Novel Dimerization of 2-Phenylindenone

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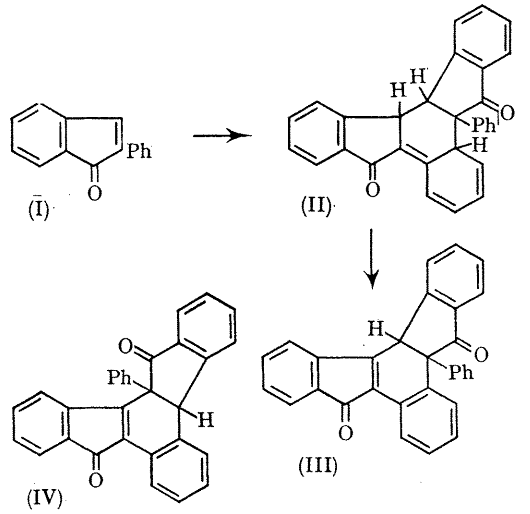
ATTEMPTED preparation of 2-phenylindenone (I) by the pyrolysis and basic dehydrohalogenation of 2-bromo-2-phenylindenone[1] or by the oxidation of 1-bromo-2-phenylindenone[2] with dimethyl sulphoxide gives instead 5a,14c-dihydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (III). Comparison with an authentic specimen, the molecular weight (410·13; mass spectroscopy), the n.m.r. spectrum, mono-oxime formation, and a blue colour with alkali supported the identity of the compound.



(I) (II) (III) (IV)

Formation of this compound (III) from 2-phenylindenone (I) occurs through a Diels–Alder reaction in which the 2-phenyl and the cyclopentene ring serve as a diene. The intermediate (II) was not isolated but undergoes dehydrogenation to compound (III).

The diketone (III) was obtained in highest yield (33%) by pyrolysis of 2-bromo-2-phenylindenone; it was accompanied by two other compounds (27%) with molecular formulae $C_{30}H_{18}O_2$ and $C_{30}H_{20}O_3$. The first of these is yellow, m.p. 243—245°, *M* 410 (mass spectroscopy) shows a non-aromatic proton at δ 3·55 in the n.m.r. in [$^2H_5$]-nitrobenzene in contrast to δ 4·83 for the diketone (III) and carbonyl absorptions at 1748 and 1700 cm.$^{-1}$ in the infrared region. These properties suggest that this compound is the second isomer possible from the Diels–Alder reaction, phenylbenz[*c*]indeno[1,2-*a*]fluorene-9,14,4b,13c-dihydro-13c-dione (IV).

The second compound is a pink solid, m.p. 324—326°, *M* 428 (mass spectroscopy) has a non-aromatic proton at δ 5·18 in its n.m.r. spectrum in [$^2H_5$]nitrobenzene and a carbonyl frequency at 1712 cm.$^{-1}$ in the i.r. region. No structural assignment for this compound has been made.

The dimerization of 2-phenylindenone (I) is novel when compared with the dimerization of indenone[4] and 3-phenylindenone,[5] both of which are reported to form truxones. N.m.r. spectra of the dimers for the latter are not in agreement with such a structure.

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