

# Generation of Bicyclo[3.2.0]hept-6-ene-2,4-diyl Radical Cations by Chemical Electron Transfer (CET) with Trisarylamminium Salts and Intramolecular Cyclobutene Trapping as an Alternative Entry to the Quadricyclane–Norbornadiene Valence Isomers

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**Abstract:** For the first time, chemical electron transfer (CET) studies have been conducted for the tricyclo[3.2.0.0<sup>2,4</sup>]hept-6-enes **2** and the quadricyclanes **3** in solution. The 2,4-dimethyl-substituted bicyclo[3.2.0]hept-6-ene-2,4-diyl radical cation **2a**<sup>•+</sup>, generated by trisarylamminium salt oxidation of **2a**, is intramolecularly trapped by the juxtaposed cyclobutenyl double bond to afford the quadricyclane radical cation **3a**<sup>•+</sup> in addition to the expected 1,2-methyl migration to the bicyclo[3.2.0]hepta-2,6-diene radical cation **6a**<sup>•+</sup>. Radical cation **3a**<sup>•+</sup> leads to the norbornadiene **4a** by valence isomerization and the bicyclo[3.2.0]hepta-2,6-diene **5a** by skeletal rearrangement. For comparison, oxidation of quadricyclane **3a** yields exclusively norbornadiene **4a**. Whereas the 2,4-diphenyl-substituted bicyclo[3.2.0]hept-6-ene-2,4-diyl radical cation **2b**<sup>•+</sup> derived from **2b** is intramolecularly trapped by the juxtaposed cyclobutenyl double bond to afford norbornadiene **4b** and bicyclo[3.2.0]hepta-2,6-diene **5b** through the quadricyclane radical cation **3b**<sup>•+</sup>, the quadricyclane **3b** yields on oxidation also **5b** besides **4b**. These experimental facts are rationalized in terms of distinct radical cation structures, namely the  $\pi$  complex (oxidation of the lateral cyclopropane bond) and trimethylene (oxidation of the internal cyclopropane bond). Their preferences are dictated by the substrate structure, i.e., tricycloheptene **2** versus quadricyclane **3** as well as by the substitution type (phenyl versus methyl) and is corroborated by AM1 calculations.

## Introduction

1,3-Cyclopentadienyl radical cations derived from 2,3-diazabicyclo[2.2.1]hept-2-ene-type (DBH) azoalkanes and bicyclo[2.1.0]pentanes (housanes) exhibit a high tendency for rearrangement by 1,2-hydrogen or 1,2-alkyl (spiroalkyl) shift, as confirmed earlier by liquid-phase PET<sup>1</sup> and recently by CET studies,<sup>2</sup> and by ESR spectroscopy on  $\gamma$ -irradiated material under matrix isolation.<sup>1a,c,3</sup> Such rearrangements do not occur in significant amounts, if at all, in the corresponding 1,3-diradicals.<sup>4</sup> While for the 1,3-cyclopentadienyl trapping experiments with dioxygen<sup>5</sup> or nitroxides<sup>6</sup> as diradical scavengers were applied as mechanistic tools, such trapping studies are rare for the corresponding 1,3-diyl radical cation intermediates. However, for other radical cation systems there do exist numerous studies on reactions with nucleophiles. Besides trapping of 1,2-radical cations through intermolecular reactions with alcohols, amines, and nitriles<sup>7</sup> or through intramolecular reactions,<sup>8,9</sup> the scaveng-

ing of distonic radical cations is also known.<sup>10</sup> It was reported recently that radical cations generated through SET from monocyclic and bicyclic azoalkanes were efficiently trapped by methanol or acetonitrile;<sup>11</sup> however, attempts to scavenge intermolecularly radical cations derived from DBH derivatives or housanes with these nucleophiles were futile.<sup>12</sup>

Previous intramolecular trapping experiments in our laboratory with an olefinic alkyl chain,<sup>13</sup> linked at the bridgehead position of DBH, also failed. Instead of addition to the 1,3-diyl centers, only two rearranged cyclopentenes were isolated. This result suggested that the rate of the intramolecular addition of the radical cation to the double bond was too low to compete with 1,2-hydrogen migration or electron back-transfer (BET) at the stage of the 1,3-diyl radical cation. Nevertheless, similar radical cation intermediates could be trapped by a hydroxy-functionalized alkyl chain and, thereby, spiro ethers were

