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Tetrasubstituted Furans from Photocycloaddition of Alkenes to 2-(1-Alkynyl)cyclohexenones

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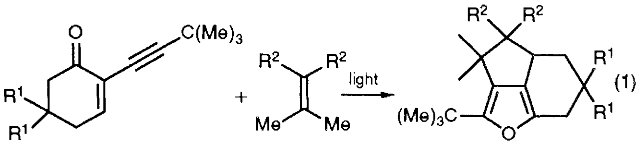
Photocycloaddition of 2-(1-alkynyl)cyclohexenones **1** and **2** with alkenes **3** and **4** furnishes tetrasubstituted furans **5–8** as the only isolated products; a suggested mechanism leads from the alkyl propynyl biradical **12** to carbene **13**, which then closes to the furan.

In recent years furans have found increasing use as intermediates in the synthesis of complex molecules,[1] and there is a general need for new methods of preparing highly functionalized derivatives of this ring system.[2] We describe here the novel preparation of tricyclic, tetrasubstituted furans in a single reaction through photochemical [3 + 2] cycloaddition of alkenes to 2-(1-alkynyl)cyclohexenones [eqn. (1)]. This is a clean, highly regioselective process, and **5–8** were essentially the only products found on addition of ketones **1** and **2** with isobutylene **3** and tetramethylethylene **4**.

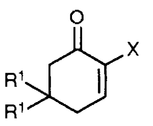
Ketones **1** and **2** were prepared from the two corresponding cyclohexenones **9a**. These were brominated[3] **9b** and converted to the cyclic acetals **10b**. The bromine atom of **10b** was exchanged for iodine **10c** on reaction with butyllithium followed by iodine, a procedure previously reported for preparation of (**10c**, R^1 = H).[4] Iodides **10c** furnished **10d** on alkylation with *tert*-butylethynyltributylstannane **11** in the presence of tetrakis(triphenylphosphine)palladium in tetrahydrofuran.[5] Removal[6] of the acetal grouping then gave ketones **1** and **2**, which were fully characterized. Each ketone was irradiated (λ ~350 nm) in benzene solution with 10 equiv. of alkene **3** or **4** to disappearance of ketone as monitored by gas chromatography (~40 h). Reaction mixtures were purified by chromatography over silica gel followed by bulb-to-bulb distillation [80 °C at 0.01 Torr (1 Torr = 133.322 Pa)]. Purified furans **5–8** were obtained in ~40% yield and were characterized spectroscopically. Especially significant data for **5–8** are the furan absorptions in ^{13}C NMR spectra at δ 155, 143, 135 and 129 (typical data); the lack of carbonyl absorption in IR spectra; and M^+ (~25%) and $(M - 15)^+$ (~45%) signals in mass spectra.



1; R^1 = H
2; R^1 = Me

3; R^2 = H
4; R^2 = Me

5; $R^1 = R^2$ = H
6; R^1 = H, R^2 = Me
7, R^1 = Me, R^2 = H
8, $R^1 = R^2$ = Me



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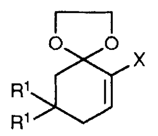
a; X = H
b; X = Br



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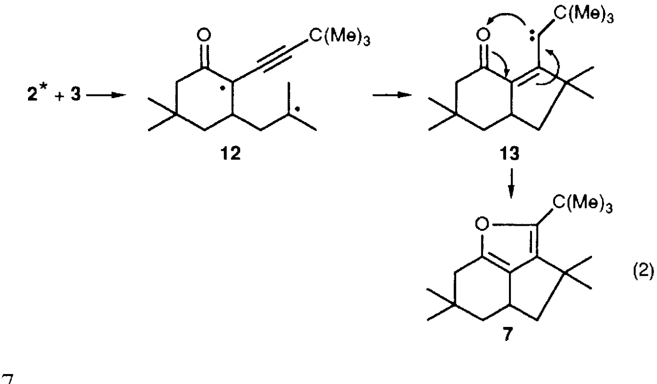
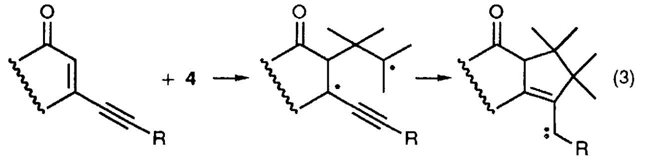
c; X = I
d; X = C≡C—C(Me)3

$Bu_3Sn—C≡C—C(Me)_3$

11

A reasonable mechanism for formation of these furans is exmplified for **7** in eqn. (2), where the suggested steps are formation of biradical **12**, 1,5 closure to carbene **13**, and then cyclization to the furan. Each step of this sequence has appropriate precedents and the combination of steps provides a new overall transformation in which three bonds are formed. Biradical **12** is an intermediate in the common [2 + 2] photochemical reaction between triplet enones and alkenes.[7] It is noteworthy that the observed regioselectivity of the cycloaddition that gives **7** and **5** can be explained by selective conversion of **12** and the analogous biradical from **1** and **3** into adducts. The alternative biradicals in which the substituted end of the isobutylene double bond has added to C(3) of the ketone either fail to form or revert completely to addends. Closure of **12** to carbene **13** exemplifies a process that we have previously observed in several different types of alkyl propynyl 1,4 biradicals.[8] As a direct analogy for the final closure, there are prior conversions of γ-carbena α,β-unsaturated carbonyl compounds to furans,[9] as well as formally related cyclizations of both all-carbon carbenes and also related species containing other heteroatoms.[10] It is also





14 **15**

possible that an acylcyclopropene intervenes between carbene and furan, in view of the known cyclization of singlet vinyl carbenes to cyclopropenes[11] and the recent discovery of the rearrangement of triplet acylcyclopropenes to furans.[12]

The steps from ketone and alkene to carbene **13** have direct analogy in the [3 + 2] photocycloaddition of alkenes with the isomeric 3-(1-alkynyl)cycloalkenones **14** [eqn. (3)].[8] In these latter additions, however, the fate of carbene **15** depends on specific structure, and in some cases several products result. A further contrast with the behaviour of **1** and **2** is that cycloadditions with **14** also furnish varying amounts of the normal [2 + 2] adducts.

The stereoselectivity of this reaction with appropriate alkenes is currently under investigation, as are the spin states of the suggested biradical and carbene intermediates.

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