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Schmidt rearrangement: Synthesis of some 3,4-dihydroquinolin-2(1*H*)-one derivatives

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ABSTRACT

*In the present study, synthesis of some (E)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1H)-ones (**4**) derived from (E)-2-arylidene-3-phenyl-2,3-dihydro-1H-inden-1-ones (**3**) via NaN_3/H_2SO_4 mediated Schmidt rearrangement in $CHCl_3$ in moderate yields has been reported. The rearrangement underwent by aryl migration without shifting of double bond from exocyclic to endocyclic position. The structural confirmation of the synthesized compounds was ascertained by spectral (IR, NMR and mass) and elemental analysis data.*

Keywords: Schmidt rearrangement; (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones; (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones.

INTRODUCTION

Schmidt reaction involves the acid-catalyzed reactions of hydrazoic acid or an alkyl azide with an electrophile which was first reported by Schmidt [1] in 1923. The reaction came to its own in the 1940's and 1950's, especially by the efforts of Smith [2] and Briggs [3]. The important feature of incorporating nitrogen into the product by Schmidt reaction has placed this chemistry among the most useful methods for the synthesis of nitrogenous compounds [4]. Literature precedent divulges various aspects of chemistry of Schmidt rearrangement by different researchers [5]. Although Schmidt rearrangement of ketones has since long been recognized as one of the useful methods for the synthesis of *N*-substituted amides and lactams [6], mechanistically related components includes an aldehyde, acid, or a carbocation generated from an alkene or an alcohol as the electrophilic part. Moreover, this transformation also finds many applications in the synthesis of a variety of heterocyclic compounds [7] and alkaloids [8]. Despite the development of various methods, the Schmidt reaction remains the most convenient and general procedure for insertion of nitrogen into the steroidal nucleus and hence provides a versatile route for the synthesis of aza steroids [9]. Although, literature records spate of publications on Schmidt rearrangement of a variety of saturated cyclic ketones, chemists in the past have exhibited only sporadic attention on the Schmidt rearrangement of *α,β*-unsaturated ketones. Keeping in view of this, we in this paper, report the results of our investigations on the synthesis of several (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (**4**) by Schmidt rearrangement of (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3**) which, in turn, were derived from 3-phenyl-2,3-dihydro-1*H*-inden-1-one (**1**). Our main aim in the present study was to examine whether (i) ketones (**3**) undergo aryl or vinyl migration and (ii) the rearrangement is accompanied by migration of double bond from exocyclic to endocyclic position or not.

MATERIALS AND METHODS

2.1 General: The chemicals (AR and LR grade) utilized in the present investigation were procured from Sigma-Aldrich, Qualigens, CDH and Spectrochem. The solvents were used as such or after necessary purification following the literature procedures. Purity of the synthesized compounds was tested by thin layer chromatography (TLC) using precoated silica gel (HF_{254}, 200 mesh) plates as stationary phase and different combinations of solvents as mobile phase. The visualization of the spots was achieved by UV fluorescence quenching. Melting points (mp °C) of the synthesized compounds were found out in open head capillaries on an electrothermal apparatus and are uncorrected. The progress of the reaction, in each case, was monitored by TLC. The synthesized compounds were characterized by employing different spectral (IR, NMR, Mass) and elemental analytical techniques. IR spectra of the synthesized compounds were scanned on Perkin Elmer Spectrum, BX II FTIR spectrometer as dry KBr pellets and absorption frequencies (ν) are stated in cm^{-1}. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Advance 300/400 MHz spectrometer at 300/400 MHz and 75/100 MHz, respectively in $CDCl_3$. The chemical shifts are reported in parts per million (δ ppm) taking tetramethylsilane (TMS) as an internal standard. The peak patterns are assigned as follows: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublet). The coupling constant (*J*) values are reported in Hertz (Hz). Elemental analyses were determined on Vario Micro Cube Elementar CHNS analyser. Elemental analytical results for C, H and N were found within ±0.4% of the theoretical values.

