BEHAVIOR OF OXOTETRAHYDROBENZO[*b*]- AND [*c*]THIOPHENES AND THEIR α-HYDROXYMETHYLENE DERIVATIVES IN THE FISCHER INDOLE SYNTHESIS

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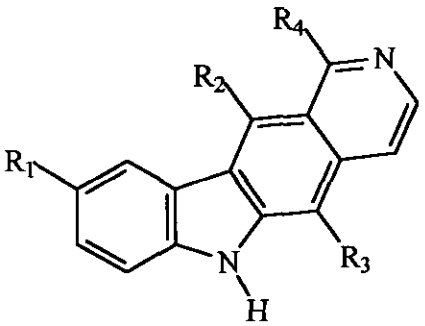
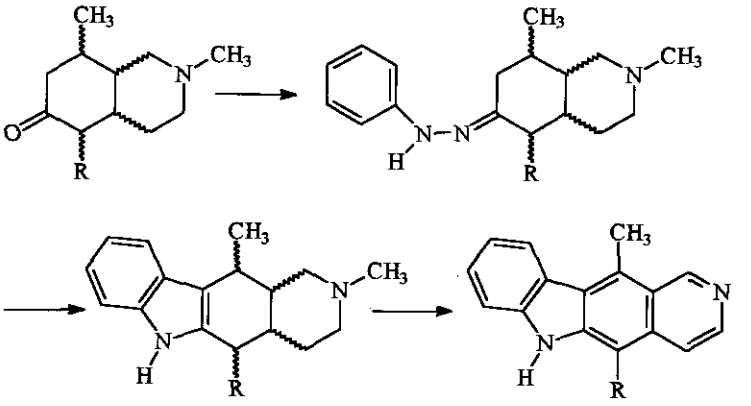
Abstract- We described an approach to thienocarbazoles *via* a Fischer indole synthesis starting directly from oxotetrahydrobenzo[*b*]- and [*c*]thiophenes or from their α-hydroxymethylene derivatives with a Japp-Klingemann reaction to make the hydrazones which are cyclised under acidic conditions.

Many studies toward the synthesis of 6*H*-pyrido[4,3-*b*]carbazoles like ellipticine, 9-methoxyellipticine or olivacine have been made in recent years and have been already reviewed.[1] Few examples of replacement of the pyridine ring in these pyridocarbazoles by other heterocycles like pyrroles[2] or pyrimidines[3] have been described. In this present paper, we present the results obtained for introducing a thiophene ring in the place of the pyridine.



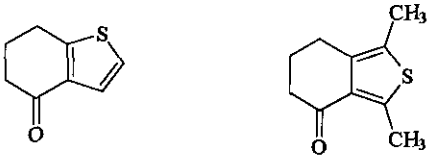
Ellipticine	$R_1 = R_4 = H$, $R_2 = R_3 = CH_3$
9-Methoxyellipticine	$R_1 = OCH_3$, $R_2 = R_3 = CH_3$, $R_4 = H$
Olivacine	$R_1 = R_2 = H$, $R_3 = R_4 = CH_3$

Our strategy was based on the work of Stilwell and Woodward.[5] They have described a approach to 6*H*-pyrido[4,3-*b*]carbazole skeleton *via* a Fischer indole synthesis, followed by a dehydrogenation (Scheme 1).



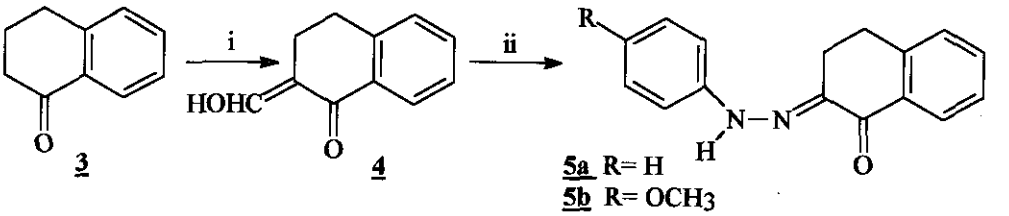
Scheme 1

In our case a Fischer indole synthesis will be applied onto keto-thiophenes (1) and (2).



1 2

During our efforts to develop a synthetic route to the thiophene analogues of ellipticine derivatives, α-tetralone (3) has been used as a readily available model compound. The synthetic route (Schemes 2 and 3) used were identical to the route applied to thienoketones (1) and (2) (Schemes 4 and 5).

