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

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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-2ene 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, β -cyanouracils, and similar systems is a known process⁵ 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 cycloaddition³ 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









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

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