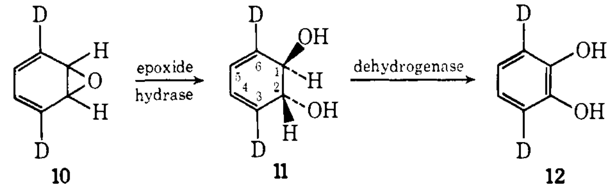
The unexpected 1,6 opening of indan oxide (**1**) necessitated a reexamination of the enzymatic hydration of benzene oxide, in which 1,6 opening would have gone undetected in previous studies.[1,3] Incubation of 1,2-benzene-3,6-^{2}H oxide (**10**, 1.06 atoms of deuterium)[12] with epoxide hydrase produced (−)-*trans*-1,2-dihydro-1,2-dihydroxybenzene-3,6-^{2}H (**11**, 1.08 atoms of deuterium) as proved by nmr spectroscopy. Enzymatic dehydrogenation[1] of **11** afforded catechol-3,6-^{2}H (**12**, 1.12 atoms of deuterium) without loss of deuterium, a clear proof that enzymatic hydration of benzene oxide does not proceed by homoallylic but *only* by 1,2-*trans* addition of water. *Isomerization of 1,2-benzene oxide-3,6-^{2}H to phenol-^{2}H (1.06 atoms of deuterium) during incubation with microsomes occurs without loss of deuterium.*



The enzymatic homoallylic hydration of an arene oxide so far is unique for 8,9-indan oxide (**1**) where steric factors may well prevent normal 1,2 hydration and cause stereospecific entry of water at the homoallylic position. Enzymatic hydrations of 16α,17α- and 16β,17β-epoxysteroids[13] and of 2,3-oxidosqualenes[14] provide further examples of control by steric factors. The significance of hepatic epoxide hydrase to drug metabolism prompts us to continue our studies on the effect of electronic and steric factors on enzymatic hydration of epoxides, and the purification and properties of the enzyme.[15]

(12) 1,4-Cyclohexadiene-3,6-^{2}H (1.10 atoms of deuterium) was purchased from Isomet Corp. and converted to **10**.[1] Deuterium was analyzed by mass spectrometry and localized by nmr spectroscopy.

(13) H. Breuer and R. Knuppen, *Biochim. Biophys. Acta*, **49**, 620 (1961).

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(15) F. Oesch, D. M. Jerina, C. R. Creveling, and J. Daly, *Fed. Proc.*, in press.

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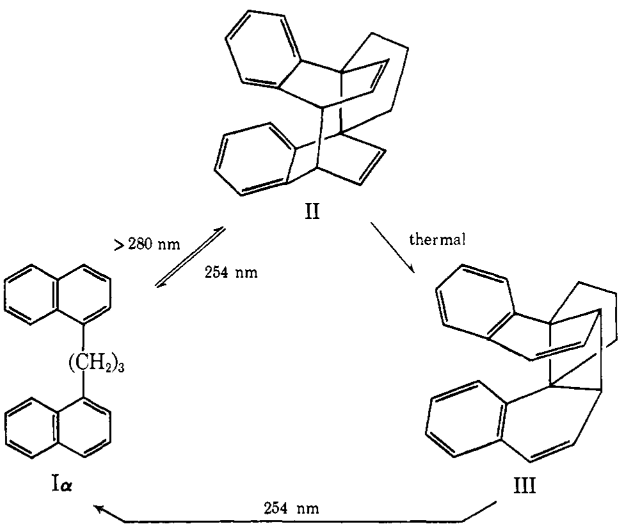
Reversible Intramolecular Photodimerization of 1,3-Bis(α-naphthyl)propane

Sir:

We have found that irradiation of 1,3-bis(α-naphthyl)-propane (Iα) results in intramolecular photodimerization of the naphthalene nuclei to give the anthracene-like dimer II. Such photodimerization has not previously been observed for naphthalene or any of its simple derivatives, although it does occur in the naphthalene paracyclophane.[1] It has been postulated[2,3] as the mode of photodimerization of various β-alkoxynaphthalenes but the structure assigned to these dimers is still in dispute.[4]