2.2 General procedure for the synthesis of (*E*)-2-arylidene-2,3-dihydro-1*H*-inden-1-ones (3): To a stirred solution of 3-phenyl-2,3-dihydro-1*H*-inden-1-one (**1**, 2.08 g, 0.01 mole) and an appropriate 4-substituted benzaldehyde (**2**, 0.01 mole) in ethanol (150 mL) was added NaOH solution (30 mL, 6.7 M) drop wise while stirring on a magnetic stirrer by maintaining the temperature of the reaction mixture below 5 °C with the aid of an ice-bath. The crude product precipitated out from the reaction mixture within a few minutes. The stirring was continued for further 30 min. at room temperature. The solid thus obtained was collected by vacuum filtration, washed with cold ethanol and then with water until the pH of the wash out was neutral, dried and recrystallized from ethanol to give the corresponding (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3**) [10] in high (84.3–93%) yields. The characterization data of the compounds (**3a–3e**) are given below.

(*E*)-2-(4-chlorobenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3a)
Yield 84.3%, mp 175–178 °C (Lit. [11] mp 174 °C); IR (KBr, cm^{-1}): 1692 (C=O, str.), 1614 (C=C, str.); ^1H NMR (400 MHz, $CDCl_3$): δ 5.22 (s, 1H, 3-H), 7.10–7.54 (m, 12H, ArH), 7.76 (d, 1H, *J* = 2.00 Hz, H_β), 7.93 (d, 1H, *J* = 7.64 Hz, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.69 (C_3), 124.10, 124.33, 125.96, 127.17, 127.60, 128.03, 128.92, 129.08, 131.61, 132.55, 134.14, 135.06, 135.97, 138.98, 141.10, 154.27 (C_{3a}), 194.36 (C_1).

(*E*)-2-(4-ethylbenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3b)
Yield 90.2%, mp 150–152 °C; IR (KBr, cm^{-1}): 1688 (C=O, str.), 1610 (C=C, str.); ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, 3H, *J* = 7.6 Hz, 4′-$CH_2\underline{C}H_3$), 2.58 (q, 3H, *J* = 7.6 Hz, 4′-$\underline{C}H_2CH_3$), 5.32 (s, 1H, 3-H), 7.08 (d, 2H, *J* = 8.16 Hz, 3′-H & 5′-H), 7.11–7.15 (m, 1H, ArH), 7.21–7.27 (m, 4H, ArH), 7.35–7.40 (m, 4H, ArH), 7.47–7.51 (m, 1H, ArH), 7.84 (d, 1H, *J* = 1.68 Hz, H_β), 7.92 (d, 1H, *J* = 7.64 Hz, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.13 (4′-$CH_2\underline{C}H_3$), 28.73 (4′-$\underline{C}H_2CH_3$), 48.84 (C_3), 124.22, 125.91, 126.93, 127.60, 127.85, 128.03, 129.01, 131.57, 131.66, 134.92, 135.78, 136.17, 137.40, 141.66, 146.33, 154.41 (C_{3a}), 194.73 (C_1).

(*E*)-2-(4-methoxybenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3c)
Yield 92%, mp 170–173 °C (Lit.[11] mp 163–165 °C); IR (KBr, cm^{-1}): 1685 (C=O, str.), 1597 (C=C, str.); ^1H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 3H, 4′-OCH_3), 5.23 (s, 1H, 3-H), 6.68 (d, 2H, *J* = 8.8 Hz, 3′-H & 5′-H), 7.07–7.54 (m, 10H, ArH), 7.74 (d, 1H, *J* = 1.68 Hz, H_β), 7.87 (d, 1H, *J* = 7.64 Hz, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.80 (C_3), 55.29 (4′-$O\underline{C}H_3$), 113.97 ($C_{3'}$ & $C_{5'}$), 124.16, 125.84, 126.76, 126.98, 127.55, 127.82, 129.02, 133.46, 134.78, 135.52, 135.80, 136.25, 141.47, 154.25 (C_{3a}), 160.83 ($C_{4'}$), 194.70 (C_1).

