cis- and *trans*-Isomerism in 2-(1-Indanylidene)indan-1-one

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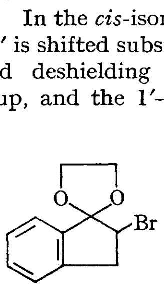
2-BROMOINDAN-1-ONE gives the ketal (I) when heated under reflux in benzene–ethylene glycol in the presence of toluene-*p*-sulphonic acid.[1] In contrast, indan-1-one undergoes self condensation. Evidence is presented here that the products isolated are the geometrical isomers, *trans*-2-(1-indanylidene)indan-1-one (II), and the corresponding *cis*-compound (III), not previously described.

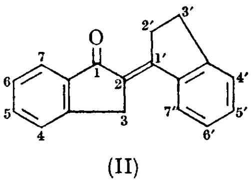
Column chromatography on silica of the crude reaction mixture from indan-1-one (5 g.) gave (*a*) compound (II) (3·10 g.); R_F 0·64 [t.l.c. on silica; benzene–ethyl acetate (9 : 1)]; yellow needles, m.p. 142·5—144·5° (lit.[1–3] 141—143°), from EtOH; i.r. (Nujol),[1,2] 1677 (carbonyl), 1610, and 1582 cm.$^{-1}$ (aromatic); u.v.[1,2] (EtOH) λ_{max} 239 mμ (ϵ 8200), 247 (8200), 344 (28,600); and (*b*) compound (III) (0·38 g.); R_F 0·75; yellow needles, m.p. 160—161°, from EtOH; i.r. (Nujol), 1668 (carbonyl), 1609, 1592, and 1557 cm.$^{-1}$ (aromatic); u.v. (EtOH); λ_{max} 344 mμ (ϵ 24,350) elemental analysis (C,H) corresponded to a molecular formula of $C_{18}H_{14}O$. The reduced ϵ value of the *cis*-compound (III) is accounted for by loss of conjugation arising from the lack of coplanarity of the two indane moieties (overlap of the carbonyl group and the C-7′ proton).

The suggested structure of each compound is supported by the n.m.r. results presented in the Table.

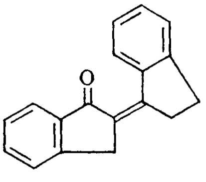
The aromatic protons at C-7 and C-7′ in the *trans*-isomer (II), and at C-7 in the *cis*-isomer (III) are shifted slightly downfield from the remaining aromatic protons, probably because of the in-plane deshielding effects of the carbonyl group, and the 1′–2 double bond on the C-7′ and C-7 protons respectively.[4] In the *cis*-isomer (III) the aromatic proton at C-7′ is shifted substantially downfield by the combined deshielding effects of both the carbonyl group, and the 1′–2 double bond. The



(I)



(II)



(III)

TABLE. τ *Values* (*deuterochloroform*)

	7′-H_1	7-H_1	4,4′,5,5′,6,6′-H_6	2′,3,3′-H_6
trans-(II)	2·10^m	2·10^m	2·45^m	6·00^s 6·40^t 6·80^t
cis-(III)	0·40^m	2·20^m	2·65^m	6·35^s 7·05^s

^{s} = Singlet; ^{t} = triplet; ^{m} = multiplet.

aliphatic proton region of the *trans*-isomer (II) is more complex than that of the *cis*-isomer (III). This complexity is thought to arise from long-range coupling[5] between the proton pairs at C-3, and C-2′; such coupling cannot occur in the *cis*-isomer.

When the *cis*-isomer (III) was heated for at least 3 hr. under reflux in benzene with toluene-*p*-sulphonic acid, an equilibrium was attained with almost complete conversion into the *trans*-isomer (II). Similarly, the *trans*-isomer (II) yielded an equilibrium mixture containing a small proportion of the *cis*-compound (III).

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