

86. Photocycloaddition of Cyclohex-2-enones to Tetramethoxyethylene: Formation of 2,2,3,3-Tetramethoxy-1-oxaspiro[3.5]non-5-enes

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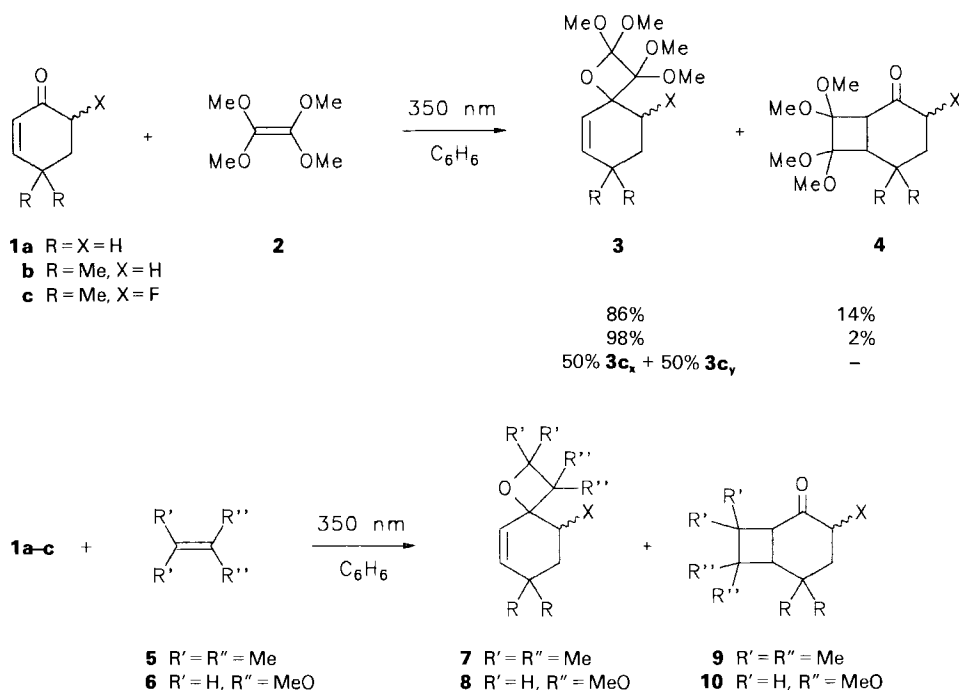
Dedicated to Prof. *Paul de Mayo* on the occasion of his 65th birthday

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Cyclohex-2-enones **1a–1c** undergo photocycloaddition to tetramethoxyethylene in benzene to afford 1-oxaspiro[3.5]non-5-enes **3** in very good yields. In MeCN as solvent, higher relative amounts of bicyclo[4.2.0]octan-2-ones **4** are formed. Results from similar experiments with the same enones and 2,3-dimethylbut-2-ene or 1,1-dimethoxyethene indicate that the driving force for oxetane formation is a sufficiently large difference in redox potentials between E_{red} of the enone and E_{ox} of the alkene. A mechanism is proposed for cycloalk-2-enone + alkene photocycloadditions wherein the cyclobutane adducts arise from an exciplex intermediate and the oxetanes from a subsequently formed contact ion-pair.

Introduction. – The generally accepted mechanism for oxetane-forming carbonyl-alkene photocycloadditions (*Paterno-Büchi* reaction [1] [2]) requires the intermediacy of a contact ion-pair. Such a species has been observed spectroscopically [3] and trapped by

Scheme 1



molecular oxygen [4]. Its occurrence is also strongly suggested by several experimental results, *e.g.* that cyclohexanone or 2-methylcyclohexanone undergo exclusive α -cleavage when irradiated in benzene saturated with 2-methylpropene, while the more easily reducible 2-fluoro- and 2-(trifluoromethyl)cyclohexanone give high yields of oxetanes under these conditions [5] [6].

As for enone + alkene oxetane-forming photocycloadditions, we had reported [7] [8] that 6-fluorocyclohex-2-enones and 5-fluorocyclopent-2-enones react with 2,3-dimethylbut-2-ene in hydrocarbon solvents to give oxetanes, either as major products or quantitatively, while, in MeCN, cyclobutane formation becomes competitive. These results have been interpreted [1] as competition in terms of configuration-specific paths for n,π^* (oxetane formation) and π,π^* enone triplets (cyclobutane formation), electron-withdrawing substituents, *e.g.* fluorine stabilizing the more polar n,π^* form. We now report that cyclohex-2-enone (**1a**) and 4,4-dimethylcyclohex-2-enone (**1b**), whose reactive (triplet) state has been suggested to be a π,π^* state [9] [10], as well as 6-fluoro-4,4-dimethylcyclohex-2-enone (**1c**) undergo photocycloaddition to tetramethoxyethylene (**2**) in benzene affording oxetanes **3** selectively (*Scheme 1*), and that the only criterion for oxetane *vs.* cyclobutane formation seems to be the difference in redox potentials between the excited enone and the alkene (E_{red} of the enone and I_p of the alkene).