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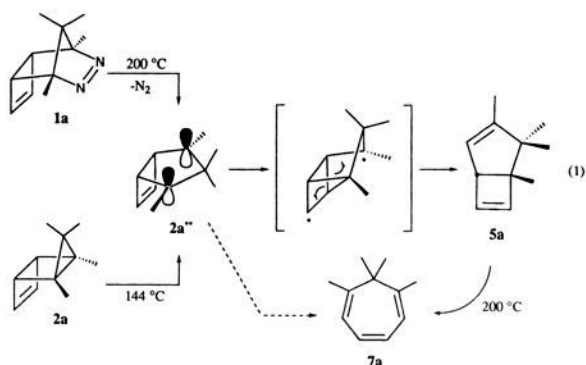
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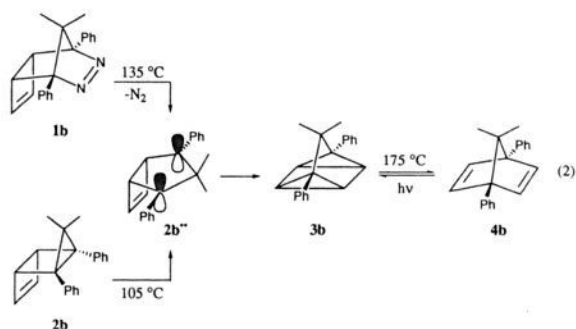
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isolated as cyclization products.<sup>14</sup> However, definitive conclusions were precluded due to the involvement of intermediary allyl cations, which mimic radical cation trapping.

In view of these uncertainties on genuine intramolecular trapping of distonic radical cation species, we searched for a suitable model and selected the tricyclo[3.2.0.0<sup>2,4</sup>]hept-6-ene ring system for the present study. On one hand, this structure contains the bicyclo[2.1.0]pentane moiety for generation of the desired 1,3-cyclopentadienyl radical cation by facile electron transfer oxidation of the central bond; on the other hand, the juxtaposed double bond through cyclobutene annelation should serve the purpose for intramolecular trapping. Furthermore and most convenient, its diradical chemistry was already examined by Paquette *et al.* in the early 1970s.<sup>15</sup> Thus, thermolysis of azoalkane **1a** (eq 1) or housane **2a** generates bicycloheptadiene **5a** and tropyliene **7a**. The products were rationalized in terms



of skeletal rearrangement. In contrast, the phenyl derivative **2b** or its azoalkane precursor **1b** yield exclusively quadricyclane **3b** on thermolysis (eq 2), which rearranges at higher temperatures further to norbornadiene **4b**. Indeed, the formation of



quadricyclane **3b** suggests intramolecular trapping of the 1,3-diradical **2b''** by the juxtaposed cyclobutene group.<sup>15</sup>

Recently we have shown that chemical electron transfer (CET) with *tris*(aryl)aminium salts constitutes an effective method to minimize electron back-transfer to 1,3-cyclopentadienyl radical cations derived from bicyclo[2.1.0]pentanes.<sup>2</sup> The intermediary 1,3-diyl radical cations are generated catalytically and rearrange regio- and diastereoselectively to the corresponding cyclopentenes.<sup>2</sup> Since intermediary donor-acceptor radical ions, i.e., contact ion pairs (CIP), solvent-separated ion pairs (SSIP), and free ions (FI), are not formed in the CET compared to the photoinduced electron transfer (PET) mode, alternative reaction channels for the 1,3-radical cation are minimized and excellent yields (>95%) of defined rearrangement products are obtained.

In the light of these relevant findings, it appeared worthwhile to examine the CET behavior of cyclobutene-annelated azoalkanes **1**, housanes **2**, and the quadricyclanes **3**. The fact that intramolecular trapping of the short-lived 1,3-diradical **2''** was demonstrated, encouraged such trapping of the hitherto unknown 1,3-diyl radical cation **2''+**! Indeed, presently we report the successful intramolecular trapping of such novel 1,3-radical cations to afford, among other rearranged products, the norbornadienes **4a,b**.<sup>16</sup> Our study provides valuable mechanistic insight into the chemical fate of radical cations derived from housanes **2** and quadricyclanes **3**.

## Results

**Synthesis of Starting Materials.** The azoalkanes **1a,b** were prepared according to the Paquette procedure<sup>15</sup> by cycloaddition of the corresponding isopyrazoles<sup>17</sup> with cyclobutadiene, which was generated *in situ* by ceric ion oxidation of cyclobutadieneiron tricarbonyl.<sup>18</sup> Hydrogenation of azoalkane **1b** with the palladium-on-charcoal catalyst afforded quantitatively azoalkane **1b**(H<sub>2</sub>).<sup>19</sup> Photolysis of azoalkanes **1** yielded tricycloheptenes **2a,b**<sup>15</sup> and tricycloheptane **2b**(H<sub>2</sub>)<sup>19</sup> (entries 1–4 and entry 6, Table 1). Quadricyclane **3b**<sup>15</sup> was obtained by thermolysis of azoalkane **1b** at 135 °C (entry 5, Table 1) and also by thermolysis of tricycloheptane **2b** at 105 °C (entry 12, Table 1). The hitherto unknown tetramethylquadricyclane derivative **3a** was obtained by benzophenone-sensitized irradiation ( $\lambda > 300$  nm) of norbornadiene **4a** (*vide infra*) and isolated by preparative GC. Norbornadiene **4b**<sup>15</sup> was prepared by thermolysis of quadricyclane **3b** at 175 °C (entry 17, Table 1).

