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N-HETEROCYCLES BY CYCLIZATION OF 2'-NHR-CHALCONES, 2'-NHR-CHALCONE DIBROMIDES AND 2'-NHR-α-AZIDOCHALCONES.

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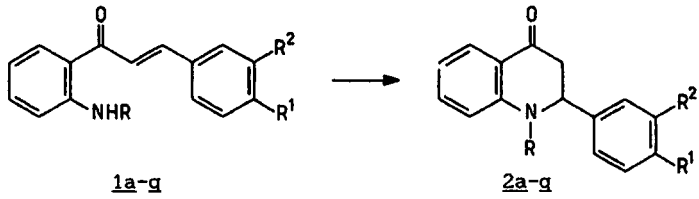
Abstract: Syntheses of six-membered N-heterocycles from 2'-NHR--chalcones, 2'-NHR-chalcone dibromides and 2'-NHR-α-azidochalcones are described and discussed.

Convenient syntheses of 2'-aminochalcone[1-4] and its 2'-amido (acetyl[2,4], benzenesulfonyl[4], tosyl[5]) derivatives and the ready cyclization of these compounds to 2-aryl-1,2,3,4-tetrahydro-4--quinolones[1-6] suggest that this is probably a useful route to related quinolones substituted in either aromatic ring. Here we summarize our experiences with the acid-(A) or base-(B) catalyzed cyclization of 2'-NHR-chalcones (1a-g)[1-11] to the corresponding 2-aryl-1,2,3,4--tetrahydro-4-quinolones (2a-g).

*To whom correspondence should be addressed



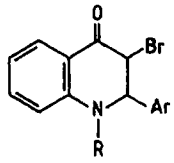
1a-g 2a-g

Compounds	R	R^1	R^2	References 1	References 2	Cyclization method
a	H	H	H	1-4	1-4,6	A
b	H	OCH_3	H	7	7	A
c	H	CH_3	H	8		A
d	H	Br	H	8		A
e	H	NO_2	H	8		A
f	H	$O\text{-}CH_2\text{-}O$		9	9	A
g	H	$O\text{-}CH_2\text{-}CH_2\text{-}O$		10	10	A
h	SO_2Ph	H	H	4	4	B
i	SO_2Ph	OCH_3	H	7	7	B
j	Tosyl	H	H	5	5,11	B
k	Tosyl	OCH_3	H	11	11	B
l	Tosyl	CH_3	H	8		B
m	Tosyl	Br	H	8		B
n	Tosyl	NO_2	H	8		B
o	Tosyl	$O\text{-}CH_2\text{-}O$		9	9	B
p	Tosyl	$O\text{-}CH_2\text{-}CH_2\text{-}O$		10		B
q	$COCH_3$	H	H	2,4	2	B

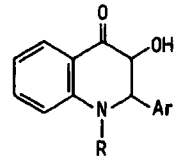
Compounds 2a-g were prepared in a reaction catalyzed by orthophosphoric acid in acetic acid whereas 2h-q were obtained by base-catalyzed cyclization of the 2'-NHR-chalcones using aqueous ethanolic sodium hydroxide. The conversion efficiency depends on the electronic character of R^1, R^2 substituents in ring B. For example: formation of 2a, b, c is almost quantitative. In the case of 2e the yield is

only 20% and other unidentified products were detected by TLC. Independently from our work McDonnell et al.[12] studied the kinetics of the ring closure of 2'-aminochalcones (1a, b, c, e) in trifluoroacetic acid (TFA) and TFA-d using NMR. The pseudo-first order rate constants determined can be compared to our data obtained on a preparative scale. The 2'-acetamidochalcone (1g) yielded 2a[4] in an acid-catalyzed cyclization. Base-catalyzed reaction, on the other hand gave 1-acetyl-2-phenyl-1,2,3,4-tetrahydro-4-quinolone (2g) in low yield[2]. Cyclization of other 2'-acetamidochalcones to 1-acetyl-4--quinolone derivatives with the above methods was not successful. Substituents in ring A can also affect the ring closure reaction. For example, 2'-amino-5'-bromo- and 2'-amino-3',5'-dibromochalcones were isomerized easily to the corresponding 6-bromo-, or 6,8-dibromo--substituted 4-quinolones in glacial acetic acid[9].

