Ring Contraction Reactions of a Non-Benzenoid Aromatic Cation and a Neutral Homoaromatic System into Benzene Derivatives

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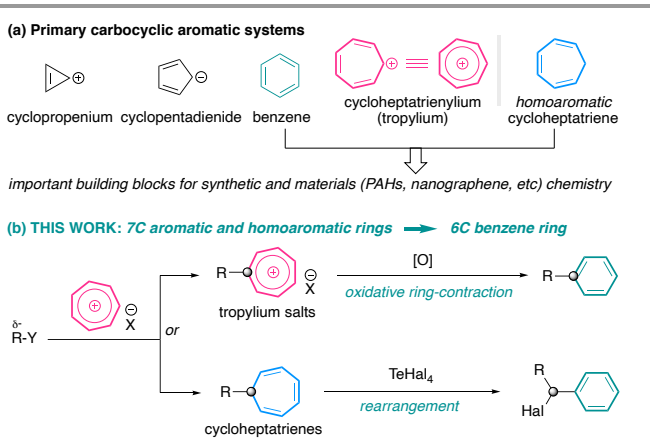
Aromaticity is one of the most intriguing concepts in organic chemistry. Simple and extended benzenoid aromatic systems have been very well established in undergraduate textbooks, and there are also mentions of non-benzenoid aromatic structures such as cyclopropenium, cyclopentadienide and cycloheptatrienylium (tropylium) ions. However, the structural relationship and the comparison of stabilization energy of such aromatic ions to benzene ring have been rarely studied and remained an underexplored area of advanced organic chemistry research. To contribute some insights into this topic, we focused on the chemical transformation, namely a ring contraction reaction, of the tropylium ion to benzene ring in this work. With an approach combining computational studies with experimental reactions, we also aim to turn this transformation into a synthetically useful tool. Indeed, this work led to the development of a new synthetic protocol, which involved an oxidative ring-contraction of tropylium ion, to formally introduce the phenyl ring onto a range of organic structures. Furthermore, the homoaromatic cycloheptatrienyl precursors of tropylium salts used in these reactions can also be rearranged to valuable benzhydryl or benzyl halides, enriching the synthetic utility of this ring-contraction protocol.

Introduction

Aromaticity, while remaining a not fully defined concept, plays an undeniably irreplaceable role in the formation, reactivity and function of organic structures.[1] The knowledge on simple as well as extended benzenoid aromatic system has been well established several decades ago, which has led to the flourishing development of their chemistry in synthetic and material chemistry.[2] Meanwhile, non-benzenoid aromatic structures such as cyclopropenium, cyclopentadienide and tropylium ions (Scheme 1a) have also been known for a long time,[3] but their relative stabilization energies to benzene remain elusive, despite being a fundamental research interest in physical organic chemistry.[4]

The recent developments in the field of polyaromatic hydrocarbons (PAHs), nanographenes or nanocarbons have identified that the inclusion of the tropylium or cycloheptatriene rings in their structures led to highly interesting properties.[5] These heptagonal occurrences often induce negative curvature or saddle-shape to the scaffolds and alter the intermolecular interactions and solid state packing, which result in fascinating contorted aromaticity, dynamic behaviours and electronic properties.[6] The neutral homoaromatic cycloheptatriene framework and the aromatic carbocationic tropylium ring can also be easily interchanged via chemical or electrochemical reactions,[5f, 7] giving the parent non-alternant PAHs useful redox properties. It is not synthetically straightforward to introduce such heptagonal defects into PAHs, given their unusual structural arrangement and the deviation from the planar hexagonal motif.[6a] On the other hand,



Scheme 1. Tropylium as an electrophilic phenyl building block.

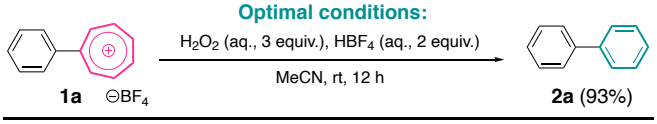
it sparks interest to develop new approaches to convert the imperfect heptagonal system into their benzenoid counterparts,[6b] which might open up completely new opto-electronic applications for these systems. Recently, there have been a number of reports on the ring-contraction or re-arrangement of specific heptagon-containing PAHs.[5f, 7a, 8] However, a systematic and practical protocol to carry out such transformations under mild conditions is still in demand.

