Tetrahedron Letters No.3, pp. 255-258, 1971. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF SOME 1,2-DIHYDRONAPHTHALENES

H. Kleinhuis, R.L.C. Wijting and E. Havinga

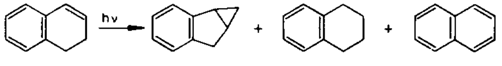
Laboratory of Organic Chemistry, The University, P.O. Box 75, Leiden, The Netherlands

(Received in UK 23 November 1970; accepted for publication 17 December 1970)

On account of recent interest in the photochemical reactivity of 1,2-dihydronaphthalenes[1,2] we wish to report the results of our experiments.

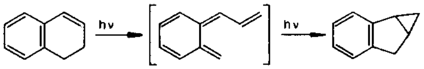
A. 1,2-Dihydronaphthalene and 1-methyl-1,2-dihydronaphthalene

Irradiation of a solution of 1,2-dihydronaphthalene (1) in ether (c = 0,2%) in a quartz vessel[3] with a 250 W high-pressure mercury lamp for 6 hr resulted in the formation of benzobicyclo[3.1.0]-hex-2-ene (2, 31%), tetralin (3, 31%), naphthalene (4, 25%) and four other products (together 2%). Recovered (1) represented 11% of the reaction mixture under these conditions. Compounds (2), (3) and (4) were isolated in a pure form by preparative glpc. The spectroscopic properties of (2) were identical with those given by Pomerantz[4] and Meinwald and Mazzocchi[5].



(1) (2) (3) (4)

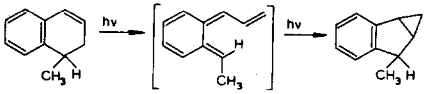
For the formation of benzobicyclo[3.1.0]-hex-2-ene Cookson, Costa and Hudec[1] proposed the following reaction scheme:



(1) (A) (2)

The occurrence of the non-aromatic intermediate (A) was consistent with their deuterium labelling experiments.

The second compound we investigated was 1-methyl-1,2-dihydronaphthalene (5). Upon irradiation of a dilute ethereal solution of (5) (for 6 hr), glpc analysis showed the presence of a new component (63%), which could be obtained pure by preparative glpc. It was assigned the structure (6) on the basis of Mass-, IR-, UV- and NMR-spectra.



(5) (6)

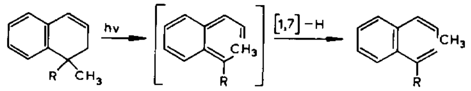
B. 1,1-Disubstituted-1,2-dihydronaphthalenes[6]

When 1-methyl-1-phenyl-1,2-dihydronaphthalene (7a) was irradiated in ether with a low-pressure mercury lamp (Hanau NK 6/20) the absorption of the starting material (at 262 nm) decreased and a new absorption band with a maximum at 252 nm appeared. From the photolysis mixture we could isolate a new compound by repeated column chromatography over Al_2O_3 (Woelm neutral, Act 1, eluent cyclohexane). This novel compound was assigned structure (8a) on the basis of its spectra: NMR (CCl_4) a 3 proton doublet of doublets at 1.63 ppm (J = 1.8 and J = 6.8 cps), a 2 proton AB system at 5.11 and 5.63 ppm (J = 1.5 cps), a 2 proton AB system - with coupled spins with the 1.63 protons - at 5.42 and 6.13 ppm (J_{AB} = 11.2 cps) and a multiplet at ∿ 7 ppm (9H); UV (isooctane) λ max 252 nm (ε = 20.000); IR revealed an ortho disubstituted benzene, a monosubstituted benzene and no trans band; MS m/e 143, 205, 220 (parent peak).

Irradiation of 1,1-dimethyl-1,2-dihydronaphthalene (7b) under the same conditions also resulted in the formation of a new compound. The physical characteristics of this photoproduct are consistent with the structure (8b).

The following reaction path is proposed (Fig. I). The parent compound - in its lowest excited singlet state - isomerises by ring opening to compound (B). This unstable intermediate undergoes a |1,7|-sigmatropic hydrogen shift to the isolated product.

Fig. I.



(7) (B) (8)

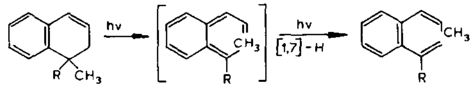
a: R = C_6H_5

b: R = CH_3

In order to elucidate the reaction mechanism we carried out a series of experiments in a low-temperature cell[7]. For measurement of spectra in the UV and visible region this cell could be placed in the sample compartment of a Cary 14 spectrophotometer. After reaching the desired temperature of -165° C a solution of 1-methyl-1-phenyl-1,2-dihydronaphthalene (7a) in MIP (methylcyclohexane-isopentane 1:3) was exposed to the light of a Philips HP 125 W mercury lamp. Following the reaction via absorption spectroscopy revealed that gradually a new absorption at 410 nm appeared and that the original absorption at 262 nm shifted to shorter wavelength (254 nm). In the course of the irradiation the 410 nm absorption reached a maximum, which could be kept unchanged in the dark for many hours at -165° C. Upon continued irradiation this maximum decreased and finally disappeared, whilst at the same time the maximum at 252 nm (due to the formation of the product (8a)) increased. The spectrum calculated for the proposed intermediate (B) in a computer-simulating process appeared to be in fair agreement with the observed one.

From the experiments described above it follows that the formation of (8) from (7) can be achieved at very low temperatures (-165° C) +). It seems unlikely that a thermal reaction should take place under these conditions and we therefore conclude that the whole process probably is photochemical. This implies that also the |1,7|-sigmatropic hydrogen shift should be a photochemical process (Fig. II).

Fig. II.



(7) (B) (8)

Full details will shortly be reported[8].

ACKNOWLEDGEMENT

The authors wish to thank Dr. J. Lugtenburg for expert help and advice in the interpretation of the NMR spectra.

REFERENCES

1. R.C. Cookson, S.M. de B.Costa and J. Hudec, Chem. Commun. 1272 (1969).
2. L. Ulrich, H.-J. Hansen and H. Schmid, Helv. Chim. Acta 53, 1323 (1970).
3. E. Havinga and J.P.L. Bots, Rec. Trav. Chim. 73, 393 (1954).

+) Irradiation under the same conditions of 1,1-dimethyl- and 1,1-diethyl-1,2-dihydronaphthalene showed the occurrence of the corresponding products. However, with these compounds the occurrence of a (B) type intermediate could not be traced.

4. M. Pomerantz, J. Am. Chem. Soc. **89**, 694 (1967).

5. J. Meinwald and P.H. Mazzocchi, ibid. **89**, 696 (1967).

6. For preparation of these compounds see: M.T. Bogert, D. Davidson and M. Apfelbaum, J. Am. Chem. Soc. **56**, 959 (1934); H. Adkins and J.W. Davis, J. Am. Chem. Soc. **71** 2955 (1949); E.A. Braude, L.M. Jackman, R.P. Linstead and G. Lowe, J. Chem. Soc. 3133 (1960).

7. G. Horsman and C.A. Emeis, Tetrahedron **22**, 167 (1966).

8. H. Kleinhuis, Thesis Leiden, to be published 1971.