Photocycloaddition of Enones to 1,3-Dienes

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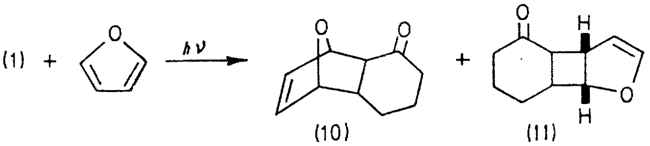
Summary It has been shown that cyclic enones undergo 2 + 2 cycloaddition to 1,3-dienes, frequently in high (0·1—0·3) quantum yield: this reaction appears to be responsible for erratic results sometimes obtained when 1,3-dienes are used as triplet quenchers.

THE photochemical annelation of cyclic enones with unactivated olefins, developed only within the past decade, has been the subject of much interest with regard to its scope and mechanism.[1] It has been generally believed that enones add to conjugated dienes either not at all, or, at best, very inefficiently,[2,3] since the triplet states of 1,3-dienes (E_T 53—60 kcal) lie well below those of most enones (E_T 66—70 kcal) and efficient collisional transfer of excitation energy should occur, resulting in quenching of the enone triplet. Indeed, a powerful tool in mechanistic photochemistry has been the use of dienes such as penta-1,3-diene and cyclohexa-1,3-diene as quantitative quenchers of triplets of $E_T > 60$ kcal.[4]

We report here our observations that cyclohex-2-enone (**1**) and cyclopent-2-enone (**2**) do in fact undergo photocycloaddition to several 1,3-dienes, usually in the 2 + 2 manner, with surprisingly high efficiency. By use of a large excess of the diene (20 : 1 mole ratio) it is possible to obtain on a preparative scale good yields of most of the adduct mixtures under conditions of high conversion. The Table gives yields of adduct mixtures obtained by irradiation of (**1**) and (**2**) with several representative 1,3-dienes, all run to essentially complete consumption of enone. There is usually observed concomitant formation of diene dimers[4b] resulting from sensitization of the diene by enone triplets. In some cases, where the energy transfer process is fairly efficient [*e.g.*, (**1**) and cyclohexa-1,3-diene] there is a rapid early build-up of diene dimer and most of the enone is consumed by cycloaddition to the diene dimers.†

to the extent of at least 85%. In the mixture from irradiation of (**1**) and cyclopentadiene, there was present a minor isomer (15%) not obtained entirely pure, whose n.m.r. data [*inter alia*, signals at τ 3·9 (2H, m) and for bridge methylene at 8·6 (2H, m)], are consistent with its formulation as a norbornene derivative.[5]



(10)

(11)

Irradiation of (**1**) or (**2**) in furan led to both 2 + 2 and 4 + 2 addition, in the ratio *ca.* 45 : 55. The stereochemistry of the 4 + 2 adduct (**10**) is a matter of some interest, since a *trans*-ring fusion would imply the intermediacy of a strained ground-state *trans*-enone *via* thermal 4 + 2 addition. However, the 4 + 2 adducts from (**1**) and (**2**) and furan proved to be thermally unstable and on attempted g.c. purification underwent retro-Diels–Alder reaction, reverting to (**1**) and (**2**), respectively, and furan. The presence of (**10**) in the product mixture from (**1**) and furan was clear from the spectral properties of the mixture, the n.m.r. signals for (**10**) at τ 3·7 (2H, A part of AA′XX′) 5·1 and 5·4 (1H each, br s, –CH–O–), and 6·5 (2H, m, $-CH_2-C{=}O$) being clearly separated from those attributable to (**11**) at τ 3·6 (1H, 2d, J 2·8, J' 1·4, $-C{=}CH-O-$), 4·8 (1H, apparent triplet, J 2·8, $-O-C{=}CH-CH-$), 5·0 (1H, 2d, J 7·4, J' 4·2, –O–CH–), and 6·7 (2H, m, $CH_2C{=}O$). The major 2 + 2 adduct, (**11**), obtained pure by g.c., was identified by comparison of the product of its hydrogenation over Pd/C with the major photoadduct from (**1**) and 2,3-dihydrofuran.

