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NOVEL PHOTOISOMERIZATION OF 5-CHLORO-1,4-DIHYDRO-9-METHYL-NAPHTHALEN-1,4-IMINE

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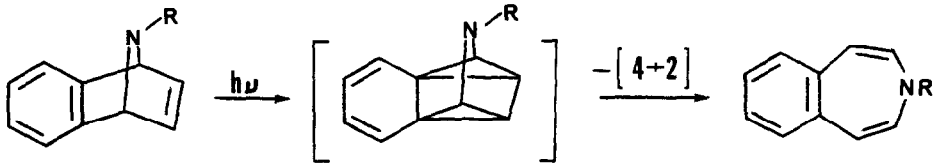
Summary: Direct photolysis of 5-chloro-1,4-dihydro-9-methyl-naphthalen-1,4-imine in cyclohexane gave a mixture of 1-chloronaphthalene and isomeric dihydrocyclobut[b]indoles 5 and 6. Dihydrocyclobut[b]indoles 5 and 6 thermally rearranged to give 1-benzazepines 7 and 8, respectively.

It is known that direct photolysis of 1,4-dihydronaphthalen-1,4-imines 1 results in their isomerization to 3-benzazepines 2 in low quantum efficiency.[1,2,3] The reaction mechanism which has been postulated is that the 3-benzazepines 2 form via a reverse [4+2] ring opening of an azaquadricyclane intermediate.[3] The reported examples of this reaction (1 → 2) involve those where the nitrogen contains an electron-withdrawing substituent (1a - c). In this paper, an example of the photolysis of a 1,4-dihydronaphthalen-1,4-imine containing an electron-donating substituent on the nitrogen is reported.