Results. – The GC-product yields from irradiations ($\lambda = 350$ nm) of enones **1a–c** and tetramethoxyethylene in benzene are summarized in *Scheme 1*. Oxetanes **3** were characterized by $^1\text{H-NMR}$ (2 olefinic H, $J(\text{H,H}) = 10$ Hz), MS (no M^+ , strong peak $[M - (\text{MeO})_2\text{CO}]^+$) and IR (absence of $\text{C}=\text{O}$). Diastereoisomers **3c_x** and **3c_y** were successfully separated by prep. GC, but an unambiguous structural assignment from NMR data alone is not possible. A *Stern-Volmer* plot in benzene using naphthalene as quencher indicates that, in the photocycloaddition of **1a** to **2**, both oxetane **3a** and cyclobutane **4a** [11] are quenched with the same efficiency. From the slope (8.93 m^{-1}), a limiting lower value of $\tau \approx 2$ ns is obtained for the triplet **1a** at 0.1M concentration. The overall rate of conversion of **1** and **2** to products in benzene and MeCN is alike in both solvents, but the

Table 1. Oxetane (Ox)/Cyclobutane (CB) Ratio and Cycloadduct Yield in Photoreactions of Cyclohex-2-enones and Alkenes

Enone	$E_{\text{red}}^{\text{a}}$	Alkene	I_p^{b}	Solvent	Ox/CB	Overall yield [%]
1a	-2.38	2	6.82	C_6H_6	6.1:1	93
				CH_3CN	1.9:1	80
		5	8.27	C_6H_6	1:19	90
1b	-2.37	2	8.56	C_6H_6	1:25	[15]
				C_6H_6	49:1	99
		CH_3CN	19:1	98		
1c	-1.96	2		C_6H_6	1:1.7	[16]
				C_6H_6	1:7	[17]
		C_6H_6	100:0	96		
		5		CH_3CN	100:0	92
				C_6H_6	9:1	[8]
		6		C_6H_6	1:4.2	94

^a) In V *vs.* Ag/Ag^+ [13].

^b) In eV, taken or estimated from [14].

Table 2. Selected Spectroscopic Data of Oxetanes **3**, **7**, and **8**

Compound	¹ H-NMR (CDCl ₃)	MS
3a	5.92 (<i>dt</i> , <i>J</i> = 10.0, 3.6, H–C(6)); 5.82 (<i>dt</i> , <i>J</i> = 10.0, 1.8, H–C(5))	244 (0.5, <i>M</i> ⁺), 133 (100)
3b	5.70, 5.62 (<i>AB</i> , <i>J</i> = 10.0, H–C(5), H–C(6)); 2.02 (<i>ddd</i> , <i>J</i> = 3.8, 9.8, 13.8, H–C(9)); 1.78 (<i>ddd</i> , <i>J</i> = 3.2, 8.4, 14.0, H–C(9)); 1.50 (<i>ddd</i> , <i>J</i> = 3.2, 9.6, 13.2, H–C(8)); 1.40 (<i>ddd</i> , <i>J</i> = 3.6, 8.4, 13.4, H–C(8))	272 (0.1, <i>M</i> ⁺), 133 (100)
3c_x	5.76 (<i>s</i> , H–C(5), H–C(6)); 4.94 (<i>ddd</i> , <i>J</i> = 1.4, 4.4, 46.8, H–C(9)); 1.93 (<i>ddd</i> , <i>J</i> = 4.4, 8.0, 14.8, H–C(8)); 1.66 (<i>ddd</i> , <i>J</i> = 1.4, 14.8, 48.2, H–C(8))	290 (0.1, <i>M</i> ⁺), 133 (100)
3c_y	5.70, 5.62 (<i>AB</i> , <i>J</i> = 10.0, H–C(5), H–C(6)); 4.98 (<i>ddd</i> , <i>J</i> = 2.0, 7.0, 49.0, H–C(9)); 1.95 (<i>ddd</i> , <i>J</i> = 6.8, 7.0, 14.4, H–C(8)); 1.70 (<i>ddd</i> , <i>J</i> = 2.2, 14.4, 37.6, H–C(8))	290 (0.1, <i>M</i> ⁺), 133 (100)
7a^{a)}	6.03 (<i>dt</i> , <i>J</i> = 10.0, 1.8, H–C(5)); 5.83 (<i>dt</i> , <i>J</i> = 10.0, 3.6, H–C(6))	180 (0.1, <i>M</i> ⁺), 43 (100)
8c^{a)}	5.94, 5.78 (<i>AB</i> , <i>J</i> = 10.2, H–C(5), H–C(6)); 5.04 (<i>ddd</i> , <i>J</i> = 2.2, 5.8, 48.6, H–C(9)); 4.45, 4.36 (<i>AB</i> , <i>J</i> = 7.0, H–C(2)); 2.01 (<i>ddd</i> , <i>J</i> = 5.8, 8.1, 14.6, H–C(8)); 1.72 (<i>ddd</i> , <i>J</i> = 2.2, 14.6, 48.2, H–C(8))	230 (0.1, <i>M</i> ⁺), 88 (100)

