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SOLID STATE ORGANIC PHOTOCHEMISTRY II.
PHOTOLYSIS OF 4,6-DIPHENYL-α-PYRONE.[1]

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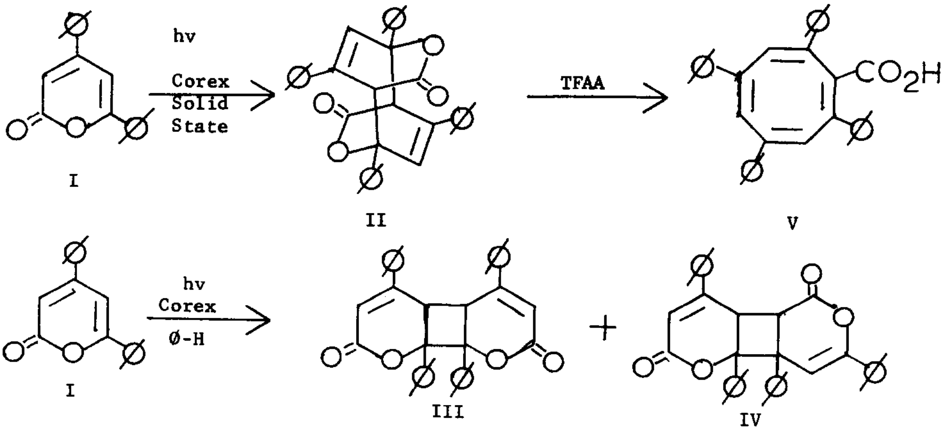
The photolysis of α-pyrones in the solution phase has received considerable attention. In this communication, we would like to present some observations regarding the solid state photolysis of α-pyrones in contrast to their solution photolysis. In addition, we would like to report an unusual rearrangement of one of the photo-products.

The photolysis of a saturated benzene solution of 4,6-dimethyl-α-pyrone yields syn and anti dimers resulting from 4 + 4 cyclo-addition and another dimer from 2 + 2 addition. These dimers, when heated to their respective melting points, decarboxylate to yield 1,3, 5,7 tetramethylcyclooctatetraene.[2]

The photolysis of a dilute ether solution of 4,5-diphenyl-α-pyrone yields 1,2,4,7 tetraphenylcyclooctatetraene via a proposed β-lactone intermediate which undergoes spontaneous decarboxylation.[3]

We have photolyzed 4,6-diphenyl-α-pyrone (I) in the solid state and as a dilute (4.0 mM) benzene solution.[4]

Scheme I



(1) I II V

(2) I III IV

As shown in scheme I, the sole product arising from photolysis (0.5 hour) of I in the solid state is the 4 + 4 anti dimer II in 100% yield based on recovered starting material.[5,6]

The structure for II was assigned on the basis of the following evidence.[7] Heating II to its melting point (168° dec) produces, in 100% yield, I, identified by mass spectral, infrared, and melting point comparisons to authentic I. The expected decarboxylation to the cyclooctatetraene does not occur in this molecule. The infrared spectrum (methylene chloride) of II shows a carbonyl stretch at 1745 cm^{-1},[8] versus 1737 cm^{-1} for I. One would expect the carbonyl of the syn isomer to come at a higher value due to dipole-dipole interaction. The ultraviolet spectrum shows $\lambda_{max}^{CHCl_3}$ at 264 nm; I has $\lambda_{max}^{CHCl_3}$ at 265 nm and λ^{CHCl_3} at 346 nm, hence the carbonyl is no longer conjugated. The poor solubility of II precluded an interpretable NMR; further, due to the high lability of II, its mass spectrum was essentially identical to that of I, even with low resolution techniques.[10]

Treatment of II with trifluoroacetic acid for ten hours at room temperature yielded (50%) a white solid identified as 1,3,5,7 tetraphenylcyclooctatetraene carboxylic acid, V, mp=238° C. The structure of V is based on the following spectral data. The infrared spectrum (KBr) showed the carbonyl stretch at 1770 cm^{-1} with weak bands at 1705 cm^{-1} and 870 cm^{-1} corresponding to the carbon-carbon double bond stretching frequency of the cyclooctatetraene ring.[11] Ultraviolet absorption shows λ_{max}^{EtOH} at 255 nm and λ^{EtOH} at 280 nm versus 273 nm for cinnamic acid. High resolution mass spectrometry shows the M^+ ion at $^m/e$ 452.1785.[12] The mass spectrum from $^m/e$ 408 on down is nearly identical to that for authentic 1,3,5,7 tetraphenylcyclooctatetraene.