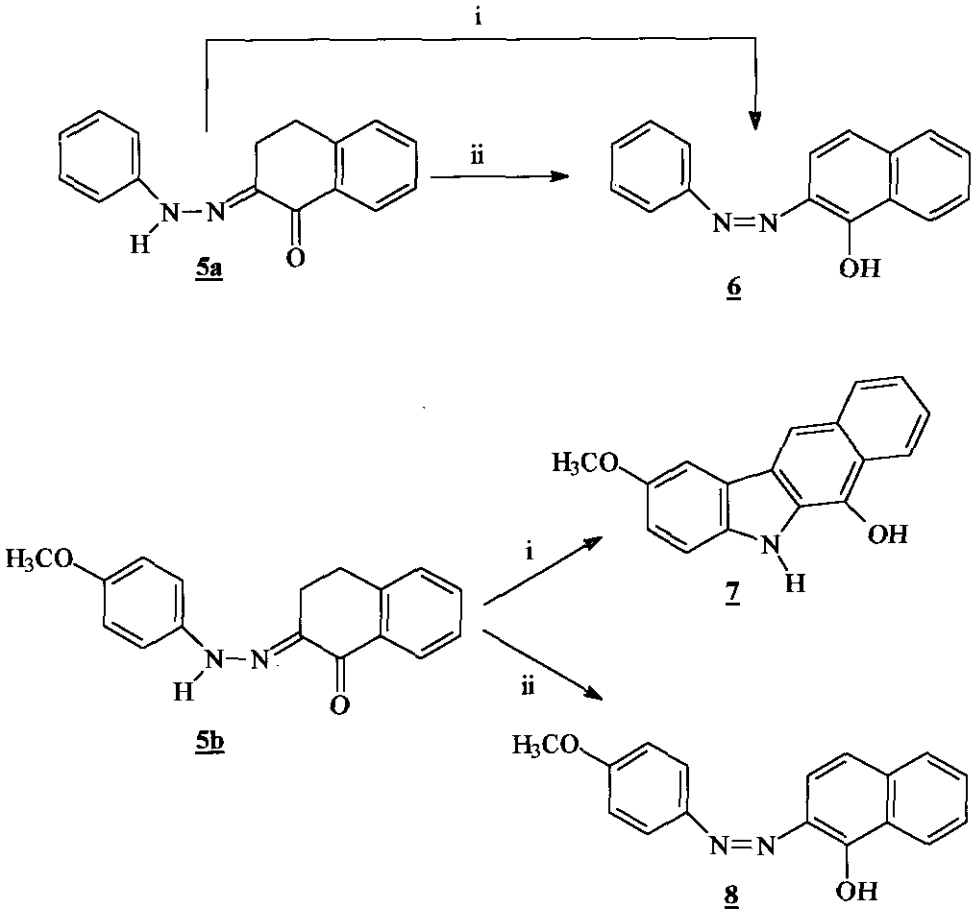


3 4 5a R= H 5b R= OCH_3

Reagents and conditions : i, $HCOOC_2H_5$, CH_3ONa, toluene; ii, *p*-R-Ph-N_2^+, CH_3COONa, CH_3OH.

Scheme 2

The Japp-Klingemann reaction [5] of 2-hydroxymethylene-1-tetralone (4) with phenyl- and 4-methoxyphenyl-diazonium chloride afforded the hydrazones (5a) and (5b) (Scheme 2). The hydrazones (5a) and (5b) were cyclised with the acidic conditions generally used.[6] The results are presented in Scheme 3. Depending of the substituent on the phenyl ring, either aromatisation or cyclisation occurred. When R= H (5a) only aromatisation to the azo derivative (6) was observed. Structure of 6 has been confirmed by aromatisation of 5a with DDQ in refluxing benzene. When R= OCH_3 (5b), then the cyclisation occurs as the only reaction. No presence of the aromatised product (8) (prepared separately using DDQ) could be detected in the reaction.