Inspired by our recent investigations on the synthetic utility of the non-benzenoid aromatic tropylium ion,[3, 7c, 9] we believe that an oxidative ring contraction reaction[7a] can be performed on the electron deficient seven-membered ring of the tropylium ($-C_7H_6^+$) ion to transform it into a phenyl ring ($-C_6H_5$). This would allow for a novel strategy to convert a seven-membered carbocycle into benzene ring, which will have tremendous potential in chemistry of heptagon-containing organic building blocks and materials. It is also an interesting transformation at fundamental level that the non-benzenoid aromatic tropylium ion is converted to the aromatic benzene ring, allowing a *formal* phenylation reaction. Our own calculations of the nucleus-independent chemical shifts ($NICS(1)_{zz}$) values[4b, 10] for tropylium ion and benzene are –27.7 and –30.8 ppm,[11] respectively, which indicate that benzene ring has higher aromaticity than tropylium ion. Hence the ring contraction reaction from a tropylium ion to a phenyl group should be energetically favourable. Herein, we report the development of a simple oxidative protocol for such chemical transformation (Scheme 1b). Furthermore, we were able to transform the homoaromatic cycloheptatriene intermediates in these synthetic sequences into useful benzyl halides, further diversifying the potential synthetic application of this method.

Results and Discussions

We started our investigation of by screening the reaction conditions to ring contract phenyl tropylium tetrafluoroborate **1a** into biphenyl **2a** in an oxidizing environment, as the tropylium moiety is electrophilic. After an extensive optimization study,[12] we established that the reaction was best carried out in aqueous/acetonitrile environment with H_2O_2 (3 equiv.) as the oxidant in the presence of HBF_4 (2 equiv.) to give the product in excellent yield of 93% (Table 1). The use of less HBF_4 or a different Brønsted acid led to lower product yields. Similarly, replacing H_2O_2 with other commonly used oxidants such as Oxone®, $(NH_4)_2Ce(NO_3)_6$, ^{t}BuOOH or even bleach also resulted in poorer efficiencies.[12]

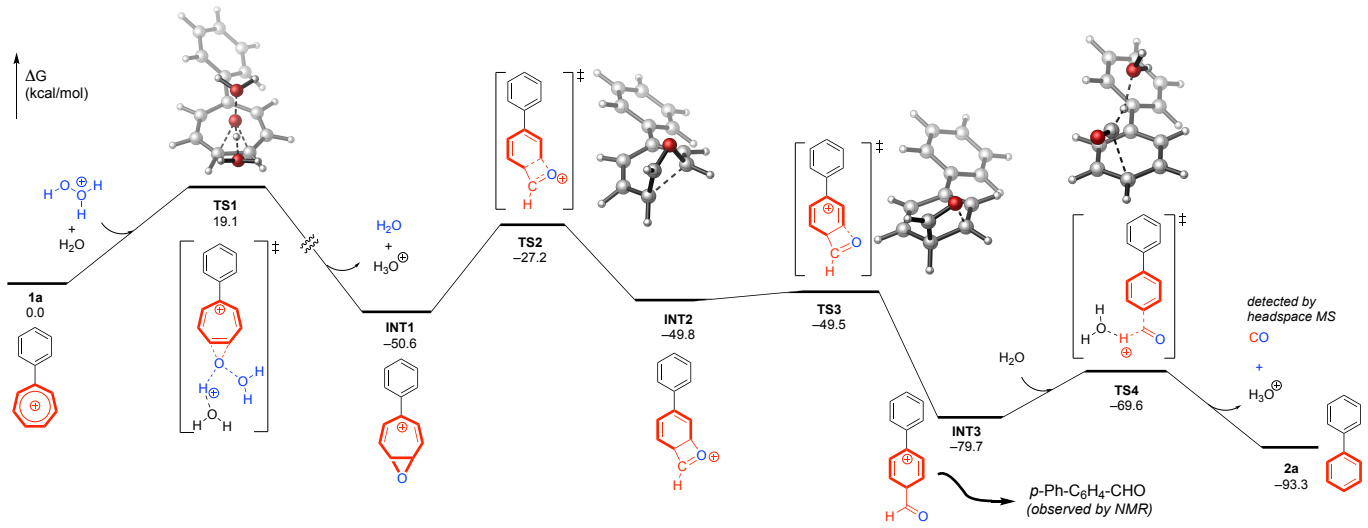
Table 1. Optimization of the oxidative ring-contraction.[a]



