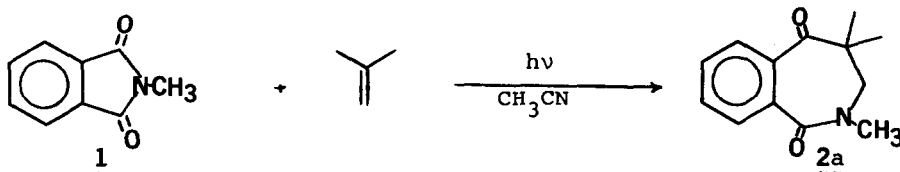


THE PHOTOCHEMICAL ADDITION OF ALKENES TO N-METHYLPHthalIMIDE
 EVIDENCE FOR ELECTRON TRANSFER QUENCHING

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We reported the photochemical addition of dienes¹ and alkenes² to N-methylphthalimide (NMP) to give 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones in what is formally a $\pi^2 + \sigma^2$ addition of an alkene to the C(O)-N bond in the imide. The reaction was found to be regiospecific with respect to the direction



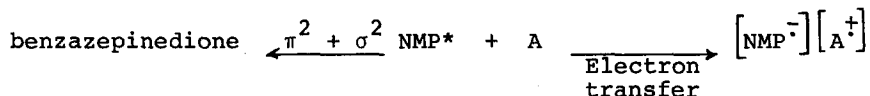
of addition of the alkene component, and selective with respect to alkene ionization potentials, i.e. only those alkenes with ionization potentials above 9 EV were reactive (Table 1). It was suggested² that electron transfer quenching

Table 1
 Benzazepinedione Formation

Alkene	Yield ^a	IP (EV)	E ^{OX} (V)	Alkene	Yield	IP (EV)	E ^{OX} (V)
	60%	9.58	2.78 ^b		0%	9.01	2.15 ^c
	46%	9.46	2.64 ^c		0%	8.95	2.05 ^b
	44%	9.23	2.39 ^c		0%	8.68	1.79 ^c
	43%	9.12	2.27 ^c		0%	8.53	1.63 ^c
	32%	9.13	2.26 ^b				

a) In acetonitrile solution, b) experimentally determined value⁸, c) calculated value.⁸

of the NMP singlet state might be taking place in those cases where the addition reaction did not occur. A possible mechanistic scheme, in which electron transfer from the alkene (A) to excited NMP gives the radical anion - radical cation pair (which subsequently back transfers an electron to regenerate starting material) in competition with the $\pi^2 + \sigma^2$ addition to give the benzazepinedione is outlined below. The electron transfer reaction will only compete



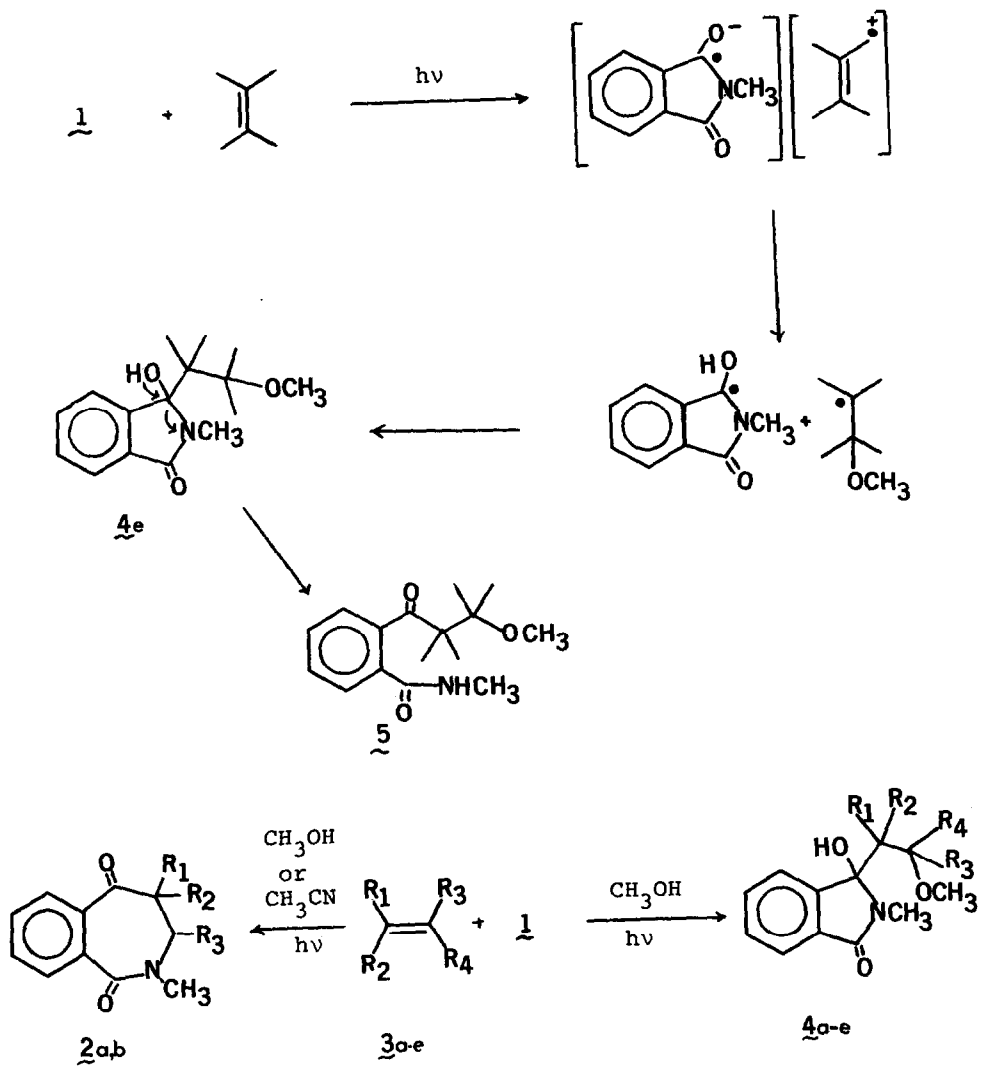
efficiently when ΔG_{ET} is negative and this can be calculated by³

