232. Oxetane vs. Cyclobutane Formation in the Photocycloaddition of Enones to Olefins. The Photoaddition of 6-Fluoro-4,4-dimethyl-2-cyclohexenone to 2,3-Dimethyl-2-butene

Preliminary Communication

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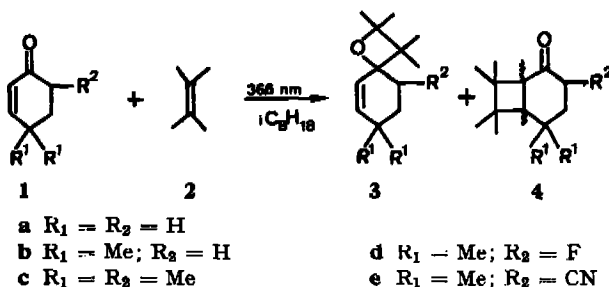Département de Chimie Organique, Université de Genève, 1211 Genève 4

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Summary. n-π* Excitation of 6-fluoro-4,4-dimethyl-2-cyclohexenone in the presence of 2,3-dimethyl-2-butene leads selectively to the formation of the corresponding oxetane. The factors which influence the oxetane vs. cyclobutane formation ratio in photoadditions of cyclic enones to olefins are discussed.

The formation of cyclobutanes *via* photoannelation of enones to olefins is a well established reaction |1–3]. Only few cases, however, are known where concurrent oxetane formation has been observed. *Chapman* has shown that equivalent amounts of oxetane and cyclobutane are formed in the photoaddition of 4,4-dimethyl-2-cyclohexenone to 2,3-dimethyl-2-butene [4] and that for the addition of the same enone to 1,1-dimethoxyethylene this product ratio depends on the solvent [5]. *Yoshida* [6] reported that the oxetane/cyclobutane ratio in the addition of 4,4-dimethyl-2-cyclopentenone to 2,3-dimethyl-2-butene decreased on changing the solvent from hexane to CH_3CN^1).

We now report report results on the photoaddition of some 2-cycloalkenones to 2,3-dimethyl-2-butene (*Scheme 1*, Table) and to other olefins. The ratio of oxetane *vs.* cyclobutane formation depends mainly on: a) the nature of the substituents in the positions vicinal to the C–C and C=O bonds (steric and inductive effects), b) the olefinic reaction partner (charge density on the olefinic carbon atom), c) the solvent.

Scheme 1

1   **2**   **3**   **4**

a $R_1 = R_2 = H$
b $R_1 = Me; R_2 = H$
c $R_1 = R_2 = Me$
d $R_1 = Me; R_2 = F$
e $R_1 = Me; R_2 = CN$

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1) The authors suggested that this dependence of the ratio is due to two distinct triplet intermediates in product formation. However conclusive evidence on this point is not available, and indeed such 'two triplet' mechanisms which have been invoked occasionally in enone and dienone photochemistry proved to be based on equivocal or even erroneous interpretations [7–10].

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Table. *Product Ratio* **3**: **4** *in* i-C_8H_{18} (**1**: *0.05 mol/l*, **2**: *0.5 mol/l*)

a	0:100		
b	52:48 [4]	**d**	90:10
c	30:70	**e**	— [2])