Entry	*Variations from optimal conditions*[b]	Yield of **2a** (%)[c]
1	no HBF_4	56%
2	H_2O_2 (1 equiv.), no HBF_4	28%
3	only 1.0 equiv. of HBF_4	81%
4	H_2SO_4 (2 equiv.) instead of HBF_4	52%
5	Oxone® (3 equiv.) instead of H_2O_2	52%
6	Oxone® (3 equiv.), no HBF_4	59%
7	CAN (3 equiv.) instead of H_2O_2	31%
8	^{t}BuOOH (3 equiv.) instead of H_2O_2	69%

[a] Conditions: **1a** (0.5 mmol), acid and oxidant in MeCN (2 mL) under ambient conditions at room temperature. [b] For further experiments on optimization studies, see page S33 in the experimental SI. [c] Yield of the isolated **2a**.

It should be noted here that the cleavage of one carbon from the seven-membered ring,[13] to retain a phenyl group on the original organic framework, is directly opposite but complementary to the elegant cycloheptatriene chemistry recently developed by the Echavarren group, in which they use Au(I) or Rh(II) catalysis to eliminate a benzene ring from cycloheptatriene derivatives to produce organometallic carbenoid complexes.[14] Thus, we were curious to understand the mechanistic insights of our own reaction, with the hope that they will lead to direct synthetic applications for this reaction as well as inform future developments in chemistry of non-traditional aromatic compounds. However, we were met with little success in our attempts to trap reaction intermediates in the conversion of **1a** to **2a**, as the reaction was in partially aqueous and oxidative environment. Thus, density functional theory (DFT) calculations[11] were carried out to locate a plausible pathway for this oxidative ring contraction. The computational studies were initiated by locating transition states for the reaction between the tropylium salt **1a** (Scheme 2) and neutral hydrogen peroxide H_2O_2. However, all transition states that we could locate are calculated to associate with very high activation



Scheme 2. Computational mechanistic elucidation of the oxidative ring-contraction reaction.

