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PROCEEDINGS

ON THE MECHANISM OF PHOTO-OXYGENATION OF SOME N-ALKYL SUBSTITUTED ISOXAZOLIDINES

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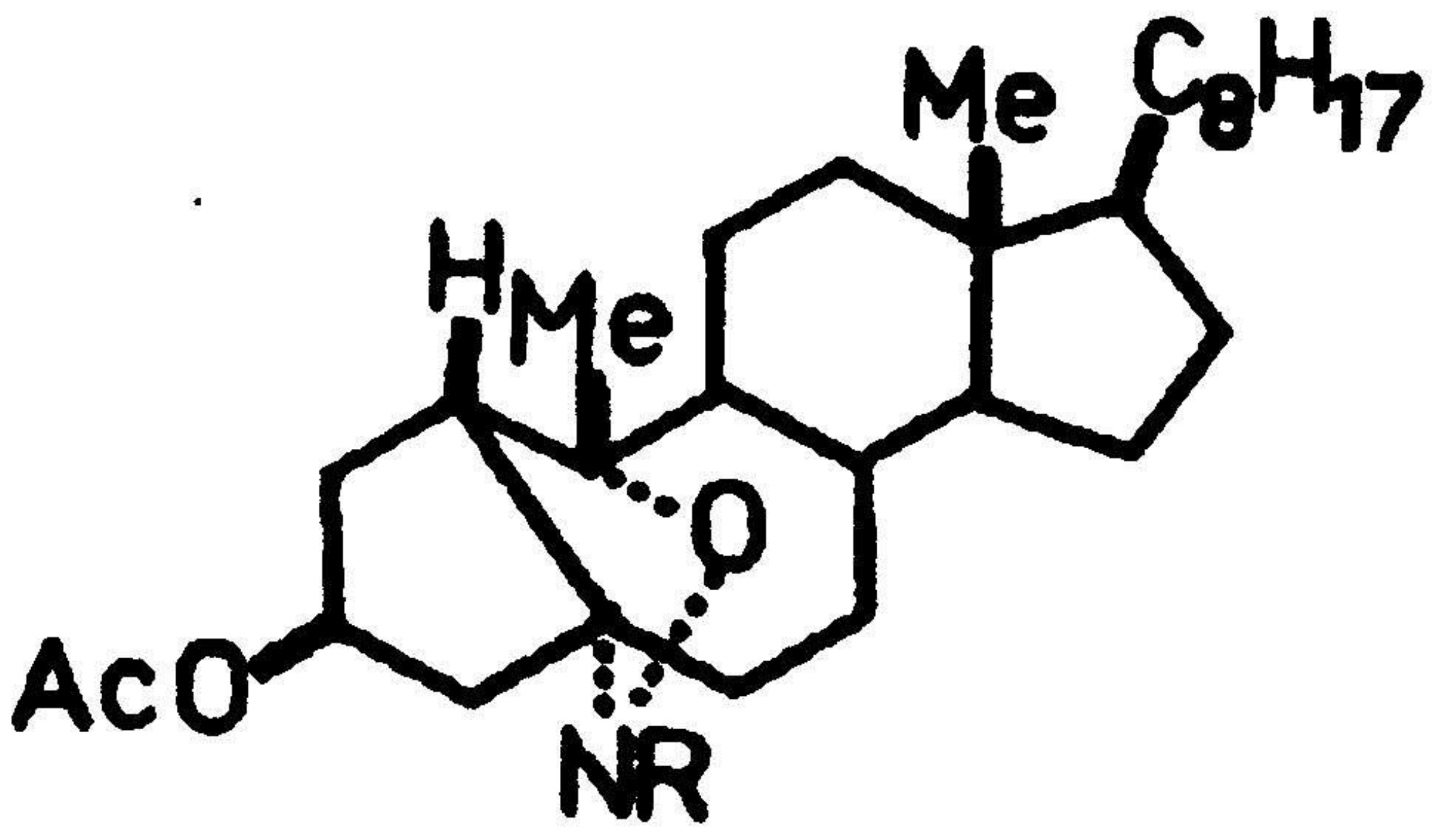
Recently we published[1,2] that u.v. irradiation of some steroidal isoxazolidines devoid of α-hydrogen atoms with respect to either heteroatom (compounds Ia-c) in various solvents in the presence of oxygen leads to azoxy and/or nitro compounds.



