Srinivasan Photoreactor with ultraviolet lamps (λ_{max} 2537 A). The solvent was removed from the resulting solution to give a yellow solid, 48 mg (96% recovery), mp 284–288° dec, whose infrared spectrum was identical with that of the starting material.

Registry No.—**3,** 15156-53-3; **4,** 15156-58-8; **6,** 15084-03-4; **7,** 15080-10-1; **8,** 15134-48-2; **10,** 15084-00-1; **12,** 15180-31-1; **13,** 15080-11-2; **15,** 15080-12-3; **16,** 15156-59-9; di-9-anthrylcarbinol, 15080-13-4; di-9-anthrylmethane, 15080-14-5; 10-bromo-9,9-dianthrylmethane, 15156-60-2; 10-bromo-9-hydroxymethylanthracene, 2606-53-3; 10-bromo-9-chloromethylanthracene, 15080-16-7; 10-chloro-9-anthroic acetic anhydride, 15156-61-3; 10-chloro-9-anthroic anhydride, 15084-01-2; 10,10′-bianthronyl, 434-84-4; 9-anthryldiazonium fluoborate, 15084-02-3.

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Photochemistry of Alkyl-β-naphthyl Ethers. Steric Inhibition in the Dimerization Reaction[1]

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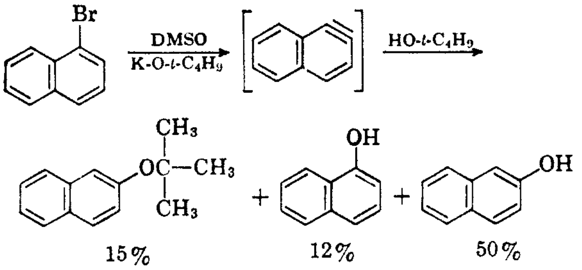
A series of alkyl-β-naphthyl ethers have been prepared and irradiated with ultraviolet light. Straight-chain ethers dimerized while the branched ethers did not. This coupled with the fact that no excimer fluorescence was observed for the branched alkyl ethers suggests that the photodimers have head-to-head structure I. It is proposed that an excited dimer (excimer III) is involved in photodimer formation.

We have previously reported that methyl-β-naphthyl ether undergoes photodimerization when irradiated by ultraviolet light.[2] The α-ether and other substituted naphthalene compounds did not dimerize.[2] The gross structure of the photodimer was believed to be similiar to that for the photodimer of anthracene.[3] The stereochemistry, however, could not be determined due to its instability to heat and its insolubility.[2] In an attempt to learn more about the structure of the photodimer, we have prepared and irradiated a series of alkyl-β-naphthyl ethers where the alkyl group varies from allyl to *t*-butyl. The straight chain alkyl ethers readily dimerized while branched chain materials failed to dimerize even after prolonged irradiation.

The starting ethers with exception to the *t*-butyl ether, were prepared by reacting the alkyl halide with β-naphthol in the presence of base.[4] The *t*-butyl ether could not be prepared by this method. The Sahyun–Cram procedure to prepare phenyl *t*-butyl ether was used for this synthesis.[5] This procedure involves an aryne generated from an aryl bromide in a solution of potassium *t*-butoxide in dimethyl sulfoxide (DMSO).[6] The more abundant α-bromonaphthalene was used in this reaction. A yield of only 15% *t*-butyl-β-naphthyl ether was isolated. No α-ether could be detected although it must be present. The major product (63%) of this reaction was a mixture of α- and β-naphthol at a ratio of about 18% α to 82% β[7] (see eq 1). This apparent ratio of α to β products



(1)

(1:4) from a 1-naphthalyne reaction is considerably different than that (1:2) found when 1-naphthalyne was prepared by a different procedure.[8] The details of this reaction and its use to prepare other naphthyl ethers and naphthols will be reported in a future communication.