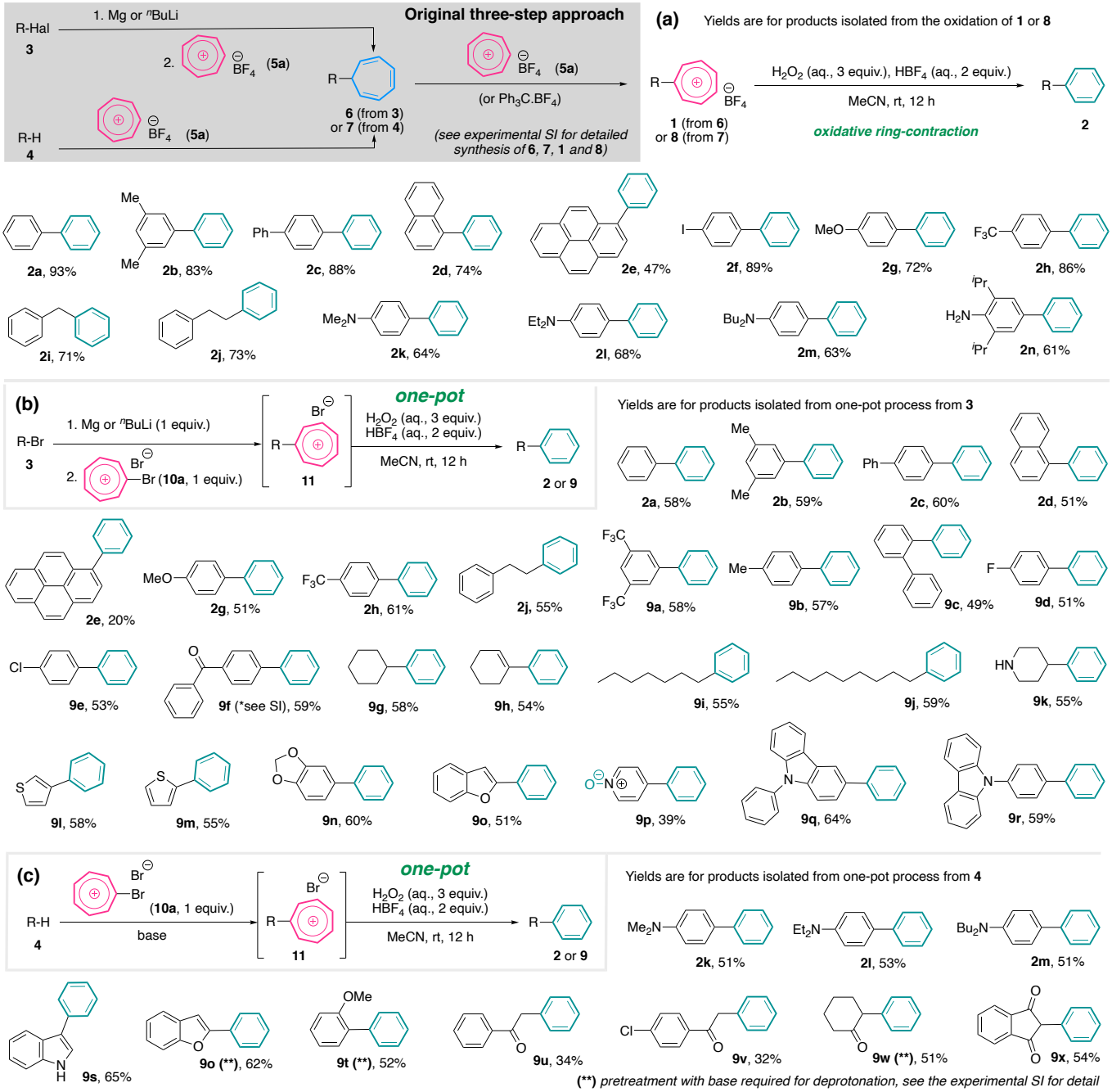
barriers (> 30 kcal/mol, see Figure S1 in the computational SI). This result is inconsistent with the experimental finding in Table 1 where we found that the reaction can occur efficiently at ambient temperature, albeit in a strongly acidic environment. We then carried out calculations with the assumption that under these reaction conditions, H_2O_2 is protonated by fluoroboric acid to generate a highly reactive species $HOOH_2^+$,[15] which indeed led to a feasible reaction pathway. The computed free energy profile and optimized structures of transition states for the reaction between the tropylium ion **1a** and the protonated hydrogen peroxide $HOOH_2^+$ are shown in Scheme 2. The reaction starts with the electrophilic addition of the $HOOH_2^+$ species to tropylium ion **1a** via transition state **TS1**, giving oxirane intermediate **INT1**. The activation energy of **TS1** is calculated to be 19.1 kcal/mol relative to **1a**. The feasible barrier of **TS1** is primarily initiated by the relatively low energy of LUMO of $HOOH_2^+$.[15a]

To proceed, calculations suggested that skeletal rearrangements[16] via transition states **TS2** and **TS3** take place, generating cyclohexadienylium intermediate **INT3**. Subsequent decomposition of **INT3** can then occur via **TS4**, giving product **2a** and CO.[17] The formation of CO molecule (M = 28) from the reaction mixture was detected by headspace mass-spectrometry, supporting this proposed mechanism of our oxidative ring contraction reaction. Our DFT calculations show that the rate-determining step is **TS2** with an overall barrier of 23.5 kcal/mol (Scheme 2). This energy barrier is consistent with our mild reaction conditions.[18] The overall reaction is calculated to be exergonic by 93.3 kcal/mol, which explains why the reaction can proceed to transform the non-benzenoid aromatic tropylium ion into the aromatic benzene ring at ambient conditions. This result is promising as the starting point for the ring contraction of complex heptagon-containing PAHs.