(*E*)-2-(4-(dimethylamino)benzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3d)
Yield 91.3%, mp 178–180 °C; IR (KBr, cm^{-1}): 1692 (C=O, str.), 1619 (C=C, str.); ^1H NMR (400 MHz, $CDCl_3$): δ 3.06 (s, 6H, 4′-$N(CH_3)_2$), 5.21 (s, 1H, 3-H), 6.86 (d, 2H, *J* = 8.8 Hz, 3′-H & 5′-H), 7.10–7.76 (m, 11H, ArH, H_β), 7.94 (d, 1H, *J* = 8.0 Hz, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.05 (C_3), 111.23 ($C_{3'}$ & $C_{5'}$), 124.36, 125.69, 126.45, 126.83, 127.32, 129.33, 131.26, 133.52, 134.12, 135.67, 135.98, 137.10, 141.32, 150.23 ($C_{4'}$), 154.47 (C_{3a}), 194.12 (C_1).

(*E*)-2-(3-hydroxy-4-methoxybenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3e)
Yield 93%, mp 223–225 °C; IR (KBr, cm^{-1}): 3425 (O–H, str.), 1697 (C=O, str.), 1625 (C=C, str.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H, 4′-OCH_3), 5.30 (s, 1H, 3-H), 5.93 (br s, 1H, 3′-OH, exchangeable with D_2O), 6.98 (d, 1H, $J_{5'6'}$ = 8.48 Hz, 5′-H), 7.10–7.70 (m, 10H, ArH, H_β), 7.92 (d, 1H, *J* = 8.0 Hz, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.75 (C_3), 55.89 (4′-O<u>C</u>H_3), 110.24 ($C_{5'}$), 116.98 ($C_{2'}$), 124.17, 125.37, 125.89, 126.95, 127.64, 127.68, 127.82, 128.99, 134.83, 135.63, 136.24, 136.53, 141.57, 145.32 ($C_{3'}$), 148.00 ($C_{4'}$), 154.36 (C_{3a}), 194.68 (C_1).

2.3 General procedure for the synthesis of (*E*)-3-arylidene-3,4-dihydroquinolin-2(1*H*)-ones (4): To a cooled suspension of an appropriate (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3**, 0.0093 mole) and sodium azide (1.30 g, 0.02 mole) in chloroform (50 mL), was added conc. H_2SO_4 (5 mL) drop wise with continuous stirring on a magnetic stirrer keeping the temperature of the reaction mixture below 40 °C. After the addition was over, the reaction mixture was further stirred at room temperature. The progress of the reaction was checked through TLC on aliquots withdrawn from the reaction mixture (after neutralization and extraction) at regular intervals of time. After completion of the reaction, contents were cooled and poured onto crushed ice. The chloroform layer was separated and aqueous layer was extracted with chloroform (3×50 mL). All the extracts were combined with chloroform layer and the contents were dried over anhydrous Na_2SO_4 which upon concentration under vacuum gave a residue that was chromatographed over a column of silica-gel (60–120 mesh) prepacked in hexane. Elution of the column with hexane:ethyl acetate (19:1, v/v) afforded a solid which upon crystallization from a suitable solvent furnished the corresponding (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (**4**) in moderate (59.3–67.5%) yields. The characterization data of the quinolinones (**4a–4f**) are given below.

