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# *Communications*

## A New Hypervalent Iodine Precursor of a Highly Strained Cyclic Alkyne. Generation and Trapping Reactions of Bicyclo[2.2.1]hept-2-en-5-yne

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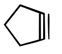
Cyclic alkynes with small rings are of considerable interest in chemistry because of their high strain and reactivity.[1] Generally, alkynes bearing more than eight-membered ring size are stable and isolable compounds, but cycloheptyne, cyclohexyne, and cyclopentyne are unstable and exist only as short-lived intermediates. Alkynes with three- and four-membered rings have not been observed experimentally. As a consequence, the smallest cyclic alkyne observed experimentally is five-membered cyclopentyne (**1**), which can be generated by reaction of 1,2-dibromopentene (**2**),[2] by oxidation of 1,2-bis(hydrazono)cyclopentane (**3**),[2a,3] and by ring expansion of cyclobutylidenecarbene (**4**).[4] However, the yields of adducts of cyclopentyne **1** with the trapping agents are low.[2−4] The unexpected side-reactions take place due to the use of the unstable precursors and the severe reaction conditions. In addition to the monocycloalkynes, strained bicycloalkynes have been also reported.[5]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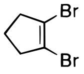

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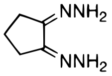

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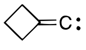

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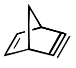
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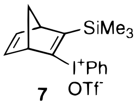

**7**

A new and excellent precursor for the generation of strained cyclic alkynes is clearly required, especially one which is stable, easy to handle, and efficient to generate a strained cyclic alkyne under mild conditions. In continuation of our studies on reactive hypervalent iodine reagents,[6,7] we have found that (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate (**5**) generates benzyne quantitatively under mild conditions.[8] This benzyne precursor **5** is stable and involves the very mild reaction conditions such as neutral medium and room temperature, giving high yields of the benzyne adducts. Thus, we have applied the benzyne precursor **5** to a cyclic alkyne system, namely bicyclo[2.2.1]hept-2-en-5-yne (**6**) which can be generated by reaction of a hypervalent iodine precursor, (phenyl)[3-(trimethylsilyl)bicyclo[2.2.1]-hept-2,5-dien-2-yl]iodonium triflate (**7**).

The previous study[8] on the benzyne precursor **5** suggests that the most suitable substrate for the generation of cyclic alkynes is the $\beta$-trimethylsilyl-substituted cyclic vinyliodonium salt. The hypervalent iodine group has an extremely high leaving ability,[9] and the trimethylsilyl group is easily cleavable by fluoride ion.[10] Accordingly, this combination constructs the alkyne precursor best.[11] To prepare trimethylsilyl-substituted cyclic vinyliodonium triflates, we examined the Diels−Alder reaction of (phenyl)[(trimethylsilyl)-ethynyl]iodonium triflate (**8**) with cyclic dienes, which provides the very convenient and direct synthesis.

First, [(trimethylsilyl)ethynyl]iodonium triflate **8**[12] was prepared according to the modified method of Bachi and Stang by using a hypervalent iodine reagent[13] readily prepared from PhI(OAc)$_2$ and trifluoromethanesulfonic acid (TfOH) or its anhydride (Tf$_2$O). Treatment of bis(trimethylsilyl)acetylene with PhI(OAc)$_2$ activated with TfOH or Tf$_2$O in dichloromethane gave alkynyliodonium triflate **8** in 72−88% yields.

Next, we examined the Diels−Alder reaction with dienes by the use of [(trimethylsilyl)ethynyl]iodonium triflate **8** according to the method of Stang.[14,15] The reaction of **8** with cyclopentadiene in acetonitrile proceeded efficiently to give (phenyl)[3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]-

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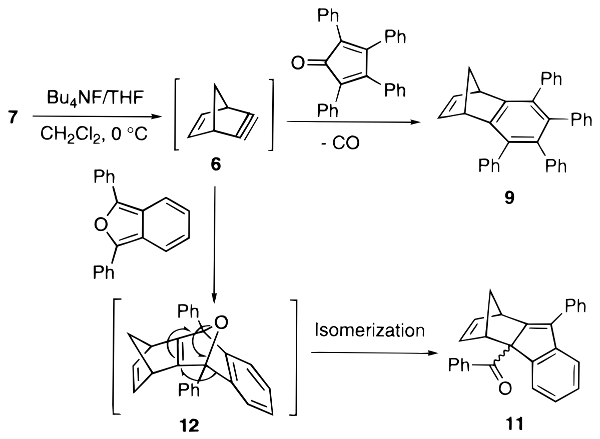
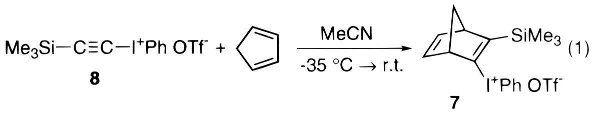
**Scheme 1**



iodonium triflate **7** in 96% yield (eq 1). The similar reaction with 1,3-diphenylisobenzofuran in dichloromethane also gave the corresponding cycloadduct in 66% yield. Unfortunately, the reactions with other dienes such as butadiene, 2,3-dimethylbutadiene, and furan did not give the cycloadducts. Although [(trimethylsilyl)ethynyl]iodonium triflate **8** is not so active, the Diels–Alder reaction of **8** with cyclopentadiene or 1,3-diphenylisobenzofuran gives the satisfactory results.