Photoadditions of (**1**)

Diene		Yield of adducts (%)[a]	Relative efficiency[b]	Number of adducts and ratio	
Cyclohexene			1·00	⩾3	
Buta-1,3-diene	(**3**)	72	0·65	5	24 : 38 : 17 : 16 : 5
Cyclopenta-1,3-diene	(**4**)	47	0·41	5	33 : 9 : 28 : 24 : 6
Cyclohexa-1,3-diene	(**5**)	16	0·3—0·35	⩾3	60 : 31 : 9
Cyclohepta-1,3,5-triene	(**6**)	30	0·04	2	25 : 75
Cyclo-octa-1,3-diene	(**7**)	78	0·58	⩾3	13 : 70 : 17
Spiro[2,5]hepta-2,4-diene	(**8**)	55	0·5	3	—
Furan	(**9**)	63	0·6	3	45 : 49 : 6
Hexa-2,4-diene		40	—	⩾4	—
Cyclo-octa-1,5-diene		66	0·7	⩾2	29 : 71

Photoadditions of (**2**)

Diene				
(**3**)	32	0·10	3	
(**4**)	27	0·15	2	37 : 63
(**7**)	56	0·3	2	15 : 62 : 23
(**9**)	47	0·5	⩾2	54 : 55

[a] Satisfactory elemental analyses and m.s. molecular weight data were obtained on all adduct mixtures, and on individual compounds when the mixtures were resolvable.

[b] Obtained by comparing the progress of irradiations of a mixture 0·25 M in (**1**) or (**2**) and 5·0 M in cyclohexene or one of the dienes; each reaction was followed to *ca.* 10% conversion. To obtain quantum yields for the addition of (**1**) to dienes, multiply the efficiency shown by the quantum yield for (**1**) + cyclohexene (0·48).[1f]

The adduct mixtures from all dienes except furan and cyclopentadiene were shown to contain only compounds resulting from 2 + 2 cycloaddition processes by hydrogenation of the adducts and comparison of the resulting saturated ketones with those obtained by photoaddition of (**1**) and (**2**) to the corresponding mono-olefins. It would be expected that 1,4-addition would be most favourable in the case of a perfectly planar, *cisoid* 1,3-diene, such as cyclopentadiene or furan. In fact, (**2**) adds to cyclopentadiene entirely in the 2 + 2 fashion (*vide infra*) and (**1**) adds 2 + 2

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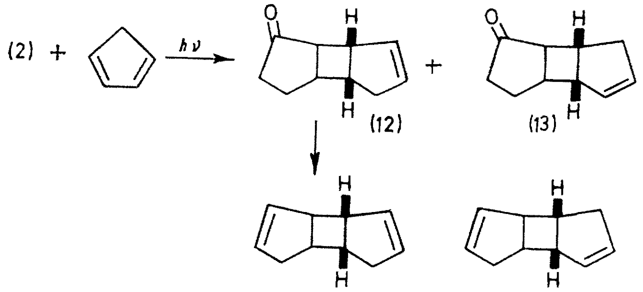
† Our observations that the ratio of adducts to diene dimers shows, if anything, a decrease on increasing the initial diene : enone ratio tenfold (2·5 : 1 to 20 : 1) support the intermediacy of enone lowest triplet states. If an enone singlet or upper triplet were involved, this ratio should increase on going to higher initial diene : enone ratios (see ref. 3c).

The orientation of the adducts from (**2**) and cyclopentadiene, and from (**1**) and cyclohexa-1,3-diene, was established by a combination of chemical degradation and synthesis. A three-step sequence of hydride reduction, tosylation, and elimination served to convert the adduct mixtures into diolefins. The individual diolefins were separated by g.c. and compared with authentic samples prepared by similar sequences from the photodimers of (**1**) and (**2**), whose structures have been rigorously proved.[6] In this way it was shown that the ratio of "head-to-head" to "head-to-tail" adducts from (**2**) and cyclopentadiene (**12** and **13**) was 63 : 37, while the two *major* adducts (those of *cis–anti–cis*-stereochemistry)[6] from (**1**) and cyclohexadiene were formed in a 69 : 31 ratio.



