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SYNTHESIS 0F CARBAZOLES FROM *O*-CYCLOHEX-2-ENYL-ANILINES.#

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Abstract : Several carbazoles **(4a-f)** have been synthesised from *o*-cyclohex-2-enylanilines by treatment with pyridine hydrotribromide in methylene chloride at 0-5 ^{0}C for 2 h followed by refluxing with Pd-C in diphenyl ether for 1 h.

The synthesis of carbazole has been reported from diphenyl amine either by photochemical cyclisation[1] or by thermal cyclisation[2] and also in the presence of iodine[3] at 350 ^{0}C. We have reported the synthesis of 1-alkoxytetrahydrocarbazoles by the Hg(II)-mediated heterocyclisation[4] of *o*-cyclohex-2-enylanilines **(2).** We now wish to report a simple and a general synthesis of carbazole and its derivatives from *o*-cyclohex-2-enylanilines **(2).**

The starting materials, *o*-cyclohex-2-enylanilines **(2a-f)** are easily prepared[4] by the acid-catalysed amino Claisen of 3-cyclohex-2-enyl-N-alkylanilines, **1** according to earlier published procedure.

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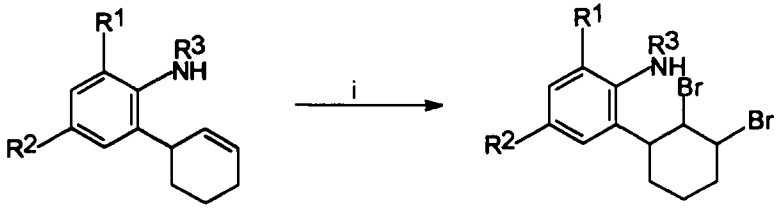
#This paper is dadicated to Professor Mrs. Asima Chatterjee, University of Calcutta on the occasion of her 80th birth anniversary.

Results and discussion :

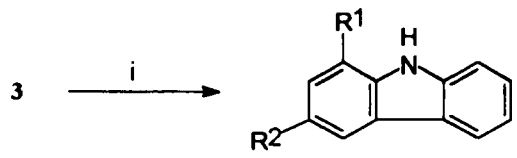
We have recently reported the regioselective cyclisation of *o*-cyclohex-2-enylphenols with pyridine hydrotribromide[5] and hexamethylenetetramine hydrotribromide[6] and also via epoxidation[7] of the cyclohex-2-enyl double bond. These observations lead us to a reasonable guide to treat *o*-cyclohex-2-enylanilines with pyridine hydrotribromide for the synthesis of carbazole derivatives. Consequently substrate **2a** was treated with pyridine hydrotribromide in dichloromethane at 0-5 ^{0}C for 2 h to give a white crystalline solid in 75% yield. This has been characterised as the dibromide **3a** from ita elemental analysis and spectral data. The other substrates **2b-f** were also similarly treated with pyridine hydrotribromide. In case of **2b**, a dibromide **3b** was obtained but in case of **2c-f** ring bromination occurred to furnish **(3c-f)** (scheme 1).



	R^1	R^2	R^3
2a,	H	Cl	Me
b,	H	Et	Me
c,	H	Me	^{t}Bu
d,	Me	H	Me
e,	H	H	Me
f,	H	H	Et

	R^1	R^2	R^3
3a,	H	Cl	Me
b,	H	Et	Me
c,	Br	Me	^{t}Bu
d,	Me	Br	Me
e,	Br	Br	Me
f,	Br	Br	Et

Scheme 1. Reagents and condition : i. $PyHBr_3$, CH_2Cl_2, 0-5 ^{0}C, 2 h



	R^1	R^2	Yield (%)	M.P. (^{0}C)
4a	H	Cl	66	200 (lit.[8] 201)
4b	H	Et	60	142 (lit.[9] 144)
4c	H	Me	68	206 (lit.[2a] 207)
4d	Me	H	62	120 (lit.[8] 120.5)
4e	H	H	70	244 (lit.[10] 245)