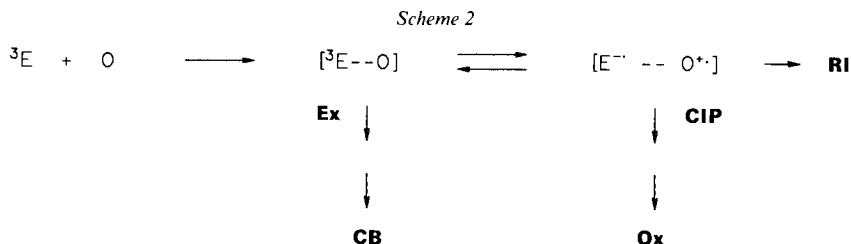
^{a)} Not isolated.

product ratio **3/4** and the overall yield are strongly influenced. In the reaction of the same cyclohex-2-enones with either 2,3-dimethylbut-2-ene (**5**) or 1,1-dimethoxyethene (**6**), *i.e.* alkenes with a much higher *I_p* than **2**, the relative amount of oxetanes **7** and **8** formed is generally much lower and that of cyclobutanes **9** and **10** correspondingly higher (*Table 1*). The spectroscopic data of all new photoproducts is summarized in *Table 2*.

Discussion. – There is essentially no published information concerning photocycloadditions of cycloalk-2-enones to alkenes of so low *I_p* as tetramethoxyethylene, and the observation concerning the preferential formation of oxetane rather than of cyclobutane is noteworthy. The synthetic use of the novel 2,2,3,3-tetramethoxy-1-oxaspiro[3.5]non-5-enes remains to be investigated.

From the results, it seems reasonable to propose a mechanism involving an exciplex (**Ex**) and a contact ion-pair (**CIP**) in equilibrium, in analogy to arene/alkene photoadditions [12]. The amount of **CIP** increases with growing difference in redox potentials (for enone reduction on the one side and alkene oxidation on the other one), cyclobutanes (**CB**) arising from **Ex** and oxetanes (**Ox**) from **CIP** (*Scheme 2*). The influence of the solvent on product distribution and the slightly lower overall yields in MeCN can be explained by the fact that, in polar solvents, **CIP** tends to dissociate into radical ions (**RI**) which could lead, in part, to unidentified products.

At all events, oxetanes are formed in enone cycloadditions to alkenes, whenever the difference in redox potentials is sufficiently high. The phantasmagoric concept of *two*



equilibrated cycloalk-2-enone triplets with different (spectroscopic) configurations (n, π^* and π, π^*) in solution at room temperature should not be retained. It is rather obvious that, for cycloalk-2-enones bearing no additional chromophor (phenyl, *etc.*), the so-called 'configuration' is of mixed character, depending on *e.g.* substitution pattern and solvent.

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Experimental Part

General. Anal. GC: 30-m SE 30 cap. column. Prep. GC: 2-m 10% QF1 on Chromosorb at 180°. ¹H-NMR: at 400 MHz. MS: at 70 eV.

Photolyses. Rayonet RPR 100 photoreactor equipped with 350-nm lamps.

Starting Materials. Cyclohex-2-enone (**1a**) and 2,3-dimethylbut-2-ene (**5**) are commercially available. 4,4-Dimethylcyclohex-2-enone (**1b**) [18] and 6-fluoro-4,4-dimethylcyclohex-2-enone (**1c**) [7], tetramethoxyethylene [19], and 1,1-dimethoxyethene [15] were synthesized according to literature.

Preparative Irradiations. Ar-degassed solns. of **1** (1 mmol) in C₆H₆ (10 ml) were irradiated for 4–6 h up to > 95% conversion (GC) of starting material.

2,2,3,3-Tetramethoxy-1-oxaspiro[3.5]non-5-ene (**3a**). After evaporation of the solvent, **3a** was obtained by prep. GC in 55% isolated yield as colorless liquid.

7,7-Dimethyl-2,2,3,3-tetramethoxy-1-oxaspiro[3.5]non-5-ene (**3b**). After evaporation of the solvent, chromatography (SiO₂, CH₂Cl₂) afforded **4a** in 78% yield as colorless liquid.

cis- and trans-9-Fluoro-2,2,3,3-tetramethoxy-7,7-dimethyl-1-oxaspiro[3.5]non-5-enes (**3c_x** and **3c_y**, resp.). After evaporation of the solvent, prep. GC afforded two fractions, the first one (**3c_x**) of > 98% purity and the second one consisting of 80% **3c_y** contaminated with 20% of **3c_x**, both colourless liquids.

Anal. Irradiations. Ar-degassed solns. of **1a** (10⁻¹ mmol) in 1 ml of solvent, containing tetradecane as standard, were irradiated, the product formation and distribution being monitored by GC. For the *Stern-Volmer* plot, naphthalene was added as quencher up to 1M concentration.

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