Acid-catalysed Photoisomerization of Alkylindens[1]

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Summary Irradiation of acidic solutions of indens containing an alkyl group at the 2-position results in the facile formation of 2-alkylideneindans

RECENT investigations of the photochemistry of substituted indens have revealed two modes of isomerization, one involving the [1,5] shift of an aromatic ring[2] and the other resulting in the transposition of C-1 and C-2[3] We report here a third photoisomerization, the acid-catalysed transformation [$h\nu$(254 nm), *ca* 0·01 M inden, MeCN (non-degassed), 0·01 M HCl] of 2-alkylindens into 2-alkylideneindans The reaction is illustrated in equations (1) and (2) (the yields shown were determined by v p c using internal standards).

A more general survey of the scope of this novel reaction is presented in the Table Though the quantum efficiencies (ϕ) are generally *ca* 0·1, note that alkyl substitution at the 3-position markedly inhibits the reaction (as it does to the previously reported C-6–C-2 phototransposition)[3a] There is also a striking effect by substituents on the aromatic ring, with the 6-methoxy-group and 5-trifluoromethyl group appreciably lowering the quantum efficiency

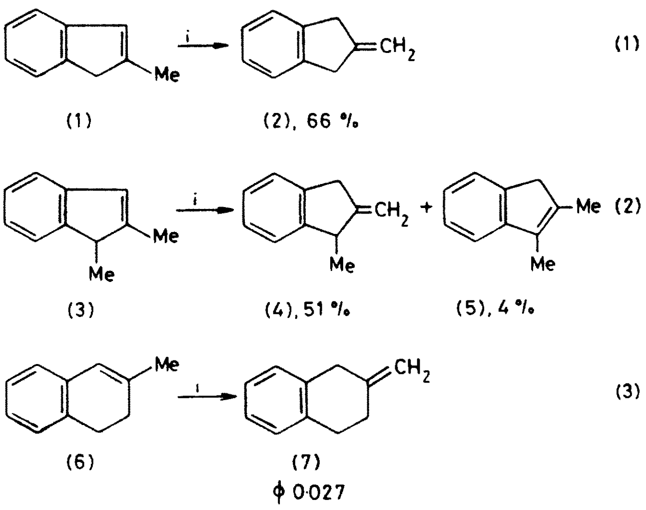
The reaction is not unique to the inden series, the dihydronaphthalene (**6**) also isomerizes under the same

TABLE Quantum efficiencies for the formation of *exo*-cyclic olefins.[a]

Reactant	Product	ϕ Product
(1)	**(2)**	0·13
(3)	**(4)**	0·10
2,3-Dimethylinden	**(4)**	0·019
2-Ethyl-1-methylinden	2-Ethylidene-1-methylindan (*E* + *Z*)	0·087
3-Ethyl-2-methylinden	1-Ethyl-2-methyleneindan	0·03
5-Methoxy-2-methylinden	5-Methoxy-2-methyleneindan	0·12
6-Methoxy-2-methylinden	,,	0·004
5-Trifluoromethyl-2-methylinden	5-Trifluoromethyl-2-methyleneindan	<0·01
6-Trifluoromethyl-2-methylinden	,,	0·085

[a] Determined at 24 ± 2 °C using 254 nm light on *ca* 0·01 M solutions of the inden in non-degassed acetonitrile containing 0·01 M HCl.

photolysis conditions [equation (3)]. However, no comparable double bond migration is observed for 2-methyl-1-phenylpropene.



(1) (2), 66 %

(3) (4), 51 % (5), 4 %

(6) (7) ϕ 0·027

i, *hν* (254 nm), MeCN, 0·01 M HCl.

Though the inden isomerization superficially resembles the photoinduced, acid-catalysed endo- to exo-cyclic olefin migrations of cyclohexenes,[4] these latter reactions proceed *via* a *trans*-cycloalkene not observable in 5-membered ring systems. [Such a mechanism cannot be eliminated for reaction (3), but the direction of the requisite protonation and the lack of 1,4-dihydronaphthalene as a product argue against a *trans*-cycloalkene intermediate.] Isomerization of the indens proceeds *via* the excited singlet-state (triplet sensitization only gives dimers) and involves protonation at C-3 [photolysis of (**1**) with DCl results in the incorporation of one deuterium atom at the benzylic position of (**2**)]. Trifluoroacetic acid also catalyses the reaction, but perchloric and sulphuric acids are ineffective. The acid is interacting with an intermediate other than the excited singlet-state since fluorescence is *not* affected by HCl. Acid-catalysed olefin-migration is accompanied by a corresponding quenching of the inden phototransposition. A detailed discussion of the mechanism of this interesting double bond migration and its relationship to the transposition will be presented in a full paper.

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