Thus, these data, coupled with elemental analysis require a dimer with the structure II.

Scheme (I) also shows the products isolated by column chromatography following dilute solution photolysis (1 hr.) of I. Compound IV is formed in 50-60% yield, III in 15-20% with 10-15% tar and 10-15% of I remaining. Increasing the concentration tenfold (40.3 mM) gives rise to about 4% II at the expense of III (8-10%). No decarboxylation occurs at either concentration.

The structures of III and IV are based on the following spectral data, coupled with elemental analyses.

Dimer III (mp 124° dec) shows a sharp carbonyl absorption in the infrared ($CHCl_3$) at 1690 cm^{-1} with additional bands present for carbon-carbon double bond stretch and carbon-oxygen single bond stretch. Ultraviolet absorption shows λ_{max}^{EtOH} at 246 nm with an intense shoulder at λ^{EtOH} 273 nm. Thus, the vinyl ether structure is no longer present; but a highly conjugated carbonyl remains. The NMR spectrum of III consists of a broad aromatic singlet (4H) at 7.87δ, a complex aromatic multiplet centered at 7.33δ (16H), a singlet at 6.30δ (2H). From the vinyl protons of I, 6.32δ(1H) and 6.80δ (1H), one can assign the 6.30δ absorption to the α, β unsaturated carbonyl fragment and the 4.76δ value to the methine protons. Again, due to lability, dimer III gives a mass spectrum essentially of the monomer (P^+ at $^m/e$ 220), but with additional new peaks, the most important coming at $^m/e$ 178 (diphenylacetylene).

Isomer IV (mp 120° dec) shows in the infrared ($CHCl_3$) a poorly resolved doublet carbonyl absorption at 1740 cm^{-1} and 1700 cm^{-1}. Ultraviolet absorption occurs at λ_{max}^{EtOH} 259 nm with a tail out to λ^{EtOH} 380 nm. The mass spectrum of IV is also essentially that of the monomer. However, low voltage, high sensitivity techniques allow peaks out to about $^m/e$ 475 to be detected. The most important of several new peaks is at $^m/e$ 178 again. These data, with elemental analysis, require structure IV.

To the authors' knowledge, this represents the first case of 4 + 4 photodimerization in the solid state. We are determining to what extent this process may be general in the solid state photochemistry of α-pyrones.

These observations represent another example of a striking difference between the photochemistry of a compound in solution and in the solid state. The usefulness of photochemistry in the solid state is pointed out here in that generally a single photoproduct is obtained. Also, it need not be a photoproduct observed in the solution photolysis. The effects of crystal structure on the photochemistry of α-pyrones are being investigated and will be reported on in the near future. The generality of the unique acid catalyzed rearrangement of the 4 + 4 photo-dimer is also being investigated.

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References

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(2) P. DeMayo, R. W. Yip, Proc. Chem. Soc., 84 (1964).

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(4) Irradiation was conducted with a water cooled, medium pressure Hanovia mercury arc lamp (450 watts) with a corex filter. Initial work with anhydrous ether as solvent was discontinued when IR and other evidence indicated I was photochemically reacting with the solvent.

(5) For a review of solid state photochemistry see: H. S. A. Gilmore, in "Physics and Chemistry of the Solid State", ed. D. Fox et al., New York, Interscience, 1963.

(6) Preliminary work on the solid state photolysis of 4,6-dimethyl-α-pyrone has shown that the 4 + 4 anti adduct is formed (2%), but, unusually, with several other (tlc) as yet unidentified products.

(7) Satisfactory elemental analyses have been obtained for all new compounds.

(8) DeMayo[9] has reported that the 4 + 4 anti dimer of 4,6-dimethyl-α-pyrone shows a carbonyl stretch at 1734 cm^{-1} whereas the syn isomer comes at 1760 cm^{-1}.

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(12) The theoretical value for $C_{33}H_{24}O_2$ is $^{m}/e$ 452.1776[13]

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