I

(a) R = H
(b) R = CH_3
(c) R = Ac

For unsubstituted isoxazolidine Ia we proposed a mechanism which involves as the primary photoprocess electron transfer from substrate to molecular oxygen. The exciplex (A) so formed undergoes internal proton transfer to give isoxazolidine radical (B) and hydroxyl radical. Rearrangement and one-electron

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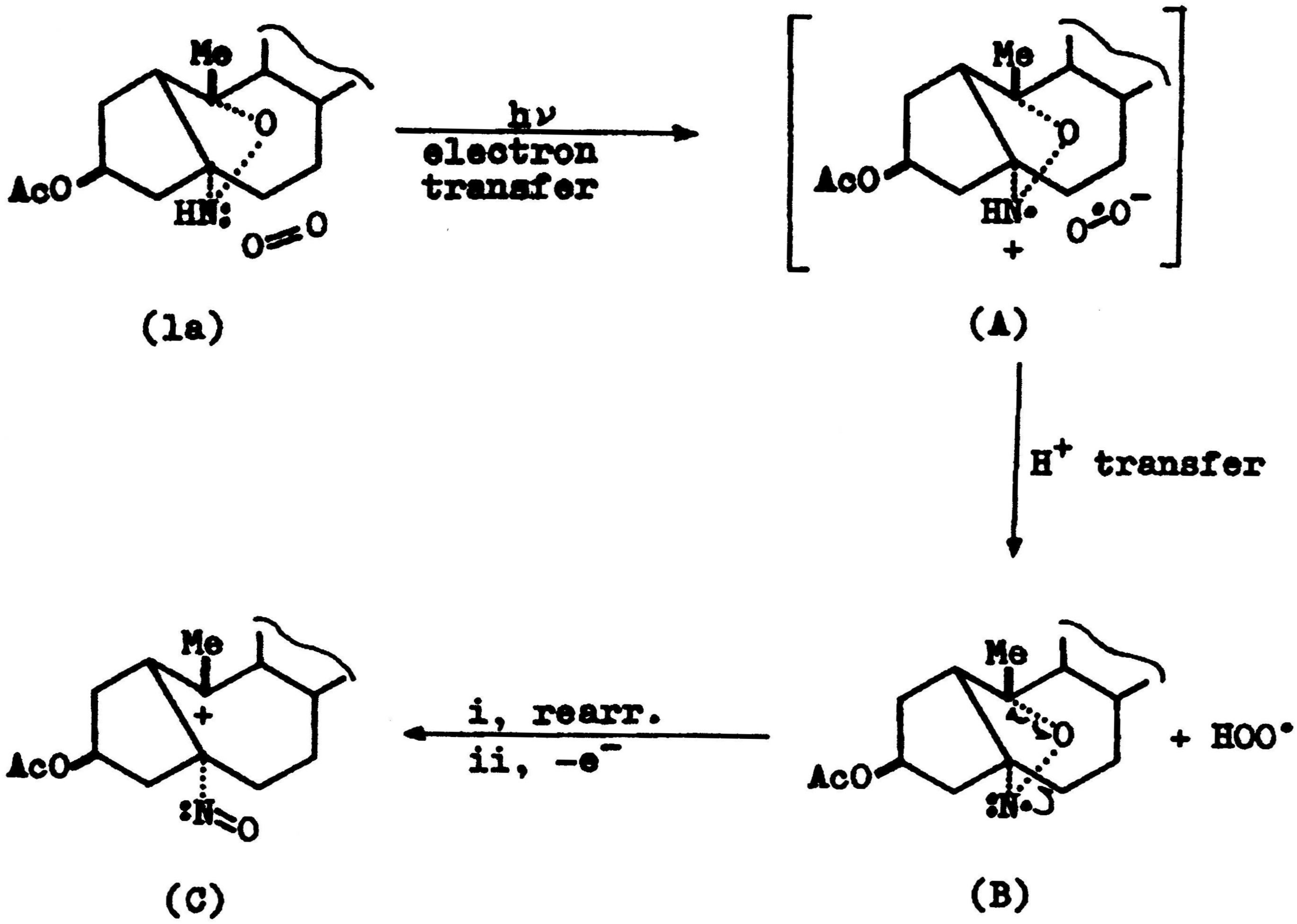
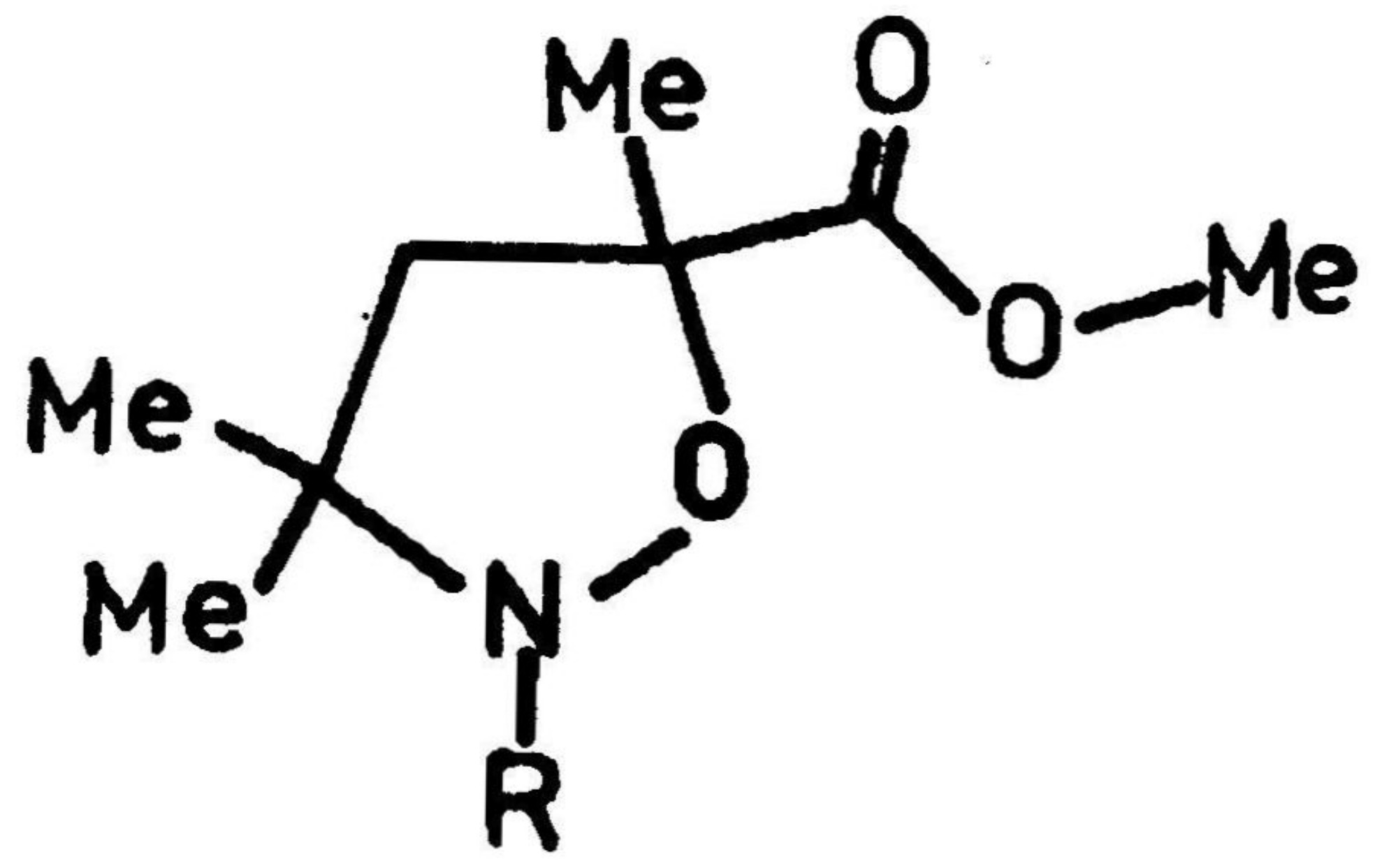