$$\Delta G_{\text{ET}} = 23.06 (E_{\text{D}}^{\text{OX}} - E_{\text{A}}^{\text{red}}) - \Delta E_{\text{OO}}$$

Using $E_{\text{A}} = -1.37\text{V}$ ⁴ and $\Delta E_{\text{OO}} = 80 \text{ kcal}$ ⁵, this equation predicts that electron transfer will be efficient in those cases where E_{D}^{OX} is less than 2.1 V in agreement with our observations.

Since it has been shown⁶ that radical cations generated by photochemical electron transfer can be trapped in alcoholic solvents, we investigated the reaction of NMP with 3a-e in methanol. Irradiation of a solution of 1 and 2-methyl-2-butene (3d) in methanol afforded a pair of diastereoisomers 4d. The lower melting diastereomer (mp = 133-4°C, 32%) showed: NMR(CDCl₃) δ 0.42 (s, 3H), 1.14 (d, 3H, J=7Hz), 3.12 (s, 3H), 3.43 (s, 3H), 3.82 (q, 1H, J=7Hz), 6.60 (s, 1H), and 7.26-7.90 (m, 4H); IR(CHCl₃) 3340 and 1685 cm⁻¹. The higher melting diastereoisomer (mp = 154-155°C, 19%) showed: NMR(CDCl₃) δ 0.50 (s, 3H), 1.16 (d, 3H, J=7Hz), 3.11 (s, 3H), 3.58 (s, 3H), 3.81 (q, 1H, J=7Hz), 5.80 (s, 1H), 7.30-7.92 (m, 4H); IR(CHCl₃) 3360 and 1700 cm⁻¹. When 2,3-dimethyl-2-butene (3e) was employed, a single product (mp = 105-106°C, 42%) was obtained and assigned the keto-amide structure 5 on the basis of spectral data: NMR(CDCl₃) δ 1.26 (s, 6H), 1.28 (s, 6H), 2.87 (d, 3H, J=5Hz, coalesced to a singlet after D₂O exchange), 3.28 (s, 3H), 6.00-6.5 (1H), 7.0-7.8 (m, 4H); IR(CHCl₃) 3460, 1672 and 1688 cm⁻¹.⁷ Compound 5 arises from the initially formed 4e by ring opening. Similarly, 3c afforded 4c as a pair of diastereomers in 28% yield. No other addition products were observed. However, when 1 was reacted with 3a in methanol a 57% yield of the $\pi^2 + \sigma^2$ product 2a was obtained in addition to 15% of 4a and reaction with 3b gave 2b in 22% yield along with 12% of 4b. Irradiation of 1 with 1-heptene in either methanol or acetonitrile gave only the $\pi^2 + \sigma^2$ product, 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione.

These results are consistent with our proposed scheme in which electron transfer quenching competes with the $\pi^2 + \sigma^2$ addition in cases in which ΔG_{ET} has small positive values, dominates the $\pi^2 + \sigma^2$ process when ΔG_{ET} is negative and is non-competitive when ΔG_{ET} has a large positive value.



- a, $R_1=R_2=\text{CH}_3, R_3=R_4=\text{H}$
- b, $R_1=R_3=\text{CH}_3, R_2=R_4=\text{H}$
- c, $R_1=R_3=\text{H}, R_2, R_4=\text{-(CH}_2\text{)}_4\text{-}$
- d, $R_1=R_2=R_3=\text{CH}_3, R_4=\text{H}$
- e, $R_1=R_2=R_3=R_4=\text{CH}_3$

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7. These materials gave acceptable (C,H,N) elemental analyses. None of the hydroxy ethers showed molecular ions in the mass spectrum but they all showed base peaks corresponding to loss of the alkyl ether chain i.e. cleavage of the bond β to the nitrogen and the hydroxy oxygen. NMR and IR data were consistent with all reported structures.
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