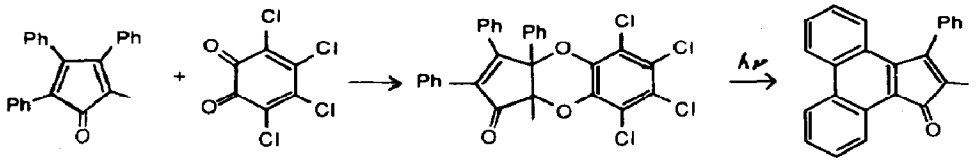
Organic Photochemical Synthesis

2-Methyl-3-phenyl-1*H*-cyclopenta[*l*]phenanthren-1-one



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1. Procedure

1.1. 5,6,7,8-Tetrachloro-3a,9a-dihydro-9a-methyl-2,3,3a-triphenylcyclopentadieno[1,2-b][1,4]benzodioxin-1-one

2-Methyl-3,4,5-triphenylcyclopentadienone (3.22 g, 0.01 mol) (note 1) and tetrachloro-1,2-benzoquinone (4.97 g, 0.02 mol) are intimately mixed and placed in a 100 ml flask which has been previously flushed with nitrogen. The mixture is heated under nitrogen in an oil bath at 170 - 180 °C for 10 min. During this time the compounds melt, lighten in colour and resolidify. The flask is removed from the oil bath and allowed to cool. The solid, an orange glass, is dissolved in the minimum amount of hot benzene, and petroleum ether (boiling point, 60 - 80 °C) is added until crystallization begins. The pale yellow material so obtained is recrystallized from cyclohexane as pale yellow needles (4.5 g, 78%) (melting point, 203 - 205 °C; ν_{max}(Nujol), 1720 cm^{-1}).

1.2. 2-Methyl-3-phenyl-1H-cyclopenta[l]phenanthren-1-one

The dioxinone (1.0 g, 0.0018 mol) from the above procedure is dissolved in propan-2-ol (500 ml), and the solution is flushed with nitrogen for 45 min prior to irradiation of the solution in an immersion apparatus with a Pyrex filter (note 2). During the 5 h irradiation (note 3) the solution, kept under an atmosphere of nitrogen, changes colour from pale yellow to red. The solvent is then removed under vacuum, and the red residue is chromatographed on alumina (20 g). Benzene elutes a red band. The solid from this is crystallized from benzene–(petroleum ether) (boiling point, 60 - 80 °C) to give 2-methyl-3-phenyl-1*H*-cyclopenta[*l*]phenanthren-1-one (0.28 g, 49%) (melting point, 166 - 168 °C; ν_{max}(Nujol), 1690 cm^{-1}).

2. Notes

(1) 2-Methyl-3,4,5-triphenylcyclopentadienone is prepared by the base-catalysed condensation of benzil and 1-phenylbutan-2-one [1].

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(2) The photolysis apparatus used is a conventional immersion apparatus with a Pyrex immersion well surrounding a 450 W medium pressure mercury arc lamp.

(3) The progress of the reaction can be monitored easily by thin layer chromatography (alumina, benzene).

3. Merits of the preparation

The free methyltriphenylcyclopentadienone does not undergo photocyclization to give the cyclopentaphenanthrenone; the benzodioxin acts as an activating group, and then is removed in the photolysis. The route can be adapted for the synthesis of other cyclopentaphenanthrenones by using a different triarylcyclopentadienone or tetraarylcyclopentadienone [2].

1 C. F. H. Allen and J. Z. van Allan, *J. Am. Chem. Soc.*, *72* (1950) 5165.
2 W. M. Horspool, *J. Chem. Soc. C*, (1971) 400.

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