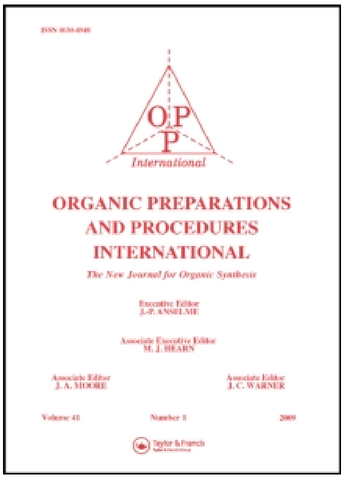

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SYNTHESIS OF 9-(P-VINYLPHENYL)-ANTHRACENE

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SYNTHESIS OF 9-(p-VINYLPHENYL)-ANTHRACENE

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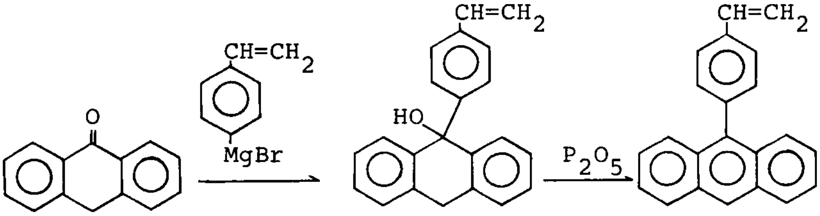
As a part of our research on organic photoconductive polymers, we synthesized a new monomer, 9-(p-vinylphenyl)-anthracene (II), via 9-(p-vinylphenyl)-9-hydroxy-9,10-dihydroanthracene (I). The later compound was prepared by applying the arylation of anthrone by a Grignard reagent.[1]



I II

Dehydration of I with P_2O_5 gave crude II, which was purified by chromatography (13% yield from anthrone). The purification of I was difficult because I tends to change to II during recrystallization. Direct treatment of the crude product from the coupling reaction of anthrone and p-vinylphenyl magnesium bromide with P_2O_5 followed by chromatography, gave

II a 37% yield from anthrone. Compound II polymerizes in solution by an initiator to give a photoconductive polymer. Studies on the polymerization will be published in future.

EXPERIMENTAL

Melting points are uncorrected. Shimazu IR-27B and Hitachi 124 spectrophotometers, and a Hitachi H-60 nmr spectrometer were used.

9-(p-Vinylphenyl)-9-hydroxy-9,10-dihydroanthracene.-To the Grignard reagent[2] prepared from p-bromostyrene[3] (2.75 g, 0.0150 mole) and Mg (0.37 g, 0.0152 g-atom) in boiling THF (16 ml) was added anthrone (2.91 g, 0.0150 mole) in THF (60 ml). After a reflux period of 3 hrs., 1.5 M HCl (24 ml) and diethyl ether (150 ml) were added to the mixture. The ether layer was separated, washed with water and dried over anhydrous sodium sulfate. The yellow residue obtained after removal of the solvent was extracted with methanol (60 ml). The extract was concentrated to one half its original volume and the resulting precipitate was removed. Crude I could be precipitated from the further concentrating of the methanol solution (about 15 ml) by cooling in ice. One recrystallization from petroleum ether (bp. 60-80°)-benzene (9:1) and twice from petroleum ether gave 1.12 g (25%) of I, mp. 132-135°.
IR(KBr, cm^{-1}): 3300 and 1150 (-OH), 907 and 990 (styrene type vinyl).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.16; H, 6.74.

9-(p-Vinylphenyl)-anthracene.-(a) About 1 g of P_2O_5 was added to the solution of I (1.12 g) in CCl_4 (22 ml). The mixture was stirred overnight at room temperature and then diluted with diethyl ether. The ethereal solution was washed with water and dried. After removal of the ether, the residue was chromatographed on a silica gel column (2.5 x 30 cm), and was eluted with petroleum ether (400 ml) and then petroleum ether-benzene (9:1). Fractions with blue fluorescence by uv irradiation (366 nm) were combined and concentrated. Recrystallization from petroleum ether-benzene (5:1) gave 0.75 g (71%) of II, mp. 166-168°.

IR(KBr, cm^{-1}): 910 and 995 (styrene type vinyl).

UV, λ_{max}(log ε): 258 (5.01), 332 (3.26), 349 (3.60), 367 (3.84), and 387 nm (3.79) in dichloromethane. 256 (5.06), 331 (3.32), 348 (3.67), 365 (3.84), and 384 nm (3.81) in ethanol.

NMR($CDCl_3$, δ): 6.90 (dd, 1H), 5.82 (d, 1H), 5.31 (d, 1H), and 8.42 (s, 1H).

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.21; H, 5.56.

(b) p-Bromostyrene (25.6 g, 0.140 mole), Mg (3.44 g, 0.141 g-atom), and anthrone (27.0 g, 0.140 mole) were allowed to react as described above. The ethereal extract was concentrated until crystals began to appear. Methanol (50 ml) was added and the resulting precipitate was removed. The solvent was evaporated and the residue was treated with P_2O_5 (about 10 g) in benzene (500 ml) as before. After chromatography (using a 3 x 130 cm column), the product (15.6 g) was recrystallized from petroleum ether-benzene (8:5) yielding 14.4 g (37%) of II, mp. 166-168°.

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