

PHOTOINDUCED CYCLOADDITIONS OF ELECTRON
 DEFICIENT NITRONES TO ALKENES

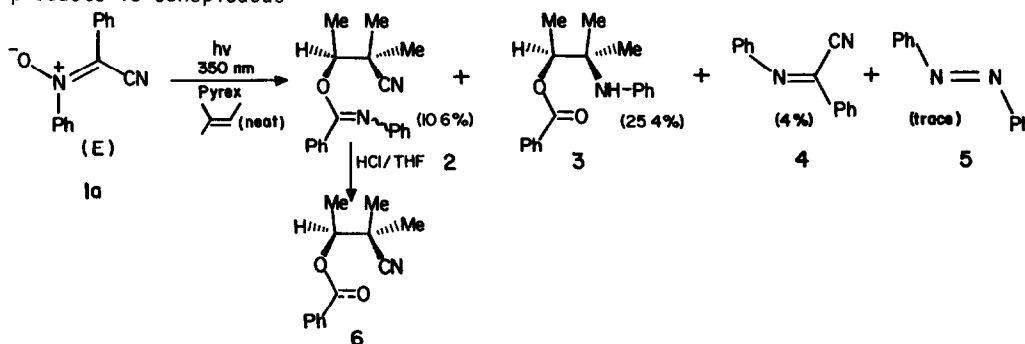
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Oxaziridines are proposed as intermediates in the photoinduced cycloadditions of electron deficient nitrones to dipolarophiles.

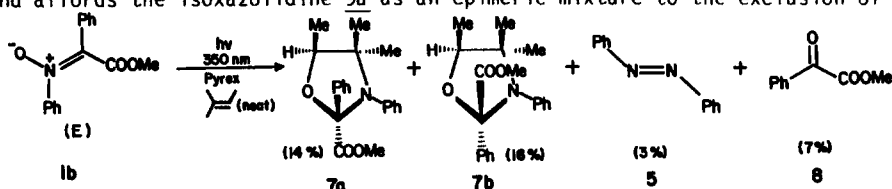
The thermal (ground state) [3+2] dipolar cycloadditions of nitrones to dipolarophiles is a widely documented process.¹ In contrast, the excited state reactions of nitrones are characterized by facile photocyclization to oxaziridines, a process often accompanied by photoinduced transformations of the latter.² We surmised that introduction of an electronegative substituent at the sp² carbon atom of a nitrone would suppress positive charge delocalization at this center, diminish the 1,3-dipolar reactivity of such substituted nitrones relative to their unsubstituted counterparts and possibly enhance the oxaziridine ring stability. Conceivably, such substitution might then be attended by an increased potential for interception of a three-center dipolar or diradical transient derived by electrocyclic opening of the oxaziridine generated by photoinduced nitrone cyclization. The photochemical studies on the substituted nitrones 1a-c³ described herein were initiated to assess the validity of these theoretical speculations.

Irradiation (350 nm)⁴ of 1a (X=CN)³ in neat 2-methyl-2-butene (7 hours) gave rise to four photoproducts identified as 2, 3, 4 and 5 which were isolated by thin layer chromatography (Silica gel or alumina, 20% ether-benzene or benzene)⁵ When the crude photolysate was hydrolyzed (2% HCl/THF) prior to thin-layer chromatographic separation, a fifth product, identified as 6 and shown to arise from hydrolysis of 2, was obtained in addition to 3, 4 and 5. It is evident that cyanoester 2 is consumed in forming 6 since the absence of the former among the hydrolysate products is conspicuous.

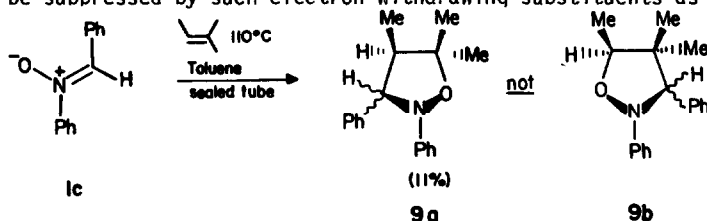


In a similar manner, irradiation (350 nm)⁴ of 1b (X=CO₂Me) in neat 2-methyl-2-butene (7 hours) followed by preparative thin layer chromatographic separation permitted isolation of four photoproducts identified as the epimeric [3+2]cycloadducts 7a and 7b, azobenzene 5 and methyl phenylglycidate (8)⁵ It is significant that neither 1a nor 1b undergoes thermal (ground state)

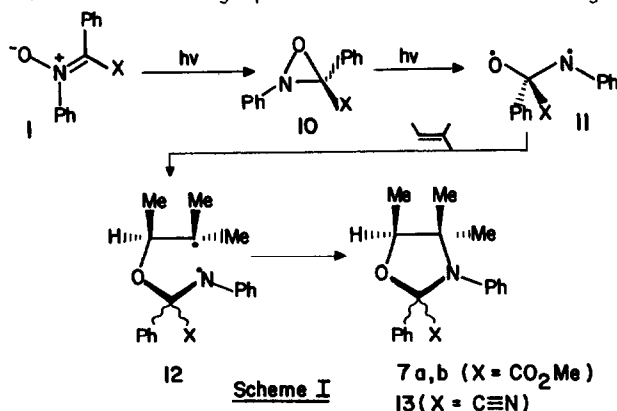
cycloadditions to the electron rich dipolarophile 2-methyl-2-butene. In contrast, however, thermal induced [3+2]cycloaddition of the parent nitron 1c (X=H) to 2-methyl-2-butene occurs readily and affords the isoxazolidine 9a as an epimeric mixture to the exclusion of the regio-



isomer 9b. These results are consistent with our initial premise that dipolar reactivity of nitrones should be suppressed by such electron withdrawing substituents as X



