The Photochemistry of 6-Nitrocholesteryl Acetate

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APART from a recent report[1] of the photochemistry of β-nitrostyrene and some related compounds, little attention has been paid to the action of ultraviolet light on non-aromatic nitro-compounds. We

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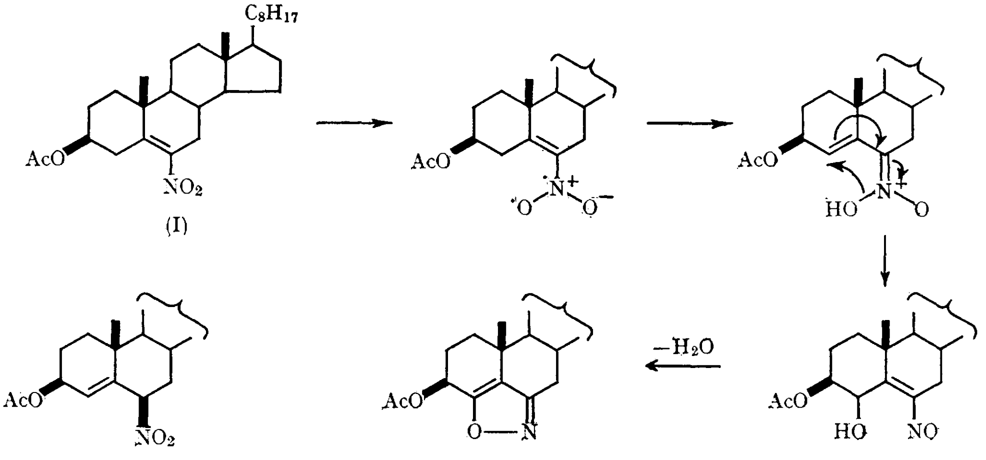
[1] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, **1964**, **9**, 585.

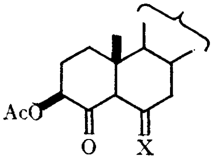
describe here some results obtained in an investigation of the photolysis of aliphatic and alicyclic nitro-compounds. For our initial study of αβ-unsaturated nitro-compounds we selected the readily available 6-nitrocholesteryl acetate (I).



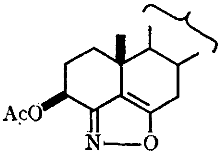
(I)

(II)

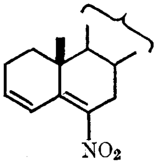
(III)



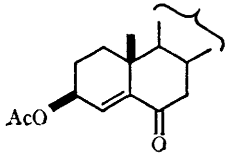
(IV) X=NH
(V) X=O



(VI)



(VII)



(VIII)

Irradiation of (I) in hexane or aqueous dioxan with light from a high-pressure mercury arc, using a pyrex filter, gave a complex mixture from which four compounds could be separated. The major product (30% yield) was 6β-nitrocholest-4-en-3β-yl acetate[2] (II), m.p. 101—102°, confirmed by acetylation of the known[3] alcohol. The formation of (II) from (I) is analogous to the photochemical deconjugation of certain αβ-unsaturated ketones.[4] To the second product (10% yield), m.p. 129—130°, we assign structure (III). The presence of the isoxazole ring was confirmed by reduction of (III) to the imino-ketone (IV), m.p. 173—175°, which could be readily hydrolysed to the diketone (V), m.p. 119—120°. The mechanistic path to (III) is very probably similar to that proposed[5] for the oxidation–reduction reactions observed in the photolysis of certain *ortho*-substituted nitrobenzenes. We exclude the alternative structure

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[2] All new compounds analysed correctly and had i.r., u.v., and p.m.r. spectra consistent with the assigned structures.

[3] W. A. Harrison, Sir Ewart R. H. Jones, G. D. Meakins, and P. A. Wilkinson, *J. Chem. Soc.*, 1964, 3210.

[4] Reviewed by O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 323.

[5] P. de Mayo and S. T. Reid, *Quart. Rev.*, 1961, **15**, 393.

(VI) for the isoxazole for the following reason. The enol nitrite, which could form[6] by isomerisation of (I) would be a necessary intermediate in the formation of (VI). The Barton reaction which the enol nitrite would then be required to undergo would involve a five-membered transition state and even in more favoured cases such a reaction has not been observed to occur.[7]

The third product (2—3% yield), m.p. 72—73°, was also obtained by pyrolysis of 6-nitrocholesteryl benzoate and is therefore 6-nitrocholesta-3,5-diene (VII). The fourth product (2—3% yield) was the known αβ-unsaturated ketone (VIII). As far as we are aware the formation of (VIII) from (I) is the first example of a photochemical Nef-type reaction.

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[6] See ref. 1 for an example of the isomerisation of an αβ-unsaturated nitro-compound to an enol nitrite.

[7] For a review of the Barton Reaction see M. Aktar, *Adv. Photochem.*, 1964, **2**, 263.