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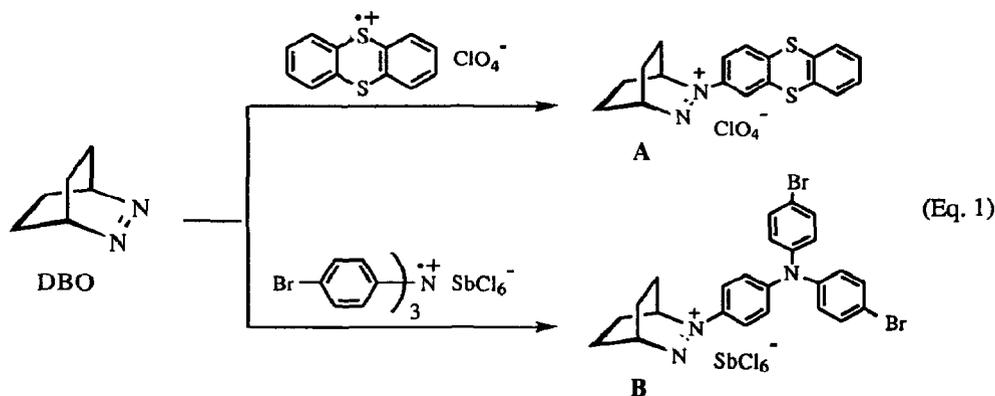
## Tris(aryl)aminium Hexachloroantimonates: Convenient One-Electron Oxidants for Chemical Electron Transfer with Bicyclic Azoalkanes and Bicyclo[2.1.0]pentanes

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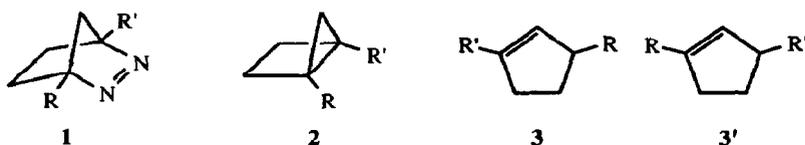
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**Abstract:** Treatment of the parent and bridgehead-substituted 2,3-diazabicyclo[2.2.1]hept-2-enes (**1a-d**) and their bicyclo[2.1.0]pentanes (**2a-d**) with catalytic amounts (2-10 mol%) of tris(aryl)aminium hexachloroantimonates afforded the corresponding cyclopentenenes (**3a-d**). A reversal in the regioselectivity of the 1,2 migration was observed for the unsymmetrical derivatives of bicyclo[2.1.0]pentane, namely **2b** (methyl substitution) versus **2c** (phenyl substitution). This surprising fact is rationalized in terms of delocalization of the positive charge into the aromatic ring for the 1,3-diyl radical cation, as corroborated by AM1 calculations.

Although the biradical chemistry of cyclic azoalkanes has been well elucidated for several decades [1], their one-electron oxidation has been attended to only the last few years [2,3]. Whereas 2,3-diazabicyclo[2.2.1]hept-2-ene or DBH (**1a**) extrudes molecular nitrogen upon one-electron oxidation, either photochemically [3d], chemically [3f] or radiolytically [2h] induced, its higher homologue 2,3-diazabicyclo[2.2.2]oct-2-ene or DBO is quite inert to such redox chemistry. For example, the difference in chemical behavior is demonstrated in the formation of adducts **A** and **B** (Eq. 1) when DBO was treated



with the well-known, isolable radical cation salts thianthrenium perchlorate ( $\text{Th}^{\bullet+}\text{ClO}_4^-$ ) or tris-(4-bromophenyl)aminium hexachloroantimonate ( $\text{TBA}^{\bullet+}\text{SbCl}_6^-$ ) [2c,f]. Indeed, it is surprising that one-electron oxidation of DBH-type azoalkanes and their bicyclo[2.1.0]pentane denitrogenation products by persistent radical cation salts has not been examined. Herein we demonstrate the convenience and scope of this methodology, when applied to the azoalkanes **1a-d** and the corresponding bicyclo[2.1.0]pentanes **2a-d** (Table 1).



