phoric acid and allowed to stand overnight at room temperature. The resulting solution was diluted with 100 ml. of water, neutralized with ammonia, and extracted with chloroform. The chloroform extract was dried with sodium sulfate, filtered, and evaporated to dryness. The residue was extracted with boiling *n*-hexane and allowed to cool. The deposited crystals were collected to give 6.9 mg. of material, m.p. 106.5–107.5° (59.1% yield). The melting point of the isolated material was undepressed on admixture with the natural hydronootkatinol; their infrared spectra were identical.

Paper chromatography of the crude reaction product revealed an intense spot for hydronootkatinol and the absence of nootkatin. Similar results were obtained with concentrated sulfuric acid.

Acknowledgment.—An acknowledgment is made to Mr. Richard Scheible for his help in collecting the necessary wood samples.

The Structure of the Solid State Photodimer of 3-Benzylidenephthalide

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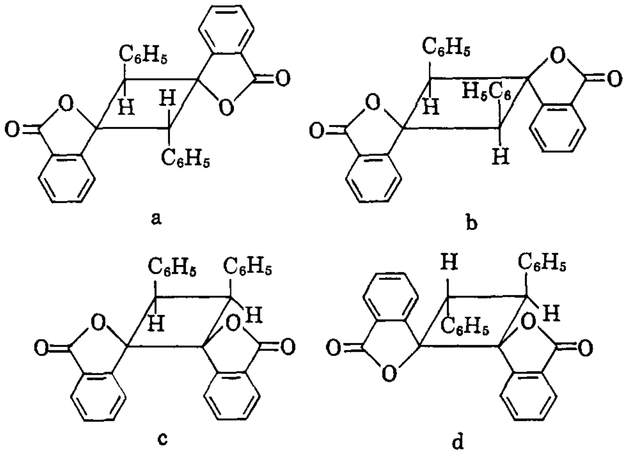
Of the wealth of photodimers which have been reported[1] the number of those whose structure has been fully elucidated remains small. With growing interest in the mechanism of the photodimerization reaction, structural delineation of photochemical dimerization products has acquired renewed importance. While the mechanism of solution photodimerization is still being debated,[2] the structural consequences of solid state dimerization are thought to be dictated by the alignment of the monomers in the crystal lattice.[3] This generalization is based only on few examples,[4–6] an extensive correlation being impossible because of the lack of photodimers whose structure can be considered as firmly established. It was deemed desirable for this reason to investigate additional photodimeric compounds, of which the photodimer of 3-benzylidenephthalide was a particularly convenient example.

3-Benzylidenephthalide was found to dimerize readily in the solid state in yields of 30% by irradiation with a 275-watt sunlamp.[7] The photodimer, m.p. 294-296°, infrared absorption at 5.64 μ, lacks vinyl proton absorption in the n.m.r. spectrum,[8] the latter exhibiting outside the aromatic region only one sharp signal at τ 4.82 (p.p.m.).

Formation of a cyclobutane ring structure is corroborated by the n.m.r. spectrum as well as by the observation that the dimer reversed to the monomer upon irradiation in solution with a Hanovia mercury arc lamp. The presence of a single aliphatic proton absorption in the n.m.r. spectrum is in accord with the expected formation of a symmetrical dimer. Rejecting from consideration the possibility of *cis–trans* isomerization,[9] the number of photodimeric structures among which the choice has to be made is reduced to a total of four, the *cis–trans* isomeric pairs of either the head–tail structure (Ia, b) or of the head–head structure (Ic, d). the following evidence establishes the structure of the photodimer as being Ia, the head–tail formulation.

Upon mild alkaline hydrolysis the photodimer was found to yield a carboxylic acid II, which readily eliminated water reverting to starting material.[10] The corresponding methyl ester, found to be somewhat more stable, was assigned the mono ester–lactone structure III on the strength of its infrared spectrum (bands at 2.90, 5.65, and 5.92 μ) and its n.m.r. spectrum, the latter providing conclusive evidence for the streochemistry of III and, hence, for that of the photodimer from which it is derived. With the loss of symmetry in the molecule, the two hydrogens become dissimilar in the ester–lactone derived from three of the four possible dimeric structures. A photodimer of structure Ib would give rise to an ester–lactone which retains a plane of symmetry and the two ring hydrogens remain in an identical environment. Of the remaining three structures, the head–head structures Ic and Id, when transformed into an ester–lactone, will have their ring hydrogens on adjacent carbons and since they are now nonequivalent, they should give rise to a doublet.[11] In fact, the ester obtained showed, in addition to the



a b

c d

I

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[1] See, for example, A. Mustafa, *Chem. Rev.*, **51**, 1 (1952); A. Schönberg, "Präparative Organische Photochemie," Springer Verlag, Berlin, 1958, pp. 22-35.