Both allyl- and *n*-butyl-β-naphthyl ethers dimerized readily when irradiated with ultraviolet light through pyrex, while the isopropyl- and *t*-butyl ethers did not. No dimerization took place in the presence of benzophenone. The dimers were very similar to the methyl-β-naphthyl ether dimer.[2] The infrared spectra of all three compounds (methyl-, allyl-, and *n*-butyl ether dimers) contained similar major bands in the following spectral regions: 2900–3100, 1625–1635, 1420–1470, 1330–1340, 1270, 1170–1200, 1140–1150, 775–780, 750–755, and 720 cm^{-1}. The major differences in the spectra can be attributed to the different alkyl (alkenyl) groups. The ultraviolet spectra were also very similar with bands at 2835, 2740, and 2315 A at about the same intensity as those reported for the methyl-β-naphthyl ether dimer.[2] Small monomer bands were observed at 3100–3300 A for both dimers. These bands greatly increased in intensity when the solution was allowed to stand for a few hours. The typical three naphthalene bands at 2600–2850 A also appeared. Both dimers also reverted to the starting ethers when heated above the melting point.

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[1] Supported by the Research Division, Brigham Young University, Provo, Utah.

[2] J. S. Bradshaw and G. S. Hammong, *J. Am. Chem. Soc.*, **85**, 3953 (1963).

[3] F. D. Greene, S. L. Misrock, and J. R. Wolfe, *ibid.*, **77**, 3852 (1955).

[4] D. S. Tarbell, *Org. Reactions*, **2**, 1 (1944).

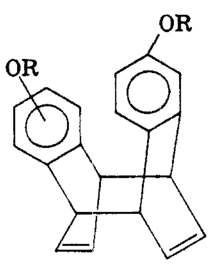
[5] M. R. V. Sahyun and D. J. Cram, *Org. Syn.*, **45**, 89 (1965).

[6] See also D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

[7] These products were probably prepared on the work-up. A considerable amount of phenol (29%) was isolated during the preparation of phenyl-*t*-butyl ether.[5]

[8] See J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **23**, 904 (1958).

These similarities in the ultraviolet and infrared spectra show that the structures of the methyl-, allyl-, and *n*-butyl ether dimers are similar. The ultraviolet spectra are similar to *o*-xylene except for a distinct bathochromic shift. Similar bathochromic shifts are observed for *o*-xylene when a methoxy group is substituted on the ring. This evidence indicates that the dimer is formed by a 1,4–1,4 dimerization of the unsubstituted ring.[2] Inhibition of dimer formation by the bulky isopropyl and *t*-butyl groups suggests that the dimers have a head-to-head structure (I). Steric inhibition would not be expected in the formation of a head-to-tail dimer (II). The disposition of the alkoxy groups may be symmetrical or unsymmetrical with respect to each other.



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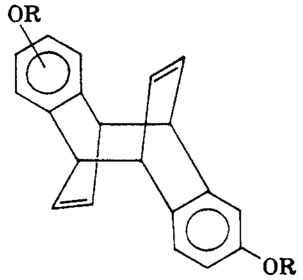
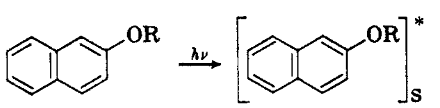


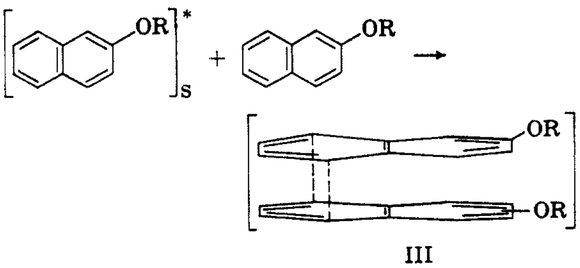
II

Owing to a complete insolubility in almost all solvents, attempts to establish the structure of the photodimers more rigorously were not successful. Solubility in methylene chloride was effected to the extent ($10^{-3}M$) that ultraviolet absorption spectra could be obtained. Even in this case, however, the dimers rather quickly reverted to the monomers. Attempts to oxidize the double bond with alkaline permanganate or ozone or to hydrogenate the double bond over platinium resulted in the recovery of the starting naphthyl ether.[2]