Scheme 2. Reagents and condition : i.Pd/C, Ph_2O, reflux, 1 h

As our efforts to cyclise *o*-cyclohex-2-enylanilines **(2a-f)** were of no avail an attempt was made to synthesise carbazole derivatives from brominated *o*-cyclohex-2-enylanilines, **(3a-f).** Therefore, substrate **3a** was treated with palladised charcoal in diphenyl ether at 220 ^{0}C for 2 h but no change was observed. The reaction was then conducted in boiling diphenyl ether (b.p. 259 ^{0}C) for 1 h to give the carbazole **4a** in 66% yield. Encouraged by the result other substrates **3b-f** were similarly treated with palladised charcoal to furnish the carbazoles **(4b-e)** in 60-70% yields (scheme 2). The thermal method described here for the synthesis of carbazole derivatives is a relatively mild and simple one.

Experimental: M.p's are uncorrected. UV absorptions were recorded on a Hitachi 200-20 spectrometer for solutions in absolute ethanol and IR spectra were run on a Perkin-Elmer 1330 apparatus using KBr discs. ^{1}H-NMR spectra were determined

for deuteriochloroform solutions with $SiMe_4$ as internal standard on Jeol Fx-100 (100 MHz) instruments at the IICB, Calcutta and on a Bruker AC-250 (250 MHz) spectrochem at the Universitat Konstanz, Germany. Elemental analyses and recording of mass spectra were carried out by R. S. I. C. (CDRI), Lucknow. Silica gel (60-120 mesh) is obtained from spectrometer, India. Pet. ether refers to the fractions of b.p. 60-80°C.

General procedure for the preparation of 3-N-alkylanilinocyclohexenes 1(a-f):

Compounds **1(a-f)** were prepared according to published procedure[4].

Compounds 1(c-f) reported earlier[4].

Compound 1a: Yield 90%, viscous liquid; $\lambda_{max.}$: 266 (log ε 3.0), 314 (log ε 2.1) nm; $\nu_{max.}$: 3020, 1620, 1520, 1100, 810 cm^{-1}; ^{1}H-NMR (100 MHz/ $CDCl_3$) δ: 1.52-1.84 (m, 4H), 1.88-2.12 (m, 2H), 2.76 (s, 3H), 4.20-4.52 (br s, 1H), 5.52-5.80 (m, 1H), 5.80-6.08 (m, 1H), 6.60-7.36 (m, 4H). Anal. calcd. for $C_{13}H_{16}ClN$: C 70.59, H 7.24, N 6.33%; found: C 70.79, H 7.54, N 6.12%.

Compound 1b: Yield 92%, viscous liquid; $\lambda_{max.}$: 258 (log ε 3.0), 266 (log ε 3.2) nm; $\nu_{max.}$: 3020, 1580, 1320, 810 cm^{-1}; ^{1}H-NMR (100 MHz/$CDCl_3$) δ: 1.20 (t, 3H, J= 7.0 Hz),1.48-2.08 (m, 6H), 2.56 (q, 2H, J= 8.0 Hz), 2.76 (s, 3H), 4.28-4.56 (br s, 1H), 5.56-6.00 (m, 2H), 6.68-7.16 (m, 4H). Anal. calcd. for $C_{15}H_{21}N$: C 83.72, H 9.77, N 6.51%; found: C 83.52, H 9.98, N 6.74%.

General procedure for the preparation of 2-(cyclohex-2-enyl)-N-alkylanilines 2(a-f):

Compounds **2(a-f)** were prepared according to published procedure[4].

Compounds 2(c-f) reported earlier[4].

