

Unexpected Influence of Mono-phenyl Substitution on the Photochemistry of β,γ -Unsaturated Oxime Acetates

Diego Armesto,*^a Antonia R. Agarrabeitia,^a William M. Horspool,^b and Mar G. Gallego^a

^a Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain

^b Department of Chemistry, The University, Dundee DD1 4HN, Scotland

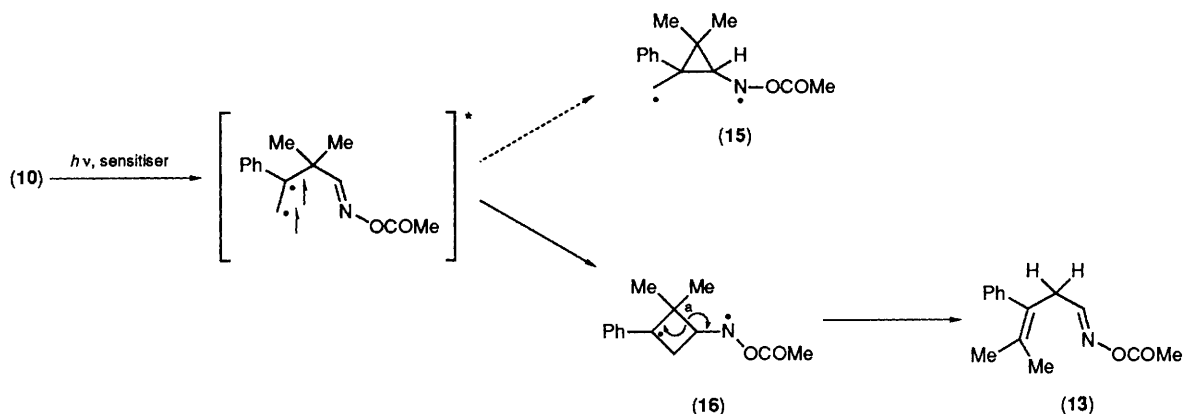
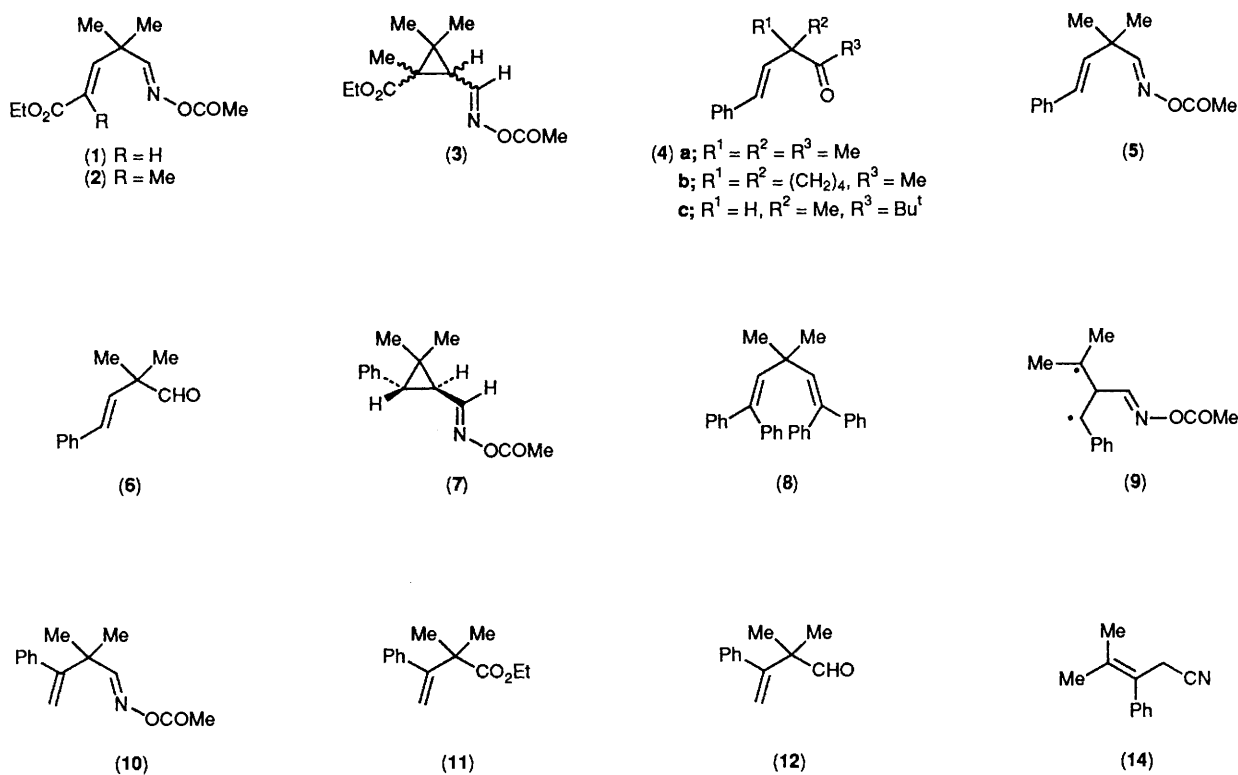
On irradiation the oxime acetate of *trans*-2,2-dimethyl-4-phenylbut-3-enal (**5**) undergoes stereospecific aza-di- π -methane rearrangement to the oxime acetate of *trans*-2,2-dimethyl-3-phenylcyclopropanecarbaldehyde (**7**), while surprisingly the irradiation of the oxime acetate of 2,2-dimethyl-3-phenylbut-3-enal (**10**) follows a different reaction path and affords the oxime acetate of 4-methyl-3-phenylpent-3-enal (**13**) by a novel 1,3-migration pathway.

