl·.

Besides their relative reactivity in aromatic substitution, ada· and *tert*-butyl· can be compared as hydrogen atom abstracting agents. Beckhaus et al.[32] have recently calculated that ada· is only slightly strained, so that it is not expected to be much more reactive than *tert*-butyl· on purely energetic grounds. Indeed, ada· might be less reactive if steric effects are considered.[31] The ability of these radicals to produce benzyl-containing products from toluene can be used to evaluate reactivity on the basis of Scheme II with k_3 representing H· abstraction. The yield of benzyl products is 27% and 34% from *tert*-butyl· and ada·, respectively.[37] Since *tert*-butyl· has available a reaction pathway which ada· does not (disproportionation), *tert*-butyl· actually must be a more reactive hydrogen abstractor if similar yields of benzyl products are to be produced. It is again assumed that k_1 is comparable for the two radicals. The reactivities become more nearly equal if the 24% product deficiency from ada· in toluene consists of nonvolatile benzyl-containing compounds. In view of the elegant work of Fischer in determining absolute rate constants for hydrogen atom transfer from toluene to *tert*-butyl·,[38] it would be interesting to apply this technique to ada·. For the present, it appears that the two radicals exhibit comparable reactivity toward toluene side-chain hydrogen abstraction.

When **1t** was photolyzed in an equimolar mixture of toluene-d_8 and C_6H_{12}, the ada–H/ada–D ratio came out 1.43. Since the isotope effect for toluene is 9.2, one readily calculates that toluene is 6.4 times more reactive than cyclohexane toward ada·. A statistical correction reveals that a benzylic H is 25 times more reactive than a secondary hydrogen, a figure which can be compared with 3.2 for methyl and 1.0 for phenyl radicals.[26] It follows that ada· is a highly selective hydrogen atom abstractor, comparable in fact to the *tert*-butylperoxy radical.[39] This selectivity contrasts sharply with the nonselectivity of ada· in halogen abstraction.[35,40]

No biphenyl was detected in benzene except upon thermolysis of **1t** at 300 °C, implying that the activation energy for aromatic ring hydrogen abstraction is large. This result is in accord with the high Ar–H bond strength and with a report[12] that methyl radicals abstract ring hydrogens from toluene only at high temperatures. The yield of biphenyl in the 300 °C thermolysis (Table I) is over 6 times greater than the 6% reported by Golzke et al. for the same type of experiment.[41]

As seen in Table IV, isotope effects for hydrogen transfer to bridgehead radicals range from about 12 to 32. These k_H/k_D values not only exceed the calculated maximum of 6.1 at 65 °C, but they are larger than any found in the literature at a comparable temperture (cf. Table IV).[42] Since isotope effects are governed by loss of stretching and bending vibrations in the transition state and a tunnel correction, one or both of these factors must be unusually large for bridgehead free radicals. Inclusion of bending modes in the calculation raises k_H/k_D from 5.1 to 9.5 for methyl radical abstractions,[43] insufficient to account for the present results. Hence, tunneling[44] is left as the most plausible explanation of our enormous isotope effects.

Tunneling arises in a hydrogen transfer when the reaction barrier is high and thin. Such a barrier might exist when the transfer is sterically hindered since compressional energy is a steep function of distance.[45] Although no good example of this effect has come to light, it is not unreasonable to invoke steric hindrance in bridgehead hydrogen transfer because these radicals are subject to considerably more F (front) strain than, say, methyl.[31] An alternate explanation for a thin barrier is that the internal strain of bridgehead radicals is suddenly relieved as they proceed to hydrocarbons. Similar reasoning could apply to a recent study of intramolecular hydrogen abstraction via a stretched transition state.[11] Although the high internal strain known in bridgehead cations[46] is calculated not to carry over to the radicals,[29,47] there is experimental evidence for internal strain at least in bo·.[48] The lower isotope effect seen in toluene than in cyclohexane (Table IV) is likely due to the fact that the C–H bond strength of cyclohexane is much closer to that of adamantane than is the bond strength of toluene.