**Electron Transfer Reactions of the Hydrocarbons **2** and **3**.** The product data are summarized in Table 1. Thus, catalytic oxidation of the bridgehead dimethyl-substituted tricycloheptene **2a** with *tris*(*p*-bromophenyl)aminium hexachloroantimonate (TBA<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>)<sup>20</sup> afforded, independent of the solvent and within the error margins, the same product distribution of 1,4,7,7-tetramethylnorbornadiene (**4a**), 3,4,4,5-tetramethylbicyclo[3.2.0]hepta-2,6-diene (**5a**), and the bicycle **6a** with two allylic methyl groups (entries 7–9, Table 1). The three reaction products were separated by means of preparative gas chromatography, and the identity of **5a** was confirmed by comparison with the literature spectral data.<sup>15</sup> The structures of the hitherto unknown 2,3,4,4-tetramethylbicyclo[3.2.0]hepta-2,6-diene (**6a**) and norbornadiene **4a** were assigned on the basis of their spectral data and homonuclear decoupling and NOE experiments. The structure of the rearrangement product **4a** follows also from the highly symmetrical nature of its NMR spectrum (see Experimental Section).

Contrary to the tetramethyl case **2a**, the diphenyl-substituted derivative **2b** afforded upon electron transfer oxidation the two products **4b** and **5b** in the nonpolar solvent chloroform (entry 10, Table 1) and in the polar acetonitrile (entry 11, Table 1) a third unknown product (18%), whose structure could not be determined due to decomposition during attempted silica gel

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**Table 1.** Product Studies of the Photolysis, Thermolysis, and Chemical Electron Transfer (CET) Reactions of the Azoalkanes **1**, Tricycloheptenes **2**, and Quadricyclanes **3**

entry	substrate		reaction conditions <sup>a</sup>	solvent	conv. <sup>b</sup> (%)	mb <sup>b</sup> (%)	product distribution (%) <sup>b</sup>						
	structure	R					2	3	4	5	6		
1		1a	Me	hv (333-364), 20 °C	CDCl <sub>3</sub>	100	>98	100					
2		1b	Ph	hv (333-364), 20 °C	CDCl <sub>3</sub>	100	>98	98	2				
3		1b	Ph	hv (333-364), 20 °C	CD <sub>3</sub> CN	100	>98	98	2				
4		1b	Ph	hv (364 nm), Ph <sub>2</sub> CO	CDCl <sub>3</sub>	100	>98	100					
5		1b	Ph	135 °C, 3 h	Cl <sub>2</sub> CCl <sub>2</sub>	>95	>97		100				
6		1b(H <sub>2</sub> )	Ph	hv (333-364), 20 °C	CDCl <sub>3</sub>	100	>98	100					
7		2a	Me	TBA <sup>+</sup> , 20 °C	CDCl <sub>3</sub>	100	95	[c]		66	10	24	
8		2a	Me	TBA <sup>+</sup> , 20 °C	CD <sub>3</sub> CN	100	95	[c]		64	11	25	
9		2a	Me	TBA <sup>+</sup> , 20 °C	CH <sub>2</sub> Cl <sub>2</sub>	100	96	[c]		64	11	25	
10		2b	Ph	TBA <sup>+</sup> , 20 °C	CDCl <sub>3</sub>	100	95	[c]		18	82		
11		2b	Ph	TBA <sup>+</sup> , 20 °C	CD <sub>3</sub> CN	100	95	[c]		30	70	[d]	
12		2b	Ph	105 °C, 3 h	CDCl <sub>3</sub>	>95	>97	[c]	98	2			
13		2b(H <sub>2</sub> )	Ph	TBA <sup>+</sup> , 20 °C	CDCl <sub>3</sub>	100	99	[c]					100
14		2b(H <sub>2</sub> )	Ph	TBA <sup>+</sup> , 20 °C	CD <sub>3</sub> CN	100	97	[c]					100
15		3a	Me	TBA <sup>+</sup> , 20 °C	CDCl <sub>3</sub>	100	97	[c]	100				
16		3b	Ph	TBA <sup>+</sup> , 20 °C	CDCl <sub>3</sub>	100	97	[c]	55	45			
17		3b	Ph	175 °C, 3 h	Cl <sub>2</sub> CCl <sub>2</sub>	>95	>97	[c]	100				

<sup>a</sup> Up to 10 mol % of oxidant (TBA<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>) for complete conversion, 10 mol % of 2,6-di-*tert*-butylpyridine was added as base. <sup>b</sup> Conversion, mass balance (mb), and product distribution (normalized to 100%) were determined by quantitative capillary GC analysis (error ca. 5% of stated value) or by <sup>1</sup>H NMR spectroscopy (error ca. 10% of stated value). <sup>c</sup> Starting material. <sup>d</sup> A third unknown product (18%) was detected by <sup>1</sup>H NMR spectroscopy but decomposed on silica gel chromatography.

chromatography. The structures of the rearrangement products 7,7-dimethyl-1,4-diphenylnorbornadiene (**4b**)<sup>15</sup> and 4,4-dimethyl-3,5-diphenylbicyclo[3.2.0]hepta-2,6-diene (**5b**) were assigned on the basis of spectral data and homonuclear decoupling and NOE experiments.