[2] P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344, 2454 (1962).

[3] T. Sadeh and G. M. J. Schmidt, *ibid.*, **84**, 3970 (1962); D. Cohen and G. M. J. Schmidt, in "Reactivity of Solids," J. H. de Boer, Ed., Elsevier Publishing Co., Amsterdam, 1961, p. 556.

[4] P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **80**, 6150 (1958) and forthcoming publication.

[5] G. W. Griffin, J. E. Bassinski, and L. I. Peterson, *ibid.*, **84**, 1012 (1962).

[6] G. M. J. Schmidt, *Acta Cryst.*, **10**, 793 (1957); H. J. Bernstein and W. C. Quimby, *J. Am. Chem. Soc.*, **65**, 1845 (1943).

[7] The dimerization of 3-benzylidenephthalide in solution has been reported to give one photoproduct of unknown structure [A. Schönberg, N. Latif, R. Moubasher, and W. I. Awad, *J. Chem. Soc.*, 374 (1950)]. In the present study it was found that three dimers resulted from solution dimerization, one in predominant amounts and none identical to Ia. The n.m.r. spectra exhibited only singlet proton signals in the 5-τ region.

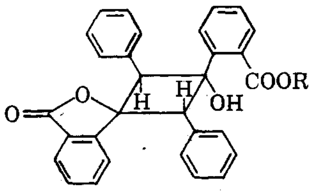
[8] The vinylhydrogen in the monomer gives rise to a signal at τ 3.62 (p.p.m.).

[9] *cis–trans* isomerization in the solid state is unlikely in this case. The cross-over mechanism *via* a cyclobutane dimeric structure advanced for the solid state isomerization of cinnamic acid (G. M. J. Schmidt, Photochemistry Symposium, Rochester, N. Y., March, 1963) cannot hold in our example, as the photodimer remains unchanged upon further irradiation. We are indebted to a referee for bringing to our attention the above unpublished results.

[10] The facile formation of photodimer precludes cyclobutane ring opening or other skeletal changes under these conditions. More vigorous base treatment caused cyclobutane ring cleavage.

[11] Coupling of vicinal nonequivalent *cis* or *trans* cyclobutane protons is expected; *cf.* ref. 2 and spectra of distilbenes in J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McHraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 290-291.

methyl ester hydrogen signals at τ 6.23 (p.p.m.), two one-proton singlets located at τ 4.52[12] and τ 5.50 (p.p.m.), the positions being invariant upon dilution. Only the ester III can give rise to such a spectrum, and hence, the structure of the photodimer must be Ia.



II, R=H
III, R=CH_3

The large difference in chemical shift between the two cyclobutane ring hydrogens appears to be the consequence of shielding effects exerted on these by the various phenyl groups, being particularly sensitive to the steric relationships between the substituents on the ring. Opening of one lactone ring appears to increase the shielding (by about 0.7 p.p.m.) experienced by, the vicinal *cis* proton, but causes a deshielding effect (by about 0.3 p.p.m.) on the *trans* hydrogen. The latter is probably the result of the altered rotational equilibrium position of the *cis* phenyl group, effected by the added steric interaction which opening of the lactone ring introduces.

Experimental

Photodimerization of 3-Benzylidenephthalide.—Solid 3-benzylidenephthalide (15 g.) was irradiated in frequently turned thin layers, for about 2 weeks with a G. E. 275-w. sunlamp. Total solid was triturated with cold benzene (75 ml.) and the filtered remaining solid (4 g., 27%) was recrystallized twice from large volumes of benzene to give the photodimer Ia as stubby needles, m.p. 294–296°. The benzene soluble solid (10 g.) was shown to be starting material.

Anal. Calcd. for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54; mol. wt., 444. Found: C, 80.81; H, 4.43; mol. wt., 451.

Base Hydrolysis of the Photodimer. Formation of II.—The photodimer (5.0 g.) was stirred with alcoholic 5% sodium hydroxide (50% water–ethanol) for 4 hr. The clear solution was cooled and neutralized with cold 10% hydrochloric acid. The precipitated solid (4.55 g.) was air-dried and was shown to consist of the monocarboxylic acid–lactone II and large amounts of starting material. II readily reverted to starting material on standing; it was not obtained in a pure state, but was converted to the methyl ester III immediately.