(*E*)-3-(4-chlorobenzylidene)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (4a)
The time required for completion of reaction was 8h; light yellow crystals (methanol), yield 67.5%; mp 110–114 °C; IR (KBr, cm^{-1}): 3367 (N–H, str.), 1675 (C=O, str.), 1603 (C=C, str.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.03 (s, 1H, 4-H), 7.01 (d, 2H, *J* = 8.1 Hz, 3′-H & 5′-H), 7.11–7.20 (m, 3H, ArH), 7.26–7.55 (m, 8H, ArH), 7.71 (s, 1H, H_β), 9.26 (br s, 1H, NH, exchangeable with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.47 (C_4), 116.12, 123.67, 125.14, 126.89, 127.12, 128.09, 128.68, 130.26, 131.51, 131.96, 133.63, 134.60, 135.28, 136.24, 138.11, 146.36, 163.25 (C_2); ESI-MS m/z: 346.1 $[M+H]^+$; *Anal*. Calcd. for $C_{22}H_{16}ClNO$ (345.82): C, 76.41; H, 4.66; N, 4.05. Found: C, 76.12; H, 4.80; N, 4.28.

(*E*)-3-(4-ethylbenzylidene)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (4b)
The time required for completion of reaction was 11h; white crystals (benzene), yield 59.6%; mp 163–166 °C; IR (KBr, cm^{-1}): 3346 (N–H, str.), 1662 (C=O, str.), 1602 (C=C, str.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (t, 3H, *J* = 7.5 Hz, 4′-CH_2<u>CH_3</u>), 2.60 (q, 3H, *J* = 7.5 Hz, 4′-<u>CH_2</u>CH_3), 5.22 (s, 1H, 4-H), 6.55 (d, 2H, *J* = 7.8 Hz, ArH), 6.64–6.82 (m, 1H, ArH), 7.03 (d, 2H, *J* = 7.8 Hz, 3′-H & 5′-H), 7.11–7.50 (m, 9H, ArH), 7.94 (s, 1H, H_β), 9.48 (br s, 1H, NH, exchangeable with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.05 (4′-CH_2<u>C</u>H_3), 28.71 (4′-<u>C</u>H_2CH_3), 48.08 (C_4), 115.71, 124.05, 125.84, 127.54, 127.85, 128.02, 128.42, 129.03, 131.69, 131.84, 134.87, 135.42, 136.04, 137.81, 145.07, 146.24, 164.31 (C_2); ESI-MS m/z: 340.17 $[M+H]^+$; *Anal.* Calcd. for $C_{24}H_{21}NO$ (339.43): C, 84.92; H, 6.24; N 4.13. Found: C, 84.68; H, 6.50; N, 4.29.

(*E*)-3-(4-methoxybenzylidene)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (4c)
The time required for completion of reaction was 11.5h; white solid (methanol), yield 61%; mp 208–211 °C; IR (KBr, cm^{-1}): 3340 (N–H, str.), 1669 (C=O, str.), 1591 (C=C, str.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H, 4′-OCH_3), 5.21 (s, 1H, 4-H), 6.92 (d, 2H, *J* = 8.4 Hz, 3′-H & 5′-H), 7.19–7.33 (m, 3H, ArH), 7.36 (d, 2H, *J* = 8.4 Hz, 2′-H & 6′-H), 7.39–7.58 (m, 6H, ArH), 7.82 (s, 1H, H_β), 9.03 (br s, 1H, NH, exchangeable with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.08 (C_4), 56.02 (4′-O<u>C</u>H_3), 113.98, 115.41, 123.57, 125.02, 127.66, 128.52, 128.70, 129.32, 130.88, 131.22, 134.06, 135.86, 136.49, 138.19, 146.55, 156.62 ($C_{4'}$), 163.53 (C_2); ESI-MS m/z: 342.14 $[M+H]^+$; *Anal*. Calcd. for $C_{23}H_{19}NO_2$ (341.40): C, 80.92; H, 5.61; N 4.10. Found: C, 80.61; H, 5.39; N 4.28.