The mechanism of this reaction most probably involves an excited singlet state as does the photodimerization of anthracene.[2,9] Indeed, the presence of benzophenone in the solution completely quenches the fluorescence of the naphthyl ether *and* stopped the formation of the photodimer.[2] In this case, the benzophenone effectively quenched the excited singlet state of the ether. It is likely that an excited ether molecule associates with a ground-state molecule to form an excited dimer III (excimer) (eq 3). This excimer then either dissociates to two ground-state ether molecules and emits radiation (excimer fluorescence) (eq 4), or new bonds are formed to create the photodimer (eq 5). Excimer fluorescence[10] has been observed in the case of methyl-β-naphthyl ether,[11] however, we failed to observe any excimer emission for the *t*-butyl ether at concentrations up to $2.5 \times 10^{-2}M$. This suggests (but does not prove) that bulky molecules inhibit the formation of naphthyl ether excimers (III) and that it is this excimer that leads to dimer formation. There is evidence in anthracene chemistry which supports this mechanism. 9-Methylanthracene photodimerizes readily and shows excimer fluorescence, while 9, 10-dimethylanthracene, which has a great deal more steric hindrance, does neither.[10,12]

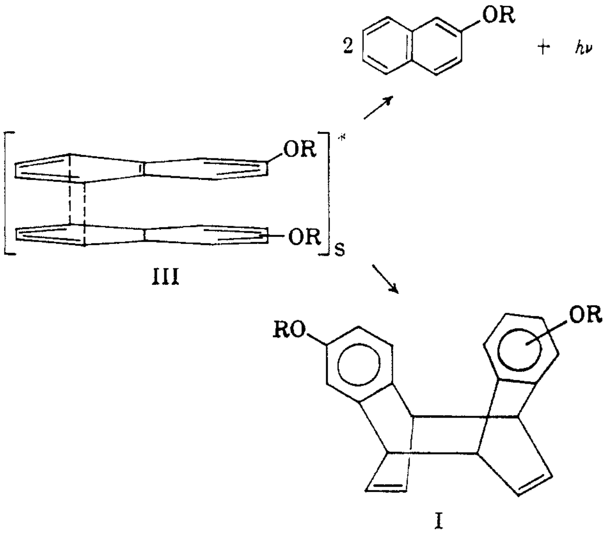


(2)



III

(3)



(4)

(5)

The fact that the allyl ether dimerized rather than rearranged is pertinent.[13,14] This result lends more support to the theory that an excimer is involved in dimer formation. If an excited dimer was not involved, some rearranged product would be expected.

Experimental Section

Materials.—β-Naphthol and the alkyl halides were purchased from Eastman Kodak or Aldrich Chemical Co. and used without purification. The solvents were all reagent grade quality. Potassium *t*-butoxide was used as purchased from Alfa Inorganics Inc. All melting points were uncorrected. Infrared spectra were taken on a Beckman IR-7 or IR-8 spectrophotometer. A Cary Model 15 recording spectrophotometer was used to obtain the ultraviolet absorption spectra. The fluorescence spectra were obtained on a Farrand spectrofluorometer.

Preparation of the Alkyl-β-naphthyl Ethers.—The procedure for the preparation of allyl phenyl ether[4] was followed in the preparation of all alkyl-β-naphthyl ethers except the *t*-butyl ether.

Allyl-β-naphthyl Ether.[15]—A mixture of 12.0 g (0.10 mole) of allyl bromide, 14.5 g (0.10 mole) of β-naphthol, 14 g of finely ground calcinated potassium carbonate, and about 40 ml of dry acetone was stirred under reflux for 8 hr. Water (50 ml) was then added and the aqueous phase was extracted three times with 50-ml portions of ether. The combined ether extracts were washed with 10% aqueous sodium hydroxide and dried over

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(9) E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955).

