ELECTRON TRANSFER PHOTOCHEMISTRY OF 1,8-NAPHTHALIMIDE AND PHENYLCYCLOPROPANE

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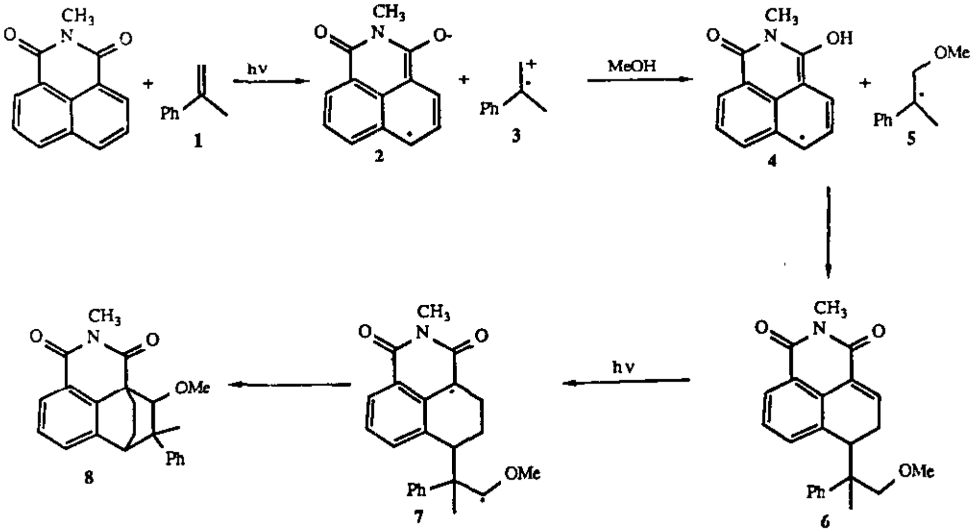
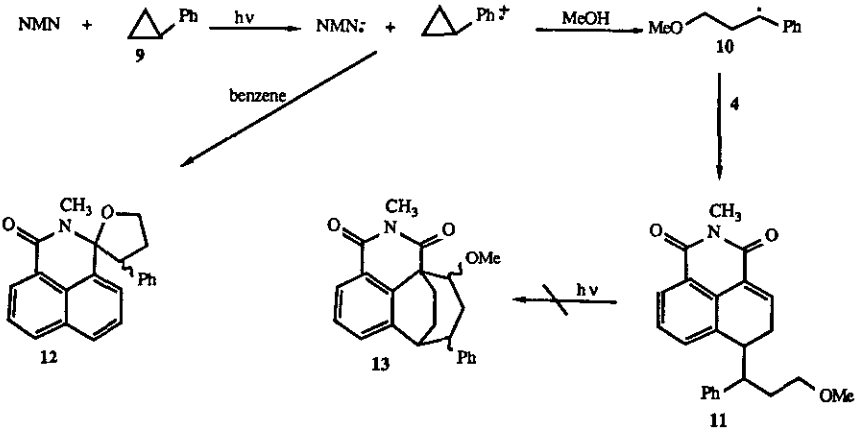
Abstract - Photolysis of N-methyl-1, 8-naphthalimide (NMN) with phenylcyclopropane in methanol gave the novel photoproduct **11**. Photoproduct **11** presents strong evidence for the formation of the ntermediate **6** proposed in the photochemistry of the NMN/2-phenylpropene system.

We previously reported that irradiation of N-methyl-1,8-naphthalimide (NMN) in the presence of 2-phenylpropene (**1**) in methanol afforded the polycyclic product **8**[1,2]. We demonstrated that the reaction proceeded by electron transfer to the radical ion pair which reacted with methanol to give the radical pair **4** + **5** which coupled to give the key intermediate **6** . *Presumably irradiation of **6**, which contains an α,β-unsaturated carbonyl system*, reacts by the well precedented H abstraction at the β carbon[3] to give the biradical **7** which closed to **8**. However attempts to isolate or obtain physical evidence for **6** were fruitless.[2] Our research on the photochemistry of aromatic imides in the presence of phenylcyclopropane[4] (**9**) suggested that **9** might be a useful substrate to generate an analog of **6**. Thus, it is well known that the radical cation of **9** undergoes nucleophilic attack by methanol to give the radical **10**[5]. Coupling of **10** with **4** would afford **11** the desmethyl homolog of **6**.