(*E*)-3-(4-(dimethylamino)benzylidene)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (4d)
The time required for completion of reaction was 10h; pale yellow crystals (benzene), yield 59.3%; mp 222–224 °C; IR (KBr, cm^{-1}): 3253 (N–H, str.), 1669 (C=O, str.), 1593 (C=C, str.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.05 (s, 6H, 4′-$N(CH_3)_2$), 5.30 (s, 1H, 4-H), 6.71 (d, 2H, *J* = 8.7 Hz, 3′-H & 5′-H), 7.11–7.60 (m, 11H, ArH), 7.91 (s, 1H, H_β), 8.75 (br s, 1H, NH, exchangeable with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.62 (4′-N(<u>C</u>H_3)$_2$), 48.07 (C_4), 111.75 ($C_{3'}$ & $C_{5'}$), 115.68, 123.19, 124.27, 125.35, 127.80, 128.15, 128.72, 131.23, 131.88, 134.56, 135.69, 136.37, 138.45,

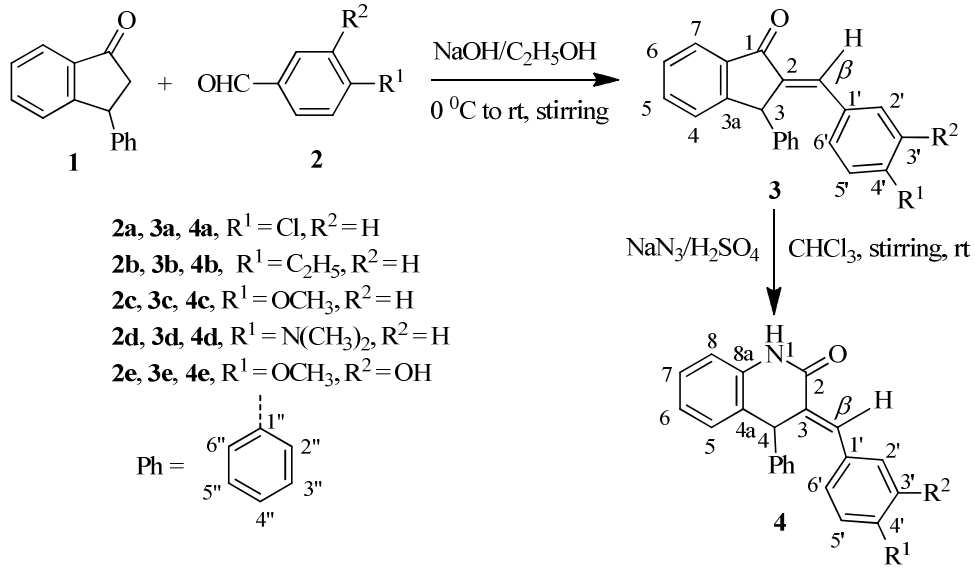
147.02, 149.52 ($C_{4'}$), 162.87 (C_4); ESI-MS m/z: 355.17 $[M+H]^+$; *Anal.* Calcd. for $C_{22}H_{16}NO$ (354.44): C, 85.14; H, 5.20; N 4.51. Found: C, 85.40; H, 4.91; N, 4.79.

(*E*)-3-(3-hydroxy-4-methoxybenzylidene)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (4e)

The time required for completion of reaction was 12h; white crystals (ethanol), yield 60.7%; mp 147–149 °C; IR (KBr, cm^{-1}): 3358 (O–H, str.), 3286 (N–H, str.), 1665 (C=O, str.), 1590 (C=C, str.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, 4′-OCH_3), 5.15 (s, 1H, 4-H), 5.74 (br s, 1H, 3′-OH, exchangeable with D_2O), 6.96 (d, 1H, $J_{5'6'}$ = 8.4 Hz, 5′-H), 7.16–7.24 (m, 4H, ArH), 7.28–7.45 (m, 7H, ArH), 7.86 (s, 1H, H_β), 9.32 (br s, 1H, NH, exchangeable with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.23 (C_4), 56.21 (4′-O<u>C</u>H_3), 111.32 ($C_{5'}$), 114.75 ($C_{2'}$), 116.23, 124.56, 125.22, 126.74, 128.43, 128.80, 130.22, 132.12, 133.56, 134.62, 135.51, 136.58, 138.23, 145.37, 146.53, 156.62 ($C_{4'}$), 163.47 (C_2); ESI-MS m/z: 358.15 $[M+H]^+$; *Anal*. Calcd. for $C_{23}H_{19}NO_3$ (357.40): C, 77.29; H, 5.36; N 3.92. Found: C, 77.48; H, 5.11; N, 4.17.