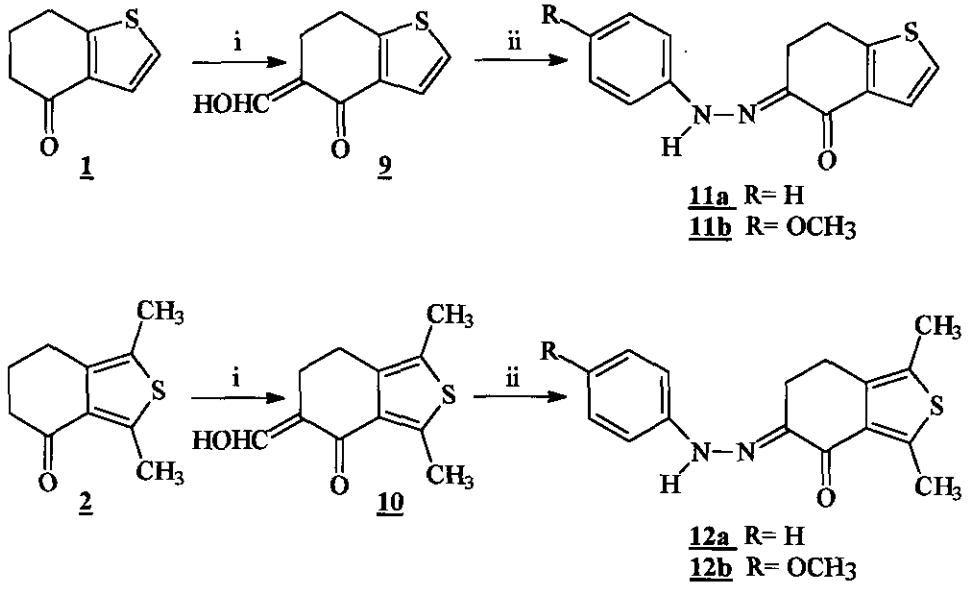


Reagents and conditions : i, THF /conc. HCl (10:1), reflux; ii, DDQ, benzene, reflux.

Scheme 3

The same route was applied to two thiophene analogues of 1-tetralone: 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene[7] (1) and 2,7-dimethyl-3-oxo-3,4,5,6-tetrahydrobenzo[*c*]thiophene[8] (2) (Scheme 4).

The hydroxymethylene derivatives (9) and (10) were transformed into the hydrazones (11) and (12) in good yields *via* a Japp-Klingemann reaction.



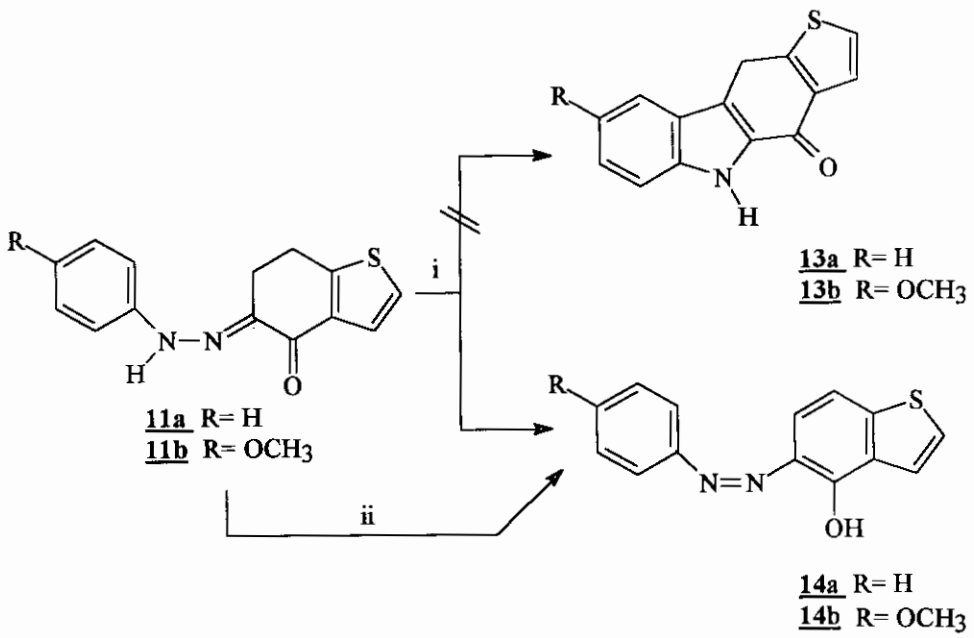
Reagents and conditions : i, $HCOOC_2H_5$, CH_3ONa, toluene; ii, *p*-R-Ph-N_2^+, CH_3COONa, CH_3OH.

Scheme 4

Treatement of compounds (11a) and (11b) with THF/conc. HCl (10:1) did not afford the desired tetracyclic structures (13a) and (13b) but led to the azo derivatives (14a) and (14b) resulting from the aromatisation of the starting material (Scheme 5). The transformation of hydrazones (11a) and (11b) with DDQ to 14a and 14b respectively confirmed the aromatisation under Fischer indolisation conditions.

In fact, aromatisation of hydrazone (11b) is already observed when the compound is recrystallised from ethanol. The same behaviour is not observed for compound (11a). If for the benzenoic analogues (5), the presence of the methoxy group in para position seems to favour the cyclisation versus aromatisation, the dehydrogenation is made easier in the case of benzo[*b*]thiophene derivative. In the case of

benzo[*c*]thiophene derivative (**12b**) cyclisation occurred normaly under acidic conditions, unfortunatly compound (**12a**) gave mainly resinification under the same conditions (Scheme 6). The azo derivatives (**16a**) and (**16b**) were prepared using DDQ in refluxing benzene (Scheme 7).



