Spiroconjugation, Dimerisation, and Ultraviolet Absorption of *o*-Quinonoid Compounds

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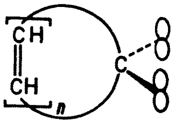
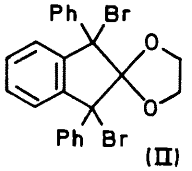
Summary The ethylene acetal of 1,3-diphenylisoindenone, 1,2,3-triphenylbenzo[*c*]phosphole 2-oxide, and 2-methyl-1,3-diphenylbenzo[*c*]phosphole 2-oxide have been generated in solution; the u.v. absorption and $(4 + 2)\pi$ dimerisation of these compounds is attributed to spiroconjugation.

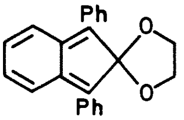
THE prediction[1,2] of spiroconjugation between the termini of a cyclic polyene and the *p*-orbitals of substituents attached to an insulating carbon atom as in (I) is supported by the properties of cyclopentadienone acetals (I; $n = 2$).[1] The effect of nonplanarity in larger polyenes *e.g.* tropone acetals is uncertain so that interpretation of their u.v. spectra in terms of spiroconjugation is less secure.[1] We report evidence for spiroconjugation in 1,3-diphenylisoindenone ethylene acetal, a planar bridged variant of (I; $n = 4$).



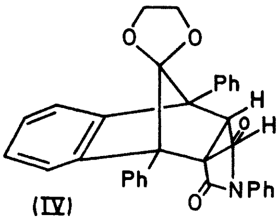
(I)



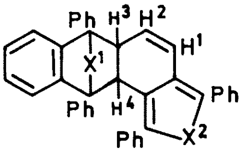
(II)



(III)

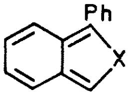


(IV)



(V) $X^1 = X^2 = C\langle{}^{O}_{O}\rangle(CH_2)_2$

(VI) $X^1 = C\langle{}^{O}_{O}\rangle(CH_2)_2$, $X^2 = CO$



(VII)

The ethylene ketal of 1,3-diphenylindan-2-one was prepared from the ketone in the usual way, and gave the dibromide (II) in reaction with *N*-bromosuccinimide. Reduction of (II) with copper powder in boiling benzene gave a violet–red colour (λ_{max} 537 nm) attributed to the isoindenone acetal (III) since trapping with *N*-phenylmaleimide gave the *endo*-adduct (IV). In the absence of a trap the acetal rapidly gave a non-crystalline dimer (V) the structure of which follows from the n.m.r. spectrum, τ 4 (d, H^1, $J = 10$ Hz), 4·22 (dd, H^2, $J = 10$ and 3·5 Hz), 5·66 (dd, H^3, $J = 8·5$ and 3·5 Hz), 5·31 (d, H^4, $J = 8·5$ Hz). Reaction of (V) in ethanol with toluene-*p*-sulphonic acid hydrate gave the cyclone (VI) which has properties [ν_{max} (Nujol) 1693 cm.$^{-1}$, λ_{max} (EtOH) 269, 336, and 493 nm (ϵ 25,400, 4520, 1970)] similar to those of tetracyclone.

The acetal (III) is more cleanly generated by reduction of (II) with sodium iodide in acetone. By this method either the dimer or *endo*-cyclopentadiene adduct of (III) are obtained (45%).

The acetal (III) absorbs at longer wavelength than the related isoindene (VII; X = CMe_2) which has λ_{max} 444 nm.† The acetal also dimerises more readily than the isoindene which has been isolated.[3] Both these differences are consistent with an increased ground-state energy of the acetal which arises by spiroconjugation.

In related work we have generated the *o*-quinonoid phosphole oxides [VII; X = P(O)Ph] and [VII; X = P(O)Me]. Cycloaddition of *trans*-1,2-diphenylbenzocyclobutene with phenylphosphonous dichloride followed by aqueous work-up gave the 1,3-dihydro-derivative of [VII; X = P(O)Ph]. Bromination with *N*-bromosuccinimide and reduction of the product with copper powder in refluxing benzene then gave [VII; X = P(O)Ph]; [VII; X = P(O)Me] was similarly prepared from methylphosphonous dichloride. The properties of these oxides are consistent with spiroconjugation. Both compounds gave dimers analogous to (V), oxide [VII; X = P(O)Ph] has λ_{max} 573 nm, and oxide [VII; X = P(O)Me] λ_{max} 550 nm. The properties of simple phosphole oxides[4] are also consistent with spiroconjugation.

Unlike the isolable isoindene (VII; X = CMe_2)[3] the sulphone (VII; X = SO_2)[5] is stable only in solution. This reduced stability and the u.v. absorption (λ_{max} 550 nm) are attributable to spiroconjugation which has previously been invoked to explain the properties of thiophen 1,1-dioxide.[6]

All new compounds have been characterised by analysis or mass spectroscopic accurate mass measurement, and have appropriate i.r., u.v., n.m.r., and mass spectra.

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† Measured for a benzene solution prepared by reduction of the corresponding dibromide with copper powder. The original author (ref. 3) do not report λ_{max}.

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