Tetrasubstituted Furans from Novel [3 + 2] Photocycloaddition of Conjugated Acetylenic α-Diketones with Alkenes

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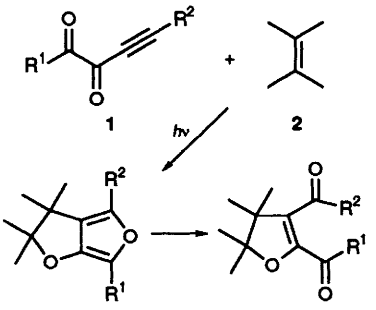
Photocycloaddition of ketones **1a–c** with tetramethylethylene **2** furnishes tetrasubstituted furans **3a–c** in isolated yields of ≈85%; a suggested mechanism for formation of **3a** involves [3 + 2] cycloaddition by way of an initial biradical **5** to form an intermediate carbene **6**, followed by cyclization to the furan.

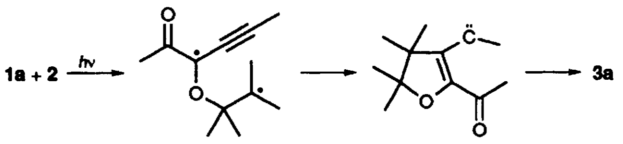
Photochemical cycloaddition of acetylenic α-diketones **1a–c** to simple alkenes yields tetrasubstituted furans as the only observed products. This reaction is a novel photochemical process that effectively provides a one-step route to bicyclic furans bearing oxygen at C3. Furans find increasing use in synthesis,[1] and new methods of preparing these heterocycles are in demand.[2] We are aware of no previous photochemical studies on conjugated acetylenic α-diketones. Irradiation of aliphatic or alicyclic α-diketones in the presence of alkenes leads to hydrogen abstraction and to both [2 + 2] and [4 + 2] cycloaddition, forming oxetanes and 1,4-dioxenes, respectively.[3]

Ketones **1a–c** were available starting from alanine (for **1a,b**) or phenylglycine (for **1c**), and propyne (for **1a,c**) or phenylacetylene (for **1b**), following a procedure for related α-diketones.[4] We purified **1a–c** using spinning-disc chromatography and characterized them spectroscopically. These ketones underwent photocycloaddition ($\lambda > 340$ nm) with tetramethylethylene **2** (10 equiv. 0.25 mol dm^{-3}) in benzene as solvent to yield ≈85% of the corresponding purified bicyclic furans **3a–c**.

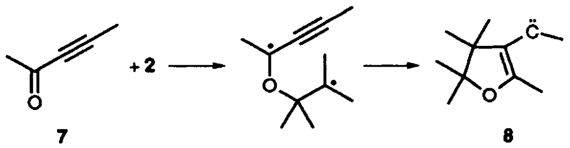


1 **2** **3** **4**

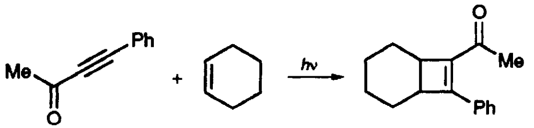
a R^1 = R^2 = Me
b R^1 = Me, R^2 = Ph
c R^1 = Ph, R^2 = Me



5 **6**



7 **8**



9 **10**

Essentially no other volatile products appeared on gas chromatography. Structures of these furans rest on their spectroscopic properties and reaction[5] with oxygen in the presence of silica gel to furnish α,β-unsaturated γ-diketones **4a–c** in high yield.

We propose that this reaction is a [3 + 2] cycloaddition followed by cyclization, as illustrated for formation of **3a**. Addition of **2** to **1a** to furnish **5** and subsequent 1,5 closure of **5** to **6** have analogy in the addition of simple α,β-acetylenic ketones to alkenes, as shown for formation of **8** from pent-3-yn-2-one **7** and **2**.[6] Cyclization of **6** to **3a** has precedent in previously observed closures of β-acylvinyl carbenes to furans.[7] Other alkyl propargyl biradicals that cyclize to vinyl carbenes, as is suggested for the closure of **5** to **6**, emanate from triplet ketones.[6,8] In line with this earlier experience, the yield of **3c** was reduced ≈25% in the presence of 0.1 mol dm^{-3} naphthalene as a triplet quencher.

It is noteworthy that this tandem cycloaddition–cyclization is successful with phenyl-substituted ketone **1b**, where the phenyl substituent is conjugated with the triple bond. In the simple β-phenyl α,β-acetylenic ketone **9** photocycloaddition of cyclohexene, tetramethylethylene, or other alkenes occurs at the triple bond to give a cyclobutene such as **10**.[9] This suggests that **9** has a π,π* reactive excited state centered on the phenylacetylene system. In contrast, formation of **3b** suggests that the reactive triplet of **1b** is an n,π* state associated with the appropriate carbonyl group. Similarly, it was conceivable that the reactive triplet of **1c** would be associated with the phenone carbonyl rather than the carbonyl group conjugated with the triple bond, and that the observed reaction would not occur. Finally, even with high concentrations of **2** (50 equiv. 1.25 mol dm^{-3}), the only observed product from **1a** is furan **3a**. In simple acetylenic ketones such as **7** intersystem crossing is sufficiently slow that high concentrations of alkene capture the singlet ynone to yield an oxetane.[6] These various observations demonstrate that simple conjugated acetylenic ketones, phenones, and α-diketones fail to provide satisfactory models for the photochemical behavior of **1a–c**, indicating that this previously unexplored chromophoric system requires further study.

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