4-Quinolones, substituted by bromine or hydroxy groups in position 3 of the heterocyclic ring were obtained from side-chain brominated or bromo-methoxylated chalcones or chalcone epoxide, respectively.



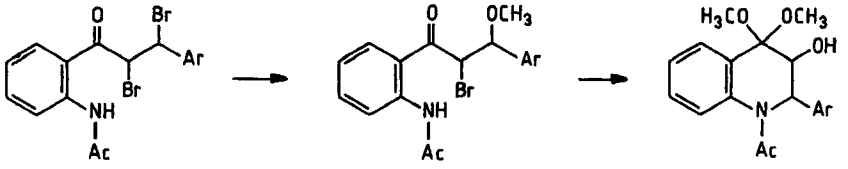
R=Ac[4], SO_2Ar[4,7], Tosyl[9,13]



R=H[4,11]

According to Donnelly and Farrell[4] 2'-aminochalcone dibromide and 2'-amino-α-bromo-β-methoxydihydrochalcone gave no heterocyclic products under typical Emilewicz von Kostanecki reaction conditions (with ethanolic KOH)[14]. As an extension of this work we studied the reactions of 2'-NHR-chalcone dibromides (3a-c, R=H, acetyl, tosyl) under the action of NaOH in H_2O-MeOH in various concentrations. We

were able to isolate a heterocyclic product in only one case. In a solution containing 1M NaOH 2'-acetamidochalcone dibromide (3b) gave rises to the formation of 1-acetyl-3-hydroxy-4,4-dimethoxy-2-phenyl--1,2,3,4-tetrahydroquinoline (5) presumably via initial formation of 2'-acetamido-α-bromo-β-methoxydihydrochalcone (4)[4,8]. Reaction of 4 with 1M NaOH in MeOH gave also 5.



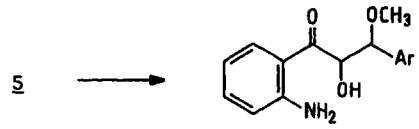
3b 4 5

In the O-heterocyclic series base-catalyzed cyclization of α-bromo-β--alkoxydihydrochalcones yielded aurone and flavone (Wheeler synthesis[15]). The structure of 5 was unambiguously established from the ^{1}H and ^{13}C NMR spectra. The >CH-CH<^{OH} fragment is evident from the presence of a well-resolved coupling of the OH signal to one of the proton signals in a substituted ethane fragment. On the other hand, the absence of a C=O resonance around 190 ppm[3,16] from, and the presence of a quaternary carbon signal at 103.39 ppm in the ^{13}C NMR spectrum clearly speaks for the presence of an acetal carbon at position 4. These spectral data are compatible with only structures 5 and 6 below:

5 6

Structure 5 was selected as the right one on the basis that a selective INEPT[17] performed by exciting the OH doublet in the ^1H spectrum gave a response at the quaternary C at 103.39 ppm. The large value of $J_{2,3}$ (6.8 Hz) establishes the relative configuration of C(2) and C(3) as trans. The assignments of C(2) vs. C(3) were deduced from a H,C COSY measurement optimized to $^1J_{CH}$ values.

Acid catalysed (HCl) hydrolysis of the dimethyl acetal 5 in methanol at room temperature promoted ring opening and 2'-amino-α--hydroxy-β-methoxydihydrochalcone (7) could be isolated from the reaction mixture.



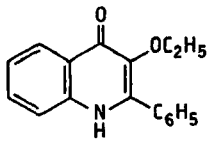
7

We also investigated ways to introduce an amino group into position 3 of the 4-quinolone ring. In the O-heterocyclic series we reported the synthesis of 3-aminoflavone from 2'-OR-chalcone dibromide via α-azidochalcone[18-20]. 2'-NHR-chalcone dibromides (3a-c) were reacted with sodium azide in DMF resulting 2'-NHR-α-azidochalcones (8a-c) in good yields.

