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INTRA- AND INTERMOLECULAR PATERNO-BUCHI REACTIONS ON PHTHALIMIDES. ISOLATION OF THE OXETANE.

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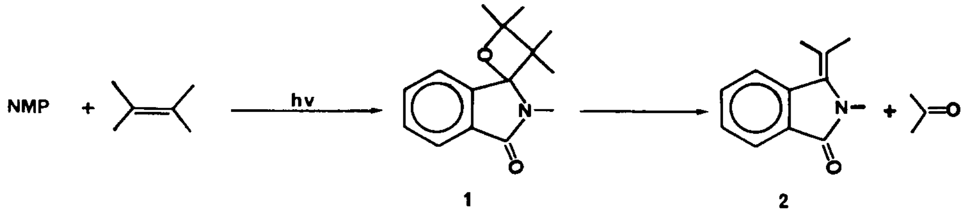
Summary. Photochemical addition of a series of alkenes to N-substituted phthalimides resulted in the formation of oxetanes which subsequently collapsed to substituted 3-methylene isoindolones.

Phthalimides undergo a series of diverse photochemical reactions[1] with alkenes, including addition to the C(O)N bond,[2] electron transfer[3] and photoreduction.[1a,4] Whereas aliphatic imides undergo efficient Paterno-Buchi reactions with alkenes,[1a] there is only one example in which a Paterno-Buchi intermediate is implicated in phthalimide photochemistry.[2b,5] We now wish to report several examples of the Paterno-Buchi process in phthalimides including two cases in which the oxetane was isolated.[6]

Irradiation of acetonitrile solutions of 2,3-dimethyl-2-butene and N-methylphthalimide (NMP) resulted in the formation of a number of products, including the oxetane (1) and the 3-isopropylidene isoindolone (2). The structure of 1 was established on the basis of its spectroscopic properties[7] and on the fact that chloroform solutions decomposed to 2[8] and acetone.

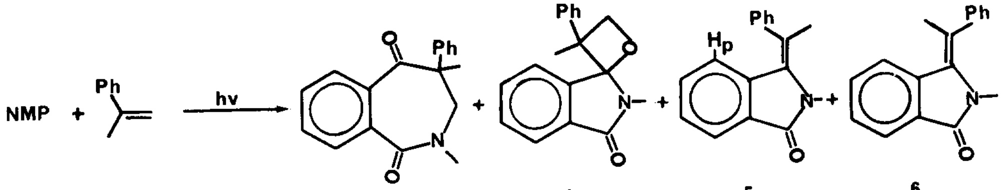


1

2

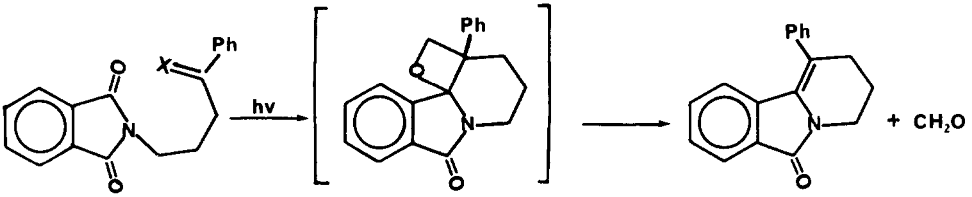
In a similar manner, irradiation of solutions of NMP and low concentrations of α-methylstyrene in acetonitrile gave four products, including the addition product 3 (60%), the oxetane 4 (4%) and its decomposition products 5 (17%) and 6 (3%). The NMR of compound 4 showed the methylene protons as doublets at δ4.60 and 5.34 and methyl resonances at δ1.77 and 2.52. The CIMS showed its base peak (M+1) at m/e 280.

The stereochemistry of 5 follows from the chemical shift of proton Hp which appears as an ortho coupled doublet at δ6.00. Models indicate that this proton should be shielded by the proximate phenyl substituent due to steric interactions which cause the phenyl group to twist out of the plane of the bicyclic system. The corresponding proton in 6 appears in the normal aromatic region of the NMR.[9]



3 4 5 6

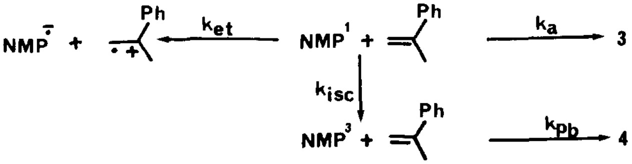
Irradiation of an acetonitrile solution of 7 led to the formation of a single photoproduct in 64% yield. The product was identified as 10 based on



7 $X = CH_2$
8 $X = O$
9
10

spectroscopic evidence and the fact that ozonolysis converted it to 8. The Paterno-Buchi intermediate 9 is a necessary intermediate in the formation of 10.

Quenching (fluorene) and sensitization (1-indanone) studies on the 2,3-dimethyl-2-butene reaction unequivocally establish that the reaction occurs through the triplet excited state of NMP. Clearly in cases such as this and the α-methylstyrene reaction, intersystem crossing must compete with electron transfer. Thus at high alkene concentrations, electron transfer quenching dominates ISC and no triplet product is observed. The situation with respect to these competing reactions is outlined below. We are continuing studies to elucidate the scope and mechanistic details of phthalimide photochemistrty.



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6. Machida, Takechi, and Kanaoka have discovered examples of intramolecular

oxetane formation. We thank them for sending us a preprint of their forthcoming publication.

7. The NMR spectrum of $CDCl_3$ solution of 7 showed methyl singlets at δ1.0, 1.2, 1.5, 1.6 and 3.2 in addition to the aromatic multiplet centered at δ7.6

8. This compound showed spectroscopic characteristics identical with those of an authentic sample.

9. Similar results were obtained with ρ-methyl-α-methylstyrene and styrene which gave decomposition products analogous to 5 and 6.

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