

HgCl₂). The dioxolane rings at the top of the molecule are exposed to attack and their oxygen atoms should be available for hydrogen bonding.

The greater reactivity of Ph₃Cr(THF)₃ as compared with **3** may imply that the former has the *trans* (or *mer*) configuration with a labile THF *trans* to Ph and labile Ph groups *trans* to one another.

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197. Photoaddition of Oxa-enones to 2-Chlorodifluoromethyl-3-chloro-3,3-difluoro-propene

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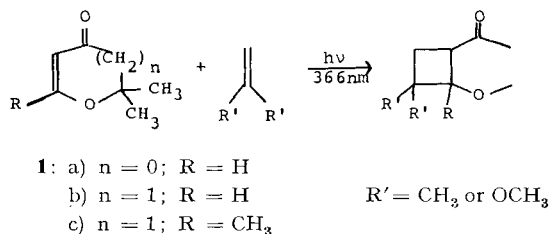
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(5. VIII. 74)

Summary. Electronic effects determine the regioselectivity in the photoaddition of oxa-enones to olefins.

Oxa-enones (**1**) have been shown to photoadd to polarized olefins such as isobutylene or 1,1-dimethoxyethylene in a regioselective manner [1]. This regioselectivity was ascribed to an electronic control – inverted charge distribution in the C–C double bond of the excited oxa-enone molecule – rather than to steric arguments alone (*scheme 1*).

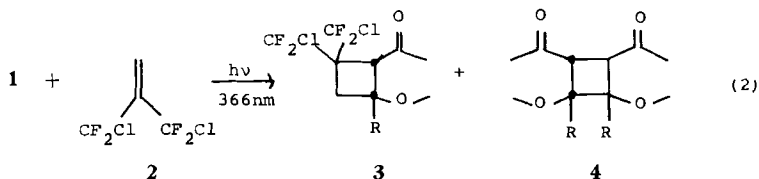
Scheme 1



Both factors, however, would have been expected to exert a parallel regiocontrol in the reactions investigated previously. In order to assess the importance of electronic *vs* steric control, 2-chlorodifluoromethyl-3-chloro-3,3-difluoro-propene (**2**) has

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Scheme 2



now been used as a suitable probe for the cycloaddition with the oxo-enones **1** (Scheme 2)²⁾.

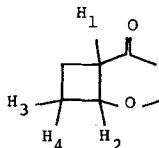
The exclusive formation of **3** and **4** in these experiments (10⁻³ mol **1** and 6.10⁻³ mol **2** in 2 ml hexane) demonstrates that indeed electronic effects determine the regio-specificity in the addition. The stereochemistry of the cyclobutanes is in accordance with an observation [5], that no *trans*-fused products are formed in the addition of enones to olefins bearing electronegative substituents. The fact that no photodimerization was observed in the additions in Scheme 1 shows that the addition of oxo-enones to electron-deficient C–C double bonds is much slower so that the photodimerization becomes competitive.

Table. Physical Data of Compounds **3**

	VPC. a)	NMR. (CDCl ₃) b)			J ₂₃	J ₂₄	IR. (CCl ₄) ν _{C=O}	ratio 3:4
		δ _{H₁}	δ _{H₂}	J ₁₂				
3a	170°	3,46	4,70	6,0	6,0	3,0	1770	1:1
3b	180°	3,34	4,60	7,0	8,0	4,0	1725	1:2
3c	180°	3,25	–	–	–	–	1720	2:3

a) 5% SE 30 on Chromosorb G-AW-DMCS

b)



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³⁾ Acrylonitrile is one of the very few olefins bearing a net electron attracting substituent which has been used so far as a partner in the photocycloadditions of enones, but either the stereochemistry of the cyclobutanes was not fully elucidated [2] [3] or the high rate of the reaction suggests a chain mechanism [3]. The title olefin **2** [4] has now been found to be better suited for such investigations in view of the absence of mesomeric effects and the fact that polymerization does not interfere, the photochemical conversion thus occurring very cleanly.