3-Oxo-1,4-diphenyl-3*H*-2-benzopyran and its Iron Carbonyl Complexes

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WE report the novel reaction of 1,3-dihydroxy-1,3-diphenylindane-2-one (I) to give 3-oxo-1,4-diphenyl-3*H*-2-benzopyran (II), a new heterocycle related to *o*-quinodimethane. The iron carbonyl complexes of (II) are of interest in connection with the recently reported complex of *o*-quinodimethane.[1]

Reaction of ninhydrin dimethyl ketal[2] with phenylmagnesium bromide, followed by mild acid hydrolysis of the product affords the dihydroxy-ketone (I). The latter undergoes rearrangement on solution in sulphuric acid, and dilution with water gives a 70% yield of the pyrone (II), m.p. 182—183°, λ_{max} (CH_3CN) 474 mμ (ϵ 10,600), ν_{max} (Nujol) 1693 and 1625 cm.$^{-1}$ The n.m.r. spectrum shows the phenyl protons (τ 2·1—2·7), and the ring A protons (τ 2·7—3·3). The mass spectrum shows an intense $M - CO$ peak and subsequent fragmentation very similar to that observed for 1,3-diphenylisobenzofuran. The chemical properties of the pyrone are in accord with the proposed structure. Reaction with dimethyl acetylenedicarboxylate gives 2,3-dimethoxycarbonyl-1,4-diphenylnaphthalene,[3] and boiling with methanol, the *cis*- and *trans*-forms of the pseudo-ester (III; $R = OCH_3$). The structure (II) is confirmed by synthesis. Oxidation of 1,3-diphenylindene[4] (with chromic acid) and of 1-hydroxy-1,3-diphenylindane-2-one[5] (with lead tetra-acetate) gives the acid (IV) which on solution in sulphuric acid and dilution with water gives (II).† Reaction of the pyrone (II) with

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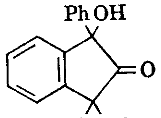
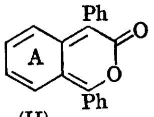
† The red substance, $C_{21}H_{14}O_2$ or $C_{28}H_{18}O_3$ described by Straus and Ehrenstein (ref. 4) is identical with (II).

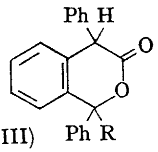
tri-iron dodecacarbonyl in boiling toluene gives two complexes in 50% yield. Both complexes, analyse as $C_{24}H_{14}FeO_5$, show ν_{max} (Nujol) *ca.* 2000 and 2060 cm^{-1}, and decompose at 200° to the pyrone (II). Thus both are iron tricarbonyl complexes of (II).



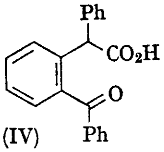
(I)



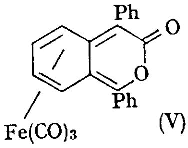
(II)



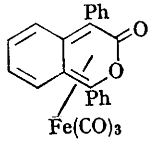
(III)



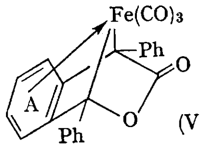
(IV)



(V)



(VI)



(VII)

The first complex, m.p. 191—193°, ν_{max} (Nujol) 1693 and 1630 $cm.^{-1}$, is assigned the structure (V). This accords with the n.m.r. spectrum which shows the phenyl protons (τ 2·3—2·8) and resonance at τ 4 (2H) and 6·2 (2H). Two structures may be written for the second complex with m.p. 182°. In addition to the π-bonded structure (VI), structure (VII) involving metal–ligand σ-bonds must be considered. Extreme valence-bond structures, such as (VI) and (VII) are both implicated in the molecular orbital description of certain diene–metal complexes.[6] The aromaticity of ring A should lead to an increased contribution from structure (VII). The properties of the complex are in accord with this prediction. The n.m.r. spectrum shows the presence of only "aromatic" protons (τ 2·0—2·8) and the i.r. spectrum (Nujol) absorption characteristic of a saturated δ-lactone at 1738 $cm.^{-1}$ The dihydro-derivative (III; R = H) shows ν_{max} (Nujol) at 1737 $cm.^{-1}$.‡ In addition the complex fails to react with tetracyanoethylene under the conditions employed for successful reaction of the dienophile with cyclo-octatetraene iron tricarbonyl.[7]

Although both complexes are stable at room temperature they undergo interconversion on brief heating in xylene solution. In the resulting mixture, complex (V) predominates.

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‡ The carbonyl absorptions of a series of $\alpha\beta$, $\gamma\delta$-unsaturated carbonyl compounds are unchanged in the corresponding iron carbonyl complexes (M. Cais and N. Maoz, *J. Organometallic Chem.*, 1966, **5**, 370).

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