

ON THE STEREOCHEMISTRY OF PHOTOADDITION BETWEEN
 α,β -UNSATURATED KETONES AND OLEFINS. III.

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ABSTRACT:--The α,β -unsaturated ketone **1** yields with allene the photocycloadduct **3** predicted by our empirical photoaddition rule and the byproduct **7**. The formation of this material may be rationalized by the sequence **1** \rightarrow **4** \rightarrow **5** \rightarrow **6** \rightarrow **7**. The isomeric ketone **2** is unreactive under the same conditions, since α addition is prohibited by the rule and β addition is severely blocked.

Some time ago we proposed^{1,2} an empirical rule which allowed the prediction of the configuration of cis-photocycloadducts between allene or other olefins and α,β -unsaturated ketones. We postulated that the configuration of the cycloadduct is controlled by a species which is trigonal in the α - and pyramidal in the β -position. This species was assumed to select the more stable configuration and to determine the configuration of the adduct. The identity of the species was uncertain. For the sake of simplicity we assumed that an additional chiral center is created in the excitation process itself and that the excited state selects the more stable one of the two epimeric configurations.

We have, however, clearly emphasized that no physical meaning should be ascribed to this assumption and that it should be regarded merely as a guideline for an empirical prediction of configuration of the cycloadduct. We mentioned already in the first communication the possibility that the configuration controlling species might be identical with the transition state of the dark reaction between the excited α,β -unsaturated ketone and the olefin and

that the process of configuration selection might be kinetic.

Three years ago de Mayo³ commented on our rule and suggested that the control of stereochemistry in photocycloaddition might depend exclusively on the steric hindrance of the approach of the olefin to the excited ketone.

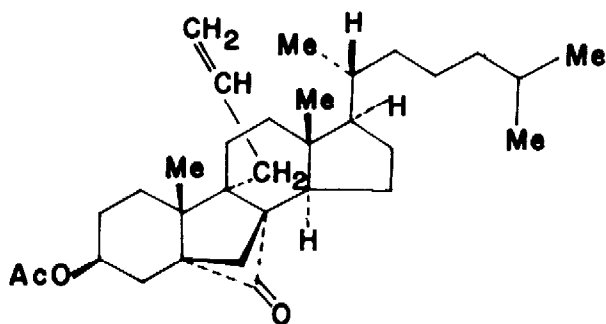
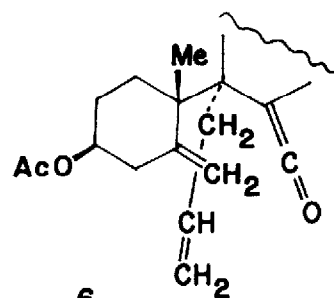
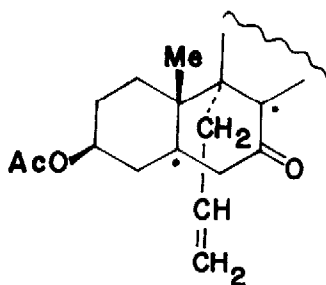
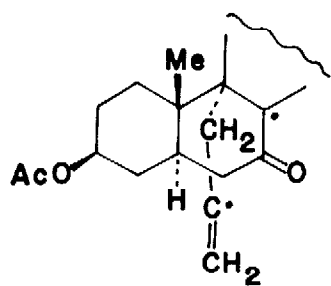
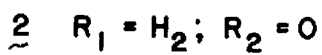
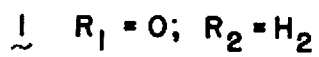
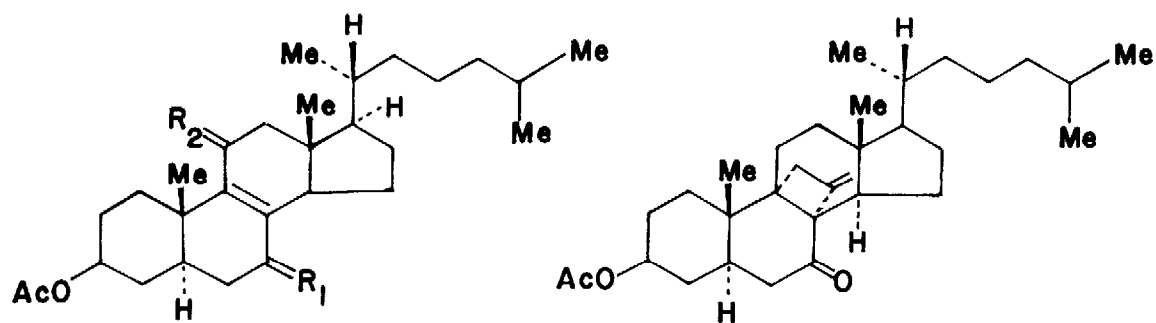
While we disagreed with this opinion on the basis of the data available to us,^{1,2} we decided to design an experiment which would show unambiguously the operation of the factors implicit in our rule. The ketones 1 and 2 contain a double bond which is extremely strongly shielded from the β side by the two angular methyls.⁴

If this shielding is the only factor to be considered in photocycloaddition the two compounds should behave essentially in the same fashion both giving α -photoadducts with allene. If, on the other hand, the addition rule operates, compound 1 should yield rapidly the α -adduct 3 while compound 2 should either give the β -adduct in spite of the shielding or it should turn out to be unreactive since α -addition is opposed by the rule and β -addition is blocked.

In the event irradiation of 1 with allene under our standard conditions for 1.5 h gave the adduct 3 (mp 119.5-120.5°C) in a yield of 72% after crystallization. The structure of 3 was determined by X-ray crystallography. A second product (mp 177-178.5°C) was isolated in a yield of 17% and recrystallized from ether-chloroform [ν : 1760, 1730 cm^{-1} (cyclobutanone, acetate)]. An X-ray crystallographic examination of this material revealed the structure 7. Its formation may be readily rationalized by the sequence 1, 4, 5, 6 and 7. Irradiation of the pure adduct 3 for several hours did not lead to any change and specifically no compound 7 was formed.

Irradiation of compound 2 with allene under the same conditions as with compound 1 for 1.5 h yielded only starting material. After 12 h a trace of an oily adduct was formed, which according to its spectral properties seemed to be a normal cycloadduct. The configuration of this material could not be investigated but it does not seem to be crucial. It is clear that α -addition was inhibited by the mechanism underlying the rule and β -addition by shielding. Whether the trace product was an α or β -adduct does not affect this conclusion.

We believe that the crucial experiment reported herein puts our empirical photoaddition rule beyond reasonable doubt. Attempts to identify the configuration controlling species by direct experiments are in progress. Until this work is finished speculations about the mechanism are clearly premature.



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5. Details about the crystallographic work and tables of the final atomic parameters are available from J. F. Blount.

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