3a-c 8a-c

	R
a	H[4]
b	Ac[4,13]
c	Tosyl[5]

The 2'-NHR-α-azidochalcones (8a-c) were reacted with NaOH in ethanol at room temperature and the reactions monitored by TLC. The conversions from 8b and 8c were complete in 24 h. Compound 8a did not react at room temperature but in boiling ethanol it gave 2-phenyl-3-ethoxy-4(1H)-quinolone (9) and 2-phenyl-4(1H)-quinolone (10). Compound 8b afforded 9 and 11b; 11c was obtained from 8c in good yield, however.



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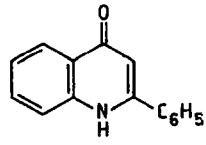

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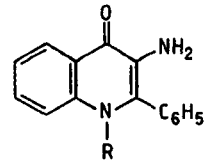


11

b R=Ac

c R=Tosyl

The formation of 11b and 11c is not surprising since the acylic NH is deprotonated upon the action of base, and an attack on the N-nucleophile is quite favourable yielding the N-substituted 3-azido--2-phenyl-1,2,3,4-tetrahydro-4-quinolone as an intermediate. Base induced nitrogen elimination[18,20] in the intermediate then yields 11b and 11c. Formation of 10 from the above intermediate can be explained through HN_3 elimination. The structures of the products were established on the basis of analytical data, and IR, NMR and mass spectra.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on a Bruker WP 200 SY spectrometer at 200 MHz for solution in $CDCl_3$, DMSO-d_6

or acetone-d_6 (internal standard TMS, δ=0.0 ppm) at room temperature. MS was obtained with a VG-7035 type mass spectrometer. IR spectra were measured for KBr discs with a Perkin Elmer 16 PC FT-IR instrument.

Synthesis of 2-aryl-1,2,3,4-tetrahydro-4-quinolones (2c-e) by the acid-catalyzed cyclization of 2'-NH_2-chalcones (1c-e)

A mixture of 2'-aminochalcone (1c-e, 3 mmol), glacial acetic acid (12.5 ml) and orthophosphoric acid (12.5 ml) was warmed at 100 ^{0}C for 20 min. After cooling the mixture was poured into iced water. The product precipiteted was purified by column chromatography on Kieselgel 60 using hexane-ethylacetate (1:1) as eluent.

2-(4'-Methylphenyl)-1,2,3,4-tetrahydro-4-quinolone (2c)

Yield: 85%, m.p. 149 ^{0}C. ^{1}H NMR 7.85 (dd,1H, H-5); 7.40-6.70 (m, 7H, aromatic); 4.70 (dd, 1H, H-2; $J_{2,3e}$= 4.0 Hz; $J_{2,3a}$= 12.0 Hz); 4.50 (bs, 1H, NH); 2.80 (m, 2H, H-3e, H-3a); 2.35 (s, 3H, CH_3)

Anal. Calcd. for $C_{16}H_{15}NO$: N, 5.90. Found: N, 5.90.

2-(4'-Bromophenyl)-1,2,3,4-tetrahydro-4-quinolone (2d)

Yield: 70%, m.p. 171 ^{0}C. ^{1}H NMR 7.90 (dd, 1H, H-5); 7.55-6.70 (m, 7H, aromatic); 4.70 (dd, 1H, H-2; $J_{2,3e}$= 4.2 Hz; $J_{2,3a}$= 10.5 Hz); 4.50 (bs, 1H, NH); 2.80 (m, 2H, H-3e, H-3a)

Anal. Calcd. for $C_{15}H_{12}BrNO$: Br, 26.44; N, 4.63.Found: Br, 25.95; N, 4.60.