For the saturated, diphenyl-substituted tricycloheptane **2b**(H<sub>2</sub>) chemical electron transfer afforded *cis*-3,4 $\alpha$ -dimethyl-2,4 $\beta$ -diphenylbicyclo[3.2.0]hept-2-ene [**6b**(H<sub>2</sub>)] as the exclusive oxidation product (entries 13 and 14, Table 1). Thus, for this substrate only 1,2-methyl migration had occurred.

Control experiments on the products confirmed that these olefins did not interconvert into each other under the employed electron transfer conditions. Furthermore, the possible involvement of acid-catalyzed rearrangement of the tricycloheptenes **2** was probed by running the CET oxidations in the presence and absence of the hindered base 2,6-di-*tert*-butylpyridine. The unaltered product distributions confirmed that acid catalysis does not play a role on the time scale of the CET experiments. When a sample without base was allowed to stand at ambient temperature for up to 24 h, a decrease in norbornadiene **4a** was observed without the formation of new products, whereas the other products persisted. However, this acid-catalyzed decomposition could be completely suppressed in the presence of the hindered pyridine base.

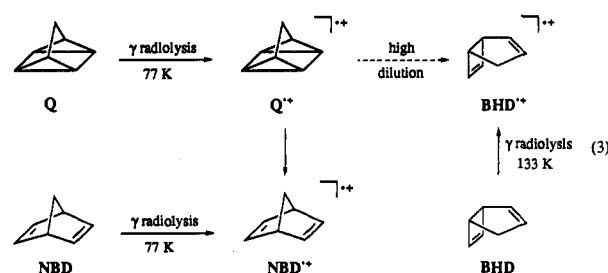
The CET oxidations of quadricyclane **3a** yielded exclusively norbornadiene **4a** (entry 15, Table 1). Its phenyl analog **3b** afforded, besides norbornadiene **4b**, also bicycloheptadiene **5b** (entry 16, Table 1).

None of the azoalkanes **1** could be oxidized by TBA<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>. Thus, the oxidation potentials of these azoalkanes are too high to permit CET with this one-electron oxidant.

## Discussion

Quadricyclane (Q) and norbornadiene (NBD) are strained valence-isomeric hydrocarbons which interconvert under appropriate conditions. The energy difference between their radical cations NBD<sup>•+</sup> and Q<sup>•+</sup> is known experimentally from

the ionization potentials of Q and NBD (7.86 and 8.43 eV) measured by photoelectron spectroscopy.<sup>21</sup> Thus, NBD<sup>•+</sup> is around 13 kcal/mol more stable than Q<sup>•+</sup>, an energy advantage similar to solution data (7 kcal/mol) based on the oxidation potentials of Q and NBD (0.91 and 1.54 V).<sup>22</sup> Therefore, it is not astonishing that the only matrix-isolated product of ionized Q was the radical cation NBD<sup>•+</sup> as confirmed by  $\gamma$  radiolysis of NBD (eq 3).<sup>21a,23,24</sup> Similarly, the gas-phase radical cations



derived from Q and NBD by electron impact were found to be mutually indistinguishable by mass spectrometry.<sup>25</sup> Nonetheless, the existence of the two distinct radical cations Q<sup>•+</sup> and NBD<sup>•+</sup> and the expected hyperfine coupling pattern for Q<sup>•+</sup> have been established by CIDNP results<sup>26</sup> and pulse radiolysis<sup>27</sup>

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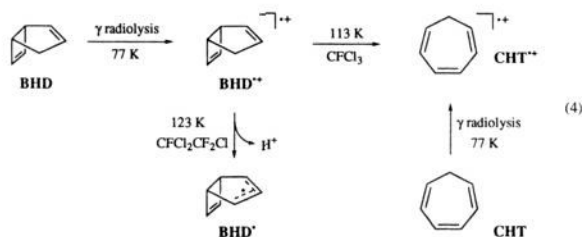
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studies in solution. Moreover, recently  $Q^{+\bullet}$  was also directly spectroscopically observed by time-resolved ESR.<sup>28</sup>