RESULTS AND DISCUSSION

The general approach towards the synthesis of quinolinones (**4**) involves an initial condensation of 3-phenyl-2,3-dihydro-1*H*-inden-1-one (**1**) with appropriate 4-substituted benzaldehydes (**2**) in base-catalyzed conditions to furnish (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3a**–**3e**) which upon subsequent Schmidt rearrangement with NaN_3/H_2SO_4 in $CHCl_3$ furnished the corresponding (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (**4a**–**4e**) in moderate yields (59.3–67.5%) (Scheme 1).



Scheme 1: Protocol for the synthesis of (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (4)

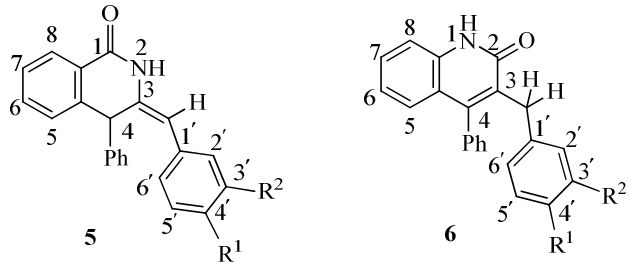
The (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3a**–**3e**) needed for the purpose were obtained by the condensation of 3-phenyl-2,3-dihydro-1*H*-inden-1-one (**1**) with appropriate 4-substituted benzaldehydes (**2a**–**2e**) in the presence of $NaOH/C_2H_5OH$ by stirring at low temperature in excellent yields (84.3–93%) according to the procedure as detailed in literature [10]. IR spectra of all the arylidenes (**3a**–**3e**) displayed the characteristic absorptions due to C=C and C=O stretchings in the regions at 1597–1625 cm^{-1} and 1685–1697 cm^{-1}, respectively which are in accord with the values reported in the literature [11,12]. The ^{1}H NMR spectra of the arylidenes (**3a**–**3e**), in each case, exhibited a characteristic one-proton doublet in the region at δ 7.87–7.94 (J = 7.64–8.00 Hz) due to C_7-H besides other aromatic and non-aromatic proton resonances (*vide* experimental). The most distinguishing feature of ^{13}C NMR spectra of **3a**–**3e**, in each case, is the presence of a signal in the region at δ 194.12–194.73 safely ascribable to C_1 [13] Another noteworthy feature is the appearance of a signal in the region at δ 154.25–154.47, which has been assigned to C_{3a}. The signals due to the remaining carbons were obtained in the expected regions (*vide* experimental).

The (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3a**–**3e**) were next converted into their corresponding (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (**4a**–**4e**) by Schmidt rearrangement. The treatment of **3** with NaN_3/H_2SO_4 in $CHCl_3$ under stirring at room temperature afforded the corresponding (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (**4**) in moderate yields (59.3–67.5%). The structures of the quinolinones (**4a**–**4e**) thus obtained were established through the analysis of their spectral (IR, ^{1}H NMR, ^{13}C NMR and mass) and analytical data.

