JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 13
1988

Novel (3 + 2) Photocycloadditions with 3-(1-Alkynyl)cyclohexenones and Tetramethylethylene

Paul Margaretha,[a]* H. J. Rathjen,[a] Steven Wolff,[b] and William C. Agosta[b]*

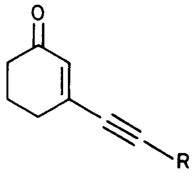
[a] *Institut für Organische Chemie, Universität Hamburg, D-2000 Hamburg 13, Federal Republic of Germany*
[b] *Laboratories of The Rockefeller University, New York, New York 10021-6399, U.S.A.*

Irradiation of 3-alkynylcyclohexenones (**3**) with tetramethylethylene gives rise to novel (3 + 2) cycloadducts that can be explained mechanistically in terms of closure of an initial biradical (**6**) to a vinyl carbene (**7**), followed by stabilization of the carbene.

There are now several photochemical reactions known in which alkyl prop-2-ynyl biradicals (**1**) undergo ring closure to vinyl carbenes (**2**), that are then transformed by some typical carbene reaction into stable products;[1] there is evidence suggesting that this ring closure occurs specifically from the triplet state.[2] We describe now a new (3 + 2) photocycloaddition of 3-alkynylcyclohexenones (**3**) with 2,3-dimethylbut-2-ene that yields adducts readily explained by this pathway in successful competition with the common (2 + 2) reaction that in cyclohexenone itself leads to cyclobutanes.[3] The only previous example known to us of photocycloaddition in an enynone involves solid-state dimerization at the double bond.[4] However, photochemical (3 + 2) cycloaddition of olefins to β-cyano α,β-unsaturated ketones, 6-cyanouracils, and similar systems is a known process[5] that is at least formally related to the reactions reported here.

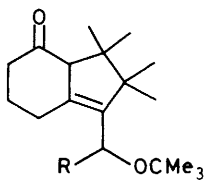
The substrates (**3a**) and (**3b**) were available in 40—60% yield through addition of the Grignard reagent from propyne or 3,3-dimethylbut-1-yne, respectively, to 3-ethoxycyclohex-2-enone, followed by acid hydrolysis. Irradiation ($\lambda > 340$ nm) of (**3a**) and 2,3-dimethylbut-2-ene in t-butyl alcohol as solvent leads to a *ca.* 2.5 : 1 mixture of (**4a**) and (**5**). The solvent adduct (**4a**) was initially a *ca.* 3 : 1 mixture of diastereoisomers that underwent some epimerization on preparative g.l.c. The 1 : 1 adduct (**5**) was a mixture of double-bond and geometric isomers, one of which (a cyclohex-3-enone) was obtained pure. These reactions can be explained in terms of the intermediates (**6**) and (**7**). Stepwise cycloaddition[3] of the olefin to triplet (**3**) leads to the biradical (**6**), which can close on the triple bond to form the vinyl carbene (**7**). Insertion into the O–H bond of solvent then gives (**4a**), while 1,4-transfer of hydrogen furnishes (**5**) as the cyclohex-3-enone. Migration of the ring double bond into conjugation with the carbonyl group on work-up (preparative g.l.c.) can give the fully conjugated system.

Similar reaction of (**3b**) in acetonitrile gives a *ca.* 2 : 1 mixture of two types of 1 : 1 adduct. The major product is a

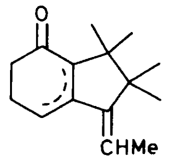


(**3**)

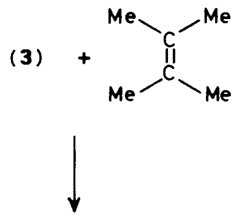
a; R = Me
b; R = Bu^t

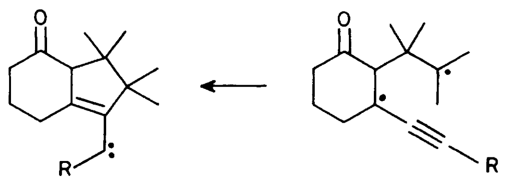


(**4**)

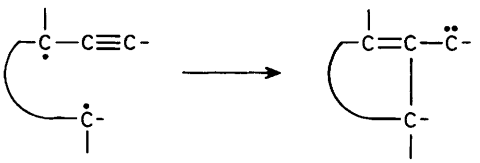


(**5**)

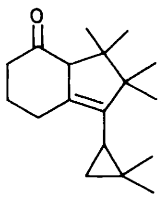




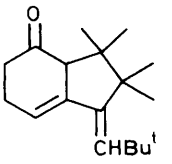
(**7**) (**6**)



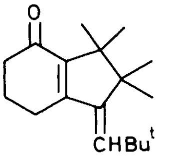
(**1**) (**2**)



(8)



(9)



(10)

1:1 diastereoisomeric mixture of cyclopropanes (**8**), C–H insertion products from (**7**; R = Bu^t). The minor adduct type, corresponding to (**5**), consisted of the hydrogen transfer product (**9**) and its double-bond isomer (**10**). Irradiation of (**3b**) and 2,3-dimethylbut-2-ene in t-butyl alcohol as solvent yields these same photoproducts, along with a small amount of the ether (**4b**).

All new compounds (**3a**), (**4**), (**5**), and (**8**)—(**10**) have been fully characterized and have spectroscopic properties compatible with the structures assigned. Data for (**3b**) are in agreement with those previously reported for this ketone prepared by another route.[6]

For support we thank the U.S. National Science Foundation (New York) and N.A.T.O. (both laboratories).

Received, 19th February 1988; Com. 8/00677F

References

1 S. Hussain and W. C. Agosta, *Tetrahedron* (Symposium-in-Print), 1981, **37**, 3305; V. B. Rao, C. Schröder, P. Margaretha, S. Wolff, and W. C. Agosta, *J. Org. Chem.*, 1985, **50**, 3881; P. Margaretha, C. Schröder, S. Wolff, and W. C. Agosta, *J. Fluorine Chem.*, 1986, **30**, 429; S. Wolff and W. C. Agosta, *J. Am. Chem. Soc.*, 1984, **106**, 2363; V. B. Rao, S. Wolff, and W. C. Agosta, *ibid.*, 1985, **107**, 521; W. C. Agosta, R. A. Caldwell, J. Jay, L. J. Johnson, B. R. Venepalli, J. C. Scaiano, M. Singh, and S. Wolff, *ibid.*, 1987, **109**, 3050; A. Rudolph, P. Margaretha, and W. C. Agosta, *Helv. Chim. Acta*, 1987, **70**, 339.

2 S. Saba, S. Wolff, C. Schröder, P. Margaretha, and W. C. Agosta, *J. Am. Chem. Soc.*, 1983, **105**, 6902.

3 S. W. Baldwin, *Org. Photochem.*, 1981, **5**, 123; A. C. Weedon, in 'Synthetic Organic Photochemistry,' ed. W. M. Horspool, Plenum, New York, 1984, pp. 61—143.

4 F. Pochat and E. Levas, *Bull. Soc. Chim. Fr.*, 1972, 4197.

5 I. Saito, K. Kanehira, K. Shimozono, and T. Matsuura, *Tetrahedron Lett.*, 1980, **21**, 2737; I. Saito, K. Shimozono, and T. Matsuura, *ibid.*, 1982, **23**, 5439; *J. Am. Chem. Soc.*, 1980, **102**, 3948; *J. Org. Chem.*, 1982, **47**, 4356.

6 J. Schwartz and Y. Hayasi, *Tetrahedron Lett.*, 1980, **21**, 1497.