In summary, we have found that ada· behaves as a reactive but selective radical toward aromatic and aliphatic solvents. Due to its electrophilicity, ada· adds more readily to aromatic rings than does *tert*-butyl· but the two radicals exhibit comparable reactivity

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[33] The possible complications of radical–arene complexes, a low *A* factor for recombination of ada· due to its spherical shape, and reversibility of k_3 are neglected.

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Table VI. Normalized Integrated Mass Spectral Peak Intensities

sample	*m/e* 135	136	137	138	ada-H/ada-D[a]
ada-H	33.90	100.0	11.55		
ada-D		28.09	100.0	11.98	
1:1 ada-H:ada-D	29.30	100.0	87.63	10.21	0.99
4:1 ada-H:ada-D	32.44	100.0	34.59	3.08	3.92 (3.48)
1:4 ada-H:ada-D	23.82	100.0	190.31	20.70	0.25
9.22:1 ada-H:ada-D	39.20	100.0	21.44		9.50 (7.92)
18.64:1 ada-H:ada-D	40.80	100.0	16.35		19.9 (15.11)
$h\nu$, 1t-1.22:1 C_6H_{12}:C_6D_{12}	33.82	100.0	14.55	1.17	32.0
$h\nu$, 1t-1:1 $PhCH_3$:$PhCD_3$	33.22	100.0	21.78		9.18
$h\nu$, 1t-1:1 C_6H_{12}:toluene-d_8	29.98	100.0	68.06	7.23	1.43
$h\nu$, 1t-toluene-d_8	7.25	35.71	100.0	13.25	0.079
$h\nu$, 1t-toluene-d_3	12.66	54.21	100.0	10.90	0.278

[a] Calculated from eq 1. Values in parentheses were calculated from eq 2 and 3.

in benzylic hydrogen abstraction. The observed products can be rationalized on the basis of the viscosity-dependent cage effect and the intermediacy of cyclohexadienyl radicals in aromatic solvents. Large isotope effects for hydrogen atom transfer to bridgehead radicals are postulated to arise from steric compression in the transition state or from strain relief as the bridgehead radicals proceed to hydrocarbons.

Experimental Section

The synthesis of azoalkanes **1t** and **2t** has been described previously.[1,41]

Adamantane-*1-d*. The general method of Kuivila was used.[49] To a flame-dried flask was added 0.60 g (2.8 mmol) of 1-bromoadamantane, 0.90 g (3.1 mmol) of tri-*n*-butyltin deuteride, and 25 mL of dry benzene. AIBN (2 mg) was added and the reaction mixture heated to reflux. After 2 h the solution was cooled to room temperature and poured into ice water and the organic phase was separated. The benzene layer was washed with brine (15 mL), dried over $MgSO_4$, filtered, and concentrated. The adamantane-*d* was recrystallized from acetone to give 0.15 g (39%); mp 258–262 °C (sealed tube).

Product Analysis. Products from **1** and **2** were analyzed on a 6 ft. by $^1/_8$ in. column of 10% SE-30 on Chromosorb W. Solutions of the known products and *n*-tetradecane were used to obtain response factors. Peak areas were determined by means of a disk integrator or an on-line computer.

Deuterium Isotope Effect. Deuterium analysis of adamantane and bicyclo[2.2.2]octane in the irradiated mixtures was performed on a Finnigan 3300 gas chromatograph/mass spectrometer. Two formulas were used to calculate the ratio of ada-H to ada-D from mass spectral peak intensities. The more reliable method depended upon knowing the mass spectrum of pure ada-H and ada-D (cf. Table VI). Using the designations h_1–h_9 for intensities of the *m/e* 136–138 peaks as shown below, eq 1 was derived.

	m/e 136	137	138
ada-H	h_1	h_2	h_3
ada-D	h_4	h_5	h_6
mixture	h_7	h_8	h_9

$$\frac{\text{ada-H}}{\text{ada-D}} = \frac{(h_8/h_7)(h_4/h_5) - 1}{(h_2/h_1) - (h_8/h_7)} \qquad (1)$$

