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C₁₂H₁₂ interconversions: two non-pyrolytic syntheses of tricyclo[5.3.2.0^{4,8}]dodeca-2,5,9,11-tetraene

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Abstract

Herein, we describe two independent and non-pyrolytic syntheses of an important C₁₂H₁₂ hydrocarbon which had been prepared previously by gas phase thermolysis of compound **6**. The first method is based on an unusual dipolar cycloaddition of dichloroketene onto bullvalene. After reductive dechlorination, a Shapiro-Heath reaction of the tosylhydrazone gave the title compound. Alternatively, compound **13** is also obtained from its isomer **6** by a Ag⁺ catalyzed reaction.

Graphical abstract

Keywords

C₁₀H₁₀ hydrocarbons; C₁₂H₁₂ hydrocarbons; Dichloroketene; Silver ion catalyzed reactions; Bullvalene

1. Introduction

The study of the class of hydrocarbons whose isomers are composed of only methane units has fascinated the chemists for a long time. In particular, the colorful chemistry and the multitude of complex structures discovered in the C₁₀H₁₀ series has been the impetus for prolonged and intensive research in the area of (CH)_n hydrocarbons.¹ The most notable C₁₀H₁₀ isomers are bullvalene,² basketene,³ snoutene,⁴ diademane,⁵ and triquinacene,⁶ the latter four being closely interrelated due to their well-documented interconversion pathways.⁵

Bullvalene, for instance, incorporates a homotropylidene, as well as a *cis*-divinylcyclopropane unit and represents a fully fluxional molecule undergoing degenerate

Cope rearrangements that render all carbon atoms and protons, respectively, equivalent on the NMR timescale. Snoutene was obtained from basketene by Ag^+ -catalyzed rearrangement, and diademane was synthesized from snoutene by photolysis;⁵ triquinacene forms from the latter either thermally, or by Ag^+ catalysis.⁶ Our work with $\text{C}_{12}\text{H}_{12}$ hydrocarbons originated during our synthetic effort to prepare cyclobutyl-annelated bicyclo[2.2.2]octane hydrocarbons to eventually obtain bridgehead halides for solvolysis kinetic studies.⁷ Since the tricyclic compound **6** was derived from one of the cyclooctatetraene dimers,⁸ and was the unwanted isomer for our purpose at the time, we fortuitously discovered a new photochemical rearrangement of **6** via direct photolysis to give a 2:1 mixture of the desired tetracyclic $\text{C}_{12}\text{H}_{12}$ isomers **8** and **9** via **7**.⁹

In another project on $(\text{CH})_{12}$ hydrocarbons, we developed a new unusual synthesis of snoutene (**3**) from the Nenitzescu hydrocarbon **10** by way of a dipolar cycloaddition with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and subsequent denitrogenation of the azo compound **12** derived from **11** by either thermolysis or photolysis.¹⁰

In continuation of our work with $(\text{CH})_{12}$ hydrocarbons we report in this *Letter* two new, non-pyrolytic methods for the synthesis of another $(\text{CH})_{12}$ isomer that has previously been accessible only from **6** by flash vacuum pyrolysis.

2. Results and Discussion

As stated above, the title compound **13** has so far been available only by gas phase pyrolysis of **6** at 480 °C (Scheme 3).¹¹

Our first synthesis of **13** is based on our previous work on dichloroketene cycloadditions onto fluxional compounds that are subject to degenerate Cope rearrangements, such as semibullvalene, barbaralane and bullvalene.¹² While semibullvalene and barbaralane gave the expected [2+2] cycloadducts, bullvalene gave an unusual cycloadduct **15** that presumably stemmed from the initial [2+2] cycloaddition product **14** which underwent ZnCl_2 isomerization to **15**. (Scheme 4). This premise was substantiated by the isolation of **14** when the dichloroketene cycloaddition was conducted in the presence of POCl_3 , a reagent that complexes ZnCl_2 . Compound **14** was then converted with added ZnCl_2 , or upon prolonged exposure to silica gel to **15**.

Compound **15** bears a remarkable structural similarity to **13** and appeared as an excellent precursor thereof. Indeed, upon dechlorination with Zn in methanol in the presence of NH_4Cl ketone **16** was obtained.¹³ It was converted to its tosylhydrazone in EtOH, and the resulting solid, after drying overnight in vacuum was subjected to a Shapiro-Heath reaction¹⁴ by treating the latter with 2 equivalents of *n*-BuLi in THF to give the desired compound **13** in 68% overall yield (from **15**).¹⁵ Compound **13** had NMR data identical to those reported by Schröder¹² (Scheme 5).

