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ABNORMAL DIMERISATION OF 2,3,4-TRIPHENYLCYCLOPENTADIENONE

R. S. Atkinson

Organic Chemistry Department, The University, Leeds. LS2 9JT

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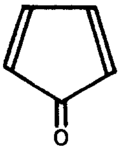
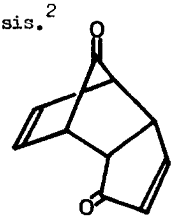
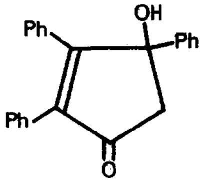
Cyclopentadienones are reactive compounds which readily dimerise unless heavily substituted.[1] Some of these dimers regenerate the monomers at higher temperatures by reversal of the Diels-Alder addition involved in their formation (I $\rightleftharpoons$ II) and an attempt has been made to classify cyclopentadienones on this basis.[2]



I



II



III

We find that dehydration of the cyclopentenolone (III) with p-toluene sulphonic acid in benzene does not give the conventional dimer analogous to (II); i.r. spectral examination of the crude reaction product showed complete absence of a band at 1770 cm.$^{-1}$ (Film) corresponding to the bridging carbonyl group. A yellow crystalline product was isolated (35%) by chromatography over alumina m.p. 260° resolid. m.p. 314-322°. Mass spectral molecular weight ($\overset{\bullet}{M}^{+}$ 616.2413 (base peak) calc. for $C_{46}H_{32}O_2$ 616.2402) shows this material to be dimeric. The i.r. spectrum (Nujol) shows a single band at 1680 cm.$^{-1}$ and the n.m.r. spectrum* only a 2 proton singlet at τ 4.23 besides aromatic protons.

Assignment of the ene-dione structure (IV) to this yellow dimer is supported by its rapid reduction with zinc in acetic acid at room temperature giving a mixture of two isolable dihydro-dimers separated by crystallisation and formulated as (V) m.p. 227-232° and (VI) m.p. 115-120°. The stereochemistry of these dihydro-dimers follows by comparison of their

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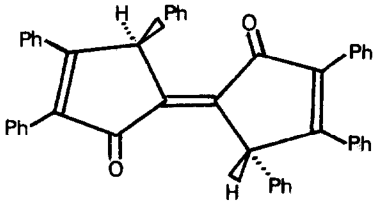
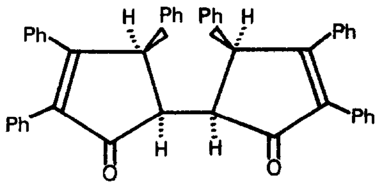
* N.m.r. spectra run in $CDCl_3$

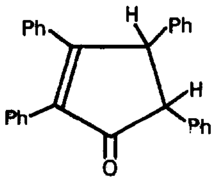
n.m.r. spectra with those of cis (VII) and trans (VIII)^{3} dihydro-tetracyclones and with the assumption of retention of stereochemistry at C3 and C3'. Thus the isomer (V) shows, besides aromatic protons, a very simple spectrum with 2 doublets (each 2 protons) at τ 5.47 and 6.97 (J 7 Hz.) compared with 2 doublets at τ 5.55 and 5.10 (J 7.5 Hz.) for (VII). Isomer (VI) shows 4 protons of differing chemical shift including 2 lower field doublets of J 7.5 and 3.5 Hz. (for (VIII), J 2.5 Hz.). The other possible isomer with the trans-cis-trans stereochemistry was not isolated and would be expected to be a minor product assuming protonation from the less hindered face.