The observed predominance of head-to-head adducts may have mechanistic implications. Since initial bond formation to the diene almost certainly takes place at one of the terminal diene carbons, it appears that initial bonding to the enone occurs to an appreciable extent at both C-2 and C-3, with that at C-3 predominating.[7]

Certain 1,3-dienes, particularly penta-1,3-diene and cyclohexa-1,3-diene, have long been used as triplet quenchers in quantitative studies of properties of triplets of enones and many other types of compounds. It has been noted recently[8] that these quenchers do not give reliable results in quantitative studies at high concentrations, with curvature of Stern–Volmer plots being observed. These results have been attributed to quenching of enone singlet excited states by dienes at the higher concentrations. While singlet quenching may be significant, our observations described here strongly suggest that chemical reaction of enone triplets with dienes at high concentrations is a major factor responsible for the erratic quenching behaviour observed under such conditions.

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[1] (a) For a review of work prior to 1968, see P. E. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50; see also, (b) P. DeMayo, J. P. Pete, and M. F. Tchir, *J. Amer. Chem. Soc.*, 1967, **89**, 5712; (c) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, 1968, **90**, 1657; (d) P. DeMayo, J. P. Pete, and M. F. Tchir, *Canad. J. Chem.*, 1968, **46**, 2535; (e) P. J. Wagner and D. Bucheck, *J. Amer. Chem. Soc.*, 1969, **91**, 5090; (*f*) P. DeMayo, A. A. Nicholson, and M. F. Tchir, *Canad. J. Chem.*, 1970, **48**, 225.

[2] N. J. Turro, "Molecular Photochemistry," Benjamin, New York, N.Y., 1965, p. 207.

[3] (a) The sensitized addition of maleic anhydride to dienes and trienes to give mixtures of 2 + 2 and 4 + 2 adducts is known; G. O. Schenck, J. Kuhls, and C. H. Krauch, *Annalen*, 1966, **693**, 20; (b) The direct irradiation of duroquinone with 1,3-dienes has been reported to give both 4 + 2 and 2 + 2 adducts, as well as their further transformation products; K. Kraft, G. Koltzenburg, and G. O. Schenck, *Tetrahedron Letters*, 1965, 353; (c) See also D. I. Schuster and D. H. Sussman, *Tetrahedron Letters*, 1970, 1657.

[4] (a) For example, P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 21; (b) *ibid.*, pp. 79—90.

[5] This material was not identical to the thermal 4 + 2 adduct of (**1**) and cyclopentadiene; however, the latter compound probably is that with the four-carbon bridge *endo–endo*, whereas the photoadduct would be expected on the basis of orbital symmetry considerations to possess the *endo–exo*-stereochemistry; see R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press New York, N.Y., 1970. If the adduct is the result of trapping a strained *trans*-enone, it should be one of the two *endo–exo*-isomers.

[6] Cyclopentenone dimers: P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2344; (b) Cyclohexenone dimers: D. Valentine, N. J. Turro, and G. S. Hammond, *ibid.*, 1964, **86**, 5202.

[7] The only experimental results presented to date having a bearing on the site of initial bonding to enone in photocycloadditions indicate that in the case studied [(**2**) to the symmetrical substrate 1,2-dichloroethylene] bonding occurs initially entirely at C-3; W. L. Dilling, T. A. Tabor, C. D. Boer, and P. P. North, *J. Amer. Chem. Soc.*, 1970, **92**, 1399.

[8] (a) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 1968, **90**, 2232; (b) D. I. Schuster, A. C. Fabian, N. P. Kong, W. V. Barringer, W. C. Curran, and D. H. Sussman, *ibid.*, p. 5027.