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Novel Synthesis of Bifurans via Furan-Forming Photocyclization of α-Diketones Conjugated with Ene-Yne

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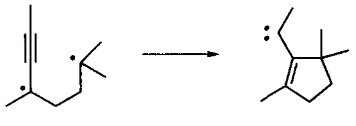
Abstract: Upon photoirradiation at 366 nm α-diketones conjugated with ene-yne undergo cyclization to furan derivatives with the formation of carbene intermediates. In protic solvents the carbene was protonated to produce furan derivatives, whereas trapping the carbene in nonprotic solvents by adjacent carbonyl group led to the formation of a novel 2,2'-bifuran derivative in a quantitative yield. © 1997, Elsevier Science Ltd. All rights reserved.

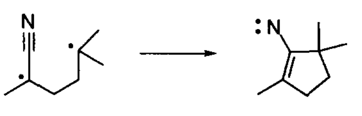
Triplet 1,4-biradicals such as **1** and **3** attached to alkyne and nitrile are known to undergo cyclization to triplet carbene **2**[1,2] (eq 1) and nitrene **4** (eq 2),[3] respectively. Such radical cyclizations so far reported are only limited to carbon-centered 1,4-biradicals. We now report herein for the first time that 1,4-biradicals **6** generated by photoexcitation of α-diketones **5** undergo a similar type of radical cyclization with a high quantum efficiency to produce furan-substituted carbenes **7** (eq 3).

We have previously reported that photoirradiation of α-diketone **8** at 366 nm in aqueous acetonitrile effectively produced furan **9** in a high yield.[4] The quantum yield for the photoreaction was 0.06. When we carried out the photoreaction of **8** in various alcohols, corresponding adducts **10**, **11**, and **12** were obtained in good yields.



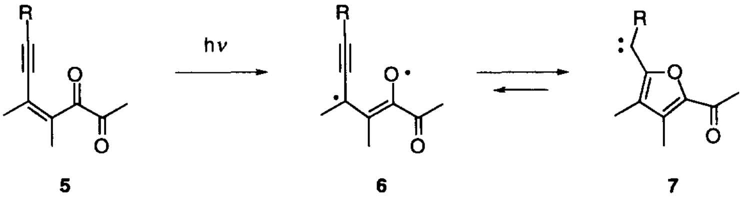
(1)

1 **2**



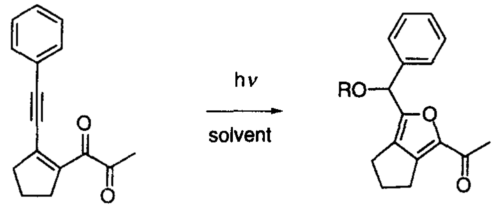
(2)

3 **4**



(3)

5 **6** **7**



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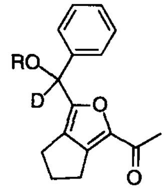
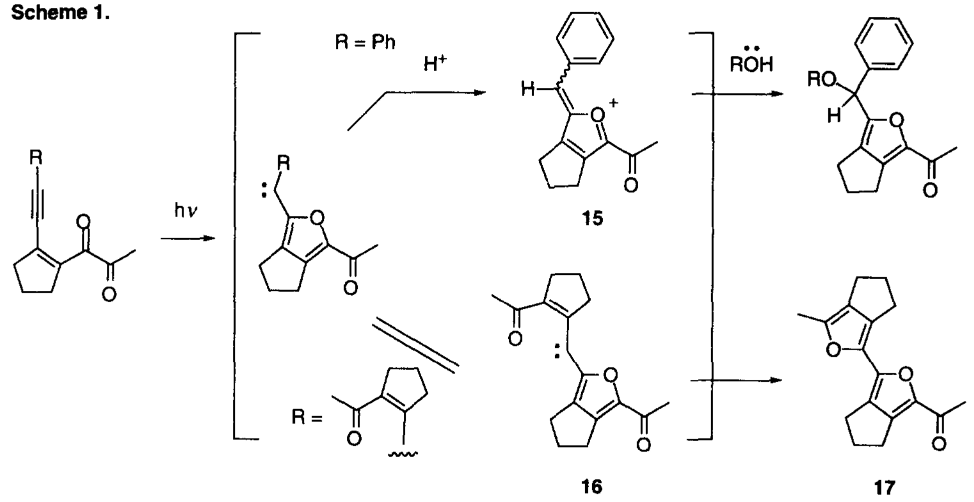


13: R = H
14: R = CD_3

solvent	product	yield (%)
aq. CH_3CN	**9**: R = H	73
MeOH	**10**: R = Me	76
i-PrOH	**11**: R = *i*-Pr	62
t-BuOH	**12**: R = *t*-Bu	49