Compound 2a: Yield 50%, viscous liquid; $\lambda_{max.}$: 251 (log ε 3.1), 308 (log ε 2.5) nm; $\nu_{max.}$: 3400, 3020, 1120, 780 cm^{-1}; ^{1}H-NMR (100 MHz) δ: 1.56-2.00 (m, 4H), 2.04-2.16 (m, 2H), 2.84 (s, 3H), 3.12-3.40 (br s, 1H), 3.40-4.00(br s, 1H), 5.56-6.12 (m, 2H), 6.50 (d, 1H, J= 8.0 Hz), 7.12-7.36 (m, 2H); m/z: 221, 223 (M^+). Anal. calcd. for $C_{13}H_{16}ClN$: C 70.59, H 7.24, N 6.33%; found: C 70.72, H 7.54, N 6.21%.

Compound 2b: Yield 70%, viscous liquid; $\lambda_{max.}$: 246 (log ε 3.2), 299 (log ε 2.6) nm; $\nu_{max.}$: 3400, 2900, 1330, 790 cm^{-1}; ^{1}H-NMR (100 MHz) δ: 1.16 (t, 3H, J= 7.0 Hz),1.24-2.20 (m, 6H), 2.56 (q, 2H, J= 8.0 Hz), 2.84 (s, 3H), 3.00-3.48 (br s, 2H), 5.64-6.04 (m, 2H), 6.60 (d,1H, J=8.0 Hz), 6.84-7.04 (m, 2H); m/z: 215 (M^+). Anal. cacd. for $C_{15}H_{21}N$: C 83.72, H 9.77, N 6.51%; found: C 83.93, H 9.99, N 6.32%.

Bromination of 2 with $PyHBr_3$, preparation of 3:

Pyridine hydrobromide perbromide [1.20 g, 4 mmol for **2e** & **2f** and 0.90 g, 3 mmol for **2 (a-d)**] was added to a stirred solution of compound **2 (a-f)** in CH_2Cl_2 (50 ml) at 0-5 °C. Stirring was continued for 2 h. It was then extracted with water and dried (Na_2SO_4). The solvent was removed and the crude mass was purified by column chromatography over silica gel. Elution of the column with pet. ether furnished product **3(a-f)**.

Compound 3a: Yield 75%, m. p. 82°C; $\lambda_{max.}$: 251 (log ε 3.2) , 306 (log ε 2.5) nm; $\nu_{max.}$: 3410, 2910, 1450, 820 cm^{-1}; ^{1}H-NMR (100 MHz/$CDCl_3$) δ: 1.68-2.80 (m, 6H), 2.84 (s, 3H), 3.40-3.60 (m, 1H), 3.64-3.88 (br s, 1H), 4.76-4.90 (m, 2H),

6.56 (d, 1H, J= 8.0 Hz), 6.96-7.28 (m, 2H). Anal. calcd. for $C_{13}H_{16}Br_2ClN$: C 40.94, H 4.20, N 3.67%; found: C 40.69, H 4.43, N 3.88%.

Compound 3b: Yield 70%, gummy mass; $\lambda_{max.}$: 245 (log ε 3.4) , 298 (log ε 2.8) nm; $\nu_{max.}$: 3410, 2920, 1510, 820 cm^{-1}; ^{1}H-NMR (100 MHz/$CDCl_3$) δ: 1.16 (t, 3H, J= 7.0 Hz), 1.68-2.36 (m, 6H), 2.56 (q, 2H, J= 8.0 Hz), 2.84 (s, 3H), 3.24-3.64 (m, 2H), 4.84-4.98 (m, 2H), 6.80 (d, 1H, J= 8.0 Hz), 6.92-7.12 (m, 2H). Anal. calcd. for $C_{15}H_{21}Br_2N$: C 48.00, H 5.60, N 3.73%; found: C 48.23, H 5.84, N 3.44%.