More vigorous hydrolysis by refluxing the basic solution for 6 hr. led to the formation of a different acid-lactone, m.p. 244–246°, characterized as being isomeric with II. The methyl ester had infrared bands at 5.65, 5.80, and 5.93 (sh) μ. It is evident that cyclobutane ring cleavage takes place under these conditions.

Preparation of III. Methyl Ester of II.—An ether suspension of II was treated with diazomethane until the color of diazomethane persisted. The considerable amount of unchanged solid remaining consisted of photodimer, to a large part formed during the diazomethane treatment. The methyl ester III was obtained in small yields from the ether solution by evaporation of the solvent *in vacuo*. Fast recrystallization from boiling benzene–petroleum ether afforded, after the less soluble photodimer had crystallized, in subsequent crops, III as small prisms. The melting point of III was that of the photodimer, with a crystalline change being observable at 180° on slow heating. The infrared spectrum of a melted sample was identical to that of the photodimer. Reversion to photodimer also took place at moderate speeds in solution; stability as a solid was good.

Anal. Calcd. for $C_{31}H_{24}O_5$: C, 78.13; H, 5.08. Found: C, 78.56; H, 5.34.

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Synthesis of a Derivative of Indolo[3,2-*b*]carbazole

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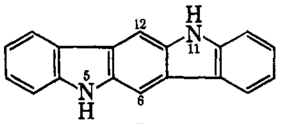
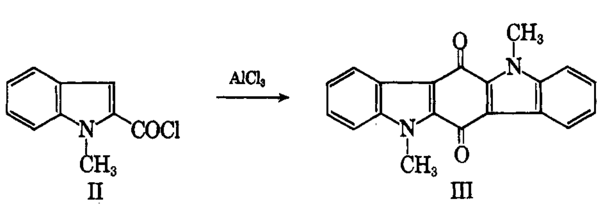
Efforts in the indolocarbazole area recently have been summarized by Grotta, *et al.*[1] (*cf.* also ref. 2), who prepared 5,11-dihydroindolo[3,2-*b*]carbazole (I) by cyclodehydrogenation of N,N′-diphenyl-*p*-phenylenediamine. Noland, *et al.*,[3,4] suggested that the condensation products resulting from the reaction of 1-methylindole with methyl isobutyl ketone and that of indole with acetophenone may be derivatives of 5,6,11,12-tetrahydroindolo[3,2-*b*]carbazole.



I

We have found that a derivative of this difficultly accessible ring system resulted readily when a solution of 1-methylindole-2-carbonyl chloride (II) in 1,2-dichloroethane was treated with aluminum chloride.[5] This reaction led to 5,11-dimethylindolo[3,2-*b*]carbazole-6,12(5*H*,11*H*)-dione (III) in 41% yield. The assignment of this structure is supported by analytical data, and ultraviolet and infrared spectra.



In connection with this problem we had occasion to examine the reduction of "urorosein sulfate" with lithium aluminum hydride. Early literature related to this compound was reviewed by Fearon and Boggust,[6] who prepared urorosein sulfate by heating indole-3-carboxaldehyde with sulfuric acid, and proposed structure IV for the free base. On the other hand, Harley-

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[12] This proton signal is not sharp, but is unresolvable.

[1] H. M. Grotta, C. J. Riggle, and A. E. Bearse, *J. Org. Chem.*, **26**, 1509 (1961).

[2] *Cf.* R. J. Brunton, F. K. Drayson, S. G. P. Plant, and M. L. Tomlinson, *J. Chem. Soc.*, 4783 (1956).

[3] W. E. Noland, C. G. Richards, H. S. Desai, and M. R. Venkiteswaran, *J. Org. Chem.*, **26**, 4254 (1961).

[4] W. E. Noland and M. R. Venkiteswaran, *ibid.*, **26**, 4263 (1961).

[5] *Cf.* the reaction of benzoyl chloride with aluminum chloride which afforded a small amount of anthraquinone: S. Coffey and J. vanAlphen in "Chemistry of Carbon Compounds," E. H. Rodd, Ed., Vol. IIIB, Elsevier Publishing Co., New York, N. Y., 1956, p. 1376.

[6] W. R. Fearon and W. A. Boggust, *Biochem. J.*, **46**, 62 (1950).