Photoisomerization of 5,5-dimethyl-3-(3,3-dimethylbut-1-ynyl)-2-(pent-4-enyl)-cyclohex-2-enone to *tert*-butyl(4,4-dimethyl-2-oxotricyclo[7.3.0.0^{1,6}]dodec-6-en-7-yl)carbene

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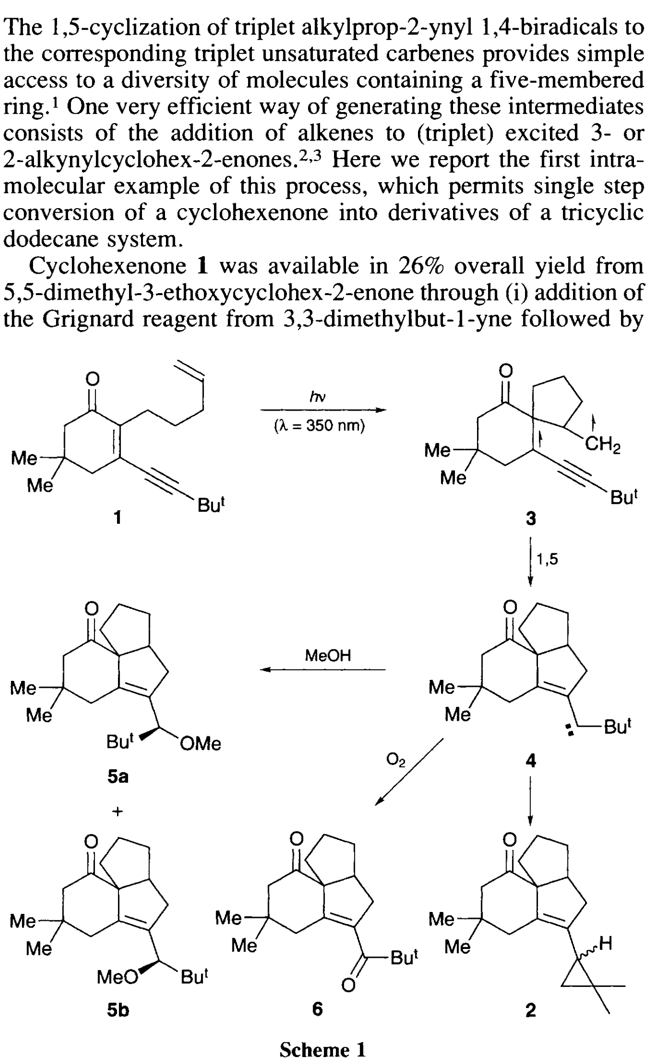
On irradiation (λ > 340 nm) cyclohexenone 1 is converted to a mixture of diastereoisomeric 4,4-dimethyl-7-(2,2-dimethylcyclopropyl)tricyclo[7.3.0.0^{1,6}]dodec-6-en-2-ones 2 *via* the title carbene 4, which can also be efficiently trapped both by methanol or by oxygen to afford methyl ethers 5a and 5b or the pivaloyl derivative 6, respectively.

The 1,5-cyclization of triplet alkylprop-2-ynyl 1,4-biradicals to the corresponding triplet unsaturated carbenes provides simple access to a diversity of molecules containing a five-membered ring.[1] One very efficient way of generating these intermediates consists of the addition of alkenes to (triplet) excited 3- or 2-alkynylcyclohex-2-enones.[2,3] Here we report the first intramolecular example of this process, which permits single step conversion of a cyclohexenone into derivatives of a tricyclic dodecane system.

Cyclohexenone **1** was available in 26% overall yield from 5,5-dimethyl-3-ethoxycyclohex-2-enone through (i) addition of the Grignard reagent from 3,3-dimethylbut-1-yne followed by acid hydrolysis, and (ii) metallation of the addition product with lithium diisopropylamide and alkylation with 5-iodopent-1-ene at −20 °C. Irradiation (λ > 340 nm) of **1** in Ar-degassed benzene (Scheme 1) affords a 3 : 1 diastereoisomeric mixture of cyclopropanes **2** (47% isolated yield). This reaction can be explained in terms of intermediates **3** and **4**. Spirocyclization of the pentenyl side chain in triplet excited **1** affords a triplet alkylprop-2-ynyl 1,4-biradical containing a cyclopentanemethyl radical moiety (**3**). The first step has precedent in the analogous cyclization of 2-(pent-4-en-1-yl)cyclohex-2-enone.[4] Biradical **3** then undergoes selective (>95% from GC) 1,5-cyclization to form the vinylcarbene **4**. Good additional evidence for formation of **4** comes from its trapping exclusively as a 1 : 2 diastereoisomeric mixture of methyl ethers **5a** and **5b** on irradiation of **1** in Ar-degassed methanol solution. Ethers **5a** and **5b** were separated by chromatography on SiO_2 with pentane–diethyl ether (25 : 1) as eluent and isolated in 22 and 54% yields, respectively.



Scheme 1

Interestingly, one new product **6** is formed selectively from **1** on irradiation in *non-degassed, i.e.* air-saturated, benzene solution. If the reaction is stopped at 40–50% conversion, diketone **6** can be isolated in 15% yield. Further irradiation leads to secondary photolytic destruction of **6**. Reactions of triplet carbenes with molecular oxygen are known to be rapid, and frequently the isolated products are carbonyl compounds.[5] In the present case, product **6** is an α,β-unsaturated ketone that is apparently photolabile under the irradiation conditions.

All new compounds **1**, **2** **5a**, **5b** and **6** have been fully characterized and have spectroscopic properties compatible with the structures assigned.

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