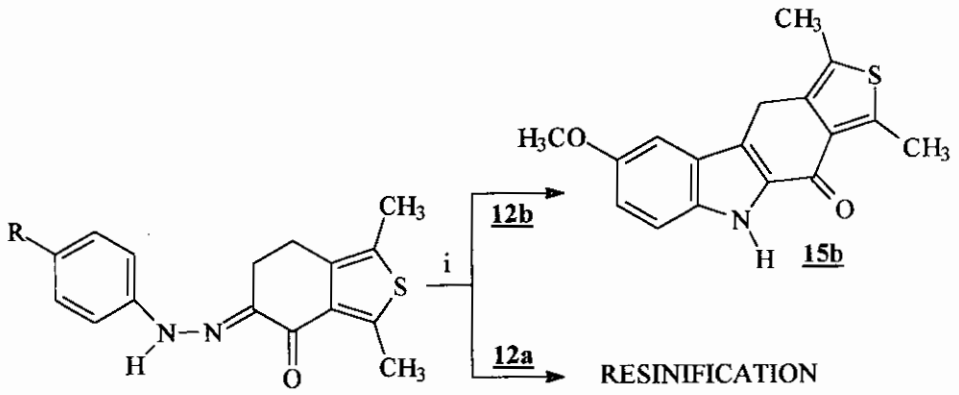
11a R= H
11b R= OCH_3

13a R= H
13b R= OCH_3

14a R= H
14b R= OCH_3

Reagents and conditions : i, THF /conc. HCl (10:1), reflux; ii, DDQ, benzene, reflux.

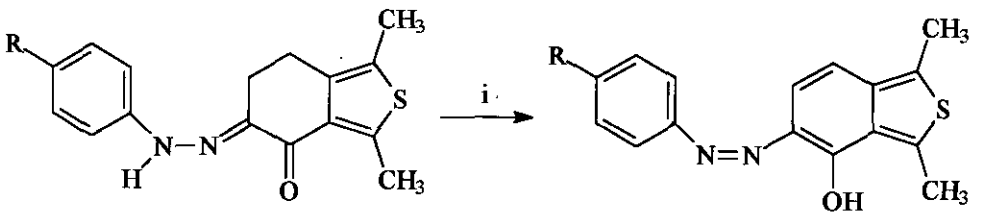
Scheme 5



12a R= H
12b R= OCH_3

Reagents and conditions : i, THF /conc. HCl (10:1), reflux.

Scheme 6



12a R= H
12b R= OCH_3

16a R= H
16b R= OCH_3

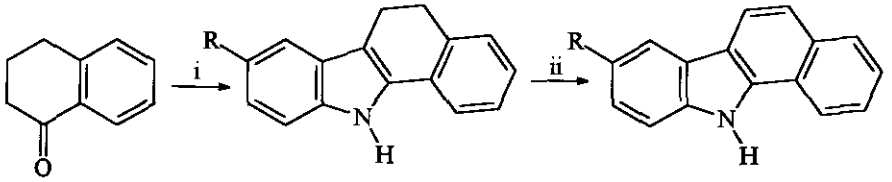
Reagents and conditions : i, DDQ, benzene, reflux.

Scheme 7

The competition between cyclisation and dehydrogenation of the arylhydrazones observed for the benzene analogues seems not to occur for thiophene compounds. Indeed, the only isolable compounds after acidic treatment of arylhydrazone benzo[*b*]thiophene derivatives (11a) and (11b) were azo compounds (14a) and (14b), in opposition to arylhydrazone benzo[*c*]thiophene derivatives (12b) and (12a) which respectively led to tetracyclic compounds (15b) and resinification with no trace of (16b) and (16a).

Fischer indole synthesis applied to the hydrazones (5), (11) and (12) was thought to allow the synthesis of analogues of ellipticine and related derivatives. We have shown that there is a competition between aromatisation to azo compounds and cyclisation.

Having the ketones (1) and (2) at hand, we decided to apply directly the synthesis on them. The reaction of 1-tetralone (3) in the Fischer indole synthesis is known[9] leading the 11*H*- 5,6-dihydrobenzo[*a*]carbazole easily dehydrogenated to the 11*H*-benzo[*a*]carbazole (Scheme 8).



