

DOUBLE BOND CLEAVAGE ON ULTRAVIOLET IRRADIATION OF $\alpha\beta$ -UNSATURATED
NITRO COMPOUNDS

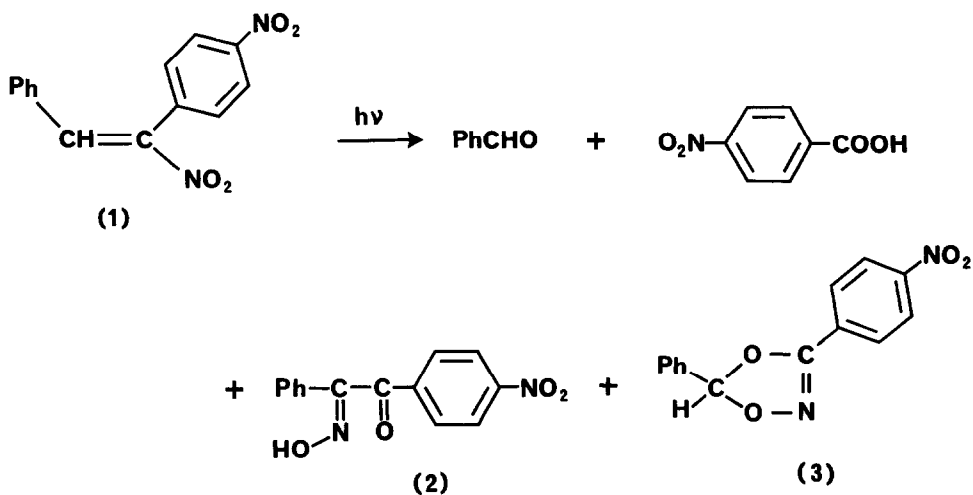
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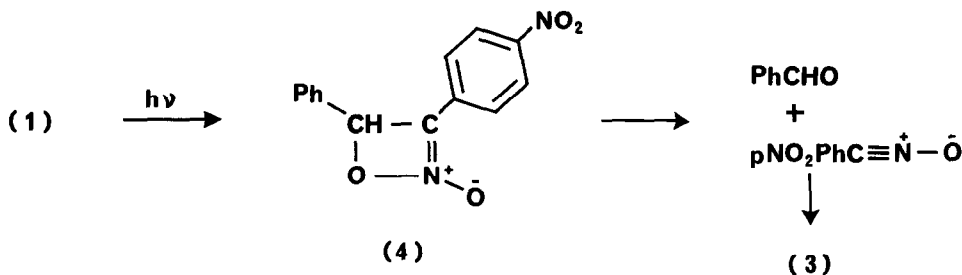
Several studies of the photochemistry of $\alpha\beta$ -unsaturated nitro compounds have shown that they undergo five main reactions, depending on their structural features and on the conditions used, isomerisation to the $\beta\gamma$ -unsaturated compound^{1,2,3}, dimerisation to give a dinitrocyclobutane⁴, isomerisation to an α -oximino ketone^{2,5,6}, conversion into an $\alpha\beta$ -unsaturated ketone^{1,2,7}, and dehydration to an isoxazole¹. We now report that in certain cases cleavage of the double bond occurs to give an aldehyde or ketone and a carboxylic acid.

During an investigation of substituent effects on the photoisomerisation of β -nitrostyrenes to α -oximino ketones, it was found that, whereas *cis*- α -nitrostilbene was converted in high yield into a mixture of isomers of benzil monooxime on irradiation (pyrex filter, medium pressure mercury arc) in acetone, *cis*- α ,4-dinitrostilbene⁸ (1) under similar conditions¹⁰ gave only 38% of the α -isomer of 2-phenyl-2-hydroxyimino-4'-nitroacetophenone¹¹ (2). Also isolated from this reaction were benzaldehyde (19%), *p*-nitrobenzoic acid (11%), and 5-phenyl-3-(*p*-nitrophenyl)-1,4,2-dioxazole¹² (3) (6%).



We suggest that benzaldehyde and the dioxazole (3) may arise as outlined below. On irradiation *cis*- α ,4-dinitrostilbene (1) yields the N-oxide (4), for which we have no direct evidence, which then breaks down to give benzaldehyde and *p*-nitrobenzoxazole. These products then combine in a 1,3 dipolar addition to yield the dioxazole (3). *p*-Nitrobenzoic acid probably arises by hydrolysis of the nitrile oxide under the acid conditions which develop during the photolysis, or from the dioxazole, shown to yield the acid under the irradiation conditions. There is analogy for the formation of the N-oxide (4) in the recent photochemical conversion of an $\alpha\beta$ -unsaturated ketone to an oxetene¹³, and in the proposed intermediacy of an oxazetene in the photochemical breakdown of an acetylenic nitrite to a nitrile and a lactone¹⁴.

Two further examples of this nitroolefin fragmentation have been found. Irradiation of *trans*- α -nitro- α' -methylstilbene¹⁵ as above led to the rapid formation of acetophenone (22%) and benzoic acid (21%), while α -nitro- α' -phenylstilbene¹⁷ behaved similarly to give benzophenone (34%) and benzoic acid (15%). The absence of products corresponding to the dioxazole (3) in these two cases would be expected if mechanisms similar to that suggested above were operating here, since benzonitrile oxide does not add to unactivated ketones¹⁸.



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- 8 Prepared by the method of Robertson. All new compounds gave satisfactory analytical data and the expected spectral properties.
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- 11 Failure to isolate the β -isomer is in keeping with our finding with α -nitrostilbene that the isomer with the hydroxyl and keto groups *anti* is formed first, and photoisomerisation to the other isomer is comparatively slow.
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