2-(4'-Nitrophenyl)-1,2,3,4-tetrahydro-4-quinolone (2e)

Yield: 20%, m.p. 194 ^{0}C. ^{1}H NMR 8.25 (dd, 1H, H-5); 7.90-6.80 (m, 7H, aromatic); 4.90 (dd, 1H, H-2; $J_{2,3e}$= 5.2 Hz; $J_{2,3a}$= 10.0 Hz); 4.55 (bs, 1H, NH); 2.80 (m, 2H, H-3e, H-3a)

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: N, 10.44. Found: N, 10.45.

Synthesis of 2-aryl-1-tosyl-1,2,3,4-tetrahydro-4-quinolones (2l-n,p) by base-catalyzed cyclization of 2'-tosylamidochalcones (1l-n,p)

A solution of 2'-tosylamidochalcone (1l-n,p; 1.6 mmol) in ethanol and aqueous NaOH (1%, 10 ml) was warmed at 60 °C for 10 min. After addition of water the precipitate crystallized from ethanol.

2-(4'-Methylphenyl)-1-tosyl-1,2,3,4-tetrahydro-4-quinolone (2l)

Yield: 80%, m.p. 161 °C. ^{1}H NMR 7.50-7.0 (m, 12H, aromatic); 5.90 (dd, 1H, H-2); 2.75 (m, 2H, H-3a, H-3e; $J_{2,3e}$= 3.9 Hz; $J_{2,3a}$= 12.0 Hz); 2.35 (s, 3H, 4'-CH_3); 2.20 (s, 3H, CH_3)

Anal. Calcd. for $C_{23}H_{21}NO_3S$: N, 3.57; S, 8.18. Found: N, 3.54; S, 8.02.

2-(4'-Bromophenyl)-1-tosyl-1,2,3,4-tetrahydro-4-quinolone (2m)

Yield:65%, m.p. 194 °C. ^{1}H NMR 7.65-7.0 (m, 12H, aromatic); 5.95 (dd, 1H, H-2); 2.70 (m, 2H, H-3a, H-3e; $J_{2,3e}$= 3.5 Hz; $J_{2,3a}$= 10.5 Hz); 2.20 (s, 3H, CH_3)

Anal. Calcd. for $C_{22}H_{18}BrNO_3S$: Br, 17.50; N, 3.06; S, 7.02. Found: Br, 17.52; N, 3.01.

2-(4'-Nitrophenyl)-1-tosyl-1,2,3,4-tetrahydro-4-quinolone (2n)

Yield: 18%, m.p. 183 °C. ^{1}H NMR 7.55-7.10 (m, 12H, aromatic); 5.90 (dd, 1H, H-2); 2.75 (m, 2H, H-3a, H-3e; $J_{2,3e}$= 3.0 Hz; $J_{2,3a}$= 11.0 Hz); 2.18 (s, 3H, CH_3)

Anal. Calcd. for $C_{22}H_{18}N_2O_5S$: N, 6.63; S, 7.58. Found: N, 6.60; S, 7.52.

2-(3',4'-Ethylenedioxyphenyl)-1-tosyl-1,2,3,4-tetrahydro-4-quinolone (2p)

Yield: 40%, m.p. 148 °C. ^{1}H NMR 7.90-6.70 (m, 11H, aromatic); 5.80 (dd, 1H, H-2); 4.10 (s, 4H, 2xCH_2); 2.90 (dd, 1H, H-3e); 2.50 (dd, 1H,

H-3a; $J_{2,3e}$= 4 Hz; $J_{2,3a}$= 12.5 Hz); 2.20 (s, 3H, CH_3)

Anal. Calcd. for $C_{24}H_{21}NO_5S$: N, 3.21; S, 7.36. Found: N, 3.25; S, 7.40.

1-Acetyl-3-hydroxy-4,4-dimethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline (5)

a.) 2'-Acetamidochalcone dibromide (3b, 2 mmol) was suspended in methanol (50 ml) and 1M NaOH (10 ml) was added under stirring. The reaction was monitored by TLC. After 1h the methanol was evaporated and the residue was extracted with chloroform. The organic phase was washed with water, dried and evaporated yielding 4[4,8] and 5, which were separated on Kieselgel 60 using hexane-acetone (7:3) as eluent.