3

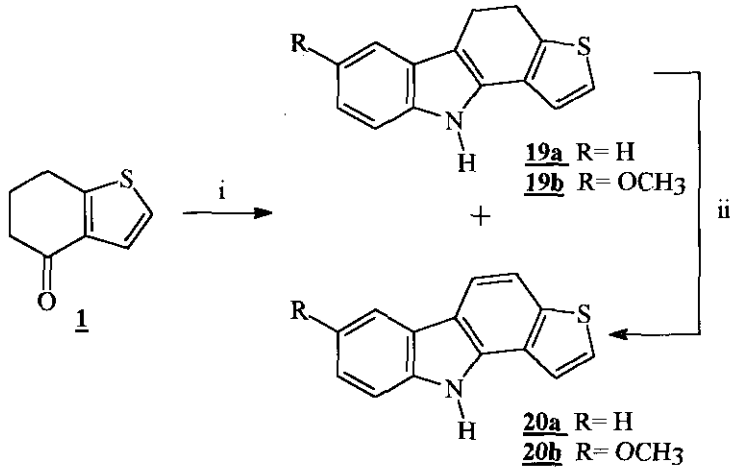
17a R= H
17b R= OCH_3

18a R= H
18b R= OCH_3

Reagents and conditions : i, *p*-R-Ph-NH-NH_2,HCl, CH_3COOH, reflux; ii, DDQ, benzene, reflux.

Scheme 8

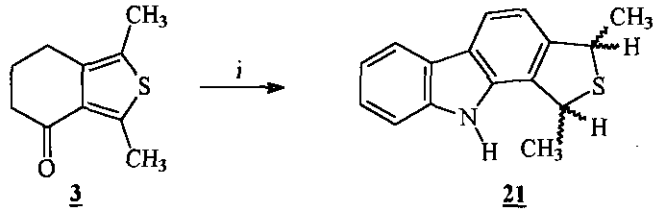
In the same reaction conditions, the 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (1) gave a mixture of the dihydro and the fully aromatic compounds (19) and (20). The presence of the two compounds was confirmed by the nmr spectrum of the reaction mixture. Other case of aromatisation during cyclisation has been already observed.[10] Separation of compounds (19) and (20) was difficult and the reaction mixture was treated with DDQ to afford only compound (20) (Scheme 9).



Reagents and conditions : i, *p*-R-Ph-NH-NH_2,HCl, CH_3COOH, reflux; ii, DDQ, benzene, reflux.

Scheme 9

Treatment of the 2,7-dimethyl-3-oxo-3,4,5,6-tetrahydrobenzo[*c*]thiophene (2) with phenylhydrazine hydrochloride in refluxing acetic acid gave the cyclisation reaction with a double bond shift giving 21, the only compound present at the end of the reaction. In this case carbazole appears taking away the electrons from the thiophene moiety (Scheme 10).



3 21

Reagents and conditions : i, *p*-R-Ph-NH-NH_2,HCl, CH_3COOH, reflux.

Scheme 10

Compound (21) is prepared with moderate yield (70%). Unfortunatly, the same reaction with 4-methoxyphenylhydrazine hydrochloride only gave resinification.

EXPERIMENTAL

^{1}H Nmr spectra were recorded using 250 MHz Bruker spectrometer. The operating frequency and the solvent are quoted in parenthesis before the chemical shift values (δ relative to internal $CDCl_3$). Mp were determined on a Kofler bench and are uncorrected. Elemental analysis were made on a Carlo Erba elemental analyser.

General procedure for the Japp-Klingemann reaction.

To a well stirred solution of sodium acetate (0.82 g, 10 mmol) in water (5 ml) was added the hydroxymethylene derivative[11] (5 mmol) in methanol (10 ml). After 10 min, a solution of the phenyldiazonium chloride derivative (5.5 mmol) is added dropwise. The precipited phenylhydrazone was collected by filtration and wasched with water.

2-Phenylhydrazone-1-tetralone (5a) : mp 82°C (from MeOH). Yield 90%. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.80; H, 5.60; N, 11.20. Found: C, 76.76; H, 5.69; N, 11.26. ^{1}H Nmr δ_H ($CDCl_3$) 2.99 (4H, m), 7.03 (1H, m), 7.33 (6H, m), 7.50 (1H, m), 8.05 (1H, d, J = 7.7 Hz) and 14.05 (1H, s).

2-(4-Methoxyphenylhydrazone)-1-tetralone (5b) : mp 115°C (from MeOH). Yield 85%. Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.85; H, 5.71; N, 10.00. Found: C, 72.93; H, 5.64; N, 9.97. ^{1}H Nmr δ_H ($CDCl_3$) 3.02 (4H, m), 3.81 (3H, s), 6.89 (2H, d, J = 8.8 Hz), 7.26 (3H, m), 7.37 (1H, t, J = 7.4 Hz), 7.48 (1H, t, J = 7.0 Hz) and 14.15 (1H ,s).