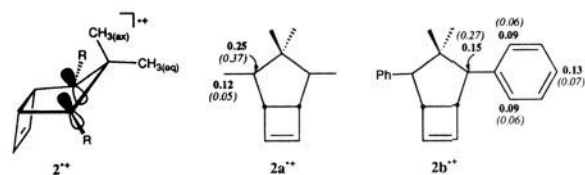
One of the key questions in the Q-NBD system concerns the rate of conversion of  $Q^{+\bullet}$  to  $NBD^{+\bullet}$ . The ESR signals of  $Q^{+\bullet}$  disappeared within 1.5  $\mu$ s after the laser pulse, but the decay process has as yet not been identified; possible pathways include (a) electron spin relaxation, (b) valence isomerization to  $NBD^{+\bullet}$ , or (c) undefined reactions with the solvent.<sup>28</sup> Although the ESR spectrum of the bicyclo[3.2.0]hepta-2,6-diene radical cation ( $BHD^{+\bullet}$ ) has been observed along with the cycloheptatriene radical cation ( $CHT^{+\bullet}$ ) in the radiolysis of highly diluted solutions of Q under matrix-isolation (eq 3),<sup>29</sup> no evidence for the conversion of  $Q^{+\bullet}$  to  $BHD^{+\bullet}$  (and also  $CHT^{+\bullet}$ ) was found in solution.<sup>28</sup> Important in this context is the observation that  $BHD^{+\bullet}$  ring-opens to  $CHT^{+\bullet}$  in the matrix (eq 4).<sup>30</sup> However, this process depends on the matrix material since in the rigid



$CFCl_3$  matrix ring-opening to  $CHT^{+\bullet}$  occurs (thus, the observation of  $CHT^{+\bullet}$  alongside  $BHD^{+\bullet}$  from  $Q^{+\bullet}$  is not surprising), while in the mobile  $CF_2ClCFCl_2$  matrix the prevalent process is deprotonation to the neutral bicyclo[3.2.0]hepta-2,6-diene-4-yl ( $BHD^{\bullet}$ ) radical by the bimolecular ion-molecule reaction, in which the proton is transferred to the neutral BHD molecule or to nucleophiles such as Cl ions.<sup>30</sup>

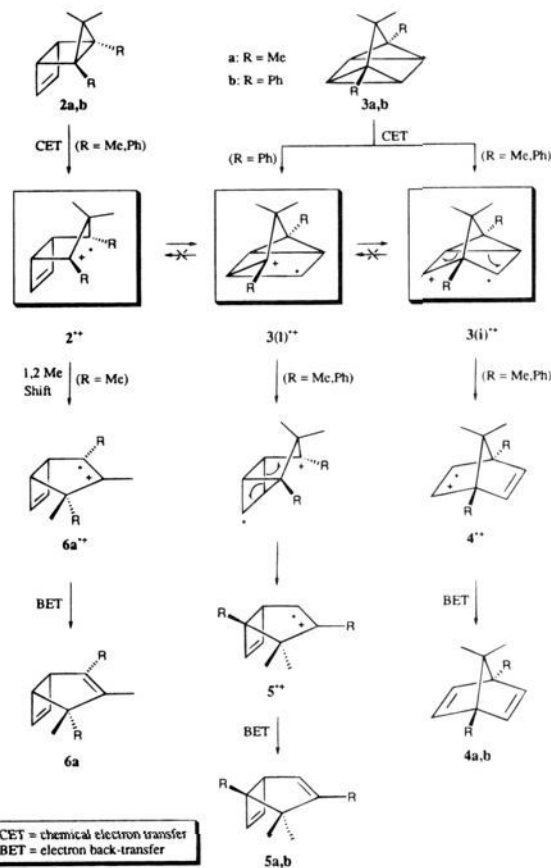
With these reported spectroscopic studies on the complexities of the interconverting radical cations of the Q, NBD, and BHD valence isomers, we shall now venture into constructing a consistent mechanistic framework of our product data in Table 1. Electron transfer from the housane **2** to the aminium salt  $Ar_3N^{+\bullet}$  generates the initially puckered 1,3-cyclopentadienyl radical cation  $2^{+\bullet}$  intermediate (Scheme 1). As established in previous studies,<sup>1</sup> the puckered conformation of the radical cation  $2^{+\bullet}$  (Figure 1) places the *syn* substituent in the preferred pseudo-axial position in almost coplanar alignment with the 2p orbital at the bridgehead positions; the pseudo-equatorial substituent is located essentially parallel to the nodal plane of the 2p orbitals. The 1,2-methyl migration of the pseudo-axial substituent should, therefore, be favored and thereby the diastereoselective formation of the bicycloheptadienes **6b**( $H_2$ ) and **6a** from the housanes **2b**( $H_2$ ) and **2a** is accounted for, after electron back-transfer (BET) either from  $Ar_3N$  or the substrate.<sup>2</sup>

AM1 calculations<sup>31</sup> for the housane radical cations **2a,b**<sup>+</sup> (Figure 1) provide support for this mechanistic rationale. The methyl derivative **2a**<sup>+</sup> possesses a higher local positive charge on each of the relevant 1,3-diyl centers than the phenyl derivative **2b**<sup>+</sup> (0.25 *versus* 0.15) due to delocalization of charge



**Figure 1.** The coplanar alignment of the *syn* substituent (pseudo-axial) with the 2p orbital lobes in the tricycloheptene radical cation  $2^{+\bullet}$  and the charge ( $q_i$ ) and spin density ( $\rho_i$ ) distributions in the radical cations **2a,b**<sup>+</sup>.