(10) See J. B. Birks and L. G. Christophorou, *Nature*, **197**, 1064 (1963) for a review of excimer fluorescence.

(11) G. S. Hammond and C. Dalton, private communication,.

(12) A. S. Cherkosov and T. M. Vember, *Opt. Spectr. U.S.S.R.* (English Transl.), **6**, 319 (1959).

(13) The photo Claisen rearrangement has been reported for the corresponding benzene compounds.[14]

(14) D. P. Kelly, J. T. Pinkey, and D. R. G. Rigby, *Tetrahedron Letters*, 5953 (1966).

(15) L. Claisen, *Ber.*, **45**, 3157 (1912).

anhydrous potassium carbonate. The ether was evaporated and the product distilled under reduced pressure, yielding 11.2 g (60%) of product bp 129–145 (1 mm). This material exhibited a small hydroxyl band in the infrared. A pure sample was obtained by careful chromatography on silica gel using pentane as eluant, $n^{30}\mathrm{D}$ 1.6033.

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.85; H, 6.89.

Isopropyl-β-naphthyl ether was obtained in a yield of 44%, mp 38–40° (lit.[16] 40–41°). This material was distilled to give a pure product.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.80; H, 7.51. Found: C, 83.80; H, 7.68.

***n*-Butyl-β-naphthyl Ether.**—A yield of 72% light yellow material was obtained. This was distilled at 120–123° (1 mm) to give a light colored solid, mp 31–35° (lit.[17] mp 33–35°).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.94; H, 8.01.

***t*-Butyl-β-naphthyl Ether.**—The procedure used by Sahyun and Cram to prepare *t*-butyl phenyl ether[5] was followed. To a stirred mixture of 120 ml of dimethyl sulfoxide, 32 ml of *t*-butyl alcohol, and 50 g (0.106 mole) of potassium *t*-butoxide in a 500-ml, round-bottom flask at 140° was added at once, 14 ml (20.7 g or 0.1 mole) α-bromonaphthalene. The reaction was extremely vigorous. After standing for 5 min, the hot dark brown solution was added to 400 ml of water. The water was cooled with ice and extracted five times with 150-ml portions of ether. The combined ether extracts were washed with water, dried, and distilled at 1 mm pressure to yield three high boiling fractions: I, bp 78–84°; II, bp 84–92°; and III, bp 92–180°. The infrared spectra of all three fractions were almost superimpossible and very similar to that of the *n*-butyl-β-naphthyl ether. These fractions were combined to give 2.5 g (15%). This material proved to be about 88% pure on analysis on a vapor phase chromatograph using an S.E. 30 column, programmed from 100 to 250°. An analytical sample was collected for irradiation, $n^{30}\mathrm{D}$ 1.5724. The product exhibited the following major infrared bands (IR-7): 3060, 2980, 2920 shoulder, 2880 shoulder, 1630, 1595, 1505, 1465, 1390, 1365, 1250, 1218, 1155, 1120, 968, 928, 916, 890, 866, 845, 815, 765 shoulder, 752, 648 cm^{-1}. The following ultraviolet spectrum was obtained (hexane) 2365 A (ϵ 7.9×10^4), 2660 (4.9×10^3), 2740 (5.4×10^3), 2835 (4.3×10^3), 3065 (1.2×10^3), 3137 (1.1×10^3), 3210 (1.3×10^3), and 3290 (6.9×10^2). The ether was found to exhibit a strong fluorescence band at 3550 A (excitation 3400 A). No additional long wave length bands were observed at concentrations up to 2.5×10^2 M.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.79; H, 7.97.

When treated with 6 N hydrochloric acid at 90–100°, the *t*-butyl-β-naphthyl ether cleaved to yield β-naphthol, mp 120–121° (mmp 120–121°). This cleavage was also observed on the vapor phase chromatograph using a column which had been used to analyze possible benzene sulfonic acids.

