REACTION OF o-AMINOPHENYLDIPHENYLCARBINOL WITH UNSATURATED ALDEHYDES

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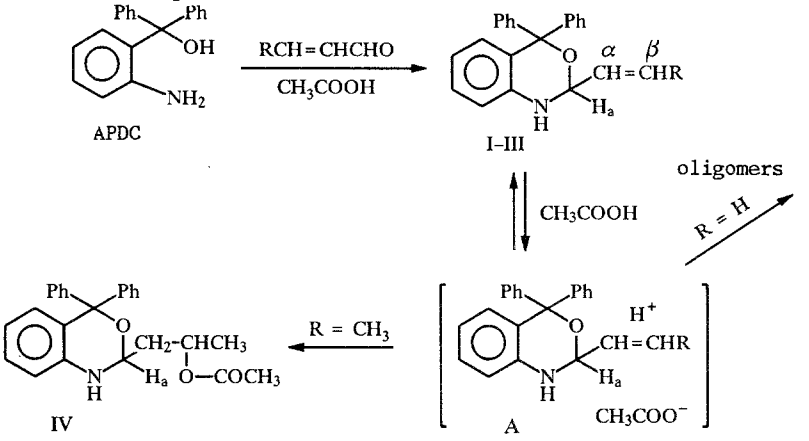
It is known that the condensation of o-aminophenyldiphenylcarbinol (APDC) with carbonyl compounds in acetic acid at 5°C leads to substituted 1,2-dihydro-4H-3,1-benzoxazines [1, 2]. We established that under conditions of the method [1] the reaction of APDC with acrolein is accompanied by cationic polymerization of 2-vinyl-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (I) with the formation of oligomers, and with crotonic and cinnamic aldehydes to give the corresponding dihydrobenzoxazines (II and III). Increasing the temperature of the reaction mixture from 5 to 20°C for an hour leads to the addition of acetic acid to compound II with the formation of the product IV.



I R = H, II R = CH_3, III R = C_6H_5

Differences in the behavior of the dihydrobenzoxazines I-III in acetic acid are determined by the nature of the substituent R and the reaction products of the carbocation A.

EXPERIMENTAL

Elemental analysis data for compounds II-IV corresponded with the calculated values.

2-(1-Propenyl)-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (II, $C_{23}H_{21}NO$). mp 126-127°C. R_f 0.36 (benzene). IR spectrum (mineral oil mull): 3400 (NH), 1120, 1070, 1050 cm^{-1} (N—C—O). UV spectrum (C_2H_5OH), λ_{max}, nm (log ε): 247 (3.99), 303 (3.57). ^1H NMR ($CDCl_3$): 7.12 (5H, s, Ph_a), 7.23 (5H, s, Ph_e), 6.65 (4H, m, C_6H_4), 4.88 (1H, d, H_a, $^3J_{HaH\alpha}$ = 5.0 Hz, 4.19 (1H, br.s, N—H), 5.64 (2H, m, $H_{\alpha,\beta}$), 1.62 ppm (3H, d, CH_3, $^3J_{CH_3H\beta}$ = 6.0 Hz. Mass spectrum, m/z (I, %), ion: 327 (33), $M^{+\cdot}$, 257 (40), $[M—CH_3CH=CH—CHO]^{+\cdot}$, 256 (100), $[257—H]^+$, 180 (31), $[257—C_6H_5]^+$. Yield 74%.

2-(2-Phenylvinyl)-4,4-diphenyl-1,2-dihydro-4H,3,1-benzoxazine(III, $C_{28}H_{23}NO$). mp 179-181°C. R_f 0.59 (benzene). IR spectrum (mineral oil mull): 3370 (NH), 1020, 1080 cm^{-1} (N—C—O). UV spectrum (C_2H_5OH), λ_{max}, nm (log ε): 255 (4.45), 285 (3.81), 294 (3.81). ^1H NMR ($CDCl_3$): 7.16 (5H, s, Ph_a), 7.28 (5H, s, Ph_e), 6.65 (4H, m, C_6H_4), 5.08 (1H, d, H_a, $^3J_{H_aH_\alpha}$ = 6 Hz), 4.37 (1H, br.s, N—H), 6.68 (1H, d, H_a), 6.38 ppm (1H, d, Hβ, $^3J_{H_\alpha H_\beta}$ = 6 Hz). Mass spectrum, m/z (I, %), ion: 389 (33), $M^{+\cdot}$, 257 (41), $[M—C_6H_5CH=CHCHO]^{+\cdot}$, 256 (100), $[257—H]^+$, 180 (29), $[257—C_6H_5]^+$. Yield 66%.

Krasnodar Polytechnic Institute, Krasnodar 350072. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1292-1293, September, 1993. Original article submitted July 28, 1993.

0009-3122/93/2909-1109$12.50

2-(2-Acetoxypropyl)-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (IV, $C_{25}H_{26}NO_3$). mp 157-158°C. R_f 0.16 (benzene). IR spectrum (mineral oil mull): 3360 (NH), 1733, 1252 cm^{-1} (CH_3—COO). UV spectrum (C_2H_5OH), λ_{max}, nm (log ε): 247 (3.93), 303 (3.52). ^1H NMR ($CDCl_3$): 7.14 (5H, s, Ph_a), 7.20 (5H, s, Ph_e), 6.65 (4H, m, C_6H_4), 5.05 (1H, m, C—H), 4.50 (1H, t, H_a, $^3J_{H_aHCH_2}$ = 5.5 Hz), 3.83 (1H, br.s, N—H), 1.93 (2H, m, CH_2), 1.63 (3H, s, CH_3—C=O), 1.02 ppm (3H, d, CH_3, $^3J_{CH_3H}$ = 6.5 Hz). Mass spectrum, m/z (I, %), ion: 387 (31) $M^{+\cdot}$, 286 (100), $[M—CH_2CH(CH_3)OC(O)CH_3]^+$, 256 (38), $[286—HCHO]^+$, 208 (38), $[286—C_6H_6]^+$. Yield 71%.

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