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PHOTO-OXIDATION OF STEROIDAL ISOXAZOLIDINES

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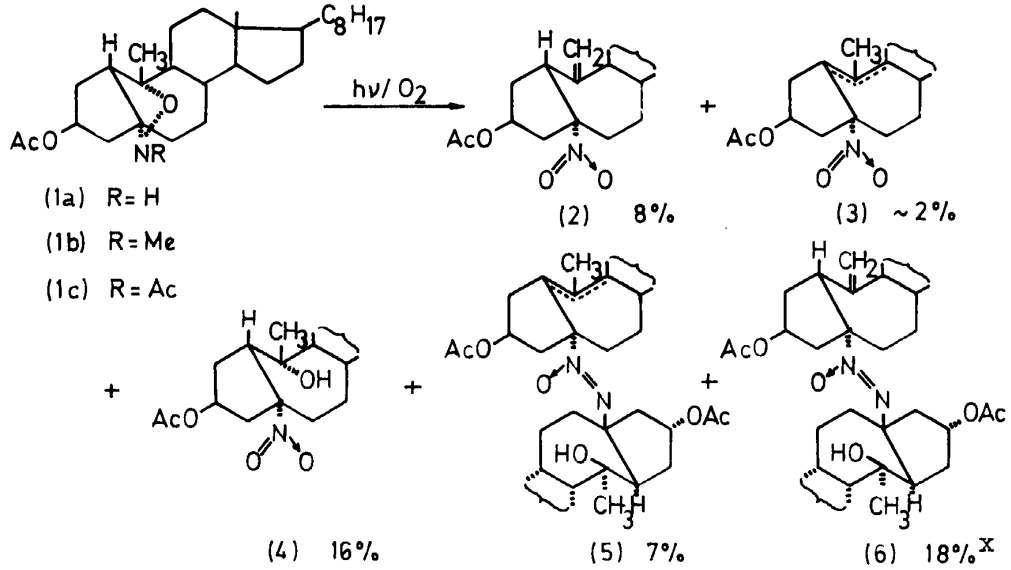
Irradiation of 5α,10α-iminoöxy-5(10→1βH)abeo-5α-cholestan-3β-ol acetate (1a) in dioxane, acetone, benzene or methanol yields in all cases a mixture from which the nitro derivatives (2), (3) and (4) and oxidodiazenes (5) and (6) could be isolated (Scheme 1).



SCHEME 1

[x]Yields indicated were obtained in a 2% acetone solution with a medium pressure mercury lamp and refer to crystallized material.

Relative yields of these products, i.e. the efficiency of the photoprocess depend on the solvent used, the most effective being in acetone or dioxane.

When irradiation is performed in an oxygenfree solution under otherwise similar experimental conditions, the disappearance of the starting isoxazolidine (1a) proceeds much slower and results in formation of a complex unresolvable mixture only. Obviously the presence of molecular oxygen is neccessary for the above photoreaction. Since isoxazolidine (1a) does not possess a chromophoric group which could accept the excitation energy, a complex pathway in which molecular oxygen is involved should be envisaged.

Irradiation of N-methyl (1b) and N-acetyl isoxazolidine (1c) gives only nitro derivatives (2) and (4).

These results and possible mechanism of the photooxidation will be discussed.