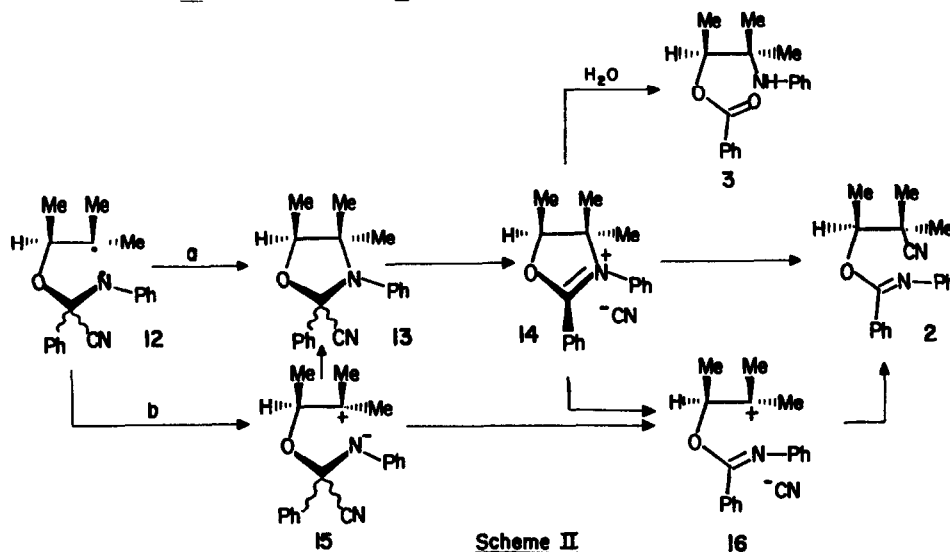
It is noteworthy that the photoinduced addition reactions described proceed in a regio-selective manner. This is clearly evident in the photoinitiated cycloaddition of 1b to 2-methyl-2-butene where the oxygen atom binds to the least substituted terminus of the double bond while nitrogen becomes attached to the alternate more highly substituted end with formation of the oxazolidines 7a and 7b. Similar behavior is observed in the addition of 1a to 2-methyl-2-butene, although clearly an obvious divergence in chemical properties is displayed by the cyano adducts from those observed for the carbomethoxy oxazolidines 7a and 7b obtained from 1b. A mechanism is advanced to rationalize the photoaddition products obtained in the case of 1a and 1b. It is proposed that the nitrones 1a and 1b initially photocyclize to the corresponding oxazolidines 10.⁷ The latter then undergo photoinduced N-O bond cleavage (Scheme I) to give the



reactive transients 11 ascribed diradicaloid character which add to the 2-methyl-2-butene in a sequential manner with formation of the intermediates 12 which cyclize to 7a, 7b, or 13 the primary photoaddition products in an ensuing step.

While the adducts 7a and 7b derived from 1b (X=CO₂Me) are sufficiently stable to be isolated and characterized, the oxazolidine(s) 13 derived from 1a (X=CN) are more labile and

undergo cleavage under the reaction conditions and/or workup. Two pathways are depicted in Scheme II to rationalize the products which arise upon opening of the presumed adducts 13 (X=CN). In path (a) it is suggested that oxazolidine(s) 13 (X=CN) formed by cyclization of the intermediate 12 may undergo ionization⁸ to the stabilized oxazolinium ion 14 followed by concerted nucleophilic attack by cyanide ion with accompanying ring-opening to give 2 an observed product. Contact of 15 with moisture present in the solvent or Silica gel during product isolation would afford 3 in a competing process. Alternatively, prior ring scission of 14 may occur to give the carbocation, which is then trapped by cyanide ion to form 2, conceivably too, the diradical 12 may undergo conversion to 15 by intramolecular electron transfer and in turn eliminate cyanide ion to give 16 and ultimately 2. Our commitment to a sequential diradical mechanism for



the observed additions is predicated on the high degree of regioselectivity which prevails and on our reluctance to reconcile this feature of these photoinduced reactions by invoking a zwitterionic transient akin to 11 in which oxygen must accommodate a positive charge.

Additional nitrones bearing electronegative substituents on the aromatic rings are presently being screened as substrates in cycloadditions of the type described and attempts are in progress to validate or refute our mechanistic proposals and characterize the transient(s) implicated using laser flash photolysis techniques.

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- 5) All new compounds gave satisfactory combustion analyses. The spectral data (pmr, cmr, ir, mass spec.) are consistent with the proposed structures. Complete structural details will be published in the full paper.
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