4-Oxo-5 -phenylhydrazone-4,5,6,7-tetrahydrobenzo[*b*]thiophene (11a) : mp 140°C (from MeOH). Yield 80%. Anal. Calcd for $C_{14}H_{12}N_2OS$: C, 65.62; H, 4.68; N, 10.93; S, 12.50. Found: C, 65.69; H, 4.57; N, 10.89; S, 12.44. ^{1}H Nmr δ_H ($CDCl_3$) 3.13 (4H, m), 6.98 (1H, t, J = 6.8 Hz), 7.15 (1H, d, J = 5.3 Hz), 7.28 (4H, m), 7.46 (1H, d, J = 5.3 Hz) and 13.62 (1H, s).

4-Oxo-5-(4-methoxyphenylhydrazone)-4,5,6,7-tetrahydrobenzo[*b*]thiophene (11b) : mp 112°C (from MeOH). Yield 80%. Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.78; S, 11.20. Found: C, 62.92; H, 5.07; N, 9.81; S, 11.26. ^{1}H Nmr δ_H (DMSO-d_6) 3.05 (4H, m), 3.72 (3H, s), 6.91 (2H, d, J = 9 Hz), 7.27 (2H, d, J = 9), 7.38 (2H, m) and 13.75 (1H, s).

2,7-Dimethyl-3-oxo-4-phenylhydrazone-3,4,5,6-tetrahydrobenzo[*c*]thiophene (12a) : mp 84-85°C (from MeOH). Yield 72%. Anal. Calcd for $C_{16}H_{16}N_2OS$: C, 67.60; H, 5.63; N, 9.86; S, 11.26. Found: C, 67.58; H, 5.66; N, 9.85; S, 11.23. ^{1}H Nmr δ_H ($CDCl_3$) 2.31 (3H, s), 2.78 (3H, s), 2.83 (4H, m), 6.98 (1H, m), 7.28 (4H, m) and 10.07 (1H, s).

2,7-Dimethyl-3-oxo-4-(4-methoxyphenylhydrazone)-3,4,5,6-tetrahydrobenzo[*c*]thiophene (12b) : mp 112-113°C (from MeOH). Yield 70%. Anal. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.49; H, 5.73; N, 8.92; S, 10.18. Found: C, 64.45; H, 5.76; N, 8.87; S, 10.19. ^{1}H Nmr δ_H ($CDCl_3$) 2.25 (3H, s), 2.71 (3H, s), 2.76 (4H, m), 3.74 (3H, s), 6.82 (2H, d, J = 9 Hz), 7.16 (2H, d, J = 9 Hz), 9.98 (1H, s).

General procedure for reaction of hydrazones with THF/conc. HCl

The hydrazone (10 mmol) was refluxed in 30 ml of THF/conc. HCl (10:1) for 2 h . The mixture was allowed to cool to room temperature. Water was added and the solid was collected by filtration.

2-Phenylazo-1-naphthol (6) : mp 135°C (from MeOH). Yield 90%. Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.42; H, 4.84; N, 11.28. Found: C, 77.36; H, 4.98; N, 11.15. ^{1}H Nmr δ_H ($CDCl_3$) 7.01 (1H, d, J = 9.4 Hz), 7.24 (2H, m), 7.47 (3H, m), 7.61 (4H, m), 8.42 (1H, d, J = 7.9 Hz) and 16.22 (1H, s).

11-Hydroxy-7-methoxy-10*H*-benzo[*b*]carbazole (7) : mp>300°C (from MeOH). Yield 75%. Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.48; H, 4.85; N, 5.32. ^{1}H Nmr δ_H ($CDCl_3$) 3.09 (3H, s), 6.07 (1H, d, J = 8.6 Hz), 6.33 (2H, t, J = 8.7 Hz), 6.42 (1H, d, J = 8.7 Hz), 6.75 (1H, s), 6.95 (1H, d, J = 7.8 Hz), 7.18 (1H, s), 7.26 (1H, d, J = 7.8 Hz), 8.52 (1H, s) and 9.38 (1H, s).

4-Hydroxy-5-phenylazobenzo[*b*]thiophene (14a) : mp 126°C (from MeOH). Yield 70%. Anal. Calcd for $C_{14}H_{10}N_2OS$: C, 66.14; H, 3.94; N, 11.02; S, 12.59. Found: C, 66.28; H, 3.87; N, 11.12; S, 12.50. ^{1}H Nmr δ_H ($CDCl_3$) 7.25 (1H, m), 7.38 (3H, m), 7.51 (2H, m), 7.64 (1H, J = 8.7 Hz), 7.69 (1H, d, J = 5.5 Hz), 7.81 (1H, d, J = 7.5 Hz) and 14.04 (1H, s).

