A Potential Chemical Source of C_2

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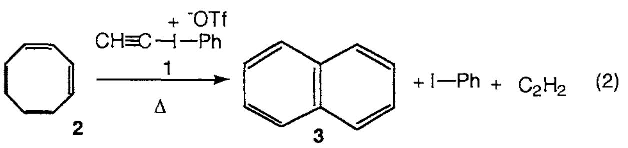
Thermolysis of ethynyl(phenyl)iodonium triflate, **1**, in the presence of cyclooctatetraene generates naphthalene in a reaction involving free C_2 or in which **1** acts as a C_2 donor.

Investigations of the mechanism of fullerene formation[1] have revived interest in small carbon clusters. Although the chemistry of atomic carbon has been extensively studied, the chemistry of simple molecular carbon species such as C_2 has received less attention.[2]

We now present evidence that ethynyl (phenyl)-iodonium triflate, **1**,[3] can serve as a source of C_2 or act as a C_2 donor. In order to investigate the possibility that **1** will undergo the exothermic decomposition to C_2 and stable products in eq 1, we

$$\underset{1}{CH{\equiv}C{-}\overset{+}{I}{-}Ph\ {}^{-}OTf} \xrightarrow{\Delta} C_2 + I{-}Ph + CF_3SO_3H \qquad (1)$$

have examined its thermolysis in the presence of compounds expected to react readily with C_2. We have recently demonstrated that arc generated C_2 reacts with cyclooctatetraene, **2**, to form naphthalene, **3**[4] and with styrene, **4**, and cycloheptatriene, **5**, to form **3** and indene, **6**, respectively.[5] These reactions, which yield easily identifiable stable products, appear well suited for detecting the intermediacy of C_2. Thus, **1** (638 mg, 1.33 mmol) and **2** (460 mg, 4.4 mmol) were placed in a pressure bottle, degassed, and heated at 65-75 °C for 4 h while the mixture gradually turned black. Analysis of an ether extract of the reaction mixture by GC, GC-MS and ^{13}C NMR revealed iodobenzene and **3** (2.4 mg, 0.019 mmol) as the only product bearing two more carbons than **2** (eq 2). An ir and NMR examination of the gaseous products revealed the presence of acetylene (0.607 mmol). Heating neat **1** or its benzene solution under similar conditions generated acetylene and iodobenzene but failed to yield **3**. Thermolysis of **1** in the presence of **4** and **5** gave **3** and **6** respectively in ~1% yield as detected by GC and GC-MS.



Much of the chemistry of C_2 that has been reported is that of a diradical. Arc generated C_2 on a 77 K matrix abstracts hydrogens to generate acetylene[6] and adds to two molecules of alkene to form eneynes.[7] In the present investigation, we observe that heating of **1** with simple alkenes such as cyclopentene invariably generates acetylene but none of the expected eneynes. If C_2 is involved in these reactions, eneyne products may be unstable or their formation may not be competitive with hydrogen abstraction to produce acetylene under these reaction conditions.

However, there is also the possibility that free C_2 is not involved and that **1** acts as a "C_2 donor" in its reaction with **2**, **4**, and **5**. It is known that alkynyl(phenyl)-iodonium salts undergo Diels Alder reaction with dienes[8] and it is possible that the reaction of **1** with **2** may proceed via a mechanism in which **1** acts as a C_2 donor without generating free C_2. Similar cycloaddition mechanisms could explain the formation of **3** and **6** in the reaction of **1** with **4** and **5**.

These studies indicate that thermolysis of **1** gives products of C_2[9] in yields comparable to those generated from arc generated molecular carbon.[4,5]

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References and Notes

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