### Scheme 1



into the aromatic ring.<sup>2</sup> A similar trend applies also in the spin densities. As a consequence, the higher positive charge on the methyl-bearing centers of the radical cation **2a**<sup>+</sup> promotes ca. 25% (entries 7–9, Table 1) 1,2-methyl migration (path  $2^{+\bullet} \rightarrow 6^{+\bullet} \rightarrow 6$  in Scheme 1) in competition with intramolecular trapping by the juxtaposed cyclobutenyl double bond (path  $2^{+\bullet} \rightarrow 3(i)^{+\bullet}$  in Scheme 1).

In comparison, for the saturated tricycloheptane derivative **2b**( $H_2$ ), 1,2-Wagner–Meerwein rearrangement represents the exclusive reaction path [100% **6b**( $H_2$ ), entries 13 and 14, Table 1], while for the tricycloheptene **2b** (entries 10 and 11) intramolecular trapping by the juxtaposed cyclobutene group occurs exclusively and affords the bicycloheptadienes **5b** and the norbornadienes **4b**. Interestingly, compared to the tetramethyl derivative **2a**, chemical oxidation of the related phenyl-substituted housane **2b** affords a much higher amount of the bicycloheptadiene **5b** than the norbornadiene **4b** (entries 10 and 11 *versus* entries 7–9, Table 1). The formation of the norbornadienes **4** unambiguously establishes that the quadricyclane radical cation  $3^{+\bullet}$  serves as an intermediate, which valence-isomerizes to the norbornadiene radical cation **4**<sup>+</sup>, as was proven for the parent system Q-NBD.<sup>21–29</sup>

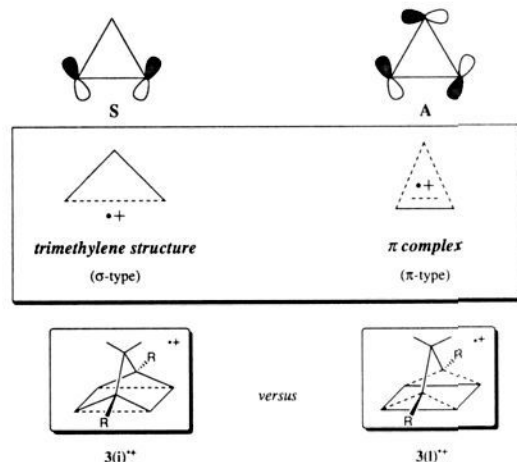
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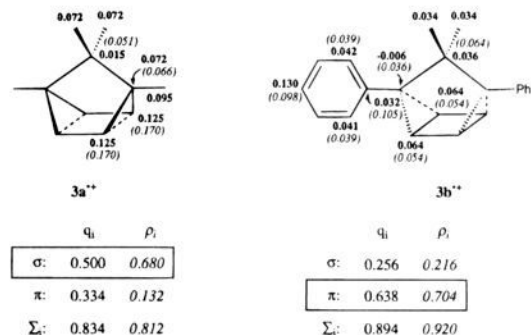


**Figure 2.** The trimethylene structure ( $\sigma$ -type) and the  $\pi$  complex illustrated for the quadricyclane radical cation  $3^{i+}$ .

Since the one-electron oxidation of tetramethylquadricyclane **3a** affords exclusively norbornadiene **4a** as rearrangement product (entry 15, Table 1), whereas its phenyl analog **5b** yields also substantial amounts (45%) of bicycloheptadiene **5b** besides the expected norbornadiene **4b** (entry 16, Table 1), the former product demands an additional precursor. We postulate that the ionized quadricyclane  $3^{i+}$  gives rise not only to the norbornadiene radical cation  $4^{i+}$  by valence isomerization but in a competing process also the bicycloheptadiene radical cation  $5^{i+}$  is produced. This simplifies the ensuing analysis since only the quadricyclane radical cation needs to be considered.

