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Trapping of a cycloheptatetraene in the reaction of atomic carbon with phenol

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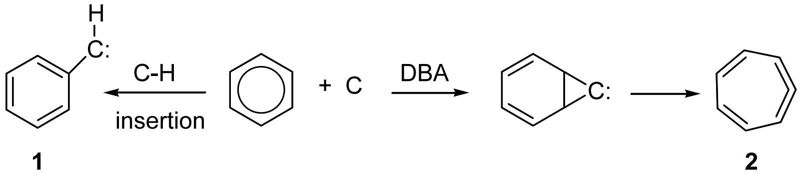
Abstract—Reaction of atomic carbon with phenol generates tropone in a reaction postulated to proceed via the hydroxycycloheptatetraenes, which rearrange to tropone. When the hydroxyphenylcarbenes are generated by the C atom deoxygenation of the corresponding aldehydes, the *meta* and *para* isomers produce tropone; the *ortho* isomer does not. © 2003 Elsevier Science Ltd. All rights reserved.

In principle, the reaction of atomic carbon with an aromatic ring can proceed via an initial C–H insertion to give a phenylcarbene **1** or by a double bond addition (DBA) to generate, after ring expansion, a cycloheptatetraene **2**. Although the situation is complicated by the well known phenylcarbene rearrangement which interconverts **1** and **2**,[1] the use of ^{11}C in the reaction with toluene[2] and the reaction of arc generated ^{13}C with benzene and *tert*-butylbenzene[3] indicate a predominance of initial C–H insertion to give a phenylcarbene which is capable of ring expanding to **2** under the reaction conditions. For example, arc generated ^{13}C atoms react with *tert*-butylbenzene by *ortho* C–H insertion to give *o*-*tert*-butylphenylcarbene which undergoes intramolecular C–H insertion to give 1,1-dimethylindane-3-^{13}C.[3] In addition, *meta* and *para* C–H insertion generates the corresponding *m*- and *p*-*tert*-butylphenylcarbenes which ring expand to the corresponding *tert*-butylcycloheptatetraenes and are trapped as *tert*-butyltropylium fluoroborate by the addition of HBF_4.[3] However, triplet C atoms in molecular beams are postulated to react with benzene by initial DBA.[4]

Since cycloheptatetraene intermediates in C atom reactions can be trapped by intermolecular proton addition,[3,5] we were interested in incorporating the acidic proton within the cycloheptatetraene in order to effect efficient intramolecular trapping. A simple way to do this is to generate a hydroxycycloheptatetraene by reacting C with phenol **3**. We now report that an intramolecular proton transfer efficiently traps the hydroxycycloheptatetraenes formed in this reaction. Thus, when C atoms are cocondensed with **3** at 77 K in a carbon arc reactor,[3] GC/MS analysis of the products reveals benzene, tropone **4**, *o*-cresol **5a**, and *m*- and *p*-cresol, **5b**,**c** (which are not separated under our GC/MS conditions). The relative yields of **4**, **5a**, and **5b**,**c**, which we feel are significant, are shown in Eq. (1). In all of our reactions of C with phenol or substituted phenols, a competing loss of OH to form benzene (benzene: **4** = 12.1) or a substituted benzene is observed. This is most likely a result of C atom deoxygenation to a phenyl radical and a hydrogen atom[6] and will not be considered further here.



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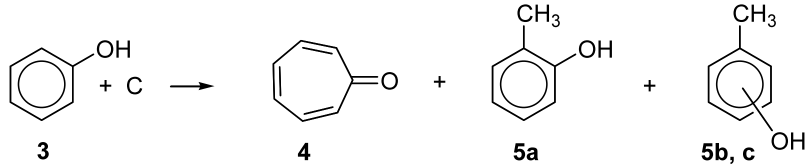