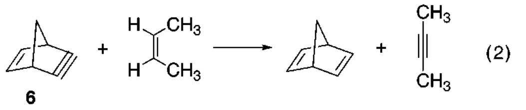


The generation of cyclic alkyne **6** was examined by the reaction of cyclic vinyliodonium triflate **7** with Bu$_4$NF in the presence of tetraphenylcyclopentadienone. Treatment of cyclic vinyliodonium triflate **7** with a THF solution of Bu$_4$NF in the presence of tetraphenylcyclopentadienone in dichloromethane gave a crystalline cycloadduct, 1,2,3,4-tetraphenylbenzonorbornadiene (**9**), in 69% isolated yield. The formation of the cycloadduct **9** strongly supports the generation of bicyclo[2.2.1]hept-2-en-5-yne **6**, which undergoes the [4 + 2] cycloaddition with tetraphenylcyclopentadienone to give the intermediate cycloadduct (**10**) followed by release of CO to form the product **9**, as shown in Scheme 1. The similar reactions giving benzocycloalkenes have been observed in the cases of cyclic alkynes such as cyclohexyne,[16] cycloheptyne,[16,17] and cyclooctyne.[2a,16] Therefore, the formation of benzoadduct **9** confirms the intervention of cyclic alkyne **6**.

Then, we conducted the reaction in the presence of 1,3-diphenylisobenzofuran which is also well-known as a trapping agent. When cyclic iodonium triflate **7** was treated with a THF solution of Bu$_4$NF in the presence of diphenylisobenzofuran in dichloromethane, the carbonyl-containing adduct (**11**) was obtained in 43% yield after isolation by column chromatography on silica gel. Surprisingly, we obtained the product different from that we have expected. According to the Wittig's reports,[2b,3] the cycloadducts derived from the reaction of 1,3-diphenylisobenzofuran with cycloheptyne and cyclooctyne are isomerized to the corresponding carbonyl compounds on heating. On the basis of these results, this carbonyl compound **11** should be formed by the similar isomerization reaction of the primary cycloadduct (**12**) derived from the reaction of bicyclo[2.2.1]hept-2-en-5-yne **6** with diphenylisobenzofuran (Scheme 1).

Since it is seemed that the use of **7** is useful for generation of cyclic alkynes, we compared the reaction of bicyclo[2.2.1]-hept-2-en-5-yne precursor **7** with those of the cyclopentyne precursors. There are three major methods generating cyclopentyne **1** from 1,2-dibromopentene **2**,[2] 1,2-bis(hydrazono)cyclopentane **3**,[2a,3] and bromomethylenecyclobutane.[4] In the reactions with 1,3-diphenylisobenzofuran, these methods give the cycloadduct in 0.5–12% yields. On the other hand, the reaction of the cyclic iodonium triflate **7** using Bu$_4$NF gives the cycloadduct, although it is isomerized one, in 43% yield. Apparently this type of cyclic iodonium triflate gives better results than the reported cyclic alkyne precursors.

Since bicyclo[2.2.1]hept-2-en-5-yne **6** is a bicyclic alkyne constructed by five- and six-membered rings, it is expected to have more strain than cyclopentyne **1**. To estimate the strain of the bicyclic alkyne **6**, we examined the $\pi$ bond strain of **6** derived by comparison to the reference molecules according to the calculation by Johnson and Daoust.[18] We considered the similar isodesmic reaction shown in eq 2 for comparison. By the calculation at MP2/6-31G* level, we got 72.7 kcal/mol of the in-plane $\pi$ bond strain. This value is between those obtained from cyclobutyne and cyclopentyne.[18] If we add the strain energy of norbornadiene, 24.0 kcal/mol,[19] as an approximation for other strain components, the total strain energy of 96.7 kcal/mol is obtained. This strain energy is much higher than that of cyclopentyne (68.1 kcal/mol) but lower than that of cyclobutyne (101.8 kcal/mol).[18] Consequently, bicyclo[2.2.1]hept-2-en-5-yne **6** is a highly strained cyclic alkyne.



In conclusion, we have succeeded in the generation of a highly strained cyclic alkyne, bicyclo[2.2.1]hept-2-en-5-yne **6**, by using the hypervalent iodine precursor **7** and found that the cyclic alkyne **6** is efficiently trapped with tetraphenylcyclopentadiene or 1,3-diphenylisobenzofuran. We believe that bicyclo[2.2.1]hept-2-en-5-yne **6** is one of the highly strained cyclic alkynes observed experimentally by the trapping reactions.

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**Supporting Information Available:** Characterization data for compounds **7**, **9**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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