Surface Photochemistry: Steric Modification of Enone Photocycloaddition by Adsorption on Silica Gel

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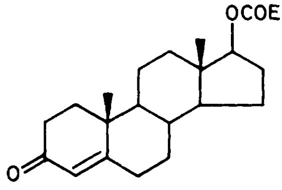
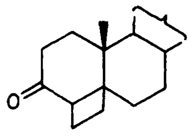
Photochemical cycloaddition of three alkenes to a steroidal enone adsorbed on silica gel is shown to be possible, and the stereochemistry of the addition is different from that in a polar solvent such as methanol which is consistent with a hindered direction of approach to the adsorbed steroid.

There is growing interest in the modified photochemistry found in molecules when in ordered or constrained systems: these include micelles, vesicles, microemulsions, monolayers, and liquid crystals in the liquid phase, whilst in the solid phase there have been reports concerned with crystalline or polymeric systems and with molecules adsorbed on surfaces. With the latter it has recently been shown[1–3] that photochemical reactions involving radical pairs follow modified routes when induced on dry silica gel. Such an effect has not been shown for a bimolecular reaction[4] other than for one case of a dimerisation.[5] Photochemical enone cycloaddition appeared to be a good candidate for such a study, and we report here that this reaction can indeed be induced on dry silica gel and that under these conditions the stereochemistry of the reaction is different from that found in solution.‡

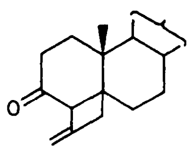
The substrate used was testosterone propionate (**1**), chosen because it was hoped that this large flat molecule with two polar functional groups would assume a position with its less hindered α face towards the bulk of the gel, leaving the normally more hindered β side open to attack. Ethylene, allene, and cyclopentene were used as addends. For comparison, the cycloaddition was carried out in methanolic solution; in the case of the additions of ethylene and cyclopentene these reactions have already been reported by Rubin.§[6] Methanol was chosen as the polar solvent to minimize or reduce the effect of the local polarity of silica gel, since it has been shown by Leermakers that silica gel approximates to methanol on the Kosower *Z* scale.[7] The results of the photocycloadditions are summarised in Table 1.



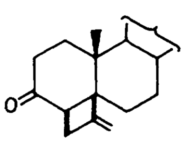
(**1**)



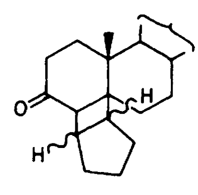
(**2**)



(**3**)



(**4**)



(**5**)

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‡ Silica gel irradiations were performed on degassed horizontally rotating cylinders with a 450 W Hg medium pressure arc through Pyrex. *Ca.* 0.1 mmol of (**1**) and 1 mmol of alkene on 3 g silica gel (Merck 60, 35—70 mesh) were used. Analyses were by g.l.c. and/or h.p.l.c.

§ Appropriate spectral data and precise masses were obtained for all new compounds reported.

Table 1. Conditions and results of the cycloaddition of (**1**) to alkenes.[a]

Alkenes	Conditions	Temp. (°C)	Conversion (%)	Products	Isomers (%)		
					4α,5α	4β,5β	4α,5β
Ethylene	MeOH	11	57	(**2**)	57	10	32
Ethylene	MeOH	—78	24	(**2**)	82	12	6
Ethylene	SiO_2	11	100	(**2**)	49	51	trace
Ethylene	SiO_2	—78	96	(**2**)	42	58	trace
Allene	MeOH	11	58	(**3**)	83	17	—
Allene	MeOH	—78	75	(**3**)	90	10	—
Allene	SiO_2	11	80	(**3**) + (**4**)	46	54	—
Allene	SiO_2	—78	97	(**3**) + (**4**)	46	53	—
Cyclopentene	MeOH	8	61	(**5**)	46	22	31[b]
Cyclopentene	MeOH	—78	67	(**5**)	53	41	6[b]
Cyclopentene	SiO_2	11	46	(**5**)	33	56	10[b]
Cyclopentene	SiO_2	—78	66	(**5**)	32	57	10[b]

[a] See footnote‡. [b] Analysed as the thermally isomerised (*cis*) isomer.

The simplest comparison is for the allene adducts (**3**) and (**4**) which are uncomplicated by ambiguity due to the presence of *trans*-isomers. Here, in the polar solution, attack from the α face was favoured by *ca.* 5 : 1 at room temperature increasing to 9.5 : 1 at −78 °C. Conversely on silica gel β attack was slightly favoured and temperature independent. The product ratio, then, had changed by about one order of magnitude. Comparison of the cyclopentene adducts is complicated by the presence of a major amount of the *trans*-isomer in methanolic solution at room temperature as opposed to its minor amount on silica gel. Methanol and the gel may be compared at −78 °C, where similar amounts of the *trans*-isomer are present, and again the product ratio shifts in favour of β approach by a factor of 2.

The addition of ethylene in methanol at room temperature also produces a large amount of the *trans*-product which is absent on silica gel. At low temperature in solution α addition is favoured by 7 : 1, whereas on silica gel at the same temperature β addition is slightly favoured.

Summarising from these preliminary observations we conclude that mixed photocycloaddition is feasible on dry silica gel; that adsorption takes place on the gel from the less hindered face (α) leaving the β-face more available for reaction and that adsorption on the silica disfavours the conformational inversion in the intermediate 1,4-biradical required for *trans* addition. Interestingly, the latter can also be achieved by lowering the temperature in methanolic solution.

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