

39. Rapid Syntheses of Hexa and Heptahelicene¹⁾

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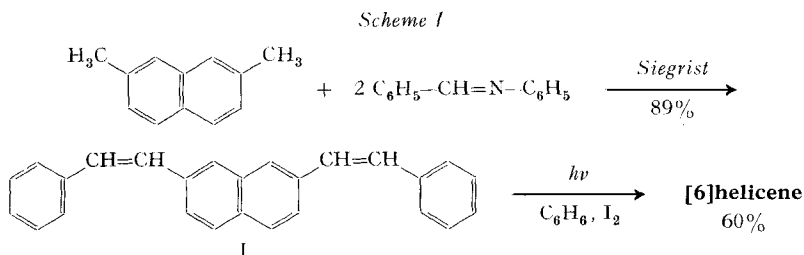
(31. XII. 70)

Summary. A two-step synthesis of hexahelicene (scheme 1; 53% over-all yield), a three-step synthesis of hexahelicene (scheme 2; 33% over-all yield), and a two-step synthesis of heptahelicene (scheme 3; 14% over-all yield) are described.

The successful double photocyclisation leading to tridecahelicene in 52% yield [2], incited us to adopt similar schemes for the preparation of hexa and heptahelicene.

The new syntheses reported in this communication are exceedingly short and simple. The required substituted ethylenes are obtained either by the *Wittig* reaction or, from methyl substituted benzenoid hydrocarbons, by the *Siegrist* 'Anil synthesis' [3].

1. *Two-step synthesis of hexahelicene: scheme 1.* Hexahelicene can be prepared in a few days from 2,7-dimethylnaphthalene *via* a *Siegrist* reaction giving 2,7-distyryl-



naphthalene (I) (89%) followed by a double photocyclisation of I (60%). Over-all yield: 53%.

In view of the present scarcity of 2,7-dimethylnaphthalene, we have carried out another synthesis of hexahelicene using readily available reagents (cf. scheme 2).

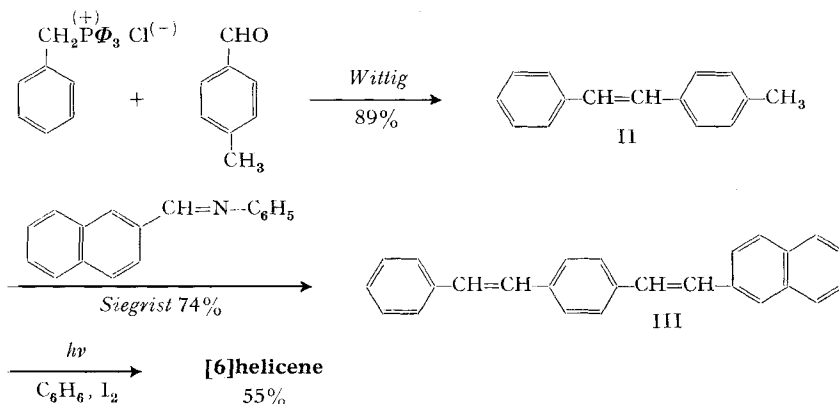
2. *Three-step synthesis of hexahelicene: scheme 2.* 4-Methylstilbene (*cis* + *trans* II), prepared by a *Wittig* reaction (89%), is condensed with N-(2-naphthylmethylene)-aniline (*Siegrist* reaction, 74%) and the reaction product (III) is submitted to a double photocyclisation (55%) to give hexahelicene in 33% over-all yield. Hexahelicene can thus be prepared, in reasonable yield, from benzyl chloride, *p*-tolualdehyde, 2-naphthaldehyde and aniline.

¹⁾ Part XXXI of 'Syntheses in the field of polycyclic aromatic compounds'; part XXX, see [1].

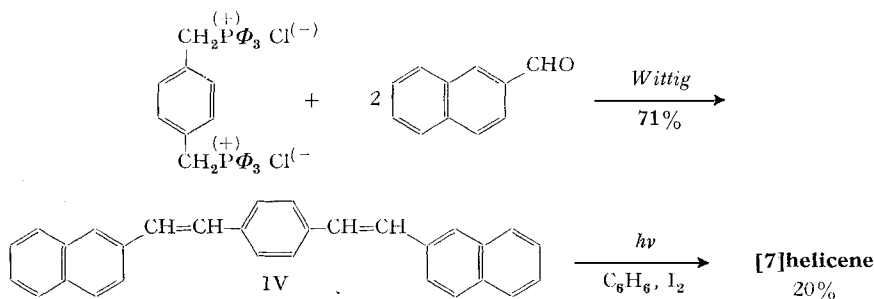
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Scheme 2



Scheme 3



3. *Two-step synthesis of heptahelicene: scheme 3.* The double photocyclisation of 1,4-bis-(2-naphthylvinyl)-benzene (IV), prepared by a double *Wittig* reaction from *p*-xylylene dichloride and 2-naphthaldehyde (71%) [4], gives a mixture of heptahelicene (20%) and dinaphtho[1,2-*a*; 1',2'-*h*]anthracene (20%).