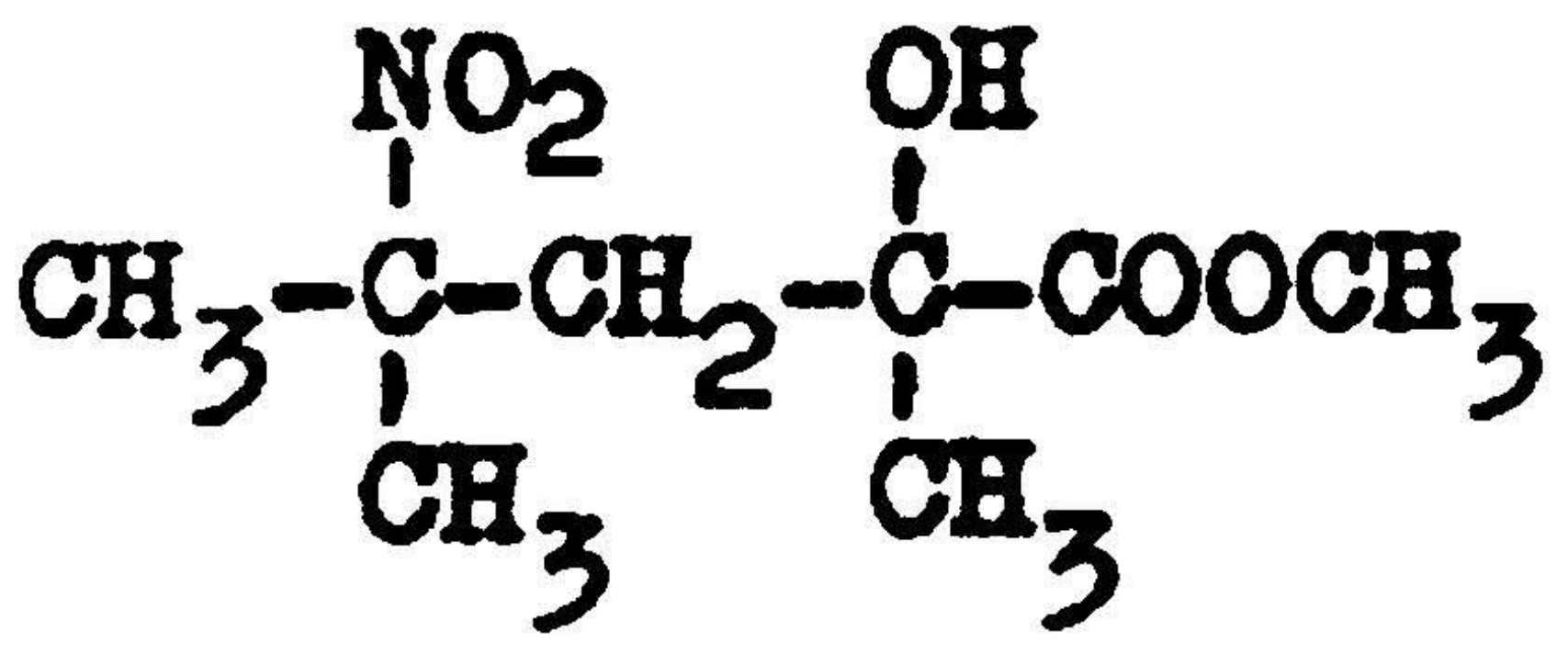
Obviously the same mechanistic path is not feasible for the N-methyl and N-acyl isoxazolidines Ib and Ic. In order to gain more insight into the reaction course of N-alkylated molecule, we investigated photochemical behaviour of a series of simple N-alkyl substituted isoxazolidines (IIa-d). Increase in reactivity in the series would indicate that C-H bond is involved in photo-oxidation[3]

II



(a) R=H (b) R=CH_3 (c) R=C_2H_5 (d) R=$CH(CH_3)_2$

It was found that irradiation of the compounds IIa-d with a medium pressure mercury lamp in ether solution gave in all cases a mixture from which nitro derivative III could be isolated.



$$CH_3-\overset{NO_2}{\underset{CH_3}{C}}-CH_2-\overset{OH}{\underset{CH_3}{C}}-COOCH_3$$

III

The obtained results can be summarized as follows:

II	$\xrightarrow{h\nu/O_2}$	III
(a)	4 h	60%
(b)	16 h	7%
(c)	"	9%
(d)	"	6%

They confirm our earlier finding that N-substituted isoxazolidines are drastically less reactive that the corresponding unsubstituted analogue and show that the basicity of the C-H bond is not the only factor which determines the efficiency of the photo-oxygenation process of N-alkyl substituted isoxazolidine molecules.

References

1. Lj. Lorenc, I. Juranić and M. Lj. Mihailović, Chem. Commun., (1977) 749.
2. I. Juranić, Ph. D. Thesis, 1977.
3. N. Kulevsky, P. V. Sneeringer and V. I. Stenberg, J. Org. Chem., 37, 438 (1972) and references therein.