The IR spectra of **4a**–**4e**, in each case, displayed a band of medium intensity in the region at 3253–3367 cm^{-1} due to N–H stretching and two strong bands in the regions at 1662–1675 cm^{-1} and 1590–1603 cm^{-1} due to C=O stretching and C=C stretching, respectively. The ^{1}H NMR spectra of **4a**–**4e**, in each case, exhibited a one-proton singlet in the region at δ 5.03–5.30 which was safely assigned to C_4-methylene protons. At the lowest field of the spectra, in each case, was located a one-proton singlet in the region at δ 7.71–7.94 easily assignable to C_{β}-H. Further, the signal due to NH was appeared as a broad signlet (exchangeable with D_2O) in the region at δ 8.75–9.48. The signals due to the remaining protons were observed in the expected regions (*vide* experimental). The ^{13}C NMR spectra of **4a**–**4e**, in each case, showed a signal in the region at δ 48.07–48.47 attributable to C_4. Another noteworthy feature was the presence of a signal, in each case, at the lowest field of the spectra, in the region at δ 162.87–164.31 which was undoubtedly ascribed to carbonyl carbon, *i.e.* C_2. The signals due to the remaining carbons were observed in the expected regions. Further, the mass spectral data and elemental analysis data of all the quinolines (**4**) were found in good agreement with their molecular formulae (*vide* experimental).

The (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3**) upon Schmidt rearrangement is expected to furnish **4** by aryl migration and **5** by vinyl migration but **4** is the sole isolable product in the present investigation. ^{1}H NMR spectral studies proved helpful to make a distinction between these structures. If **5** had been obtained by Schmidt rearrangement of **3** through vinyl migration, then C_8-H must have appeared in the downfield region in ^{1}H NMR spectra as evidenced earlier by Blanco *et al*. [14] but no such signal in the downfield region was observed in the isolated products **4a**–**4e**, and C_8-H appeared in the region below δ 7.60, therefore, formation of **5** stands rejected.

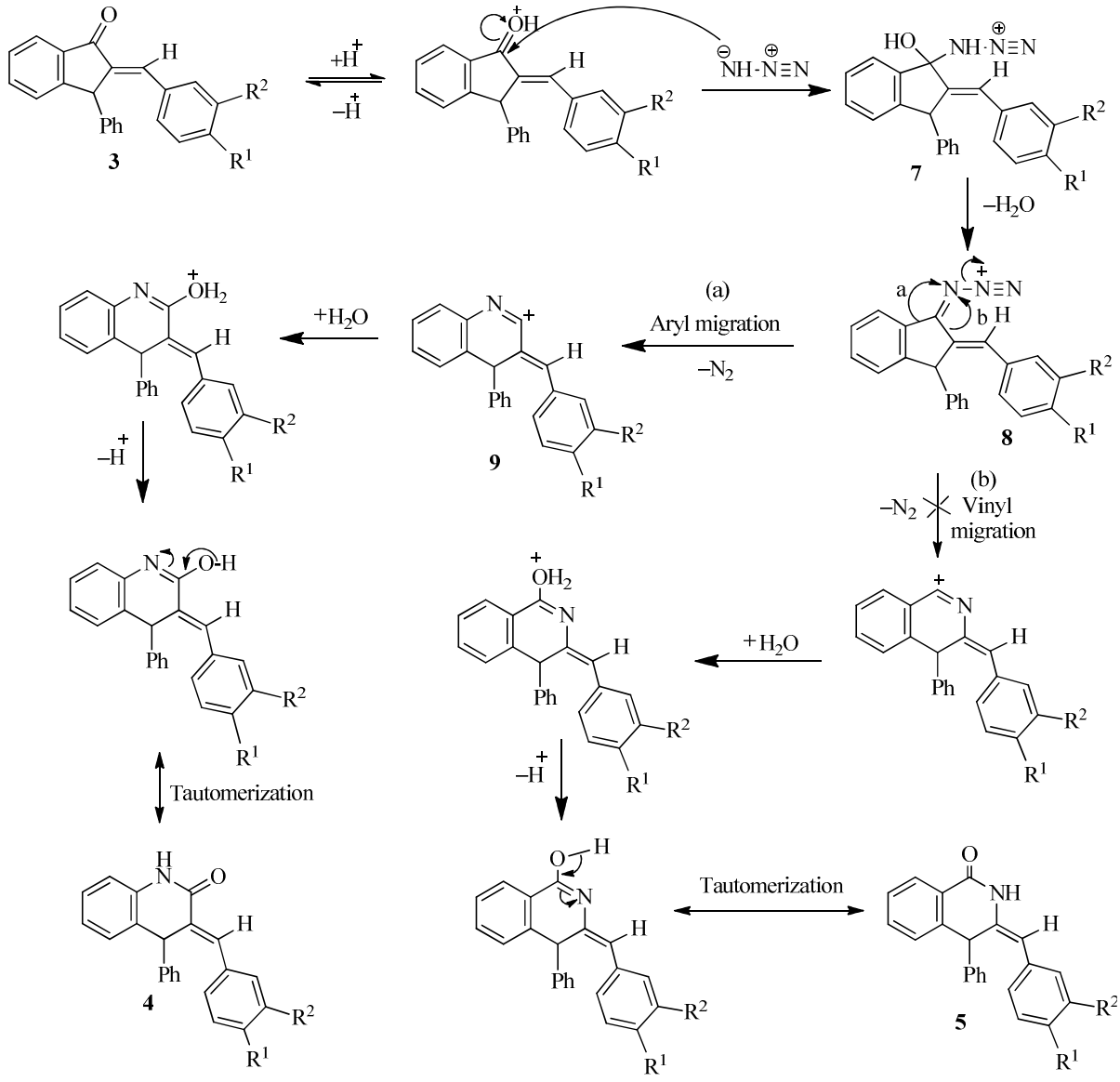
One more intriguing point which deserves attention here is that during the Schmidt rearrangement of **3**, the possibility of movement of *α,β*-unsaturated double bond from exocyclic to endocyclic position to give quinolinone (**6**) can not be avoided. If this migration had happened, it must have exhibited a two-proton signal due to C_3-benzylic CH_2 group and a resonance characteristic of the C_4-vinylic proton in the ^{1}H NMR spectra of the product formed. However, such types of resonances were not observed in the present investigation. Thus, it can be stated without any reservation that there occurs no movement of *α,β*-unsaturated double bond from exocyclic to endocyclic position during the Schmidt rearrangement of **3**.