Having the mechanistic insights of the tropylium moiety to the phenyl ring (Scheme 2) and the optimal conditions of the oxidative ring-contraction (Table 1) in hand, we subsequently applied this reaction to a range of substituted tropylium substrates (**1** or **8**, Scheme 3a), which can be derived from their corresponding aryl/alkyl halides **3** or electron-rich arene precursors **4** in two steps (see pages S4-S5 in the experimental SI for detail). The reaction efficiency did not change much with substitution of the tropylium ring, giving phenylated products **2a**-**n** in good to excellent yields.

Undoubtedly, the synthetic sequence to get to tropylium salts **1**/**8** from **3**/**4** is lengthy and not atom-economic. Therefore, we spent some effort on making the protocol more synthetically practical. Thus, we decided to employ bromotropylium bromide **10a** (Schemes 3b-c), which we previously used as halogenating or esterification/amidation reaction promoters.[9a-c] After an extensive optimization study, we found that a stoichiometric amount of **10a** could react with the organometallic reagents from aryl halides **3** or react directly with arenes **4** to form intermediates **11**. As the second bromine was able to dissociate off from the newly formed cycloheptatriene ring,[19] **11** can serve a synthetic equivalent of tropylium salts **1**/**8**, eliminating the need for a lengthy synthetic sequence. Subsequently, the *in situ* generated **11** was directly subjected to the oxidative ring contraction conditions developed in Table 1 to form the phenylated products (Schemes 3b-c).

Using this new one-pot protocol, we were able to convert a selected number of aryl halides and arenes to their corresponding phenylated products (**2a**-**2m**, Scheme 3b). The product yields of this direct one-pot protocol were slightly lower than the yields of similar products formed from pre-synthesized tropylium precursors **1** or **8** (Scheme 3a). We also further investigated a range of new aryl and alkyl halide precursors, most of them worked efficiently with this procedure to give products **9a**-**9x** in moderate to good yields (Scheme 3b). Functional groups vulnerable to the organometallic reagents or the oxidative conditions such as ketone (**9f**) or amino (**9k**) groups required protection.[12] Several types of heterocyclic systems, such as thiophene (**9l**-**m**), benzodioxole (**9n**), benzofuran (**9o**) and carbazole (**9q**-**r**), were compatible with this phenylation protocol via the organometallic pathway. Indole and benzofuran worked relatively well via the C-H functionalization pathway, giving products **9s** and **9o** in good yields. Pyrrole and furan substrates did not work[20] but the reaction was possible on a pyridine substrate, although the oxidative conditions led to the *N*-oxide pyridine product (**9p**). Most interestingly, this one-pot protocol was applicable to C-H functionalization of ketone substrates, giving phenylated products **9u**-**x**, albeit in lower yields (Scheme 3b). This type of α-phenylation reaction on carbonyl compounds is not straightforward and normally required transition metal-catalyzed or complex umpolung processes.[21]

