

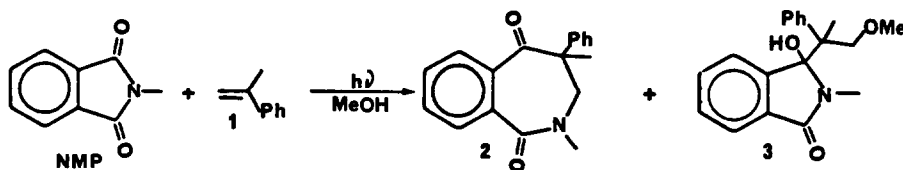
NOVEL PHOTOADDITION OF  $\alpha$ -METHYLSTYRENE TO N-METHYL-1,8-NAPHTHALIMIDE  
IN METHANOL. FORMATION OF A TETRACYCLIC ADDUCT.

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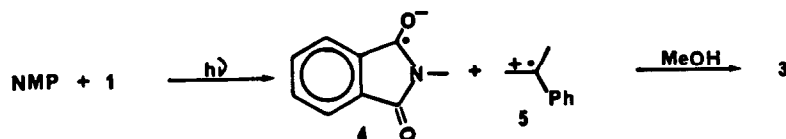
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Photolysis of 1,8-naphthalimide and  $\alpha$ -methylstyrene in methanol results in the formation of a novel tetracyclic product via initial electron transfer.

The photochemistry of N-methylphthalimide in the presence of  $\alpha$ -methylstyrene is characterized by the formation of two products in methanol solution.<sup>1,2,3</sup> The benzazepinedione products such as 2 have been shown to arise

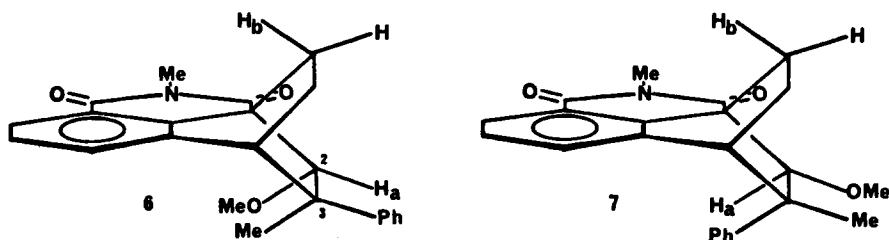


via a concerted 2+2 addition<sup>3,4</sup> whereas 3 results from initial electron transfer to the radical anion-radical cation pair which is subsequently trapped by methanol.<sup>2,5</sup>



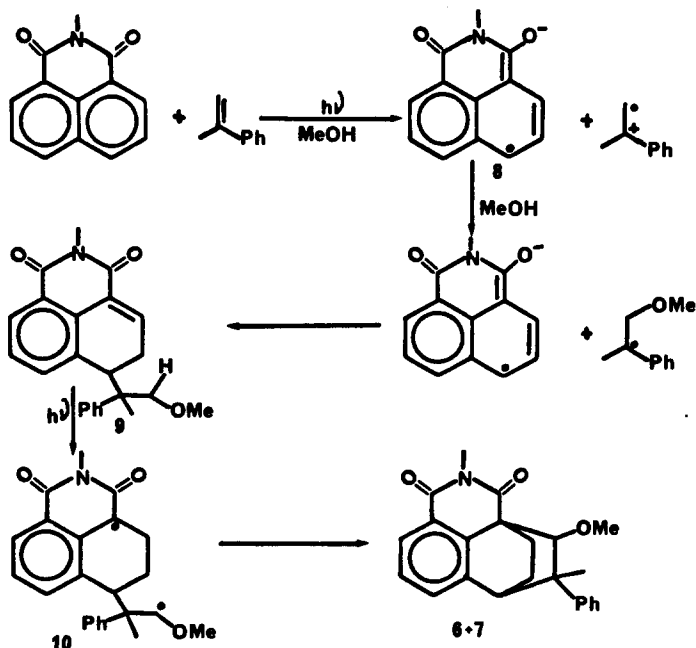
In an attempt to determine the scope of these reactions we investigated the photochemistry of N-methyl-1,8-naphthalimide (NMN) in the presence of 1. Irradiation of NMN and 1 in methanol solution through pyrex afforded a pair of products 6 and 7 each in 20% yield. The NMR spectrum ( $\text{CDCl}_3$ ) of 7 showed: NMR  $\delta$  7.99 (dd, 1,  $J=8\text{Hz}$ ,  $J=2\text{Hz}$ ), 7.32-6.90 (m, 7), 3.60 (d, 1,  $J=2\text{Hz}$ ), 3.41 (s, 3), 3.38 (s, 3), 3.29 (t, 1,  $J=3\text{Hz}$ ), 2.96-2.83 (m, 1), 2.54-2.41 (m, 1), 1.60 (s, 3), 1.57-1.30 (m, 2). The NMR spectrum of 6 was similar showing:  $\delta$  8.11 (dd, 1,  $J=8\text{Hz}$ ,  $J=2\text{Hz}$ ), 7.63-7.26 (m, 7), 4.74 (s, 1), 3.44 (s, 3), 3.40 (t, 1,  $J=3\text{Hz}$ ), 3.33 (s, 3), 2.20-2.07 (m, 1), 1.94-1.80 (m, 1), 1.44-1.10 (m, 2), 0.84 (s, 3).