Compound 3c: Yield 78%, m. p. 82°C; $\lambda_{max.}$: 223 (log ε 3.5) nm; $\nu_{max.}$: 3400, 2900, 1400, 800 cm^{-1}; ^{1}H-NMR (250 MHz/$CDCl_3$) δ: 0.95 (t, 3H, J= 7.3 Hz), 1.39-2.11 (m, 9H), 2.27 (s, 3H), 2.50-2.60 (m. 1H), 2.87-2.99 (m, 2H), 3.10-3.30 (br s, 1H), 3.90-3.94 (m, 1H), 4.86 (s, 1H), 5.20(s, 1H), 6.94 (s, 1H), 7.27 (s, 1H). Anal. calcd. for $C_{17}H_{24}Br_3N$: C 42.32, H 4.98, N 2.90%; found: C 42.55, H 5.19, N 2.66%.

Compound 3d: Yield 70%, m. p. 100°C; $\lambda_{max.}$: 225 (log ε 3.6), 259 (log ε 3.3) nm; $\nu_{max.}$: 3400, 2910, 1420, 800 cm^{-1}; ^{1}H-NMR (100 MHz/$CDCl_3$) δ: 1.28-2.04 (m, 6H), 2.20 (s, 3H), 2.76 (s, 3H),3.00-3.28 (br s, 1H), 3.80-4.04 (m, 1H), 4.76-4.96 (m, 1H), 5.12-5.28 (br s, 1H), 6.72 (s, 1H), 7.26 (s, 1H); m/z: 437,439, 441, 443 (M^+). Anal. calcd. for $C_{14}H_{18}Br_3N$: C 38.18, H 4.09, N 3.18%; found: C 38.02, H 4.32, N 3.43%.

Compound 3e: Yield 80%, m. p. 114°C; $\lambda_{max.}$: 225 (log ε 3.6), 251 (log ε 3.1), 306 (log ε 2.5) nm; $\nu_{max.}$: 3400, 2900, 1410, 1150, 800 cm^{-1}; ^{1}H-NMR (100 MHz/$CDCl_3$) δ: 1.60-2.60 (m, 6H), 2.80 (s, 3H), 3.08-3.48 (br s, 1H), 3.80-4.00

(m, 1H), 4.76-4.92 (m, 1H), 5.08-5.24 (br s, 1H), 7.24 (d, 1H, J= 2.0 Hz), 7.60 (d,1H, J= 2.0 Hz); m/z: 501, 503, 505, 507, 509 (M^+). Anal. calcd. for $C_{13}H_{15}Br_4N$: C 30.89, H 2.97, N 2.77%; found: C 30.72, H 3.20, N 2.99%.

Compound 3f: Yield 76%, m. p. 112°C; $\lambda_{max.}$: 223 (log ε 3.6), 288 (log ε 2.8) nm; $\nu_{max.}$: 3400, 2900, 1400, 800 cm^{-1}; ^{1}H-NMR (100 MHz/$CDCl_3$) δ: 1.28 (t, 3H, J= 7.0 Hz), 1.68-2.52 (m, 6H), 2.80-3.20 (m, 3H), 3.80-4.00(m, 1H), 4.80-4.92 (m, 1H), 5.08-5.24 (br s, 1H), 7.24 (d, 1H, J= 2.0 Hz), 7.60 (d,1H, J= 2.0 Hz). Anal. calcd. for $C_{14}H_{17}Br_4N$: C 32.37, H 3.28, N 2.70%; found: C 32.58, H 3.51, N 2.45%.

General procedure for the preparation of carbazole, 4.

To a solution of **3** (0.5 mmol) in diphenyl ether (5 ml) was added 0.25 g of palladised charcoal (10 %) and the reaction mixture was refluxed for 1 h.Then this was subjected to column chromatography over silica gel. Elution of the column with pet. ether removed diphenyl ether and the product 4 was obtained as a white crystalline solid in 60-70% yields by eluting the column with benzene-pet. ether (1:3). The compounds **4(a-e)** were characterised by comparison of their m. p. , mmp. and co-ir with authentic samples.

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