5, **6:** R^1 = Br, C_2H_5, OCH_3, NO_2, $N(CH_3)_2$; R^2 = H, OH; Ph = C_6H_5

All these arguments support the formation of (*E*)-3-arylidene-4-phenyl-3,4-dihydroquinolin-2(1*H*)-ones (**4**) by Schmidt rearrangement of (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3**) through aryl migration in which configuration around C=C bond is retained.

Although the mechanism transformation of **3** → **4** has not been unraveled in the present investigation, reaction is envisaged to occur through an initial protonation of carbonyl group followed by nucleophillic attack by hydrazoic acid to furnish the intermediate (**7**) which subsequently undergoes loss of a molecule of water to give the intermediate (**8**). The intermediate (**8**) undergoes aryl migration to furnish carbocation (**9**) which upon nucleophillic attack by H_2O followed by loss of a proton and subsequent tautomerization gives the quinolinone (**4**) (Scheme 2).



$R^1 = Cl, C_2H_5, OCH_3, N(CH_3)_2$; $R^2 = H, OH$; $Ph = C_6H_5$

Scheme 2: Plausible mechanism of formation of (*E*)-3-arylidene-3,4-dihydroquinolin-2(1*H*)-ones (4) by Schmidt rearrangement of (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (3)

CONCLUSION

In conclusion, we have carried out the synthesis of (*E*)-3-arylidene-3,4-dihydroquinolin-2(1*H*)-ones (**4**) by NaN_3/H_2SO_4 mediated Schmidt rearrangement of (*E*)-2-arylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-ones (**3**) in $CHCl_3$ at normal temperature under stirring. The rearrangement has occurred by aryl migration without shifting of the exocyclic double bond to endocyclic position.

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