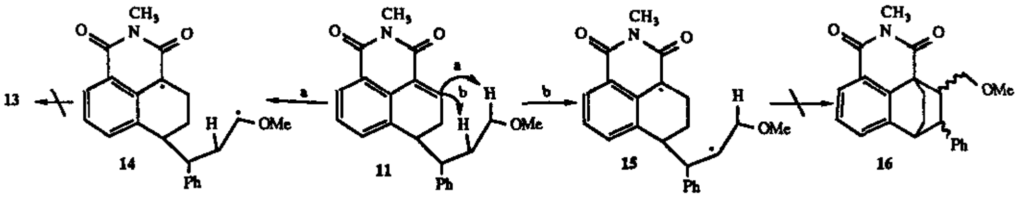


Irradiation of NMN and **9** in benzene gave a product which was assigned structure **12** (9%) on the basis of spectroscopic data[6] and comparison with data from known analogs formed from **9** and N-methylphthalimide or N-methyl-2,3-

naphthalimide[4]. When the reaction was carried out in methanol **12** was not formed, but a new pair of isomers were isolated (33%, 19%) which were assigned structure **11** on the basis of spectroscopic data[8,9]. Although the isolation of **11** provides strong evidence for the intermediacy of **6** in the formation of **8**, we were surprised by the observation that **11** failed to undergo photocylization to **13**. Although the reasons for this lack of reactivity of **11** are not obvious there are several points[4] that should be considered.



There are two routes the reaction can take. Abstraction of hydrogen by the β carbon *via* path a can take place by a disfavored seven membered transition state to give a radical stabilized by oxygen (**14**) which would close, again through a seven membered intermediate to give **13**. Alternatively, abstraction of hydrogen by the β carbon *via* path b can take place through a favored six membered transition state to give the less stabilized secondary radical (**15**) which could again close through a favored six membered transition state to **16**. Although the six membered transition state should favor the reaction, models indicate that in the transition state for biradical closure the additional steric bulk of the methoxy methylene group (over the methoxy group in the corresponding transition state for closure to **8**) disfavors this closure. For biradical closure through the seven membered transition state, models indicate that there are severe steric interactions between the methylene groups in the incipient bicyclo[3.2.2]nonane system which will prevent biradical closure, possibly allowing efficient reverse hydrogen atom transfer to regenerate **11**. Obviously these factors result in the lack of photoreactivity which allows us to be able to isolate **11**.



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6. **12**: Colorless needles. mp 210 - 212 °C. ^{1}H-nmr (200 MHz, $CDCl_3$) δ 2.40 (1H, m),2.75 (1H,m), 3.21 (3H,s), 3.45 (1H,t,J=8.2 Hz), 4.58(1H,m) 4.78 (1H, m), 6.50 - 8.00 (11H, m); ν max ($CHCl_3$) cm^{-1} 1660; ms (m/z) 329 (M+). High Resolution ms: Calculated for $C_{22}H_{19}NO_2$: 329.1416, Found: 329.1423.p

7. Prolonged irradiation in acetonitrile resulted in the slow decomposition of NMN to a variety of minor uncharacterized products. No **12** was formed. Presumably the delocalized radical anion of NMN is not sufficiently nucleophilic to open the radical cation of **9**.

8. **11a**: Colorless oil. ^{1}H-nmr (200 MHz, $CDCl_3$) δ 1.72 (2H, m), 2.46 (2H, m), 2.81 (2H, m), 2.98 (1H, m), 3.05 (1H, m), 3.05 (3H, s), 3.42 (3H, s), 7.10 - 8.10 (8H, m), 7.71 (1H, m); ν max ($CHCl_3$) cm^{-1} 1710, 1675; ms (m/z) 361 (M+). High Resolution ms: Calculated for $C_{23}H_{23}NO_3$: 361.1678, Found: 361.1668.

   11b: Colorless oil. ^{1}H-nmr (200 MHz, $CDCl_3$) δ 1.90 (2H,m), 3.10 (6H, m), 3.15 (3H, s), 3.38 (3H, s), 6.8 - 7.5 (9H, m); ν max ($CHCl_3$) cm^{-1} 1710, 1675; ms (m/z) 361 (M+). High Resolution ms: Calculated for $C_{23}H_{23}NO_3$: 361.1678, Found 361.1670.

9. Products **11a** and **11b** are also obtained from mixtures of methanol-acetonitrile with somewhat decreased efficiency. It has been established[4,5] that the radical cation of **9** reacts efficiently with methanol.

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