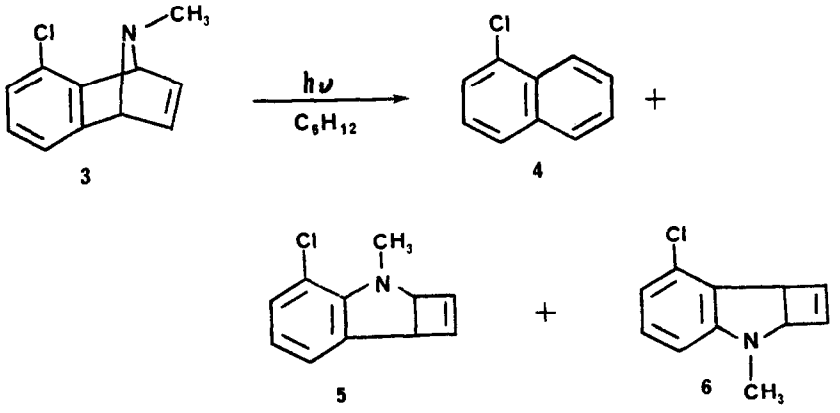


1a; R = CO_2t-Bu
b; R = CO_2CH_3
c; R = Tos

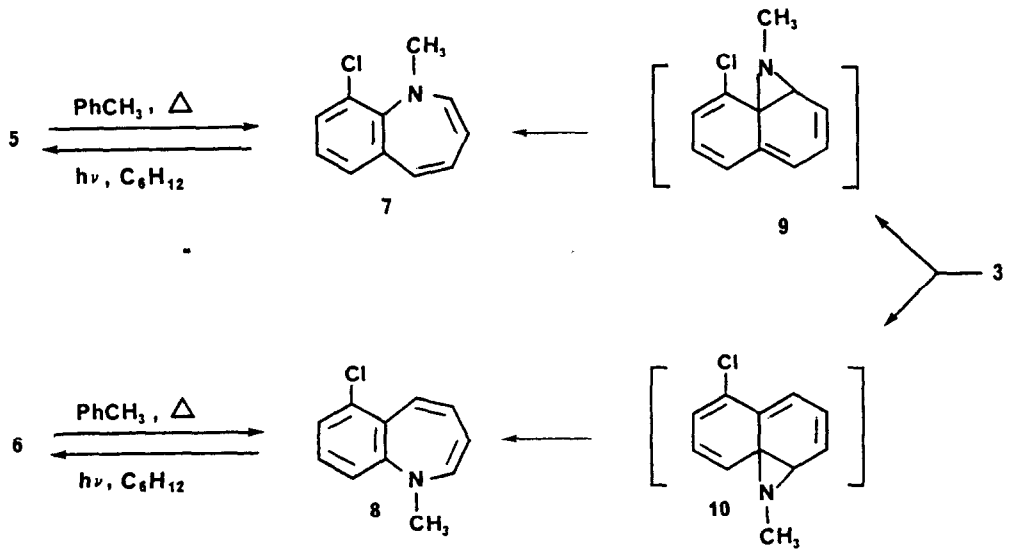
2

In an attempt to synthesize 3-benzazepines photochemically, 5-chloro-1,4-dihydro-9-methyl-naphthalen-1,4-imine (3) was prepared and photolyzed. Treatment of m-dichlorobenzene in dry THF at -40°C with 1.05 equiv of nBuLi over 40 min[4] followed by the addition of 1.1 equiv of N-methylpyrrole and subsequent stirring at rt for 3.5 h gave 3 in 38% yield after chromatography.[5] A solution of 1,4-dihydronaphthalen-1,4-imine 3 (1.02 g, 5.3 mmol) in cyclohexane (120 mL) was irradiated under argon for 27 h in a quartz vessel using a high pressure Hanovia 450 W Hg lamp. Flash chromatography led to the isolation of 1-chloronaphthalene 4[6] in 22% yield, dihydrocyclobut[b]indoles[7] 5 and 6 in 10% and 12% yields, respectively, as well as 11% recovered starting material 3. The structures of the dihydrocyclobut[b]indoles 5 and 6 were assigned based on ^1H and ^{13}C NMR. These assignments are

supported by the similarity of their ^{1}H NMR spectra with those reported for analogous heterocyclic systems.[8] No 3-benzazepine was detected by ^{1}H NMR in the reaction mixture.



Both dihydrocyclobut[b] indoles 5 and 6 rearranged when heated in refluxing toluene to the corresponding 1-benzazepines[9] 7 and 8 in 90-95% yields. This thermal behavior is consistent with that known for related systems.[10] Also, 1-benzazepines 7 and 8 were quantitatively converted back to their corresponding dihydrocyclobut[b]indoles 5 and 6 by photolysis in cyclohexane in a quartz vessel using a 450 W Hg lamp for 3 h.[11]



The formation of dihydrocyclobut[b]indoles 5 and 6 from the photolysis of 1,4-dihydronaphthalen-1,4-imine 3 may be rationalized as proceeding through intermediate naphthazirines[12] 9 and 10. This may occur either through a radical-type mechanism or a photochemically "allowed" [1,3] sigmatropic rearrangement. Ring opening and aromatization would then lead to 1-benzazepines 7 and 8 as intermediates. As was discussed, 1-benzazepines 7 and 8 do photoisomerize to their corresponding dihydrocyclobut[b]indoles 5 and 6 under the reaction conditions. The formation of 1-chloronaphthalene (4) may be rationalized as occurring through the photodeamination[13] of the naphthazirine intermediates 9 and 10.

This is the first reported example of a photochemical transformation of a 1,4-dihydronaphthalen-1,4-imine to dihydrocyclobut[b]indoles and a naphthalene. The products observed here are different than those observed by Swenton and coworkers[1,2] in their systems presumably due to the electron donating methyl group on the nitrogen. However, the mechanism of this photoreaction is uncertain.