4-Hydroxy-5-(4-methoxyphenylazo)benzo[*b*]thiophene (14b) : mp 135-136°C (from MeOH). Yield 70%. Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 63.30; H, 4.28; N, 9.95; S, 11.21. ^{1}H Nmr δ_H ($CDCl_3$) 3.89 (3H, s), 7.02 (2H, d, J = 9.0 Hz), 7.37 (1H, d, J = 5.5 Hz), 7.45 (1H, d, J = 8.7 Hz), 7.67 (1H, d, J = 5.5 Hz), 7.76 (1H, d, J = 8.7 Hz), 7.84 (2H, d, J = 9.0 Hz) and 14.67 (1H, s).

1,3-Dimethyl-4-hydroxy-6-methoxy-10-oxo-9*H*-thieno[3,4-*b*]carbazole (15b) : mp>300°C (from MeOH). Yield 75%. Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.68; H, 5.05; N, 4.71. Found: C, 68.71; H, 5.01; N, 4.72. ^{1}H Nmr δ_H (DMSO d_6) 2.42 (3H, s), 2.81 (3H, s), 3.82 (3H, s), 4.05 (2H, s), 7.02 (1H, dd, J = 7.5 and 2.5 Hz), 7.22 (2H, m) and 7.47 (1H, d, J = 9 Hz).

General procedure for the preparation of compounds (17), (19)/(20)* and (21).

To a well stirred suspension of the substituted phenylhydrazine hydrochloride (4.6 mmol) in glacial acetic acid (15 ml) at 80°C was added dropwise a solution of the ketone (4.2 mmol) in glacial acetic acid (5 ml). The mixture was heated at reflux for 3 h and after cooling, added in small portions to cold water (200 ml) with stiring. The solid was collected and recrystallized.

* As in this case, compounds (19) and (20) were obtained (yield 80%) in a mixture inseparable by chromatography, the mixture of 19 and 20 was directly treated with DDQ in refluxing benzene.

5,6-Dihydro-11*H*-benzo[*a*]carbazole (17a) : mp 157°C (from MeOH). Yield 80%. Anal. Calcd for $C_{16}H_{13}N$: C, 87.67; H, 5.93; N, 6.39. Found: C, 87.71; H, 5.89; N, 6.38. ^{1}H Nmr δ_H ($CDCl_3$) 3.07 (4H, m), 7.27 (7H, m), 7.57 (1H, d, J = 7.3 Hz) and 8.22 (1H, s).

8-Methoxy-5,6-dihydro-11*H*-benzo[*a*]carbazole (**17b**) : mp 184-185°C (from MeOH). Yield 75%. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.93; H, 6.02; N, 5.62. Found: C, 81.91; H, 6.06; N, 5.68. ^{1}H Nmr δ_H ($CDCl_3$) 3.05 (4H, m), 3.92 (3H, s), 6.86 (1H, dd, J = 8.6 and 2.2 Hz), 7.01 (1H, d, J = 2.2 Hz), 7.23 (5H, m) and 8.13 (1H, s).

1,3-Dimethyl-1,3-dihydrothieno[3,4-*a*]carbazole (**21**) : mp 170°C (from MeOH). Yield 70%. Anal. Calcd for $C_{16}H_{15}NS$: C, 75.88; H, 5.92; N, 5.53. Found: C, 75.85; H, 5.93; N, 5.55. ^{1}H Nmr δ_H ($CDCl_3$) 1.68 (3H, d, J = 7.5 Hz), 1.76 (3H, d, J = 7.5 Hz), 4.74 (1H, q, J = 7.5 Hz), 4.93 (1H, q, J = 7.5 Hz), 7.08 (1H, d, J = 8.2 Hz), 7.18 (1H, t, J = 7.8 Hz), 7.52 (1H, d, J = 8.2 Hz), 8.02 (1H, d, J =8.2 Hz), 8.09 (1H, d, J = 7.8 Hz) and 11.25 (1H, s).

***General procedure for dehydrogenation using* DDQ.**

A mixture of the hydrogenated compound (10 mmol) and DDQ (2.27 g, 10 mmol) was refluxed in dry benzene (50 ml) for 1 h . The solvent was evaporated under vacuum and the residue was poured in 100 ml of dichloromethane and the hydroquinone was filtered through a pad of Cellite. Concentration of the filtrate a gave crude product which was purified by chromatography on *alumina with dichloromethane* as eluent.