Several conclusions can be drawn from the data in the Table. First it can be seen that for the unsubstituted compound **1a** the rate[3]) of oxetane formation cannot compete with that of cyclobutane formation, which in turn is retarded by the introduction of methyl groups in C(4) (**1b**). This appears to be primarily an effect due to steric control. While the shift towards more cyclobutane formation in **1c** can be due to the steric hindrance by the methyl at C(6), it becomes obvious that the inductive effect of the fluorine in the same position (**1d**) strongly enhances the rate of oxetane *vs.* cyclobutane formation. This is most probably due to the fact that the carbonyl carbon atom is now more electrophilic and therefore better suited for bond formation with the olefinic carbon atom. This interpretation is supported by the observation that oxetane formation with cyclopentene is largely reduced. Thus, no oxetane at all has been detected in the addition of **1b** [12] or of 4,4-dimethyl-2-cyclopentenone in our hands to this olefin. Even **1d** gives less than 25% oxetane with cyclopentene. Making the rough assumption that in the addition of either the C=O or the C=C bond of the enone to olefins steric interactions will increase in like manner with increasing bulkiness of the olefin, it can be concluded that oxetane formation is favoured by higher electron density on the carbon atom of the olefinic partner. Similar correlations are found using isobutene as olefin. No oxetanes are formed with **1a** [13], **1b** and **1c**, but only a mixture of cyclobutane derivatives and alkylated cyclohexanones. In the case of **1d** again 20% oxetane is formed. Interestingly, in all these reactions the *trans*-fused cyclobutane is formed in much higher amounts than the *cis*-fused isomer. Discussions of these findings are given elsewhere [3] [9].

Increasing the polarity of the solvent also largely reduces the amount of oxetane formed, *e.g.*, less than 20% **3d** are formed in CH_3CN. This can be explained by complexation or dipolar interactions between the C=O group and solvent molecules, thus reducing the susceptibility of the carbonyl group towards reaction with the olefin.

It is interesting to note that compound **3d** is easily converted to the alkylated methylenecyclohexadiene **5** (*Scheme 2*). While such oxetane cleavages are known for

Scheme 2

3d   **5**
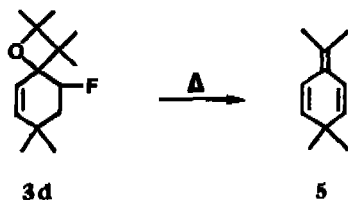
[2])   No photoadducts of compound **1e** [11] are formed owing to predominant deactivation via photoenolization. These results will be discussed in a forthcoming communication.

[3])   Quantum yield measurements for the reactions discussed and for a similar series of compounds will be reported in the full paper, together with complete experimental details concerning isolation and identification of all photoadducts.

dienone derivatives [14], this is the first time that such a transformation is observed for an oxetane derivative of an enone. It is unknown if elimination of HF is concerted with or occurs after the cleavage of the four-membered ring.

Experimental Part

Compound **1a** was obtained from *Fluka AG.* and purified by distillation. **1b** and **1c** are described in [15] [16].

Preparation of **1d**: 7.6 g (0.05 mol) 6-formyl-4,4-dimethyl-2-cyclohexenone [11] were treated with an excess of $FClO_3$ in 100 ml CH_3OH at 0°. Subsequent work-up as described in [17] gives **1d** in 70% yield, the product being identical with the one recently obtained from 3-fluoro-3-butene-2-one [18]. UV. (i-C_8H_{18}): $\lambda_{max} = 335$ nm ($\varepsilon = 24$).

Preparation of **3d**: Irradiation (366 nm) of a solution of **1d** (0.005 mol) and **2** (0.05 mol) in 100 ml i-C_8H_{18} on 50 h with a 250 W Hg-lamp followed by distillation (80°/0.2 Torr) gave **3d** in 90% yield (contaminated with 10% **4d**). – NMR. (CCl_4): 5.78 ($d \times d$) (1) ($J = 10$ and 3); 5.52 (d) (1) ($J = 10$); 4.82 ($d \times d \times d$) (1) ($J = 49$, 8 and 3); 1.80 (m) (2); 1.29 (s) (6); 1.14 (s) (6); 1.04 (s) (6).

Preparation of **5**: bulb to bulb distillation (150°/760 Torr) under N_2 of 1 mmol **3d** gives **5** in 75% yield (GC. purity = 80%). Purification by prep. GC. (5% SE-30 on Chromosorb G, 140°). – NMR. (CCl_4): 6.30 (d) (1) ($J = 10.6$); 5.40 (d) (1) ($J = 10.6$); 1.80 (s) (3); 1.05 (s) (3). – UV. (i-C_8H_{18}): $\lambda_{max} = 256$ nm ($\varepsilon = 12,000$) with a shoulder at 263 nm. – MS.: 148, 133 ($M^+ - CH_3$).

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