

THE PHOTODIMERIZATION OF 2,3-DIHYDRO-2,6-DIMETHYL-4-PYRONE

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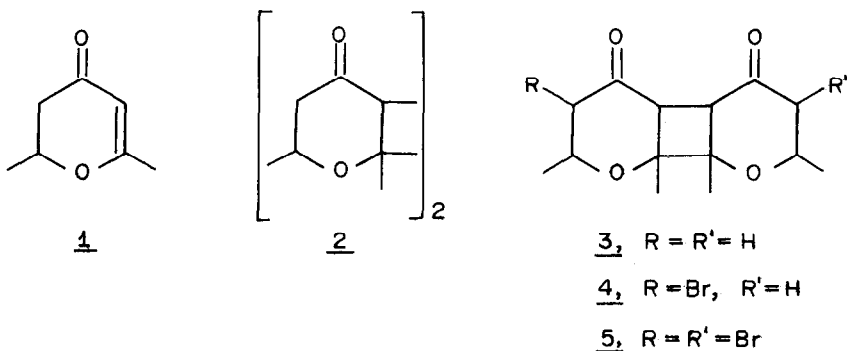
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The photodimerization of  $\alpha,\beta$ -unsaturated ketones to give cyclobutanes has long been known (1), but the structural details of such photodimers have been elucidated only recently (2-4). The photodimerization of 2,6-dimethyl-4-pyrone is egregious in proceeding with orientational and stereospecificity to give a cis-syn-cis head-to-tail product (2). With the purpose of defining which of the special structural features of this monomer - the presence of two ethylenic double bonds or an annular oxygen atom - is responsible for this circumstance, we have investigated the photodimerization of 2,3-dihydro-2,6-dimethyl-4-pyrone (1).

Irradiation of an aqueous 12% solution of 1 [ $\lambda_{\max}$  263 m $\mu$  ( $\epsilon$  14,000)] (5) under nitrogen in Pyrex tubes with a Hanovia 450-w medium pressure mercury arc lamp led to the deposition after 4 weeks of a crystalline mixture of photodimers [72%; an additional amount (ca. 25%) of this mixture was obtained from the aqueous solution]. Fractional crystallization from polar solvents gave dimer A, (6) m.p. 163-164°, and a eutectic mixture, m.p. 130-133°, of dimers A and B (1:4). Repeated crystallization of this mixture from hexane gave dimer B, m.p. 133-134°; from the combined mother liquors was obtained a crystalline mixture of A and B and dimer C. This dimer was not isolated in pure form, but the latter mixture was enriched in C by countercurrent distribution between cyclohexane and water to give a 1:2.5:6.5 mixture of A, B, and C. The ratio of these dimers in the original reaction product was ca. 9:15:1.

The spectra of the dimers showed that they are all of the cyclobutane

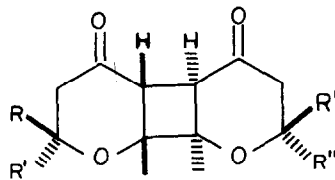
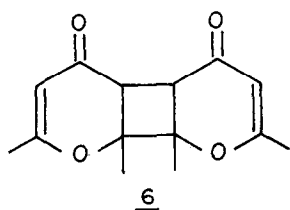


type (2). The n.m.r. signals assignable to the two cyclobutane protons of B appeared as a doublet of doublets ( $\delta$  2.92 and 3.06 ppm,  $J$  6 Hz), demonstrating that B has the head-to-head orientation 3. Although the corresponding protons in the spectrum of A gave rise to a singlet ( $\delta$  3.05 ppm), this was shown to belong to the head-to-head series (3) also by its conversion with bromine to a monobromo derivative 4, whose spectrum showed a doublet of doublets ( $\delta$  3.07 and 3.78 ppm,  $J$  5 Hz). This was confirmed by the observation that a  $^{13}\text{C}$ -H satellite signal ( $J$  126 Hz) for the cyclobutane protons of A appeared as a doublet ( $J$  7 Hz).

Treatment of A and B with boiling pyridine caused no change in these compounds. That enolization involving the cyclobutane hydrogen atoms can occur was demonstrated by treatment of A with boiling  $\text{D}_2\text{O}$ -pyridine (1:9) when six hydrogen atoms can be exchanged for deuterium. Thus the pyran and cyclobutane rings of A and B must be cis fused.

Bromination of A with two molar equivalents of bromine gave the dibromo derivative 5, m.p. 168-170° dec, which on dehydrobromination with boiling pyridine gave 6, m.p. 181-182°; the same product could be obtained directly from A by treatment with N-bromosuccinimide in carbon tetrachloride. Treatment of B under the latter conditions also gave 6, confirming that A and B are both in the head-to-head series and establishing that they are both syn or both anti with respect to the fusion of the pyran rings to the cyclobutane ring. Irradiation of 6 in dilute ethanolic solution led to the

formation of 2,6-dimethyl-4-pyrone; had 6 had the syn stereochemistry it would be expected to undergo facile photochemical ring closure to a cage compound [cf. (2)]. It is concluded that A and B have the cis-anti-cis stereochemistry shown in 7-9, which represent all the head-to-head structures



7,  $R = R'' = \text{CH}_3$ ,  $R' = R''' = \text{H}$

8,  $R = R''' = \text{H}$ ,  $R' = R'' = \text{CH}_3$

9,  $R = R''' = \text{CH}_3$ ,  $R' = R'' = \text{H}$

with this stereochemistry (apart from corresponding enantiomorphs). Dimer B may immediately be assigned structure 7, since in its n.m.r. spectrum each of the five chemically different kinds of protons gives rise to two groups of signals. Both 8 and 9 have a two-fold axis of symmetry, absent in 7, that results in the equivalence of a particular type of proton in one pyran ring with the corresponding type in the other. The spectrum of A shows only five single groups of signals, corresponding to the assignment to it of structure 8 or 9. Catalytic hydrogenation of 6 gave C as the only tetrahydro product. This dimer must then also have structure 8 or 9, as confirmed by the fact that its n.m.r. spectrum shows only five single groups of signals. Further, consideration of the geometry of 6 leads to the conclusion that its preferred mode of adsorption on the hydrogenation catalyst should lead to its reduction to 8 rather than 9. Dimer C is accordingly assigned structure 8 and dimer A then has structure 9.

The photodimerization of 1 thus leads exclusively to head-to-head cis-anti-cis products in striking contrast to 2,6-dimethyl-4-pyrone and in close analogy with 3-aryl-2-cyclohexenones (3). The presence of the additional double bond in the pyrone must be a critical factor in determining the unusual course of its photodimerization. Its presence could,

of course, affect the nature of the excitation step and/or the reaction of the excited state with a ground state molecule (7). That the nature of the photodimers obtained from 1 is determined, at least in part, by thermodynamic rather than kinetic control is indicated by the observation that irradiation of dilute ethanolic solutions of dimers A, B, and C leads to their interconversion.

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6. Satisfactory elemental analytical data have been obtained for all compounds characterized by m.p.
7. The dichotomy is not due to the use of water as solvent for the photodimerization of 1, since water is one of several solvents in which 2,6-dimethyl-4-pyrone gives a cis-syn-cis head-to-tail photodimer exclusively.