**a** (R = R' = H); **b** (R = Me; R' = H); **c** (R = Ph; R' = H); **d** (R = R' = Me)

**Table 1:** Product Studies of the Chemical Electron Transfer Oxidation of the Azoalkanes **1**, Bicyclo[2.1.0]pentanes **2**, and Cyclopentenes **3**

entry	substrate	oxidant <sup>[a]</sup>	conv. <sup>[b]</sup> (%)	mb <sup>[b]</sup> (%)	product distribution <sup>[b]</sup>	
					<b>3</b>	<b>3'</b>
1	<b>1a</b>	TDA <sup>•+</sup>	100	82	100	
2	<b>2a</b>	TDA <sup>•+</sup>	100	75	100	
3	<b>2b</b>	TBA <sup>•+</sup> [c]	100	89	>99	<1
4	<b>2b</b>	HClO <sub>4</sub> [d]	77	90	<1	>99
5	<b>2c</b>	TBA <sup>•+</sup> [c]	100	90	23	77
6	<b>2c</b>	HClO <sub>4</sub> [d]	75	95	<1	>99
7	<b>2d</b>	TBA <sup>•+</sup> [c]	100	98	100	
8	<b>3b'</b>	TDA <sup>•+</sup>	100	[e]	[e]	

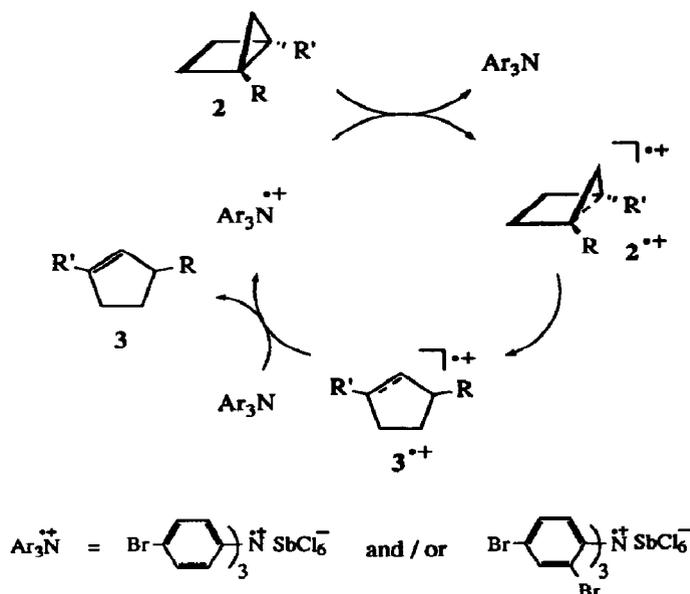
[a] Reaction conditions: 2-10 mol% oxidant, CH<sub>2</sub>Cl<sub>2</sub>, 1 min, 10 °C; [b] conversion, mass balance and the product distribution were determined by quantitative capillary GC, error  $\pm 3$  % of the stated value; [c] 10 mol% 2,6-di-*tert.*-butylpyridine was added as base; [d] reaction conditions: 2 N HClO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 1 h, 20 °C; [e] unidentified higher-molecular-weight material was formed, which went undetected by capillary GC.

Contrary to the reaction of DBO with *tris*(2,4-dibromophenyl)aminium hexachloroantimonate (TDA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup>, E<sub>ox</sub> = 1.47 V vs. SCE) [4], treatment of DBH (**1a**) with catalytic amounts (2-10 mol%) of TDA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> led to rapid nitrogen gas evolution and gave within few seconds and in high yield (82%) cyclopentene (**3a**) as the exclusive oxidation product (entry 1). The same product **3a** was observed also in high yield (75%) when the parent bicyclo[2.1.0]pentane (**2a**) was submitted to these redox conditions (entry 2).

When the substituted azoalkane derivatives **1b-d** were treated with catalytic amounts of TDA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup>, only intractable higher-molecular-weight material was formed, whereas the less powerful radical cation salt TBA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> (E<sub>ox</sub> = 1.03 V vs. SCE) [4] failed in oxidizing these azoalkanes. A control experiment confirmed that only cyclopentenes with an isolated double bond like **3a-c** were not oxidized by TDA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> (entry 8), whereas the substituted cyclopentenes **3b',c',d** persisted towards TBA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup>.

In the bicyclo[2.1.0]pentane series, at least one bridgehead substituent is necessary for oxidation by TBA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> (entries 3,5,7). Since also here catalytic amounts of oxidant was enough to achieve complete conversion within few seconds, we propose the catalytic cycle displayed in Scheme 1. Thus, electron transfer from housane **2** to Ar<sub>3</sub>N<sup>•+</sup> initiates the cycle, followed by subsequent 1,2 Wagner-Meerwein rearrangement of the radical cation **2**<sup>•+</sup>. Electron back-transfer from Ar<sub>3</sub>N to **3**<sup>•+</sup> forms cyclopentene **3** and Ar<sub>3</sub>N<sup>•+</sup> and completes thereby the catalytic cycle. Alternatively, electron back-transfer can also occur according to  $2 + 3^{•+} \rightarrow 2^{•+} + 3$ , but differentiation between these two pathways is difficult at the moment.