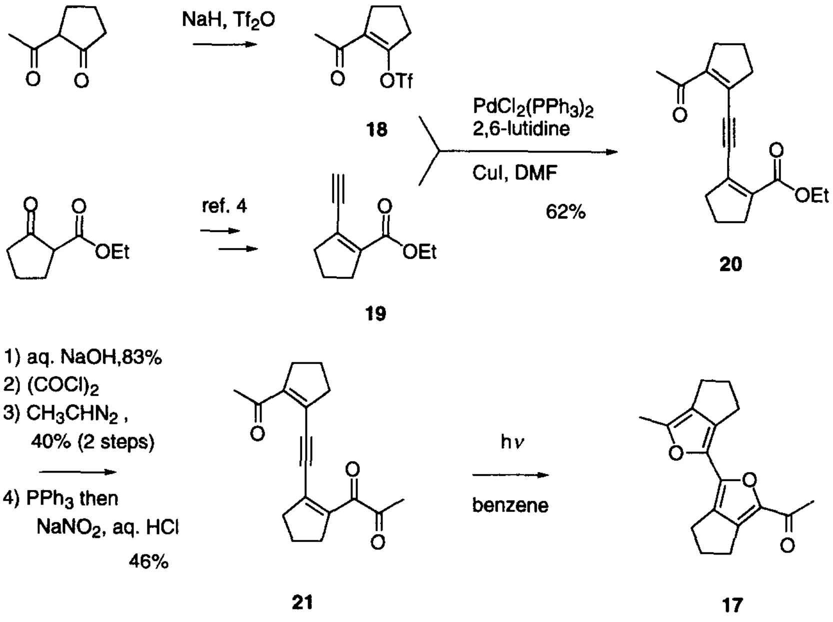
The photoirradiation of **8** in acetonitrile–D_2O (1 : 1) (99.8% atom D) produced alcohol **13**, in which the deuterium was incorporated exclusively into the benzylic position (>95% atom D). A similar incorporation of deuterium was observed with alcohol **14** when CD_3OD was used as a solvent. Since it is well established that a variety of electron rich carbenes react with alcohols by way of proton transfer,[5] it is highly likely that the photoreaction of **8** in protic solvents involves protonation of the carbene at the benzylic position followed by addition of alcohol or water to the resulting cationic species (*e.g.*, **15**) (Scheme 1).

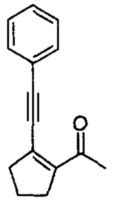
Scheme 1.



In order to confirm the carbene formation as an intermediate, the photoreaction of **8** was examined in nonprotic solvents. In spite of the efficient photocyclization of **8** to furan derivatives in protic solvents, the photoreaction in dry benzene or tetrahydrofuran was very sluggish. Attempts to trap the carbene with hydrogen donors such as tri-*n*-butyltin hydride and tris(trimethylsilyl)silane or with various alkenes were unsuccessful to result in a decomposition of the starting material **8**. These results seemed to suggest that the cyclization of 1,4-biradical to carbene (*e.g.*, **6**→**7**) would be a reversible process.[6] In order to trap carbene intermediate intramolecularly in nonprotic solvents, we have designed α-diketone **21** with the expectation that the putative carbene would undergo simultaneous cyclization to result in a formation of the second furan ring (*e.g.*, **16**→**17** in Scheme 1).[7] Synthesis of **21**[8] was accomplished by transformation of ester group of **20**, which was prepared by a coupling of alkyne **19** with enol triflate **18**, into α-diketone functionality *via* α-diazo ketone (Scheme 2). Upon photoirradiation of **21** at 366 nm in benzene, 2,2'-bifuran **17**[9] was obtained in a quantitative yield.

Scheme 2.

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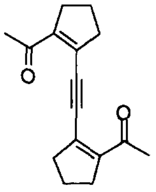
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In order to gain further insight into the mechanism of the photoreaction, we carried out following experiments. Replacement of the α-diketone functionality in **8** by monoketone completely changed the course of the photoreaction. Thus, the photoreaction of monoketone **22** in methanol produced mainly an intermolecular [2+2] photocycloadduct, whereas symmetric diketone **23** was stable under photoirradiation in benzene or aqueous acetonitrile. These results suggest that the photocyclization of **8** and **21** requiers the involvement of triplet α–diketone which gives rise to the formation of triplet 1,4-biradical.

In summary, we have uncovered a novel type of photoreaction of α-diketones conjugated with ene-yne to produce α-furyl carbenes, which could be efficiently trapped by protic solvents or adjacent carbonyl groups to produce novel 2,2'-bifuran derivatives in one step.

References and Notes

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(8) **21**: UV (CH_3CN) λ_{max} 335 ($\varepsilon = 1.41\times10^4$); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 1.90$ (quint, 2H, $J = 7.7$ Hz), 2.00 (quint, 2H, $J = 7.7$ Hz), 2.40 (s, 3H), 2.48 (s, 3H), 2.68–2.81 (8H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 21.82$, 22.09, 26.01, 29.40, 32.49, 33.32, 39.64, 39.73, 95.52, 98.32, 131.82, 138.57, 143.17, 149.36, 190.87, 196.99, 200.86; HRMS calcd for $C_{17}H_{18}O_3$ (M^+) 270.1255, found. 270.1243.

(9) **17**: UV (CH_3CN) λ_{max} 362 ($\varepsilon = 2.28\times10^4$); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 2.24$ (brs, 3H), 2.39 (s, 3H), 2.36 (m, 2H), 2.45 (m, 2H), 2.50 (m, 2H), 2.77–2.82 (4H), 2.87 (t, 2H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 12.86$, 23.03, 24.32, 24.85, 26.20x2, 31.50, 32.03, 129.38, 130.34, 133.79, 134.45, 141.18, 142.17, 143.20, 145.09, 197.71; HRMS calcd for $C_{17}H_{18}O_3$ (M^+) 270.1255, found. 270.1220.

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