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Photoaddition of Vinyl Ethers to N-Methylphthalimide. Competing 2 + 2 Processes.

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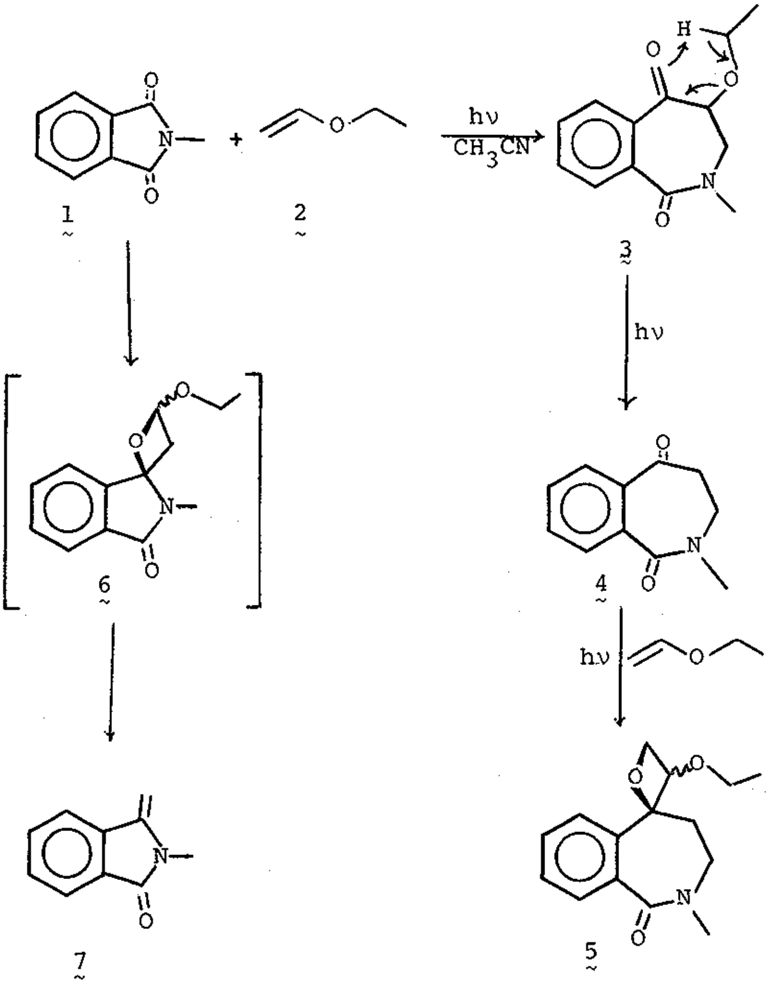
The photochemical addition of vinyl alkyl ethers to N-methylphthalimide to give 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones in a $\pi^2 + \sigma^2$ process is found to compete with the $\pi^2 + \pi^2$ Paterno-Buchi reaction in this system.

The photochemical reactions of phthalimides have been the subject of numerous recent reports. The system undergoes a variety of photoreactions common to other carbonyl compounds including Type II and photoreduction reactions.[1] We recently reported[2] the novel addition of a series of dienes to N-methylphthalimide (1) to give 6-substituted 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones in what is formally a $[\pi^2 + \sigma^2]$ process.

In this paper we report the reaction of vinyl ethers with 1. Irradiation of 1 and a 50-fold molar excess of ethyl vinyl ether in acetonitrile solution with a 450W Hanovia lamp gave three products which were identified as 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione (4[2], 8% yield), 3-methylene-2-methylazaindanone (7, 7% yield) identified on the basis of its NMR($CDCl_3$) δ7.40-7.90 (m, 4H), 5.19 and 4.81 (AB pattern,



J=2Hz) and 3.28 (s, 3H), which was identical with that of an authentic sample,[3] and the oxetane 5 (9% yield, m.p. 134-135°C) whose structure was based on the following spectral properties: NMR($CDCl_3$) δ7.23-7.78 (m, 4H), 4.59, 4.30 and 3.99 (ABX pattern, J_{AB}=4.6Hz, J_{AX}=J_{BX}=6.8Hz), 3.70-3.02 (m, 6H), 3.12 (s, 3H) and 1.20 (t, 3H); IR($CHCl_3$) 1640 cm^{-1}; m/e 259.[4]

Compound 4 arises via initial $[\pi^2 + \sigma^2]$ photochemical addition of 2 to 1 followed by subsequent type II cleavage of the primary photoproduct 3.[2] The secondary photoproduct 5 is generated by a Paterno-Buchi[5] reaction on 4 and this was confirmed by irradiating a mixture of 4 and 2 which afforded 5 in 47% yield.

Competing with the formation of 4 is the direct $\pi^2 + \pi^2$ Paterno-Buchi reaction of 2 with 1 to afford 6.[6] Compound 6 is sufficiently unstable to the reaction conditions that it decomposes to 7,[10] which is observed.

Irradiation of 1 with n-butyl vinyl ether gave the corresponding (to 5) butyl oxetane, 4 and 7 in 4%, 20% and 10% yields respectively. However, when the reaction was attempted with isopropenyl ethyl ether or 1,1-dimethoxy ethylene, alkenes which we expected to be more reactive, no benzazepinediones were formed. The reasons for this selectivity are being investigated.

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4. This material gave acceptable elemental analysis (C,H,N).

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6. We have not observed this process with dienes[2] or alkenes,[7] however, intramolecular oxetane formation has been observed on irradiation of N-alkenylsuccinimides[8] but not in the corresponding N-alkenylphthalimides.[9]

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11. The formation of **6** corresponds to one of two possible modes of addition to the carbonyl group in **1**. We do not observe the isomeric product or decomposition products from it.

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