IV

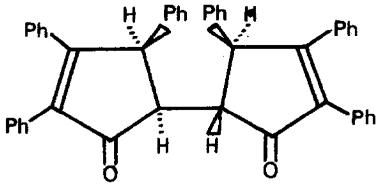


V

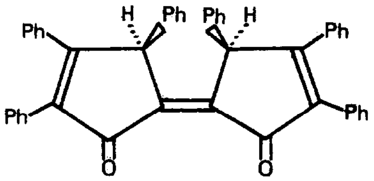


VII H cis

VIII H trans



VI



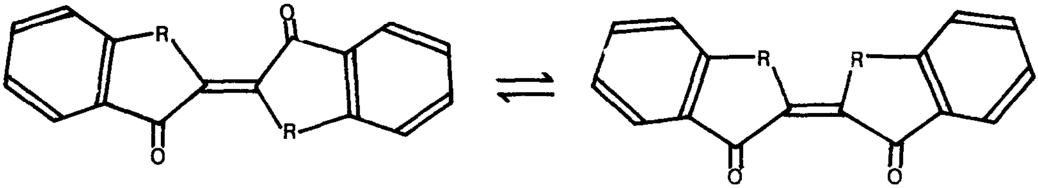
IX

A striking property of dimer (IV) was its conversion into the photo-isomer (IX) on standing for 4 hr. in benzene in sunlight. The conversion was complete as judged by u.v. and the photo-isomer (IX) was isolated as an orange yellow crystalline solid in 75% yield. In its n.m.r. spectrum the 2 proton singlet shows an upfield shift of 1.35 τ compared to that in dimer (IV) which may be ascribed in large part to the removal of the benzylic hydrogens from the deshielding influence of the adjacent carbonyl groups. In the i.r. spectrum (Nujol) the carbonyl band frequency is raised to 1704 cm.$^{-1}$.

On heating the photo-dimer in the solid state for 2 minutes at 185° quantitative re-conversion to dimer (IV) occurred. Reduction of the photo-dimer with zinc in acetic acid at room temperature gives the same two dihydro-dimers (V) and (VI) suggesting that the stereochemistry at C3 and C3' is unchanged in the photo-isomerisation.

In dimer (IV) the two phenyl groups have been assigned a trans relationship. The n.m.r. spectrum of the photo-dimer in which these two phenyl groups are now cis supports this; the character of the aromatic proton signal was altered from a narrow multiplet (τ 3.0-2.6) in (IV) to one more splayed out in (IX) (τ 3.3-2.6). Our interpretation of this observation is a mutual shielding between the cis phenyl groups due to their close proximity.[4]

It is instructive to compare the interconversion of (IV) and (IX) with the behaviour of various indigos of general formula (X).



X R = O, S, Se, NMe

Although cis-indigo itself has never been isolated, probably due to its rapid re-conversion to the trans form, indigos containing various hetero atoms have been isolated in cis and trans forms.[5,6,7] Comparison of their u.v. and i.r. data and of cis and trans dibenzoylethylenes[8] agree well with (IV) and (IX); the cis isomer has the carbonyl band at higher frequency in the i.r. and the u.v. absorption at shorter wavelength. However these cis-indigos isomerise to the trans at temperatures far below* that in the present case. The greatly decreased thermal stability of cis-(X) is due to the resonance interactions possible between lone pair electrons of R and the carbonyl groups which lead to greater single bond character for the central double bond.

Dimer (IV) proved to be identical with the yellow dimer previously obtained from cyclopentenolone (III) by dehydration using acetic acid-sulphuric acid 50:1[9] and assigned the normal dimeric structure (II). Using a higher concentration of sulphuric acid the major product is a blue dehydro-dimer[10] and only small quantities of (IV) are obtained.[11]

This mode of dimerisation is obviously restricted to cyclopentadienones bearing at least one ring hydrogen. In the present case, the reversibility of the normal mode of dimerisation ($I \rightleftharpoons II$) would allow the triphenylcyclopentadienone to be siphoned off to form

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* cis-Thioindigo (Ref 6) isomerises to the trans in 32 hr. at room temperature.

dimer (IV). Both 3-t-butyl and 2,4-di-t-butylcyclopentadienone give normal dimers corresponding to (II)[12] as do the 2-alkyl-3,4-diphenylcyclopentadienones.[13]

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