Derivatives of Isoindenone

By J. M. Holland and D. W. Jones*

(*Department of Organic Chemistry, The University, Leeds*, LS2 9JT)

Summary 1,3-Diphenylisoindenone has been generated as an unstable intermediate in three ways and its dimerisation and cycloaddition reactions have been investigated.

Isoindene and its derivatives have been implicated as intermediates in several reactions,[1] and a stable derivative[2] and metal complex[3] have been reported. The related isoindenones (I) offer attractive possibilities of mesomerism (II) and valence isomerism (III), and have potential in the synthesis of benzonorbornenone[4] and benzocyclobutadiene derivatives. The properties of 1,3-diphenylisoindenone (I; R = Ph) are of interest in connection with the recently reported 1,3-diphenylbenzo[*c*]thiophen 2,2-dioxide.[5]

Dehydration of the acyloin (IV) in boiling acetic anhydride[6,7] in the presence of certain dienophiles leads to adducts of the intermediate 1,3-diphenylisoindenone (I; R = Ph). Thus with *N*-phenylmaleimide as trap the adduct (V), m.p. 223—224°, is obtained. The assigned *endo*-configuration of the adduct follows from its n.m.r. spectrum where, as a result of shielding by the imide moiety,[6,7] two aromatic protons (H_a) appear at τ 3·5—3·8. Although (V) could conceivably arise by more than one route its formation from singlet 1,3-diphenylisoindenone (I; R = Ph) is indicated by the stereospecific additions observed in trapping experiments with dimethyl maleate and dimethyl fumarate.†

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† Although n.m.r. experiments indicated that 0·8% of the *cis*-adduct could be detected easily, no trace of this compound was seen in crude reaction mixtures from dimethyl fumarate addition.

When the acyloin (IV) is dehydrated in the absence of dienophiles, the dimer (VI) of 1,3-diphenylisoindenone is formed. Its mass spectrum shows $M - \mathrm{CO}$ and $M - 2\mathrm{CO}$ fragments as well as a pronounced $M/2$ peak. Thermal dissociation of (VI) provides a most convenient source of 1,3-diphenylisoindenone. Thus reaction of (VI) with dimethyl acetylenedicarboxylate in boiling xylene gives 2,3-bismethoxycarbonyl-1,4-diphenylnaphthalene in 85% yield. Under the same conditions, reaction of (VI) with *N*-phenylmaleimide gives the adduct (V) in 75% yield.

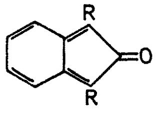
Chemical evidence for the structure (VI) was obtained by controlled photochemical decarbonylation to the ketone (VII), m.p. 269—270°. In deuteriochloroform the phenyl protons resonate at τ 2·4—2·8 and the phenylene protons at 3·0—3·4, indicating the *syn*-configuration for (VII). On brief heating at its m.p. (VII) is converted into the cyclo-octatetraene (VIII), m.p. 235—236°. Oxidation of (VIII) with chromium trioxide in acetic acid gives *o*-dibenzoylbenzene in quantitative yield. The dimer (VI) probably has the *anti*-configuration as the aromatic protons appear as one signal at τ 2·7.

The dimer (VI) is formed at room temperature by reduction of the dibromide (IX; R = Ph) with either sodium amalgam or copper powder. In neither of these experiments was the intermediate 1,3-diphenylisoindenone detected by the appearance of colour.

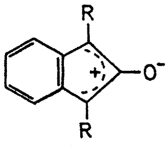
The easy dimerisation of 1,3-diphenylisoindenone and related *o*-quinonoid compounds[8,9] is surprising for both 4π-electron components must be used suprafacially.[10] To test the role of structure (II), a 2π-electron system,[11] in the dimerisation of (I; R = Ph), 1,3-diphenylisoindenone was generated by iodide reduction of the dibromide (IX; R = Ph) and trapped with cyclopentadiene. In addition to dimer (VI) only the *exo*- and *endo*-adducts‡ corresponding to structure (X; R = Ph) were obtained. 2,5-Dimethyl-3,4-diphenylcyclopentadienone reacted only as dienophile with 1,3-diphenylisoindenone generated by acetic anhydride dehydration of the acyloin (IV). The adduct (58% yield) had m.p. 230—232°. When generated by iodide reduction (I; R = Ph) fails to react with 1,3-diphenylisobenzofuran. Thus dimerisation is the only easy (4 + 4) cycloaddition of 1,3-diphenylisoindenone.

1,3-Dibromoisoindenone (I; R = Br) may be generated by iodide reduction of the tetrabromide (IX; R = Br) and trapped as the adduct (X; R = Br) with cyclopentadiene.

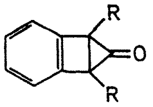
Iodide reduction of the dibromide (IX; R = H) in the presence of cyclopentadiene gives a poor yield of the iso-indenone adduct (X; R = H). The main product of this reaction is the adduct (X; R = I, R = H) derived from 1-iodoisoindenone.



(I)



(II)



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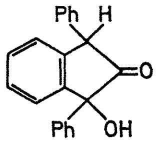
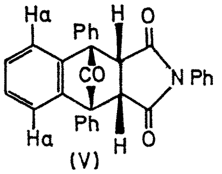
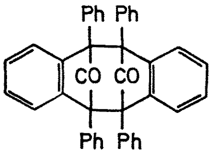


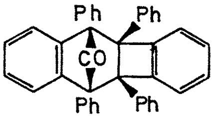
(IV)



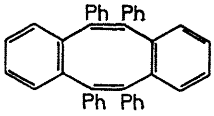
(V)



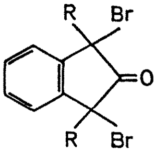
(VI)



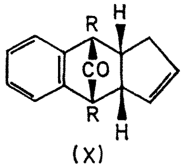
(VII)



(VIII)



(IX)



(X)

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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‡ The n.m.r. spectra of the adducts are closely similar to the spectra of the corresponding adducts obtained from 1,3-diphenyliso-benzofuran and cyclopentadiene.

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