Heptahelicene can thus be synthesised in 14% over-all yield starting from *p*-xylylene dichloride and 2-naphthaldehyde.

An attempt to prepare the intermediate 1,4-bis-(2-naphthylvinyl)-benzene by a double *Siegrist* condensation between *p*-xylene and N-(2-naphthylmethylene)-aniline failed.

Experimental. – 1. *Scheme 1.* – 1.1. *2,7-Distyrylnaphthalene (I).* 3.95 g (25 mmoles) of 2,7-dimethylnaphthalene dissolved in 100 ml of dimethylformamide (freshly distilled over calcium hydride) and 8.95 g (50 mmoles) of N-benzylidene-aniline in 100 ml of anhydrous dimethylformamide are added successively (dropwise), with vigorous stirring and under dry nitrogen, to 11.2 g (100 mmoles) of potassium *t*-butoxide. The mixture is heated progressively to 90–95° and this temperature is maintained constant for one hour. The red mixture is then cooled to 10°, and water (150 ml) and 10% HCl (150 ml) are added successively (dropwise). The yellow precipitate is filtered, washed with methanol (200 ml) and dried under vacuum. Light yellow powder: 8.3 g (98% yield). One crystallisation from dioxan affords 7.5 g (89%) of pure 2,7-distyrylnaphthalene. White crystals, m. p. 260–261°. Mass spectrum: molecular ion *m/e* 332.

$\text{C}_{26}\text{H}_{20}$ (332.4) Calc. C 93.94 H 6.06% Found C 93.5 H 6.1%

1.2. *Hexahelicene: double photocyclisation of I*. A solution of 0.2 g (0.6 mmole) of 2,7-distyryl-naphthalene (I) in 1000 ml of benzene containing 6 mg (0.024 mmole) of iodine is irradiated at room temperature in a pyrex reactor (stirring) with an *Hanovia* 450 W medium pressure mercury lamp for $1\frac{3}{4}$ hour. The reaction product is chromatographed on alumina (petroleum ether, b.p. 60–70°). Hexahelicene (first pale fluorescent fraction) is then crystallised from petroleum ether (b.p. 60–70°). Pale yellow crystals, m.p. 240–242°, 120 mg (60%).

2. *Scheme 2*. – 2.1. *4-Methylstilbene (II)*. A Wittig reaction between *p*-tolualdehyde and triphenylbenzylphosphonium chloride carried out in absolute methanol in the presence of lithium methoxide gave a mixture of *cis* + *trans* 4-methylstilbene in 89% yield.

This hydrocarbon (*cis* + *trans* mixture) had previously been prepared by *Schlosser & Christmann*, in 88% yield, by the 'salt free ylid Wittig reaction' [5].

2.2. *1-Styryl-4-(2-naphthylvinyl)-benzene (III)*. For the condensation of 4-methylstilbene (II) with N-(2-naphthylmethylene)-aniline [3c], potassium *t*-butoxide was used instead of potassium hydroxide. Yield: 74%, m.p. 268–268.5° (Litt.: 71%, m.p. 266–267°).

2.3. *Hexahelicene: double photocyclisation of III*. The photocyclisation of 1-styryl-4-(2-naphthylvinyl)-benzene (III) was carried out as described above, but for the temperature of the solution which was kept near boiling point during irradiation ($1\frac{1}{2}$ hour). Hexahelicene, purified by chromatography, was isolated in 55% yield.

The yield remained unchanged when the photolysis was prolonged to $2\frac{1}{2}$ hours.

3. *Scheme 3*. – *Heptahelicene: double photocyclisation of IV*. A boiling solution of 150 mg of 1,4-bis-(2-naphthylvinyl)-benzene (IV) [4] (m.p. 328–329°, from 1-methylnaphthalene) in 5 l of benzene containing 6 mg of iodine is irradiated (pyrex well, *Hanovia* 450 W medium pressure mercury lamp) for 1 hour. The solvent is distilled and the reaction product chromatographed on alumina (petroleum ether, b.p. 60–70°).

First fraction (weak bluish-green fluorescence): heptahelicene, m.p. 254–255°, 20% yield.

Second fraction (blue fluorescence): dinaphto[1,2-*a*; 1'2'-*h*] anthracene, m.p. 230–231°, 20% yield.

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