The photoisomerization of Iα was discovered during a study of the fluorescence of various dinaphthylalkanes, designed to yield information about the geometric requirements for intramolecular excimer formation. Only the symmetrical 1,3-dinaphthylpropanes Iα and the corresponding β-naphthyl isomer Iβ, which can form perfectly overlapping sandwich pairs, exhibit strong excimer interaction.[5] The small (*ca.* 4 kcal) activation energy involved in excimer formation has been attributed to the rotation barrier in the propane chain. At temperatures above −30°, where the excimer is the main fluorescent species, the fluorescence of Iα is much more subject to thermal quenching than is that of Iβ.

The absorption spectra of solutions of Iα as irradiation[6] proceeds at 25° clearly indicate that a photochemical reaction is occurring. The absorption spectrum of Iβ is not changed under these conditions. The spectra of a degassed 10^{-3} *M* solution of Iα in methylcyclohexane are shown in Figure 1. The absorption decreases to 20% of its original value within 15 min and reaches a steady state (18%) within an hour. It appears that a small amount of Iα remains.

If this solution is heated briefly or allowed to stand overnight, the spectrum changes to curve 3. Irradiation of either this solution or the original unheated solution with a low-pressure Hg lamp (primarily 254 nm, through the quartz portion of the apparatus) regenerates the initial spectrum of Iα (curve 4). The lower absorbance of the solution thus obtained relative to that of the original is suggestive of a photostationary state. These data indicate that upon irradiation Iα forms a compound, II, having a weaker absorbance. Further, II is thermally unstable and gives III (λ_{max} 265

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(1) H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **91**, 2374 (1969); **89**, 2270 (1967).

(2) J. S. Bradshaw and G. S. Hammond, *ibid.*, **85**, 3953 (1963).

(3) J. S. Bradshaw, N. B. Nelsen, and D. P. Rees, *J. Org. Chem.*, **33**, 259 (1968).

(4) M. Sterns and B. K. Selinger, *Aust. J. Chem.*, **21**, 2131 (1968).

(5) C. J. Dempster and E. A. Chandross, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. PHYS 25.

(6) A Rayonet reactor (N. E. Ultraviolet Co.) was used; the lamps were low-pressure Hg (400 W total) with a phosphor whose emission peaks at 300 nm. Irradiation was through Pyrex in a sealed degassed apparatus which had 1- and 10-mm quartz absorption cells attached.

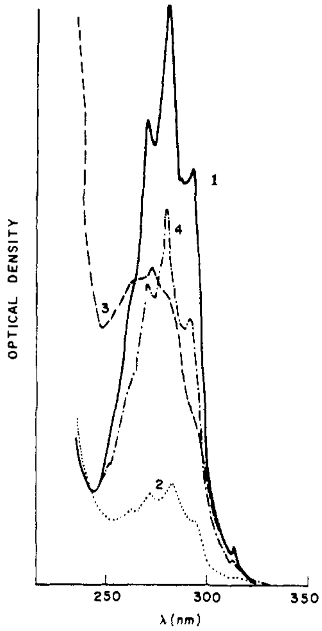


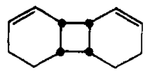
Figure 1. Absorption spectrum of 10^{-3} M Iα in methylcyclohexane (degassed), curve 1; after irradiation at 300 nm, curve 2; after heating to *ca.* 75°, curve 3; after irradiation at 254 nm, curve 4. The operations were sequential.

nm, higher ϵ). Both II and III are converted substantially to Iα upon irradiation with 254-nm light.