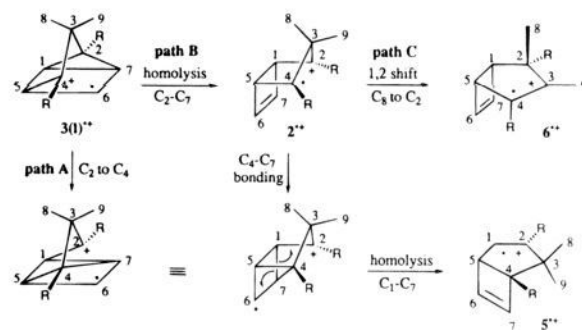
The electronic structure of the quadricyclane radical cation  $Q^{i+}$  provides some insight on its dichotomous chemical behavior, for which the nature of the highest occupied molecular orbital (HOMO) of the parent radical cation is most revealing. As a simplified theoretical model let us consider cyclopropane, for which two structure types apply, which formally are derived from a pair of degenerate HOMOs (Figure 2). On one hand, the radical cation with a symmetric (S) singly occupied MO (SOMO) possesses a weakened (and thus lengthened) bond between a pair of carbon atoms, which is described as a trimethylene species with a one-electron bond between the terminal methylene groups ( $\sigma$ -type radical cation); on the other hand, a radical cation with an antisymmetric (A) orbital as SOMO is best described as a  $\pi$  complex between ethylene and a methylene radical cation ( $\pi$ -type radical cation). Two of its carbon-carbon bonds would be weakened (and thus lengthened), whereas the third one would be strengthened (and shortened).<sup>32</sup> Applied to the quadricyclane skeleton one obtains two distinct radical cations, in which either the internal (i) cyclopropane bond [as in  $3(i)^{i+}$ ] or a lateral (l) one [as in  $3(l)^{i+}$ ] is oxidized.

The trimethylene-type structure has been assigned to many cyclopropane radical cations, based on either CIDNP<sup>32</sup> or low-temperature ESR spectra.<sup>33</sup> The existence of the  $\pi$  complex-type structure has also been established by CIDNP studies. However, to observe such transients spectroscopically, additional stabilization is essential, either by incorporation into an aromatic system like in the benzenorcaradiene case<sup>32a</sup> or by double benzyl



**Figure 3.** Charge ( $q_i$ ) and spin density ( $\rho_i$ ) distributions in the radical cations  $3a,b^{i+}$ .

## Scheme 2



stabilization like in the spirocyclopropylfluorene derivative.<sup>32c</sup> These structural features may explain why phenyl substitution in the housane **2b** or quadricyclane **3b** radical cations favor the  $\pi$  complex and increase, thereby, the proportion of bicyclo[3.2.0]heptadiene product **5** compared to the methyl derivatives **2a** and **3a** (entries 10 and 16 *versus* 7 and 15).








AM1 calculations<sup>31</sup> on the quadricyclane radical cations  $3a,b^{i+}$  corroborate this anticipation, as reflected by the charge and spin density distributions in the radical cations (Figure 3). As is evident for the tetramethyl-substituted quadricyclane  $3a^{i+}$ , the summed positive charges ( $q_i$ ) and spin densities ( $\rho_i$ ) are centered mostly on the trimethylene part of the molecule ( $\sigma$ -type radical cation), whereas for the phenyl derivative  $3b^{i+}$  they are mostly on the  $\pi$  complex ( $\pi$ -type radical cation). Consequently, the preferred transition state for rearrangement of the radical cation  $3a^{i+}$  possesses the trimethylene structure, whereas  $3b^{i+}$  the  $\pi$  complex.

There remains the question of the rearrangement process in the laterally oxidized quadricyclanes  $3a,b(l)^{i+}$  to afford the bicycloheptadiene radical cations  $5a,b^{i+}$ . In principle, two options are possible (Scheme 2): along path A the skeletal rearrangement of  $3(l)^{i+}$  involves a 1,3-shift of the  $C_2-C_7$  bond to the distonic 1,4-radical cation and subsequent  $C_1-C_7$  bond homolysis to afford  $5^{i+}$ , while along path B homolysis of the  $C_2-C_7$  bond leads first back (see Scheme 1) to  $2^{i+}$  and  $C_4-C_7$  bonding followed by  $C_1-C_7$  homolysis to  $5^{i+}$ . The latter sequence  $3(l)^{i+} \rightarrow 2^{i+} \rightarrow 5^{i+}$  (path B) has been proposed in the radiolysis of Q at high dilution and low temperatures.<sup>29</sup> Were this to take place, in competition (path C) some  $6^{i+}$  would be expected by a  $C_8$  to  $C_2$  1,2-shift. As a matter of fact,

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**Table 2.** Heats of Formation [ $\Delta H_f$  (kcal/mol)] for Some Relevant Valence Isomers of the  $C_7H_8$  Hydrocarbons