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References

1. P.D. Rosso, J. Oberdier and J.S. Swenton, Tetrahedron Lett., 42, 3947 (1971).
2. J.S. Swenton, J. Oberdier and P.D. Rosso, J. Org. Chem., 39, 1038 (1974).
3. G. Kaupp, J. Perreten, R. Leute and H. Prinzbach, Chem. Ber., 103, 2288 (1970).
4. S. Seki, T. Morinaga, H. Kikuchi, T. Mitsuhashi, G. Yamamoto and M. Oki, Bull. Chem. Soc. Jpn., 54, 1465 (1981).
5. Compound 3: colorless solid; mp 71-3°C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.45-6.72 (m, 5H), 4.75 (bs, 1H), 4.55 (bs, 1H), 2.20 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) 144.03, 143.05, 138.90, 137.97, 126.49, 125.36, 121.54, 118.17, 72.64, 70.88, 36.69.
6. Compound 4 was identical by ^{1}H NMR, IR and GC/mass spectrum to an authentic sample of 1-chloronaphthalene.
7. Compound 5: yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.05 (d, 1H, J=7.9 Hz), 6.98 (d, 1H, J=7.4 Hz), 6.64 (t, 1H, J=7.8 Hz), 6.40-6.35 (m, 1H), 6.14-6.09 (m, 1H), 4.42 (dd, 1H, J_1=3.7 Hz, J_2=1.5 Hz), 4.37-4.32 (m, 1H), 3.13 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ 149.45 (s), 143.38 (d), 136.87 (d), 135.19 (s), 129.64 (d), 122.72 (d), 119.89 (d), 117.86 (s), 70.73 (d), 51.16 (d), 38.31 (q).
Compound 6: yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.98 (t, 1H, J=8.1 Hz), 6.52 (d, 1H, J=8.1 Hz), 6.49-6.46 (m, 1H), 6.21 (d, 1H, J=8.1 Hz), 6.05-6.01 (m, 1H), 4.61 (dd, 1H, J_1=3.8 Hz, J_2=1.4 Hz), 4.33-4.30 (m, 1H), 2.87 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ 153.62 (s), 142.28 (d), 135.32 (d), 127.49 (s), 125.11 (s), 129.63 (d), 116.33 (d), 105.46 (d), 67.90 (d), 50.03 (d), 32.41 (q).
8. H. Igeta, H. Arai, H. Hasegawa and T. Tsuchiya, Chem. Pharm. Bull., 23, 2791 (1975).
9. Compound 7: yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.23 (d, 1H, J=7.9 Hz), 6.89 (t, 1H, J=7.9 Hz), 6.72 (d, 1H, J=7.5 Hz), 6.42 (d, 1H, J=11.3 Hz), 5.97 (dd, 1H,

J_1=11.3 Hz, J_2=5.8 Hz), 5.84 (d, 1H, J=7.1 Hz), 5.27 (t, 1H, J=6.4 Hz), 3.12 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ 145.09, 144.94, 140.93, 131.75, 131.15, 130.82, 127.05, 125.41, 115.04, 41.17.

Compound 8: yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.08 (t, 1H, J=8.1 Hz), 6.96 (d, 1H, J=8.1 Hz), 6.85 (d, 1H, J=11.1 Hz), 6.59 (d, 1H, J=8.1 Hz), 6.16 (dd, 1H, J_1=11.1 Hz, J_2=5.1 Hz), 5.55 (d, 1H, J=7.7 Hz), 5.25 (dd, 1H, J_1 = 7.7 Hz, J_2=5.1 Hz), 2.89 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ 156.04, 144.01, 131.67, 130.88, 129.59, 127.49, 124.33, 115.44, 114.24, 39.99.

10. M. Ikeda, K. Ohno, T. Uno and Y. Tamura, Tetrahedron Lett., 21, 3403 (1980).
11. For the photolysis of the related N-carbomethyoxy azepines to 2-carbomethoxy-2-azabicyclo [3.2.0]-hepta-3,6-dienes see: L.A. Paquette and D.E. Kuhla, J. Org. Chem., 34, 2885 (1969).
12. This type of an intermediate has been postulated in the thermolysis of 1H-1-benzazepines to 1-naphthylamines: M. Ikeda, K. Ohno, M. Takahashi, T. Uno, Y. Tamura and M. Kido, J.C.S. Perkin I, 741 (1982).
13. For an example of photodeamination of aziridines see: A. Padwa and L. Hamilton, J. Amer. Chem. Soc., 89, 102 (1967).

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