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SYNTHESIS OF 2-ARYL-1,5-DIHYDRO-1-AZAPYRENE DERIVATIVES

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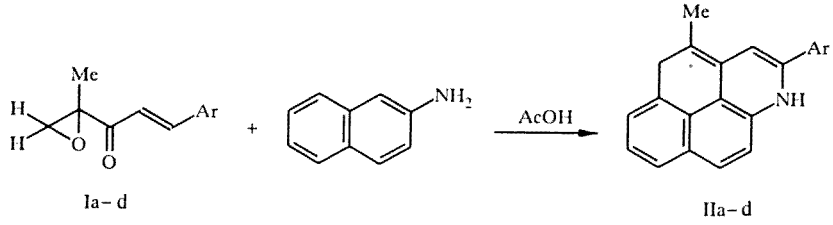
Aliphatic amines react with epoxyenones to give 3-hydroxy-4-piperidinones or 3-hydroxy-3-acetylpyrrolidones [1]. Depending on the solvent, the amine adduct is formed either at the double bond or epoxide ring (as a result of its opening) in the first step [2]. Aniline behaves similarly under the conditions of this reaction [3]. We have found that the reaction of epoxyenones Ia-Id with β-naphthalene in acetic acid proceeds further and gives only 2-aryl-1,5-dihydro-1-azapyrenes. The proposed mechanism for the formation of these compounds involves addition of the amine at the epoxyenone double bond and subsequent condensation–alkylation of the naphthylamine fragment involving the carbonyl group and epoxide ring.



Ia–d IIa–d

I, II a Ar = Ph, b Ar = *p*-MeC_6H_4, c Ar = *p*-$EtOC_6H_4$, d Ar = *p*-ClC_6H_4

4-Methyl-2-(*p*-ethoxyphenyl)-1,5-dihydro-1-azapyrene (IIc). A sample of 2.86 g (0.02 mole) β-naphthylamine was added to a solution of 4.64 g (0.02 mole) Ic in 30 ml acetic acid in an argon atmosphere. The mixture was maintained at room temperature for 48 h. The crystalline precipitate of azapyrene IIc was filtered off, washed with 2-propanol, and dried. The yield of IIa was 7.30 g (95%), mp 177-178°C. IR spectrum: 3430 cm^{-1} (N–H). PMR spectrum (in $CDCl_3$): 1.25 (3H, t, $\underline{CH_3}CH_2$, J = 7.0 Hz), 1.33 (3H, s, 4-Me), 3.40 (2H, s, ring CH_2), 3.92 (2H, q, $CH_3\underline{CH_2}$, J = 7.0 Hz), 6.14 (2H, m, H_{arom}), 6.86 (3H, m, H_{arom}), 7.30 (4H, m, H_{arom}), 8.20 ppm (1H, m, H_{arom}).

Products IIa, IIb, and IId were obtained by analogous procedures.

4-Methyl-2-phenyl-1,5-dihydro-1-azapyrene (IIa) was obtained in 91% yield, mp 184-185°C. IR spectrum: 3430 cm^{-1} (N–H). PMR spectrum (in $CDCl_3$): 1.33 (3H, s, 4-Me), 3.40 (2H, s, ring CH_2), 6.07 (2H, br.s, H_{arom}), 6.67 (1H, d, J = 8.0 Hz, H_{arom}), 7.28 (6H, m, H_{arom}), 8.20 ppm (1H, m, H_{arom}).

4-Methyl-2-(*p*-methylphenyl)-1,5-dihydro-1-azapyrene (IIb) was obtained in 93% yield, mp 152-153°C. IR spectrum: 3430 cm^{-1} (N–H). PMR spectrum ($CDCl_3$): 1.30 (3H, s, 4-Me), 2.16 (3H, s, Me_{Ar}), 3.36 (2H, s, ring CH_2), 6.04 (2H, br.s, H_{arom}), 6.64 (3H, m, H_{arom}), 7.06 (4H, m, H_{arom}), 8.20 ppm (1H, m, H_{arom}).

4-Methyl-2-(*p*-chlorophenyl)-1,5-dihydro-1-azapyrene (IId) was obtained in 96% yield, mp 176-177°C. IR spectrum: 3430 cm^{-1} (N–H). PMR spectrum ($CDCl_3$): 1.33 (3H, s, 4-Me), 3.36 (2H, s, ring CH_2), 6.00 (2H, m, H_{arom}), 6.57 (1H, d, J = 8.6 Hz, H_{arom}), 7.16 (6H, m, H_{arom}), 8.16 ppm (1H, m, H_{arom}).

The elemental analysis data were in accord with the calculated data.

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