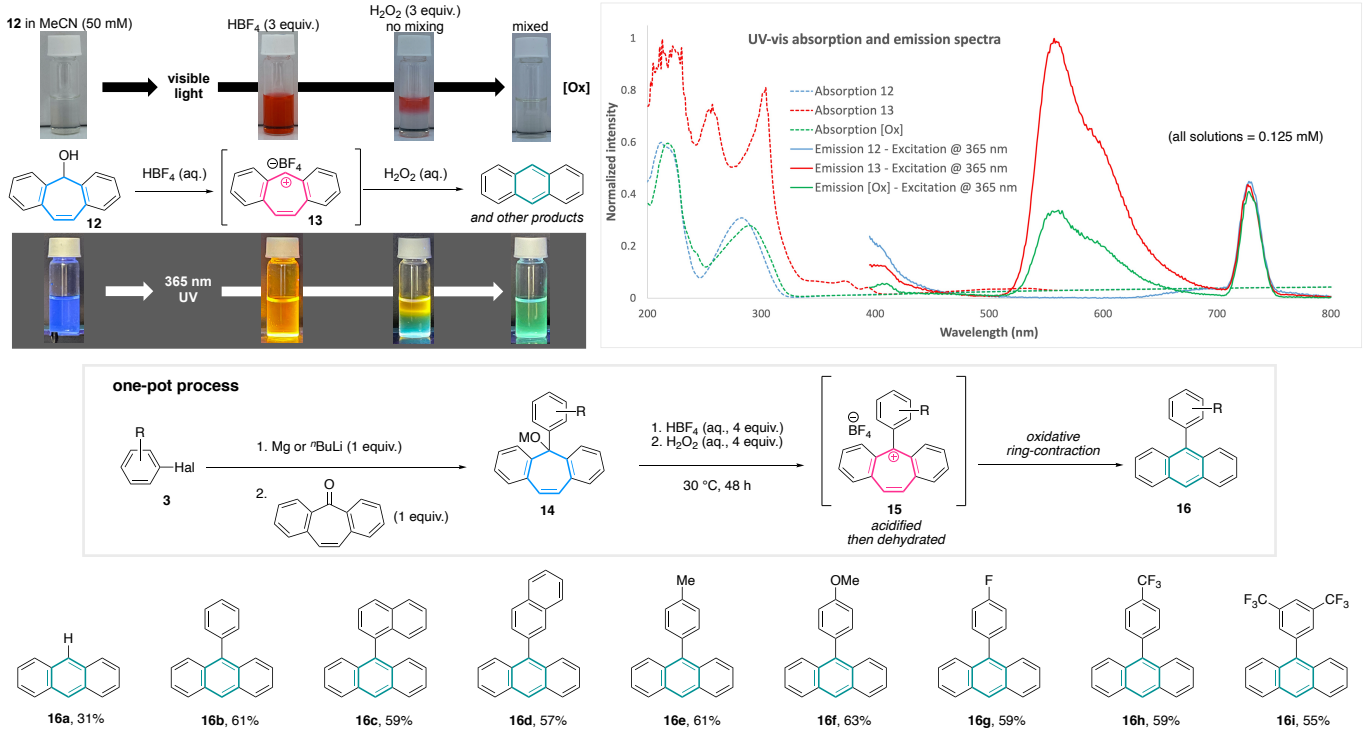


Scheme 3. One-pot *formal* phenylation reaction substrate scope.

Our oxidative ring contraction process could potentially be used in other applications than the formal phenylation reaction. For example, when we subjected suberenol **12** to similar reaction conditions (Scheme 4), we observed an interesting shift in colors and photoluminescences of the solution. Suberenol **12** solution in acetonitrile is colorless under visible light but weakly light-blue luminescent under 365 nm UV irradiation. When an acid was introduced, a protonation and dehydration process occurred to generate a cationic dibenzosuberenylium species **13**, which has similar reactivity to the tropylium ion. This solution immediately turned bright red under visible light and yellow luminescent under 365 nm UV light upon acidification. When being exposed to an oxidizing environment such as H_2O_2, **13** was oxidized to anthracene, and a number of other polyaromatic by-products, which instantly turned the solution colorless and yellow-green luminescent. The UV-vis absorption and emission spectra of these solutions are also included in Scheme 3c.[12] Further studies to adapt this simple redox-sensitive system to sensing or imaging application of oxidants in biological environments are currently underway.

On the other hand, this protocol can be employed to install anthracene framework onto aryl halides in a similar fashion to the formal phenylation developed earlier. Indeed, treatment of organometallic derivatives of aryl halides **3** with suberenone,

