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PHOTOCYCLIZATION OF NAPHTHYL PHENYL ETHERS

Wm. A. Henderson, Jr. and Arnold Zweig
Central Research Division
American Cyanamid Company
Stamford, Connecticut, U.S.A.

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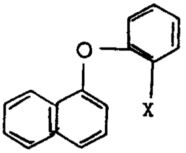
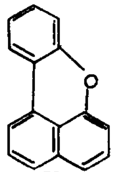
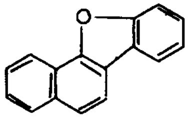
In an effort to extend our understanding of the mechanism of photocyclization reactions (1) we have investigated the photolysis of phenyl 1-naphthyl ether (Ia) and *o*-chlorophenyl 1-naphthyl ether (Ib). These compounds are of considerable interest since they have available two alternative modes of photocyclization; closure on the 8-position of naphthalene giving a compound with a new, non-aromatic six-membered ring, benzo(k,l)xanthene (II), or closure on the 2-position of naphthalene giving a compound with a new, aromatic five-membered ring, benzo(b)naphtho(2,1-d)furan (III). Although photocyclodehydrogenations and photocyclodehydrohalogenations to give both five- and six-membered rings have been reported, closures to six-membered rings being more numerous, no previous study has afforded such a choice of ring closure paths.



Ia, X=H
Ib, X=Cl



II



III

Compounds Ia (2), II (3) and III (4) have been described in the literature, but compound Ib has not previously been reported. It was synthesized, b.p. 135-140°/0.1 mm, in 18% yield by heating a mixture of 1-bromonaphthalene, *o*-chlorophenol, potassium hydroxide and copper powder to 210° for two hours(5). The ultraviolet absorbtion spectrum of Ib(6) was very similar to that of Ia(6) as were its fluorescence and phosphorescence emission spectra(7). However, the photochemical behavior of the twp compounds was markedly different.

When a benzene solution of Ia was irradiated for 24 hours with 254 mμ light, there was no evidence of photoreaction, even in the presence of added iodine and oxygen. Conversely, on irradiation for a few minutes with 254 mμ light in benzene, Ib afforded a yellow solution with intense blue fluorescence. After 18 hours of irradiation, evaporation of the solvent and chromatography of the residue gave only recovered starting material plus a 45% isolated yield (79% spectroscopic yield) of III, m.p. 102-103°, reported(4) 103°. The ultraviolet spectrum was identical to that of III reported in the literature(8). No spectral evidence for the presence of II, which absorbs at longer wavelengths than III, could be found.

The quantum yield for photocyclization of Ib in benzene, determined spectroscopically, was $3.2\text{x}10^{-3}$. This is almost an order of magnitude higher than the quantum yield of photocyclization of 1-(o-chlorophenyl)naphthalene under the same conditions(1). Other chloroaromatics which can only undergo intermolecular reaction with the solvent benzene are far less reactive (1,9). The high reactivity of Ib and the direction of ring closure must thus result from the intramolecular nature of the reaction and the aromatic stablization of the product.

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3. R. A. Friedel, Appl. Spec., 11, 13 (1957).
4. J. N. Chatterjea, J. Indian Chem. Soc., 34, 347 (1957)
5. Elemental and mass spectrographic analyses for this compound were satisfactory.
6. For Ib, λmax(ε) in methanol; 320 (1390), 312 sh (1980), 306 sh (3210), 292 sh (6330), 287 (6530), 281 (7050), 278 sh (6640). For Ia, λmax(ε) in methanol; 321 (1130), 312 sh (1,670), 307 sh (2,740), 289 (6,400), 283 (6,780), 277 (6,800).
7. The fluorescence and phosphorescence of $5\text{x}10^{-4}$M solutions of Ia and Ib at 77°K were obtained by excitation at 313 mu. Ia showed fluorescence λmax at 311(0-0), 324, 330, 338, 344 and 354 mu while Ia had λmax at 312(0-0), 324, 329, 335, 343, 352, and 366 mu. Both compounds showed phosphorescence shoulders at 480 mu; Ia had peaks at 487, 522, 537 (sh) and 563 mu while Ib had peaks at 487, 526, 537 (sh) and 556 mu. The phosphorescence lifetime was 1.5 sec for Ia and 1.6 sec for Ib under the conditions employed. We thank J. B. Gallivan for assistance with these measurements.
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