

Photocyclisation of 2-(*o*-Methoxyaryl)-3-methylcyclohex-2-enones with Elimination of the *ortho*-Methoxy-group

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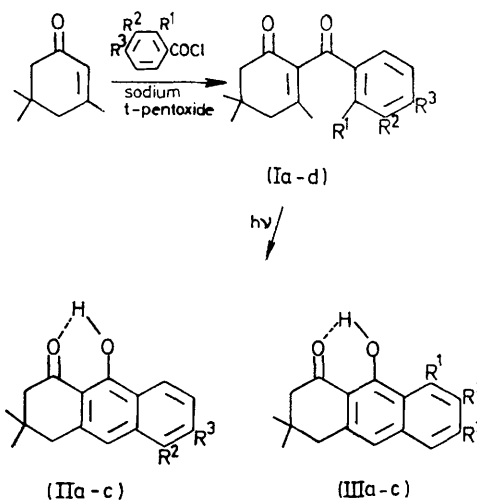
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Summary Irradiation of 2-(*o*-methoxyaryl)-3-methylcyclohex-2-enones results in a nonoxidative intramolecular cyclisation and simultaneous demethoxylation to give 9-hydroxy-3,4-dihydroanthracen-1(2*H*)-ones.

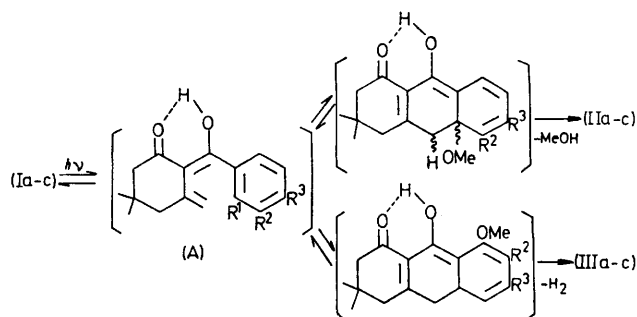
7.24 (s, 2H, CH₂), 7.53 (s, 2H, CH₂), and 8.98 (s, 6H, Me₂); λ_{max} (EtOH) (log ϵ), 259 (4.18), 267 (4.20), 286 (3.54), and 297 nm (3.57); ν_{max} (CHCl₃) 1620, 1600, and 1570 cm⁻¹, *m/e*

ELIMINATION of the *ortho*-substituted methoxy-group during the photocyclisation of benzanilides, which is thought to be characteristic of the anilide system, has recently been demonstrated.¹ However, similar behaviour has not been reported in the stilbene system,²⁻⁴ although elimination of *ortho*-substituted methyl and halogeno-groups is known.^{2a,3} In connection with a study on photochemistry of 3-substituted cyclohex-2-enones,⁵ we found that irradiation of the 2-aryl-3-methylcyclohex-2-enones (Ia-c) caused photocyclisation and simultaneous elimination of the *ortho*-methoxy-group.

Compounds (Ia-d) were synthesised in moderate yield by treating isophorone with aryl chloride in the presence of sodium *t*-pentoxide in benzene. Irradiation of a 0.4% degassed ether solution of (Id) with a 350 W high-pressure mercury lamp in a sealed quartz vessel for 40 h afforded the ketone (IIa) [green fluorescent crystals, m.p. 97–98°; τ (CDCl₃) -4.04 (s, 1H, OH), 1.57–3.03 (m, 5H, ArH),



240 (M^+)]. When (Ia) was irradiated similarly, cyclisation with simultaneous elimination of the *ortho*-methoxy-group took place to give (IIa) and a small amount of compound (IIIa) [m.p. 149—150°; τ (CDCl_3) —5.10 (s, 1H, OH), 2.38—3.28 (m, 4H, ArH), 6.01 (s, 3H, OMe), 7.22 (s, 2H, CH_2), 7.48 (s, 2H,



SCHEME

CH_2), and 8.97 (s, 6H, Me_2), ν_{max} (CHCl_3) 1625, 1610, and 1578 cm^{-1}]. This demethoxycyclisation was also observed with compounds (Ib and c) which gave compounds (IIb), m.p. 153—154°, and (IIc), m.p. 159—160°, together with a small amount of compounds (IIIb and c). Irradiation of (Ia—d) with oxygen bubbling through the ether solution decreased the yield of cyclisation products and gave many byproducts (t.l.c.). The results are summarised in the Table.

We suggest that compounds (IIa—c) and (IIIa—c) are formed from (Ia—c) by the mechanism in the Scheme, the enone (I) undergoing reversible photoenolisation to the enol (A) which is cyclised by a nonoxidative mechanism¹ and

TABLE
M.p.
($t/^\circ\text{C}$) of
(I)

	Conditions	% of (II)	% of (I)	
a	R ¹ =OMe, R ² =R ³ =H	122—123° Degassed O ₂	51 17	30 22
b	R ¹ =R ² =OMe, R ³ =H	101—102° Degassed	35	35
c	R ¹ =R ² =OMe, R ³ =H	115—116° "	15	47
d	R ¹ =R ² =R ³ =H	102—103° O ₂	30 19	36 23

the *ortho*-methoxy-group accelerating the aromatisation step to (IIa—c). It has been reported that irradiation of 2-methylbenzophenone, which is an aromatic analogue of (A), caused cyclisation^{6—8} through photoenolisation.⁹ However, the yield of the anthracenone produced was only 1% on oxygen flashing the solution previously irradiated.⁶ The cyclisation of the photo-enol (A) might occur more readily than that of 2-methylbenzophenone because the loss of resonance stabilisation of enolisation in (Ia—c) is less than in 2-methylbenzophenone, or because the enol (A) is readily formed owing to stabilisation by intramolecular hydrogen bonding.

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