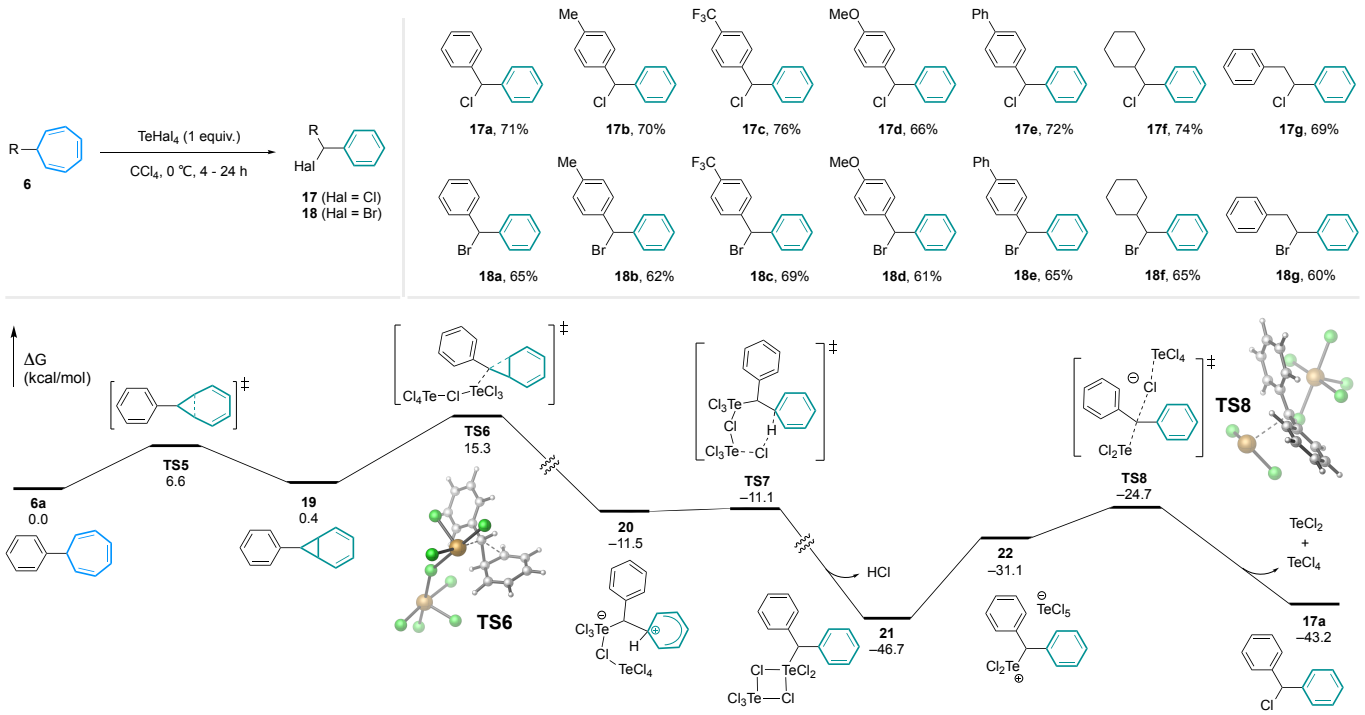
followed by the oxidative reaction with H_2O_2/HBF_4 in the same pot afforded 9-aryl substituted anthracenes **16** in moderate to good yields (Scheme 4). The reaction likely proceeded through the nucleophilic addition of organometallic reagents to suberenone to form adducts **14**, which underwent acidification and dehydration under acidic conditions to give suberenylium intermediates **15**. Presumably, the subsequent oxidative ring-contraction occurred at the 4,5-C-C double bond of the seven-membered ring to give anthracene products. In the case of non-substituted system like **13**, there might be other competing processes at the non-hindered benzhydrylium position, leading to lower yield of product **16a**.



Scheme 4. (top) Sensing of oxidative environment; (bottom) One-pot *formal* installation of anthracene moiety to aryl halides.

In parallel to the oxidative ring contraction to furnish the *formal* phenylation reaction, we also further explored the synthetic application of cycloheptatrienyl intermediates (**6**, Scheme 3a). As mentioned earlier, the Echavarren group has already reported elegant studies in this area with their Au(I) or Rh(II)-catalyzed conversion of cycloheptatriene moiety to carbene.[14] Other notable synthetic applications of cycloheptatriene include fluxional carbon cages[22] by the McGonigal group and bromoallenes[23] by Gandon, Bour and co-workers. Based on our earlier work on installation and subsequent functionalization of cycloheptatrienes,[9k] we set out to examine the rearrangement of the cycloheptatriene moiety into benzyl halide, which are valuable synthetic precursors. We attempted to facilitate this transformation by a range of Lewis acidic halide salts such as $PHal_3$, $BHal_3$, $AlHal_3$, $GaHal_3$, $TiHal_4$ and $FeHal_3$ but found that tellurium(IV) halides[24] were the most effective reagents for this purpose. Thus, we were able to convert a range of aryl or alkyl cyloheptatrienes **6** to benzhydryl or benzyl halides **17** and **18** in good to high yields using a stoichiometric amount of $TeHal_4$ in CCl_4 solvent (Scheme 5).