A colorless crystalline product consisting of nearly pure II crystallizes upon irradiation of an almost saturated degassed solution (at *ca.* 15°) of Iα in methylcyclohexane. Since II is thermally labile it is impossible to obtain it completely free from III. The uv spectrum of II exhibits a broad plateau (285–265 nm, $\epsilon \leq 2000$), reminiscent of dianthracene[7] and consistent with the assigned structure. We have assigned the *syn* structure to II because it appears to be formed from the excimer which undoubtedly has the configuration of greatest overlap. The uv spectrum of the *anti* isomer would probably resemble that of *o*-xylene more closely than does the spectrum of II.

The nmr spectrum of II ($CDCl_3$, 10°) is also in accord with this structure: τ 7.3–8.3 (m, 3.3, propyl chain); 6.3 (m, 1, methine); 3.9, 3.65, 3.1–3.5 (unsym d, m, $J = 6$, vinyl, vinyl, aromatic). It is not possible to obtain meaningful ratios of vinyl to vinyl or to aromatic protons because the chemical shifts are so similar. This similarity of the vinyl protons is expected for structure II. Decoupling the methine proton yields an AB quartet for the vinyl protons with the two halves centered at τ 3.55 and 3.90. The absorption (τ 3.55) coupled to the methine proton together with its absorption at τ 6.3 are similar to those (τ 3.52 and 6.09) reported for the corresponding protons in benzobicyclo[2.2.2]octadiene.[8]

The cyclobutane isomer III is obtained by boiling the crude photoproduct from Iα in $CHCl_3$ followed by crystallization from $CHCl_3$–hexane (mp 179–181° dec).[9] Its spectra indicate that it is the Cope rearrangement product of II. The uv spectrum of III has a broad band at 265 nm (ϵ 1.02 × 10^3), which is similar to that of 1,2-dihydronaphthalene (259 nm, ϵ 9.55 × 10^3).[10] The hypochromism is attributed to interaction between the two chromophores.[11] The nmr spectrum ($CDCl_3$) of III exhibits peaks at τ 7.5–8.2 (m, 3, propyl chain), 6.7 (m, 1, methine), 4.45 (unsym d of m, 1, nonbenzylic vinyl), 3.8 (unsym d, 1, benzylic vinyl), 3.1–3.5 (m, 4, aryl), and is in accord with that expected for structure III. Both the methine and vinyl protons of III absorb upfield from those of II. The chemical shifts for these protons in the model system IV (τ 7.12 and 4.25, respectively) are similarly shifted upfield from those in benzobicyclo[2.2.2]octadiene.[12] Cyclobutane III reverts slowly to Iα upon melting, but is stable in solution at 100° for at least 1 hr.



IV

Consideration of the steric strain in the corresponding hypothetical photoisomers of Iβ suggests that 1, 1′, 2, 2′ (2 + 2) addition should be as available to the intramolecular excimer from Iβ as to that from Iα. Since Iβ shows no tendency to photoisomerize, the (2 + 2) cycloaddition product, III, probably does not result directly from the Iα excimer, even though some of it is always found in the initial photolysate.

Species such as 1,2-di-α-naphthylethane and 1,4-di-α-naphthylbutane, which do not exhibit excimer fluorescence at 25°, do not photodimerize. We also found no evidence of photodimerization upon irradiation of pure liquid α-methylnaphthalene. The stabilization of the intramolecular excimer provided by the propane chain, attributable to a decrease in the entropy of association, appears to be responsible for these differences in behavior. The dimerization reaction obviously has an activation energy, and the normal naphthalene intermolecular excimer is too short-lived at room temperature for bond formation to occur. Self-quenching of naphthalene also decreases as the temperature increases.[13] The thermal instability of the excimer is a reflection of the increasing free energy of the excimer with temperature, due to the $T\Delta S$ term. We also photolyzed 1,3-diphenylpropane but found no sign of photodimerization; however, some fulvene derivative apparently was formed.

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[9] *Anal.* Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80; mol wt, 296. Found: C, 93.48; H, 6.94, mol wt, 296 (osmometric in CCl_4).

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Excimer Fluorescence and Dimer Phosphorescence from a Naphthalene Sandwich Pair

Sir:

The question of the possible existence of triplet excimers, analogous to the well-known singlet excimers,