In a previous study¹ we demonstrated that the monosubstituted 1-aza-1,4-diene (**1**) is unreactive in the aza-di- π -methane rearrangement. However, the incorporation of a second substituent at the 5-position gave a diene (**2**) which was again reactive, yielding the cyclopropanes (**3**). The failure of the monosubstituted compound to undergo rearrangement was interpreted as an example of triplet excited state deactivation by a free rotor since the energy from the sensitiser will be transferred solely to the alkene moiety. Others have reported similar difficulties, *e.g.* Cerfontain and co-workers² have reported the failure of (**4**) to undergo the oxa-di- π -methane rearrangement under sensitised conditions. As in our example the energy is transferred to the alkene group. There are of course many examples of the di- π -methane reaction where the triplet state is deactivated by free rotor effects.³

In order to obtain further evidence on the feasibility of the free rotor effect we have examined the photochemical behaviour of the 1-aza-1,4-diene (**5**). This has a phenyl group

at C-5 and this functionality ensures that triplet energy will be transferred to the alkene moiety. The synthesis of (**5**) was achieved by the conversion of the known aldehyde (**6**)⁴ into the corresponding oxime acetate. The sensitized irradiation of (**5**)[†] was efficient and gave a single photoproduct in high yield (71%), after chromatography on silica gel. This product was identified as the cyclopropane (**7**). The evidence from the NMR spectra indicates that the reaction is stereospecific and yields only the *trans*-isomer. This result is surprising in view of the failure with the previous compound (**1**). It could be argued that the phenyl group on the 5-position is larger than an ester group and this difference in bulk is sufficient to suppress the

[†] All new products gave satisfactory microanalytical results. The irradiations were carried out in benzene with acetophenone as sensitizer in an immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp.



Scheme 1

free rotor effect. However, this argument does not stand up to comparison with results from the di- π -methane reaction of the tetraphenyl 1,4-diene (8) where the triplet state is unreactive.⁵ The stereospecificity of the reaction is also a surprise since in the photochemistry of (2) the corresponding cyclopropane derivative (3) is obtained as a mixture of *cis* and *trans* diastereoisomers. A possible explanation could be that the cyclisation of the intermediate 1,3-diradical (9) takes place only in the *trans*-arrangement because of the large difference in size between the phenyl group and the hydrogen.

The successful cyclisation of (5) prompted a study of the 1-aza-1,4-diene (10) in which the 5-position is unsubstituted. The absence of substituents on this carbon makes this a good example for free rotor activity in the excited state and the incorporation of a phenyl at the 4-position still ensures that triplet energy will be transferred to the alkene moiety. This

compound is readily prepared by Reformatsky reaction of ethyl 2-bromo-2-methylpropanoate with acetophenone, dehydration to the alkene (11), reduction to the alcohol followed by oxidation to the aldehyde (12), and conversion to the oxime acetate (10).

Irradiation of (10) using acetophenone sensitization brought about smooth and efficient conversion to a single photoproduct. The reaction mixture was separated by chromatography on silica gel and yielded the new compound (62%) and starting material (37%). The photoproduct was readily identified as the oxime acetate of 4-methyl-3-phenylpent-3-enal (13). This compound slowly decomposes at room temperature by elimination of acetic acid to give the nitrile (14). The identification of the photoproduct as (13) clearly shows that the diene (10) does not undergo the aza-di- π -methane process and an alternative reaction mode is

operative. This alternative path is outlined in Scheme 1; energy transfer from the sensitiser affords, as always, the triplet alkene. Conventional bridging would yield a biradical (15) in which there was minimal stabilisation. The molecule, therefore, follows a path which forms a better biradical (16) rather than (15) by attack of the methylene radical at the oxime acetate carbon atom. This route yields the cyclobutane intermediate (16) which subsequently ring-opens by rupture of bond 'a' to yield the diene (13). This result is the first example of a 1,3-migration of an oxime acetate group in β,γ -unsaturated oxime acetates.

As far as we are aware, behaviour of this type has not been observed in the di- π -methane systems. It seems that this alternative reaction path is the result of the formation of a better biradical. The consequences of such a reaction and possible extensions to other systems are currently under study.

We thank the Dirección General de Investigación Científica

y Técnica of Spain (Grant No. PB 89/0144) and NATO (Grant 1764/89) for financial assistance.

Received, 28th February 1990; Com. 0/00925C

References

- 1 D. Armesto, W. M. Horspool, and M. G. Gallego, *Tetrahedron Lett.*, 1990, **31**, 2475.
- 2 A. J. A. van der Weerd and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, 1988, **96**, 247.
- 3 S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.
- 4 A. J. A. van der Weerd and H. Cerfontain, *Tetrahedron*, 1981, **37**, 2121.
- 5 H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, 1969, **91**, 1718.