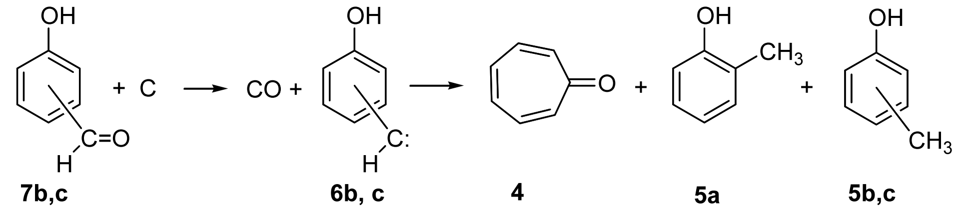
1 : 0.03 : 0.03 (1)

It has been reported that generation of the *m*- and *p*-hydroxyphenylcarbenes **6b** and **6c** from the pyrolysis of the corresponding tetrazoles at 530–700°C results in **4**[7,8] with only traces of **4** observed from *o*-hydroxyphenylcarbene **6a**.[8] It may be that the C atom reaction forming **4** proceeds via carbenes **6** in which ring expansion to the corresponding hydroxycycloheptatetraenes is followed by intramolecular proton transfer to give **4**.

In order to investigate the behavior of carbenes **6a**–**c** when they are individually generated by C atom reactions, we have examined the C atom deoxygenation of the *o*, *m*, and *p*-hydroxybenzaldehydes **7a**–**c** by atomic carbon, a well known method of generating carbenes.[9,10] Deoxygenation of **7b** and **7c** gives **4**, **5a**, and **5b**,**c** in the relative yields in Eq. (2). However, deoxygenation of **7a** generates only **5a**.

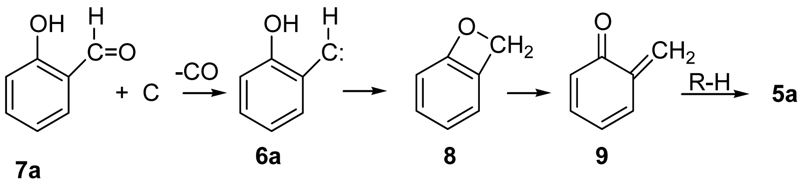
The formation of **4** in the deoxygenation of **7b**,**c** is explained by ring expansion of the corresponding carbenes **6b**,**c** to the hydroxycycloheptatetraenes followed by proton transfer to give **4**.[†] The formation of **5b**,**c** is interesting as these compounds are not observed when **6b**,**c** are generated by gas phase pyrolysis.[7,8] In the present experiments, we feel that **6b**,**c** decay to their triplet states on the 77 K surface. Hydrogen abstraction by triplet **6b**,**c** produces **5b**,**c**. While this pathway can also produce **5a** from triplet **6a**, rearrangement of **6a** to benzoxetete **8** followed by ring opening to *o*-quinomethide and subsequent H abstraction (Eq. (3)), a route postulated in the gas phase pyrolysis of **5**,[7,8] is also likely.[11,12] The fact that **5a** is generated in the deoxygenation of **7b** and **7c** indicates that **6b** and **6c** rearrange to **6a** under the energetic deoxygenation conditions.[13] Since deoxygenation of **7a** fails to generate **4**, we conclude that **6a** does not ring expand to hydroxycycloheptatetraene but rearranges to **8** (Eq. (3)).

The reactions shown in Eqs. (2) and (3) demonstrate that carbenes **6** produce substantial (30–100%) of the cresols **5** when generated under these conditions. Since direct reaction of C with **3** produces mainly **4** with only ~6% of **5**, it may be that some of the **4** generated in this reaction results from DBA, which bypasses carbenes **6**. Labeling experiments designed to evaluate this possibility are in progress. However, the current results provide additional evidence for cycloheptatetraene intermediates in the reaction of C with aromatics. While carbenes **6b** and **6c** are clearly the precursors of these cycloheptatetraenes in the deoxygenations, it is not yet clear that these carbenes are intermediates in the reaction of C with **3**.



(2)

From **7b**: 1.0 : 0.12 : 0.22
From **7c**: 1.0 : 0.22 : 0.12



(3)

[†] A referee has pointed out that proton transfer in the hydroxycycloheptatetraenes could be intermolecular, occurring on warm up of the 77 K matrix.

Acknowledgements

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