2-(4-Methoxyphenylazo)naphtol (**8**) : mp 106°C (from CH_2Cl_2). Yield 90%. Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.42; H, 4.84; N, 11.28. Found: C, 73.31; H, 4.98; N, 11.15. ^{1}H Nmr δ_H ($CDCl_3$) 7.01 (1H, d, J = 9.4 Hz), 7.24 (2H, m), 7.47 (3H, m), 7.61 (4H, m), 8.42 (1H, d, J = 7.9 Hz) and 16.22 (1H, s).

2,7-Dimethyl-3-hydroxy-4-phenylazobenzo[*c*]thiophene (**16a**) : mp 84-85°C (from CH_2Cl_2). Yield 75%. Anal. Calcd for $C_{16}H_{14}N_2OS$: C, 68.08; H, 4.96; N, 9.93; S, 11.35. Found C, 68.12; H, 4.87; N, 9.94; S, 11.28. ^{1}H Nmr δ_H ($CDCl_3$) 2.47 (3H, s), 2.91 (3H, s), 7.09 (1H, t, J = 7.1 Hz), 7.39 (6H, m) and 15.13 (1H, s).

2,7-Dimethyl-3-hydroxy-4-(4-methoxyphenylazo)benzo[*c*]thiophene (16b) : mp 112-113°C (from CH_2Cl_2). Yield 70%. Anal. Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.38; H, 5.13; N, 8.97; S, 10.25. Found C, 65.43; H, 5.07; N, 8.88; S, 10.28. ^{1}H Nmr δ_H ($CDCl_3$) 2.48 (3H, s), 2.92 (3H, s), 3.82 (3H, s), 6.92 (2H, d, J = 9.0 Hz), 7.38 (3H, m), 7.53 (1H, d, J = 8.3 Hz) and 15.21 (1H, s).

11*H*-Benzo[*a*]carbazole (18a) : mp 213°C (from CH_2Cl_2). Yield 90%. Anal. Calcd for $C_{16}H_{11}N$: C, 88.48; H, 5.07; N, 6.45. Found C, 88.53; H, 4.98; N, 6.49. ^{1}H Nmr δ_H ($CDCl_3$) 7.32 (1H, t, J = 7.6 Hz), 7.46 (1H, t, J = 8.2 Hz), 7.58 (1H, d, J = 8.6 Hz), 8.03 (1H, d, J = 7.3 Hz), 8.15 (3H, m) and 8.84 (1H, s).

8-Methoxy-11*H*-benzo[*a*]carbazole (18b) : mp 218°C (from CH_2Cl_2). Yield 85%. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.58; H, 5.26; N, 5.67. Found C, 82.51; H, 5.24; N, 5.72. ^{1}H Nmr δ_H ($CDCl_3$) 3.97 (3H, s), 7.09 (1H, d, J = 8.6 Hz), 7.48 (1H, d, J = 8.6 Hz), 7.58 (4H, m), 8.00 (1H, d, J = 7.8 Hz), 8.09 (1H, d, J = 8.4 Hz), 8.12 (1H, d, J = 7.2 Hz) and 8.77 (1H, s).

10*H*-Thieno[3,2-*a*]carbazole (20a) : mp 225°C (from CH_2Cl_2). Yield 70%. Anal. Calcd for $C_{14}H_9NS$: C, 75.33; H, 4.03; N, 6.27; S, 14.35. Found C, 75.36; H, 3.98; N, 6.29; S, 14.25. ^{1}H Nmr δ_H ($CDCl_3$) 7.21 (1H, t, J = 7.5 Hz), 7.39 (1H, t, J = 7.5 Hz), 7.58 (1H, d, J = 8.1 Hz), 7.73 (1H, d, J = 8.1 Hz), 7.82 (1H, d, J = 4.5 Hz), 7.91 (1H, d, J = 4.5 Hz), 8.11 (1H, d, J = 8.1 Hz), 8.15 (1H, d, J = 8.1 Hz) and 11.81 (1H, s).

7-Methoxy-10*H*-thieno[3,2-*a*]carbazole (20b) : mp 240°C (from CH_2Cl_2). Yield 60%. Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.66.Found C, 71.27; H, 4.48; N, 5.58; S, 1.59. ^{1}H Nmr δ_H ($CDCl_3$) 3.85 (3H, s), 7.04 (1H, dd, J =9 and 2.5 Hz), 7.51 (1H, d, J = 9 Hz), 7.69 (2H, m), 7.81 (1H, d, J = 5.5 Hz), 7.88 (1H, d, J = 5.5 Hz), 8.11 (1H, d, J = 8.4 Hz) and 11.75 (1H, s).

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