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 study[1] 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-workers[2] 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

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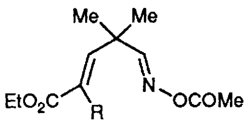
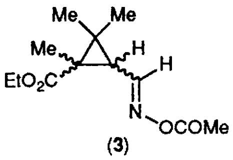
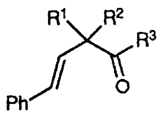
† All new products gave satisfactory microanalytical results. The irradiations were carried out in benzene with acetophenone as sensitizer in an immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp.



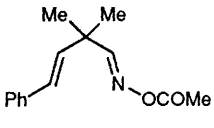
(**1**) R = H
(**2**) R = Me



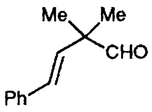
(**3**)



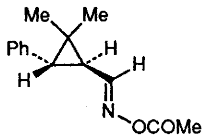
(**4**) **a**; $R^1 = R^2 = R^3 = Me$
b; $R^1 = R^2 = (CH_2)_4, R^3 = Me$
c; $R^1 = H, R^2 = Me, R^3 = Bu^t$



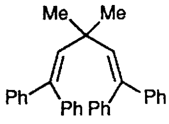
(**5**)



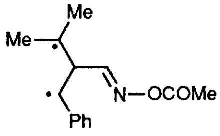
(**6**)



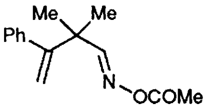
(**7**)



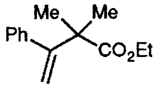
(**8**)



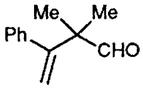
(**9**)



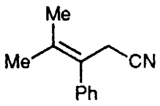
(**10**)



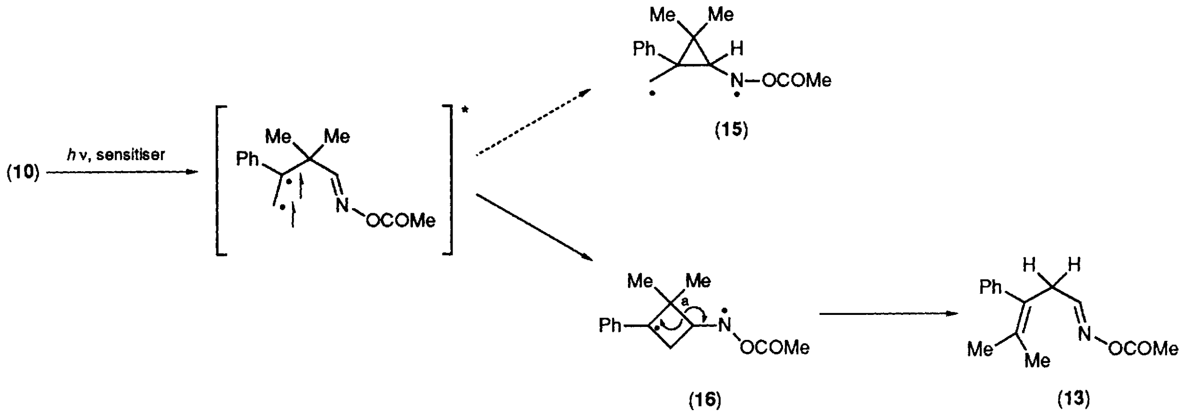
(**11**)



(**12**)



(**14**)



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.

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