Synthesis of Model Aryltetralin Lignans: Adducts of o-Methylbenzophenone with Unsymmetrical Dienophiles

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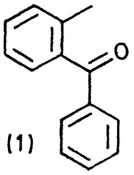
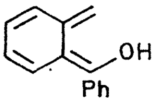
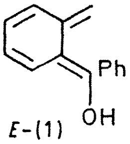
Summary Photoirradiation of *o*-methylbenzophenone in the presence of unsymmetrical dienophiles yields aryltetralin adducts of defined configuration and structurally related to natural lignans.

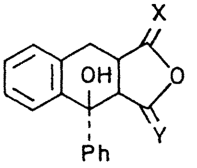
SINCE the demonstration[1] that some *o*-alkylbenzophenones may undergo photoenolization, there has been considerable interest in the mechanism of formation and nature of transient intermediates.[2–5] Recently, evidence for the formation of both enols *Z*-(**1**) and *E*-(**1**) from (**1**) has been provided, the former being shorter lived in aprotic solvents owing to internal ketonization.[3b] Chemical evidence for the longer lived enol *E*-(**1**) exists from the structure of the product (**2**) obtained by irradiation of (**1**) in the presence of maleic anhydride.[6]

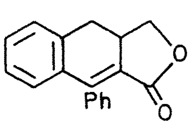
There has been little exploitation of this reaction in synthesis,[6,7] and only symmetrical dienophiles have been used as Diels–Alder traps of the photoenols. The synthesis of lignans of the arylnaphthalene (*e.g.* helioxanthin[8]), aryldihydronaphthalene (*e.g.* collinusin[9]), and aryltetralin (*e.g.* otobain[10]) classes prompted a study with particular regard to stereospecific lactone formation. We have found

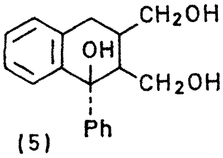

(1)

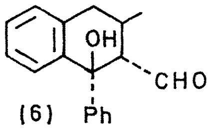

Z-(1)

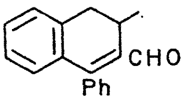

E-(1)

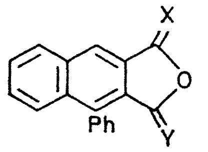

(2) X = Y = O
(3a) X = H_2, Y = O
(3b) X = O, Y = H_2


(4)


(5)


(6)


(7)


(8a) X = H_2, Y = O
(8b) X = O, Y = H_2

that when *o*-methylbenzophenone (**1**) is irradiated (Hanovia 8A-1 high-pressure lamp, Pyrex filter) in benzene under reflux with 4-hydroxybut-2-enoic acid lactone[11] (an unsymmetrical dienophile previously reported as rather unreactive[12]) the only isolated product (50% yield) was an adduct, m.p. 144—145° to which we attribute the structure (**3a**) (i.r. and n.m.r. spectra). Chemical evidence, excluding structure (**3b**), was obtained by treatment of the adduct with hydrochloric acid in methanol to effect rapid and quantitative dehydration to the known aryldihydronaphthalene lactone (**4**).[13] The relative configurations at the three asymmetric carbon atoms were established by reduction of the adduct with lithium aluminium hydride to yield a triol (**5**), m.p. 132—136°, identical with that obtained by similar reduction of the anhydride (**2**) of established stereochemistry.[6] The same carbonyl orientation in adduct formation was observed in irradiation of (**1**) in the presence of the unsymmetrical and *trans*-dienophile, crotonaldehyde, to give as the sole isolated product (27%) the aldehyde (**6**), m.p. 156—157°, which also was readily dehydrated by heating with florisil in benzene, to yield the conjugated aldehyde (**7**), m.p. 115—116°, ν_{max} (KBr) 1656 cm^{-1}.

With regard to general aspects of lignan synthesis, 1-hydroxyphenyltetralins are readily aromatized to phenylnaphthalenes [*e.g.* (**3a**) → (**4**) → (**8a**)], and lactones of type (**8a**) can be conveniently converted into the isomeric lactones (**8b**) by reduction with lithium aluminium hydride followed by silver carbonate–Celite oxidation.[8]

Satisfactory elemental analyses were obtained for all compounds.

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