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ESTABLISHMENT OF THE COUPLING POSITION IN 1-INDENYLIDENETRIPHENYLPHOSPHORANE FOR FORMATION OF AZO AND PHOSPHOCYANINE DYES

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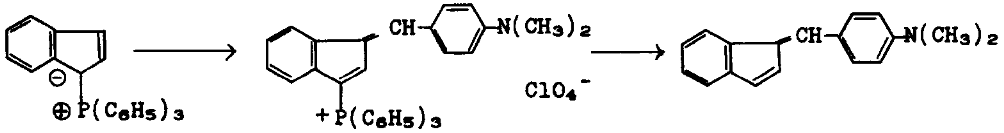
Crofts and Williamson[1] have described the synthesis of 1-indenylidenetriphenylphosphorane (I) and the reaction of this hydrolytically stable phosphorus ylide with diazonium salts to give azo dyes. They were uncertain about the location of the coupling site in I. Work on I in this laboratory has shown that it reacts with cyanine intermediates to form phosphocyanines as does cyclopentadienylidenetriphenylphosphorane[2] and has established the position in I both for cyanine and for azo coupling.

Heating stoichiometric quantities of I, triethyl orthoformate, and sodium perchlorate to the boiling point in pyridine containing a trace of glacial acetic acid, cooling, dilution with water, and recrystallization of the separated solid from chlorobenzene gave a 26% yield of [3-(1-indenylidenetriphenylphosphorane)]-[1-(3-indenyltriphenylphosphonium)]monomethinephosphinine perchlorate, dark red crystals which lost chlorobenzene at 130-133°, resolidified, and decomposed at 250-253°. [Calc'd. for $C_{55}H_{41}ClO_4P_2\cdot 2C_6H_5Cl$: C, 73.8; H, 4.68; Cl, 9.79; P, 5.70. Found: C, 73.8; H, 4.4; Cl, 9.9; P, 5.3. $\lambda_{max}^{CHCl_3}$ (log ε) 557 mμ (4.85), 585 mμ (4.82).] Similar treatment of I and sodium perchlorate with three moles of p-dimethylaminobenzaldehyde gave a 26% yield of 1-p-dimethylaminobenzylidene-3-indenyltriphenylphosphonium perchlorate (II), green crystals which lost chlorobenzene at 124-130° and decomposed at 244-247° [Calc'd. for $C_{36}H_{31}ClNO_4P$: C, 71.2; H, 5.11; Cl, 5.84; N, 2.30. Found (dried at 110° for 30 hr): C, 71.6; H, 5.0; Cl, 5.6; N, 2.2. $\lambda_{max}^{CHCl_3}$ (log ε) 535 mμ (4.74).]

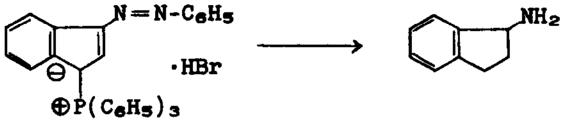
Hydrolysis of II for 6 hr with excess potassium hydroxide in boiling aqueous ethanol, concentration under vacuum, and chromatography of the benzenesoluble portion of the residue on silica gel gave 1-p-dimethylaminobenzylideneindene (III) (28% yield), mp and mmp with an authentic sample[3] 160-161.5°, and triphenylphosphine oxide (21% yield), mp 154-156°.

Hydrogenation of the hydrobromide of phenylazoindenylidenetriphenylphosphorane (IV) in methanol containing platinum oxide gave aniline, triphenylphosphine, and a small amount of 1-indanamine (V), which was isolated by V.P.C. and identified by mass spectral comparison with an authentic sample.[4]

The degradations of II to III and of IV to V show that the reactive position in 1-indenylidenetriphenylphosphorane is at C_3.



I II III



IV V

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