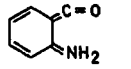
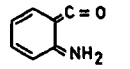
b.) 2'-Acetamido-α-bromo-β-methoxydihydrochalcone (4[4,8], 2.3 mmol) was suspended in methanol (50 ml) and 1M NaOH (10 ml) was added. The reaction was carried out as above. The yield of 5 is ~25% m.p. 132 ^{0}C. IR(KBr): 3650(OH), 1650(C=O), 1100(acetal) cm^{-1}. MS: m/z; 327(0.2; M^+); 310(0.25; M-17); 267(0.4; M-60); ^{1}H NMR 7.50-7.10 (m, 9H, aromatic); 4.04 (dd, 1H, H-3); 3.90 (d, 1H, H-2; $J_{2,3}$= 6.8 Hz); 3.20 (d, 1H, OH; $J_{3,OH}$= 3.0 Hz); 3.09 (s, 3H, OCH_3); 2.83 (s, 3H, OCH_3); 1.99 (s, 3H, $COCH_3$). ^{13}C NMR 83.34 (C-2); 79.60 (C-3); 103.39 (C-4); 119.62 (C-4a); 126.11* (C-5); 125.37* (C-6); 130.03 (C-7); 124.25* (C-8); 141.20 (C-8a); 138.84 (C-1'); 127.84 (C-2'/6'); 128.36 (C-3'/5'); 127.84 (C-4'); 50.18 and 56.28 (OCH_3); 159.62 (C=O); 20.91 (CH_3)

*Interchangeable assignments

Anal. Calcd. for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.28. Found: C, 69.55; H, 6.43; N, 4.26.

2'-Amino-α-hydroxy-β-methoxydihydrochalcone (7)

Compound 5, (0.17 mmol), methanol (10 ml) and 10% HCl (1.5 ml) was stirred at room temperature for 48h. The reaction mixture was

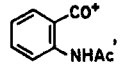
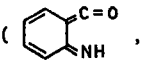
neutralized with 10% NaOH. The methanol was evaporated and than extracted with $CHCl_3$. After evaporation the residue was a syrup. Yield 65%. IR(KBr): 3646(OH), 3454, 3352(NH_2), 1618(C=O) cm^{-1}. ^1H NMR 7.30-6.60 (m, 9H, aromatic); 6.15 (bs, 2H, NH_2); 5.45 (d, 1H, H-β); 4.55 (d, 1H, H-α; $J_{H\alpha,H\beta}$= 4.6 Hz); 3.62 (d, 1H, OH; $J_{H\beta,OH}$=7.5 Hz); 3.28 (s, 3H, OCH_3). MS: m/z, 271 (M^+, 0.1); 255 (M-16, 0.1); 239 (M-32, 20); 120 ( ,100); 93 (( -HCN), 27)

General procedure of 2'-NHR-α-azidochalcones (8a-c)

2'-NHR-chalcone dibromide (3a-c, 2 mmol) was dissolved in abs DMF (10 ml) and sodium azide (6.5 mmol) was added under stirring at room temperature. After 24h the reaction mixture was diluted with water.

2'-Amino-α-azidochalcone (8a) Yield: 80%, syrup. IR(KBr): 3480, 3358(NH), 2114(N_3), 1616(C=O) cm^{-1}. ^1H NMR 7.90-6.70 (m, 9H, aromatic); 6.35 (s, 1H, H-β); 5.30 (m, 2H, NH_2, deuterable).

Anal. Calcd. for $C_{15}H_{12}N_4O$: N, 21.20. Found: N, 20.42.

2'-Acetamido-α-azidochalcone (8b) Yield: 96%, m.p. 130 °C (from ethanol). IR(KBr) 3360(NH), 2120(N_3), 1700, 1625(C=O) cm^{-1}. ^1H NMR 9.95 (s, 1H, NH, deuter.); 8.50-7.10 (m, 9H, aromatic); 6.35 (s, 1H, H-β); 2.2 (s, 3H, $COCH_3$). MS: m/z(%), 306 (M^+, 0.1); 278 ($(M-N_2)^+$, 37); 263 ($(M-CH_3CO)^+$, 7); 162 ( , 71); 119 ( ,43)

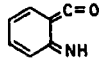
Anal. Calcd. for $C_{17}H_{14}N_4O_2$: N, 18.28. Found: N, 18.19.