					
$\Delta H_f$	92	80	63	58	44
Ref.	34a	34a	34a	34a	34b

1,3-cyclopentadienyl radical cations, generated by the oxidation of simple bicyclo[2.1.0]pentanes, react exclusively in the latter way (path C).<sup>1,2</sup> However, the corresponding hydrocarbon **6** is only observed for the methyl derivative by starting from the tricycloheptene **2a** (entries 7–9) and never by starting from the quadricyclanes **3** (entries 15 and 16). Therefore, the barriers between **2**<sup>•+</sup> and **3**<sup>•+</sup> appear to be large and path B thereby improbable. Although the corresponding 1,3-diradical **2**<sup>••</sup> was proposed to rearrange to bicyclo[3.2.0]heptadiene **5** by C<sub>4</sub>–C<sub>7</sub> bonding followed by C<sub>1</sub>–C<sub>7</sub> homolysis (eq 1),<sup>15</sup> for the radical cation this pathway is uphill in energy. Experimental hydrogenation heats<sup>34</sup> for the parent  $C_7H_8$  valence isomers (Table 2) reveal that the tricycloheptene **2** should be about 12 kcal/mol higher in energy than the quadricyclane **3**. Moreover, our AM1 calculations suggest that the quadricyclane radical cation **3b**<sup>•+</sup> is about 5 kcal/mol of lower energy than the tricycloheptene radical cation **2b**<sup>•+</sup>.<sup>35</sup> Consequently, path A should be favored over path B.

The formation of **5**, especially of the methyl derivative **5a**, by starting from **2** needs special consideration, because the oxidation of **3a** yields exclusively **4a** (entry 15). In the case of **3a**, the oxidation takes place at the internal cyclopropane bond [what one would expect and what also the calculations suggest (see Figure 3)] to yield **3a(i)**<sup>•+</sup>, which then valence-isomerizes to the norbornadiene radical cation **4a**<sup>•+</sup>. In contrast, by starting from **2a**, the first quadricyclane intermediate is **3a(l)**<sup>•+</sup>, in which the lateral cyclopropane bond is oxidized. As postulated, this laterally oxidized quadricyclane radical cation yields the bicycloheptadiene radical cation **5a**<sup>•+</sup> through skeletal rearrangement. Thus, although the internally oxidized quadricyclane radical cation **3a(i)**<sup>•+</sup> may be favored (see entry 15 and the AM1 calculations for **3a**<sup>•+</sup>), the intramolecular trapping yields first the **3a(l)**<sup>•+</sup> intermediate, which generates **5a**<sup>•+</sup> or isomerizes to

**4a**<sup>•+</sup> via **3a(i)**<sup>•+</sup>! For the phenyl derivative **2b**, the first quadricyclane intermediate is again the laterally oxidized radical cation **3b(l)**<sup>•+</sup>, which rearranges either to **5b**<sup>•+</sup> or isomerizes to **4b**<sup>•+</sup> via **3b(i)**<sup>•+</sup>. Note in Table 1 (entries 10 and 11 versus entries 7–9) that tricycloheptene **2b** affords a much higher amount of bicycloheptadiene **5** compared to tricycloheptene **2a**. In line with this observation, in the case of the phenyl quadricyclane **3b** one obtains **5b** besides **4b**, which indicates that **3b(l)**<sup>•+</sup> and **3b(i)**<sup>•+</sup> have similar energies. Therefore, the barrier between **3b(l)**<sup>•+</sup> and **3b(i)**<sup>•+</sup> has to be small, whereas between **3a(l)**<sup>•+</sup> and **3a(i)**<sup>•+</sup> it appears to be large. Consequently, the heats of formation should have the qualitative order **2b**<sup>•+</sup> > **3b(l)**<sup>•+</sup> ≈ **3b(i)**<sup>•+</sup> for the phenyl case and **2a**<sup>•+</sup> > **3a(l)**<sup>•+</sup> > **3a(i)**<sup>•+</sup> for the methyl case.

In conclusion, an alternative entry to the valence-isomeric quadricyclane–norbornadiene system has been opened through intramolecular trapping by the juxtaposed cyclobutene group of the bicyclo[3.2.0]hept-6-ene-2,4-diy radical cation **2**<sup>•+</sup>, which was generated by chemical electron transfer (CET) from the tricyclo[3.2.0.0<sup>2,4</sup>]hept-6-enes **2** with trisarylamminium salts. However, the quadricyclane radical cation **3**<sup>•+</sup> gives rise not only to the norbornadiene radical cation **4**<sup>•+</sup> by valence isomerization of **3(i)**<sup>•+</sup>, but in a competing process also the bicycloheptadiene radical cation **5**<sup>•+</sup> is produced from **3(l)**<sup>•+</sup> through skeletal rearrangement. Thus, for the first time the rearrangement of the quadricyclane radical cation to the bicycloheptadiene radical cation has been observed in solution and thereby we confirm its ESR detection in the previous matrix studies.<sup>29</sup> AM1 calculations suggest two transition states for product formation, namely the trimethylene structure [**3(i)**<sup>•+</sup>] favored for the methyl derivatives **2a** and **3a** or the  $\pi$  complex arrangement [**3(l)**<sup>•+</sup>] preferred by the phenyl substrates **2b** and **3b**.

**Supporting Information Available:** Experimental data (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(35) The  $H_f$  values are 165.8 kcal/mol for **2b** and 156.9 kcal/mol for **3b**, whereas they are 367.2 kcal/mol for **2b**<sup>•+</sup> and 362.6 kcal/mol for **3b**<sup>•+</sup>.