It was curious to us how tellurium(IV) halides can promote this rearrangement. However, this reaction proved to be challenging for experimental mechanistic studies. Therefore, DFT calculations were performed to elucidate the reaction mechanism between phenyl cycloheptatriene **6a** and $TeCl_4$. Our studies indicated that $TeCl_4$ prefers to exist in a dimeric species Te_2Cl_8 in CCl_4 solvent.[25] The dimerization of $TeCl_4$ is calculated to be exergonic by 5.2 kcal/mol. The rearrangement of cycloheptatriene starts with the ring contraction from **6a** to form norcaradiene species **19** via **TS5**. The low activation energy of **TS5** (6.6 kcal/mol) is consistent with the fact that the norcaradiene–cycloheptatriene equilibrium can occur rapidly at room temperature.[26] The second step is the electrophilic addition of Te_2Cl_8 to norcaradiene species **19** via **TS6** giving **20**, followed by rapid a proton abstraction to generate intermediate **21**. The activation barrier of **TS6** is calculated to be 15.3 kcal/mol relative to **6a**. Theoretically, the typical route to form chlorodiphenylmethane product **17a** from species **21** is to go through a reductive elimination transition state. However, we could not locate any reductive elimination transition state for such transformation. Our DFT calculations revealed that a different reaction pathway is possible, where structural arrangement of **21** can occur, giving a contact ion-pair intermediate **22**. This undergoes a heterolytic cleavage of Te–C bond and nucleophilic attack of $TeCl_5^-$ anion via **TS8** to form product **15a**. **TS8** is calculated to be the rate-determining step of this reaction with the activation barrier of 22.0 kcal/mol relative to **21**. The formation of $TeCl_2$ in this computational pathway agrees well with known chemical reactivity of $TeCl_4$.[24]



Scheme 5. Ring-contraction rearrangement of cycloheptatrienes and proposed mechanistic pathway.

Conclusions

In conclusion, we have developed a new protocol to allow the conversion of tropylium and cycloheptatriene rings into benzenoid system. This protocol exploited the versatile electrophilicity and oxidizing ability of tropylium ion to construct the seven-membered ring framework and subsequently contract one carbon from that to produce the phenyl ring. It is an interesting transformation at fundamental level in that the non-benzenoid aromatic tropylium ring is converted to the aromatic benzene ring. Anthracene moiety can be incorporated in a similar fashion using suberenone as a building block. This work also paves the way for further applications of cycloheptatrienes derivatives in organic synthesis. We are currently working on the incorporation of substituted tropylium ions onto organic structures and transforming them into polyaromatic frameworks and will report the outcomes in due course.

Author Contributions

The manuscript was written through contributions of all authors. DJML, AHD, NNHT and RDC carried out all experimental work; TVN conceived the ideas and designed the project; BKM carried out all computational studies. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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17. From **INT3**, a deprotonation process can occur to give 4-phenylbenzaldehyde. Our calculations suggest that this 4-phenylbenzaldehyde product and biphenyl **2a** are kinetically and thermodynamically controlled, respectively. Under these reaction conditions, 4-phenylbenzaldehyde can be reverted to biphenyl **2a** via a two-step pathway with an activation barrier of 21.7 kcal/mol. Moreover, the emission of CO also drives the reaction to the formation of biphenyl **2a**, preferably. See Scheme S1 in the computational SI for detailed discussion.
18. This activation energy barrier is higher than the value reported by Dulova and co-worker (10.5 kcal/mol, ref. 13a). However, our system was a substituted tropylium ion and the reaction was carried out in MeCN solvent, which is different than Dulova's unsubstituted system in aqueous environment.
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