With **13**, now available by a non-pyrolytic method, we turned our attention to the thermal isomerization of **6** to **13**. Paquette et al. reported in a series of papers¹⁶ that silver (I) ions effectively catalyze skeletal rearrangements of strained polycyclic systems by the interaction of the atomic orbitals of Ag^+ directly with a set of strained σ bonds leading to concerted

skeletal rearrangements (e.g., conversion of basketene to snoutene), although de Meijere postulated a stepwise mechanism involving carbocation intermediates for the Ag^+ catalyzed isomerization of diademane to triquinacene.⁶ We deemed it worthwhile to attempt a Ag^+ catalyzed isomerization of compound **6**, since silver (I) ions are known to interact with strained σ bonds endowed with enhanced p-character and bring about isomerizations that otherwise would be thermally forbidden in the ground state. Since compound **6** does contain a strained cyclopropane ring, we decided to put the above-mentioned considerations to test by treating **6** with AgClO_4 in chloroform. Upon stirring the mixture in the dark overnight at room temperature, compound **6** quantitatively rearranged to **13**. We propose that Ag^+ attaches itself to the cyclopropane ring to give the carbocation **17** which then undergoes the observed rearrangement to deliver **13** (Scheme 6).

Our silver (I) catalyzed conversion of **6** to **13** mimics the thermolytic rearrangement in terms of the result (Scheme 3). Schröder had postulated a mechanism shown in Scheme 7.¹¹

We postulate here an alternative mechanism for the thermal rearrangement of **6** to **13** that is quite similar to the ionic mechanism depicted in Scheme 6 through diradical intermediates instead of carbocations. The cleavage of the strained cyclopropane bond leads to the allyl radical **20**; an allyl shift gives **21**, and a 1,5 shift of the cyclobutene ring would satisfactorily account for the formation of **13**, as shown in Scheme 8.

3. Conclusions

The fascinating chemistry of $(\text{CH})_n$ hydrocarbons extends to the $(\text{CH})_{12}$ representatives in terms of the varied structures in this class of hydrocarbons as well as their diverse interconversion mechanisms via photochemical, thermal and metal ion catalyzed pathways. We have uncovered two new independent syntheses for one of the important members of the $(\text{CH})_{12}$ family; the first one features bullvalene, a $(\text{CH})_{10}$ hydrocarbon as precursor by a formal replacement of the cyclopropane bond by an etheno bridge taking advantage of an unusual ZnCl_2 -catalyzed rearrangement of the initial [2+2] dichloroketene cycloadduct **14**. The second pathway is a one-step conversion of **6** to **13** under Ag^+ catalysis. The mechanism offered for this reaction is consistent with other silver ion catalyzed rearrangements of compounds containing strained rings. Our studies also shed light on the mechanism of the thermal isomerization of **6** to **13**, rendering an entirely analogous rearrangement involving radical intermediates as the most plausible pathway.

Acknowledgments

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Tetrahedron

- Two new syntheses of an important $C_{12}H_{12}$ hydrocarbons are described
- The first of these features an unusual transannular addition of dichloroketene onto bullvalene
- The second is a direct conversion of an isomer of the title compound via Ag^+ catalysis
- Reasonable mechanism are offered for the Ag^+ catalyzed reaction and the thermal isomerization

Figure 1.
Some notable $C_{10}H_{10}$ hydrocarbons

Scheme 1.

Photochemical conversion of **6** to **8** and **9** via **7**.

Scheme 2.

Synthesis of snoutene **3** from **10** via PTAD dipolar cycloaddition

Scheme 3.
Synthesis of **13** by gas phase pyrolysis of **6**

Scheme 4.
Dichloroketene addition to bullvalene

Scheme 5.
Synthesis of **13** from **15**

Scheme 6.

Postulated mechanism for the Ag^+ catalyzed rearrangement of **6** to **13**.

Scheme 7. Schröder's mechanism for the thermal conversion of **6** to **13**

Scheme 8.

Alternative mechanism for the thermal isomerization of **6** to **13** via diradical intermediates **20** and **21**