Inserting the known ratios from Table VI reduced this formula to ada-H/ada-D = $(0.281R - 1)/(0.1155 - R)$, where R is h_8/h_7. Its accuracy was checked by analysis of five known mixtures which gave good agreement with the actual ada-H/ada-D ratios (cf. Table VI). A method which we employed earlier did not require knowing the individual spectra of ada-H and ada-D but it gave reasonable answers only when the percentage of deuterium was small. The formulas were as follows:

$$\text{ada-H} = \frac{h_8 \pm h_8^2 - 4h_7h_9}{2} \qquad (2)$$

$$\text{ada-D} = h_9 - 0.11(\text{ada-H}) \qquad (3)$$

Tritiated Cyclohexane. In order to ensure that the same impurities were present in cyclohexane and cyclohexane-*t*, both were prepared from the same bottle of bromocyclohexane. The Grignard reagent[50] from 132 g of freshly distilled bromocyclohexane was added slowly with good stirring to 20 mL of ice-cold water. A 20-mL portion of 10% HCl was added to dissolve all solids. The organic layer was washed with water, twice with aqueous $NaHCO_3$, twice with aqueous $KMnO_4$, and three times with saturated NaCl solution and finally dried over $MgSO_4$. The cyclohexane was distilled through a 30-cm glass helices packed column (bp 80 °C). Tritiated cyclohexane was prepared in the same manner from 2 g of bromocyclohexane and 0.33 mL of T_2O. The dried ether layer was combined with the "cold" cyclohexane and the product was again distilled through the 30-cm column. The yield was 50 mL of "hot" cyclohexane which showed no impurities by GC except 0.5% cyclohexene. Its specific activity was determined by scintillation counting as 5.68×10^{10} dpm/mol.

Tritium Isotope Effect. The tritium isotope effect was measured in three separate experiments, of which the following is typical. Azo-1-adamantane (147 mg) was dissolved in 3.0 mL of cyclohexane-*t* and the solution was degassed and sealed in a Pyrex tube. After irradiation at 65 °C for 5 h with a 500W mercury short-arc lamp through a Corning 7-60 glass filter, UV analysis showed that no azoalkane remained. The tube was opened and the solvent was removed by bulb-to-bulb distillation. To the residue was added 1 mL of cyclohexane-h_{12}, which was then distilled off to aid removal of cyclohexane-*t*; this procedure was repeated. The majority of the white solid residue was dissolved in 0.3 mL of toluene, some of the biadamantane remaining behind. Adamantane was isolated from this solution by preparative GC on a $^1/_4$ in. × 8ft OV-17 column programmed from 80 to 230 °C at 2°/min. Because biadamantane tended to plug the detector, it was operated at 400 °C with the injector at 300 °C. The collected adamantane was sublimed, yielding 25.8 mg of product. The efficiency of the scintillation counter was determined as 56% and the background as 25 counts/min (cpm). The isolated adamantane gave 4920 cpm corresponding to a specific activity of 4.59×10^7 dpm/mol. Dividing this value into the *a* of cyclohexane-*t* and dividing the result by the statistical factor of 12 gave an isotope effect k_H/k_D of 103.1. The two other experiments gave values of 112.3 and 104.3; however, these are considered less reliable because the isolated yield of adamantane was low (plugging of detector).

Determination of Cage Effect. An evacuable two-chamber cell was constructed for this purpose, the chambers being separated by a break seal. The lower one, a square cuvette, contained the radical scavenger and the upper one contained a solution of **1t** in toluene. Both chambers were degassed and sealed under vacuum and the absorbance of the scavenger (2,2,6,6-tetramethyl-1-oxypiperidine) was determined. *cis*-Azoadamantane was then generated by irradiating the upper chamber at 0 °C. The seal was broken and the **1c** was allowed to warm up in the presence of scavenger. A visible spectrum revealed the amount of scavenger remaining while determination of the nitrogen evolved gave the amount of **1c** which had decomposed.

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Registry No. **1t**, 24325-56-2; **2t**, 78497-37-7; ada•, 2819-03-6; bo•, 2697-21-4; H, 1333-74-0; D, 7782-39-0; $PhCH_3$, 108-88-3; c-C_6H_{12}, 110-82-7.

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