Photolysis of 3-Triphenylmethyl-Δ^2-isoxazolines: a New Method for CC-Double Bond Cleavage

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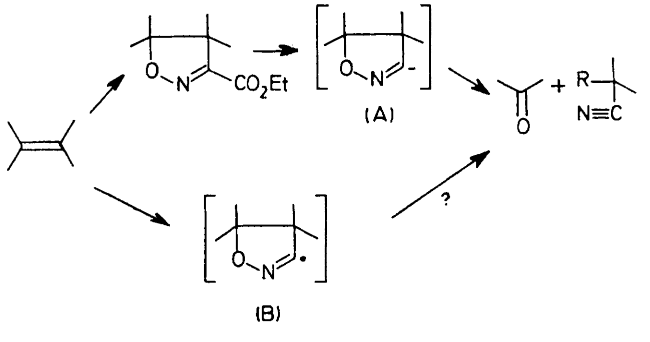
Summary U.v. irradiation of triphenylmethyl-Δ^2-isoxazolines, formed by 1,3-dipolar addition of triphenylacetonitrile oxide to olefins, results in the elimination of the Ph_3C group and subsequent fragmentation of the heterocycle to give a carbonyl compound and a nitrile.

In the preceding communication[1] a new procedure for the cleavage of olefinic double bonds involving the addition of ethoxycarbonylformonitrile oxide followed by hydrolysis of the ester and thermal decarboxylation is described.



The intermediacy of an anionic species of type (A) in the last step of process was presumed. In connexion with a study of the mechanism of this reaction and in search for a lower-temperature alternative we became interested in the behaviour of the one-electron analogue (B) of anion (A). Photolysis of a 3-triphenylmethyl-Δ^2-isoxazoline, wherein the bond between the heterocycle and the triphenylmethyl group would be susceptible to homolytic cleavage, appeared to be the most promising route to this free radical.

Suitable model compounds to test this hypothesis were obtained by the addition of the thermally stable nitrile oxide (**2**)[2]† (2 g) to the 3-methylene steroid (**1**)[3] (2 g) in dioxan solution (100 ml; 2 days; 60 °C), whereby a (1 : 1) mixture (87% yield) of the two epimeric isoxazolines (**3**), m.p. 218—220 °,‡ and (**4**), m.p. 130—132 °C, was formed.

U.v. irradiation§ of (**3**) and/or (**4**) in benzene solution ($5{\cdot}4 \times 10^{-3}$ M) led to the ketone (**8**) in 43—48% yield. These results are in agreement with the assumption that the radical (**5**) is formed and show that its reactivity is similar to that of the anion (A).[4]

Under the same conditions 2-triphenylmethyl-5-phenyl-Δ^2-isoxazoline, m.p. 154—157 °C, and 2-triphenylmethyl-4,5-diphenyl-Δ^2-isoxazoline, m.p. 153—155 °C, formed from styrene and *trans*-stilbene respectively, yielded varying amounts of benzaldehyde (characterised as its 2,4-dinitrophenylhydrazone).

A synchronous conversion of the free radical (**5**) into the ketone (**8**) is improbable from orbital symmetry considera-

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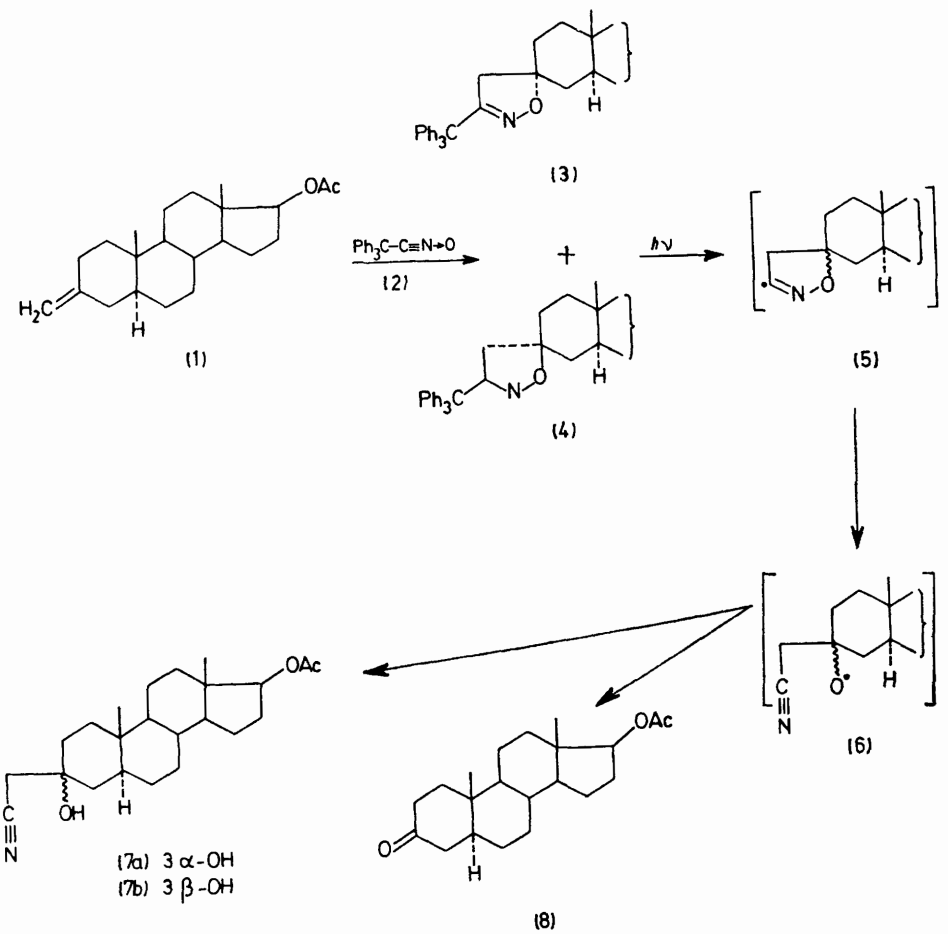
† Easily accessible from triphenylacetaldehyde by oximation and treatment with Br_2–NaOH in CCl_4 at 0 °C.

‡ All new compounds had spectroscopic (i.r., n.m.r., mass, and u.v.) and analytical data in agreement with the given structures.

§ Medium-pressure TQ 150 Hanau u.v. lamp, standard quartz equipment, argon atmosphere.



tions, so we postulate a two-step reaction involving the formation of the oxyl radical (**6**) and its subsequent fragmentation. Evidence for this mechanism derives from irradiation experiments in cyclohexane (a better hydrogen donor): a 5% yield of each of the cyanohydrins (**7a**), m.p. 215—218 °C, and (**7b**), m.p. 180 °C, was obtained from (**3**) and (**4**) respectively in addition to *ca.* 30% of ketone (**8**).

The reaction sequence (**1**) ⟶ (**8**) represents another method for 'non-oxidative' double bond cleavage.[1]

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[1] J. Kalvoda and H. Kaufmann, preceding communication.

[2] H. Wieland and B. Rosenfeld, *Annalen*, 1930, **484**, 236.

[3] F. Sondheimer and R. Mechoulam, *J. Amer. Chem. Soc.*, 1957, **79**, 5029.

[4] The photochemistry of 3,5-diphenyl-Δ^2-isoxazoline is discussed by Y. Ito and T. Masuura, *Tetrahedron*, 1975, **31**, 1373.