The aqueous reaction mixture (dimethyl sulfoxide, potassium *t*-butoxide, etc.) was acidified with concentrated hydrochloric acid and extracted with ether. The dried ether extract was evaporated yielding 8.9 g (63% based on naphthol) of a foul-smelling, semisolid material. The infrared spectrum of this material contained both α- and β-naphthol bands. By comparing this spectrum with those of known mixtures, it was determined that the mixture contained about 18% α- and 82% β-naphthol.

Dimerization Experiments.—All ethers were dissolved in benzene and/or absolute ethyl alcohol, degassed (1 mm), and sealded under vacuum in pyrex tubes. The tubes were fastened to an immersion well, lowered into distilled water and irradiated with a Hanovia 450-w medium pressure mercury lamp. The pertinent details of each reaction are as follows.

Dimerization of Allyl-β-naphthyl Ether.—A 17.5% yield of a white solid was obtained in 72 hr, mp 170–172°. This solid, when heated above the melting point in vacuum, decomposed to the starting ether (infrared spectra were superimpossible). The starting ether was recovered unchanged from the dimerization solution. A 12% yield of the photodimer was also isolated after 2 months of irradiation by sunlight. No dimer was formed in the presence of benzophenone. The infrared spectrum (KBr) of the dimer was similar to methyl-β-naphthyl ether photodimer[2] with major bands at 3070, 3010, 2950, 2900, 1625, 1475, 1455, 1420, 1330, 1270, 1185 shoulder, 1175, 1140, 1005, 990, 920, 775, 750, 720, 700 cm^{-1}. The ultraviolet spectrum was obtained (methylene chloride) as follows: 2315 A (ϵ 1.9×10^4), 2740 (2.8×10^3), 2835 (2.9×10^3). Small naphthyl ether bands also appeared at 3130 A (ϵ 2.9×10^2) and 3275 (3.4×10^2). After standing for 18 hr the following ultraviolet spectral bands were found: 2320 A (ϵ 2.6×10^4), 2635 (3.2×10^3), 2740 (4.1×10^3), 2825 (4.0×10^3), 3130 (1.0×10^3), and 3275 (1.1×10^3) (molecular weight of the monomer was used in these calculations).

Dimerization of *n*-Butyl-β-naphthyl Ether.—A 46% yield of fine white crystals was isolated after 48 hr, mp 166–168°. When heated above the melting point *in vacuo*, the dimer decomposed to starting material, mp 31–33°, mmp 31–33°. The infrared spectrum of this photodimer was similar to the other dimers with major bands at 3070, 3010, 2950, 2900, 2870, 1635, 1465, 1450, 1340, 1270, 1190, 1180, 1150, 1140, 1060, 1025, 960, 930, 780, 755, 718, 695 cm^{-1}. Ultraviolet absorption spectrum (methylene chloride) contained the following bands: 2315 A (ϵ 2.1×10^4), 2770 (3.6×10^3), and 2840 (4×10^3). In addition small naphthyl ether bands appeared at 3150 A (ϵ 3×10^2) and 3290 (3.6×10^2).

Attempted Photodimerization of Isopropyl- and *t*-Butyl-β-naphthyl Ethers.—No products were obtained from these ethers after more than 72 hr of continuous irradiation. Quantitative amounts of the starting materials (infrared spectra were superimpossible) were isolated in each case.

Registry No.—Allyl-β-naphthyl ether, 3698-15-5; isopropyl-β-naphthyl ether, 15052-09-2; *n*-butyl-β-naphthyl ether, 10484-56-7; *t*-butyl-β-naphthyl ether, 15052-11-6.

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[16] J. W. B. Reesor and G. W. Wright, *J. Org. Chem.*, **22**, 375 (1957).

[17] E. Wenkert, R. D. Youssefyeh, and R. G. Lewis, *J. Am. Chem. Soc.*, **82**, 4675 (1960).