Clearly, the spectra indicated that 6 and 7 were adducts of NMN + 1 + MeOH. Surprisingly the IR spectra of 6 and 7 showed strong absorptions at 1710 and 1675 and 1720 and 1685  $\text{cm}^{-1}$  respectively demonstrating that the imide moiety was intact. The structure of 6 was unequivocally established by an X-ray diffraction determination <sup>6</sup> study which indicated that 6 had the structure and stereochemistry shown. The stereochemistry of the diastereoisomer 7 was deduced



from NMR. In compound 6,  $H_a$  appears as a singlet at  $\delta$  4.74 whereas  $H_a$  in 7 appears as a doublet due to W coupling with  $H_b$  ( $J_{ab}=2\text{Hz}$ ) establishing that the stereochemistry at C2 in 7 has been inverted from that in 6. This assignment is consistent with the chemical shifts of the protons involved i.e.  $H_a$  in 6 appears as a singlet at  $\delta$  4.74 whereas in 7  $H_a$  is strongly shifted upfield to  $\delta$  3.60 due to the anisotropy of the aromatic ring. The C3 methyl group in 7 at  $\delta$  1.60 is shifted far downfield from the corresponding methyl group in 6 ( $\delta$  0.84)

Scheme 1

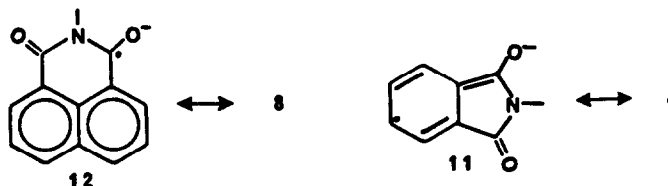


showing that stereochemistry is again inverted at C3 (i.e. the C3 methyl and H<sub>a</sub> are trans in both compounds).

We suggest the mechanism outlined in Scheme 1 to rationalize the formation of 6 and 7. Initial electron transfer and addition of methanol to radical cation 5 affords a radical pair which couples to intermediate 9. It is in the coupling step that the stereochemistry at C-3 is determined resulting in the formation of both diastereoisomers.

We suggest that 9 undergoes the well known  $\beta$ -hydrogen abstraction reaction of  $\alpha,\beta$ -unsaturated ketones<sup>7</sup> affording biradical 10 which can collapse to 6 and 7. The methoxy-phenyl vs methoxy-methyl interactions in 10 establish the relative stereochemistries at C2 and C3 in 6 and 7.

The differences in the regiochemistry of NMP and NMN reactions is particularly interesting in that the NMP radical anion reacts exclusively at the carbonyl group whereas the NMN radical anion reacts exclusively on the aromatic ring<sup>8</sup>: Presumably this regioselectivity reflects the locus of the radical anion in both systems. One rationale that explains this difference is that delocalization of the NMP radical anion into the ring (11) destroys aromaticity whereas that is not the case with 8. Photochemical investigations on the



isomeric naphthalimides and EPR studies now in progress on NMP and NMN should clarify the relationship.

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