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PHOTOCHEMISTRY OF *aci*-NITRO COMPOUNDS

J. T. Pinhey*, E. Rizzardo, and G. C. Smith

Department of Organic Chemistry, University of Sydney, Sydney 2006, Australia

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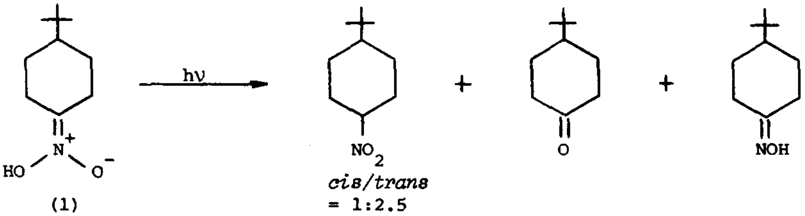
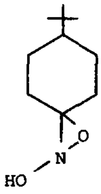
Although there has been considerable interest in the photochemistry of nitrones[1], aromatic amine N-oxides[1], and azoxy compounds[1], there have been no reports of the behaviour of the related *aci*-nitro compounds on irradiation. This is no doubt due to the instability of these compounds, especially non-conjugated ones, which are required for a study of the photochemistry of the isolated chromophore.

We have now found that 4-*t*-butyl-*aci*-nitrocyclohexane[2] (1) [m.p. 115-117° dec., λ_{max}^{dioxan} 234 nm (ε 9400), ν_{max}^{Nujol} 2800-2300 and 1657 cm^{-1}], which is readily prepared from a mixture of *cis*- and *trans*-4-*t*-butylnitrocyclohexane[3], is remarkably stable, being unchanged after keeping at room temperature for several weeks. The only nitronic acids of similar stability reported so far are stabilised either by conjugation or by the presence of bulky neighbouring groups[4]. Although unstable in protic solvents, (1) could be recovered unchanged from benzene after 4 hours at room temperature, and therefore this was the solvent used for the photolysis.

Irradiation (125-W medium pressure mercury arc, 1h, 0.25% solution) of (1) in anhydrous benzene (room temp., under N_2, complete reaction) produced *cis*-4-*t*-butylnitrocyclohexane (14%), *trans*-4-*t*-butylnitrocyclohexane (35%), 4-*t*-butylcyclohexanone (14%) and 4-*t*-butylcyclohexanone oxime (33%). It has been shown that the ketone is not arising from the oxime, and that both nitro compounds are quite stable under the reaction conditions. We believe that, in analogy with the photochemical behaviour of nitrones[1,6], the ketone arises from thermal or



photochemical breakdown of an intermediate N-hydroxyoxaziridine (2), formed from a $\pi\pi^*$ singlet state of (1), while loss of oxygen from (1) to give the oxime possibly proceeds through a triplet state. There is a precedent for the proposed breakdown of (2) in the photochemical formation of a ketone from an oxime *via* an oxaziridine[7], and in the suggested route to nitrenes formed on photolysis of quinone imine N-oxides[8].



(2)

The thermal conversion of a nitronic ester into an oxaziridine has been demonstrated[9] and it seems likely that a similar reaction occurs with the nitronic acid (1), since it yields the ketone (12%) together with the mixture of 4-*t*-butylnitrocyclohexanes (82%, *cis/trans* = 1:2.5) when heated briefly at 255° under nitrogen in biphenyl. Significantly, the oxime was not produced in the pyrolysis.

We have found that the highly stable nitronic acid, 9-*aci*-nitrofluorene[10], behaves similarly to (1) on irradiation as above (*t*-butyl alcohol as solvent), yielding fluorenone (62%) and its oxime (22%). Two minor products of the reaction were shown to be 9,9'-dinitro-9,9'-bifluorene[11] (3) (4%) and 9,9'-bifluorenylidene[12] (4) (6%). The dinitro compound (3) is probably formed by radical dimerisation, while (4) has been shown to be produced on irradiation of (3).

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