Scheme 1



Analogous to the photochemically induced oxidation [3a], we have observed that the chemical oxidation of the unsymmetrically methyl-substituted bicyclo[2.1.0]pentane **2b** (entry 3) yielded exclusively 3-methylcyclopentene (**3b**) and only traces of 1-methylcyclopentene (**3b'**). This contra-thermodynamically regioselective 1,2 hydrogen migration (entry 4) was rationalized in terms of an essentially localized positive charge at the incipient tertiary center during the formation of the 1,3-diyl radical cation **2b<sup>•+</sup>**.

In contrast, the related 1-phenylbicyclo[2.1.0]pentane (**2c**) gave with TBA<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> (entry 5) 1-phenylcyclopentene (**3c'**) as the major product and not 3-phenylcyclopentene (**3c**). Again, protonation of the housane **2c** with 2N HClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> yielded **3c'**, the thermodynamically more stable olefin (entry 6). This result suggests that the positive charge is essentially localized at the secondary carbon site of the 1,3-diyl radical cation and not at the tertiary benzylic position !

AM1 calculations on the radical cations **2b,c<sup>•+</sup>** provide a rationale for these divergent results, as reflected by the charge and spin density distributions in the radical cations **2b,c<sup>•+</sup>** (Figure 1).

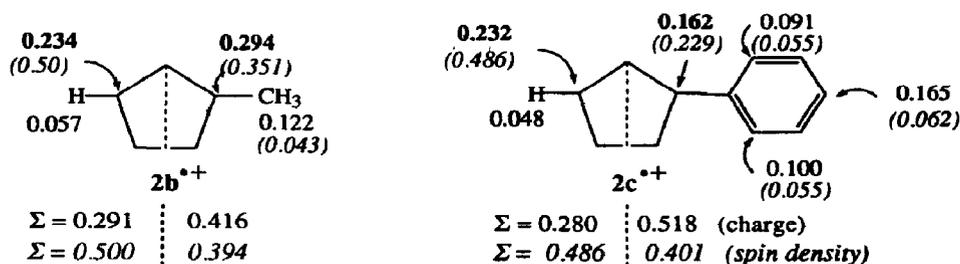


Figure 1: Charge and spin density distributions in the radical cations **2b,c<sup>•+</sup>**

As is evident for the methyl derivative **2b<sup>•+</sup>**, the absolute as well as the relative positive charge is localized on the tertiary site of the 1,3-diyl radical cation, whereas the spin density is centered mostly on the secondary center. While the positive charge and the spin density for the phenyl analogue **2c<sup>•+</sup>** change only nominally on the hydrogen-bearing carbon, on the benzylic position it is drastic. Thus, the relative positive charge is higher on the phenyl- than on the hydrogen-bearing site; but due to delocalization into the aromatic ring, the absolute value of the charge on the crucial 1,3-diyl center is reversed, i.e. in the radical cation **2b<sup>•+</sup>** it is larger (0.294 versus 0.234) at the methyl-bearing center, while in **2c<sup>•+</sup>** it is larger (0.232 versus 0.162) at the hydrogen-bearing site. Consequently, sufficient positive charge resides on the secondary center to promote 1,2 hydrogen migration to this site. That the relative size of the charge coefficients (Figure 1) does not quantitatively reproduce the ratio of the regioisomeric cyclopentenones **3** and **3'** may derive from stereoelectronic as well as from conformational effects of the phenyl group in the radical cation **2c<sup>•+</sup>**.

In summary, the chemical oxidation of DBH-type azoalkanes **1**, especially of the corresponding bicyclo[2.1.0]pentanes **2**, by *tris*(aryl)ammonium hexachloroantimonates proceeds catalytically in a clean manner to afford the rearranged cyclopentenones **3** in high yields. Since the reactions can be run on relatively large scale (> 100 mg), this oxidative rearrangement constitutes a useful synthetic strategy for tailor-made substrates. Furthermore, a reversal in the regioselectivity of the 1,2 hydrogen migration was observed, when methyl was substituted by the phenyl group. This is rationalized in terms of delocalization of the positive charge at the benzylic position into the aromatic ring.

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