2'-Tosylamido-α-azidochalcone (8c). Yield: 82%, m.p. 131-133 °C (from ethanol). IR(KBr): 3254(NH), 2120(N_3), 1626(C=O) cm^{-1}. ^1H NMR 8.95 (s, 1H, NH, deuter.); 7.85-7.0 (m, 13H, aromatic); 5.70 (s, 1H, H-β); 1.9 (s, 3H, CH_3). MS: m/z, 418 (M^+)

Anal. Calcd. for $C_{22}H_{18}N_4O_3S$: N, 13.38. Found: N, 13.05.

2-Phenyl-3-ethoxy-4(1H)quinolone (9) and 2-phenyl-4(1H)-quinolone (10)

2'-Amino-α-azidochalcone (8a, 1.5 mmol), NaOH (8%, 1ml) was boiled in ethanol (15 ml) for 5h. The mixture was neutralized with acetic acid and extracted with CH_2Cl_2. After evaporation the residue was purified by column chromatography using hexane-ethylacetate (4:1) as eluent.

Compound 9. Yield: 50%, m.p. 136-138 °C. IR(KBr):3338(NH), 1622(C=O) cm^{-1}. ^1H NMR 7.70 (m, 1H, NH, deuter.); 7.30-6.50 (m, 9H, aromatic); 3.50 (q, 2H, CH_2); 1.25 (t, 3H, CH_3). MS: m/z (%), 265 (M^+, 4); 264 (M-1, 20); 236 ($(M-C_2H_5)^+$, 14); 220 ($(M-OC_2H_5)^+$, 22); 119 ( , 8)

Anal. Calcd. for $C_{17}H_{15}NO_2$: N, 5.23. Found: N, 5.49.

Compound 10. Yield 35%, m.p. 249-251 °C (lit. m.p. 249-251[21]). IR(KBr):3420, 3064(NH), 1632(C=O) cm^{-1}. ^1H NMR 11.80 (s, 1H, NH, deuter.); 8.20-7.30 (m, 9H, aromatic); 6.35 (s, 1H, H-3). MS: m/z (%), 221 (M^+, 100); 220 ($(M-1)^+$, 30); 193 $(M-28)^+$, 63)

Anal. Calcd. for $C_{15}H_{11}NO$: N, 6.32. Found: N, 6.57.

1-Acetyl-3-amino-2-phenyl-4-quinolone (11b) and 2-phenyl-3-ethoxy--4(1H)-quinolone (9)

2'-Acetamido-α-azidochalcone (8b, 1.5 mmol) and NaOH (8%, 1ml) in ethanol (15 ml) was reacted at room temperature for 24h. The mixture was neutralized and than extracted with CH_2Cl_2. After evaporation the residue was purified by column chromatography on Kieselgel 60 with hexane-acetone (4:1). Compound 11b. Yield: 35%, m.p. 159-161 °C. IR(KBr): 3328(NH), 1698, 1622(C=O) cm^{-1}. ^1H NMR (acetone-d_6) 7.50-6.50 (m, 9H, aromatic); 5.50 (m, 2H, NH_2, deuter.); 2.10 (s, 3H, $COCH_3$). MS: m/z(%), 278 (M^+,1), 236 ($(M-CH_3CO)^+$, 10), 220 $(236-14)^+$, 40), 119 ($C_6H_5C{\equiv}CNH_2$, 24)

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: N, 10.06. Found: N, 9.57.

From the reaction mixture 9 was also isolated. Yield 28%, m.p. 138 °C.

1-Tosyl-3-amino-2-phenyl-4-quinolone (11c)

A mixture of 8c (1 mmol) and NaOH (80%, 1ml) in ethanol (50 ml) was kept at room temperature for 24h. After addition of water and acetic acid a crystalline product (11c) was obtained. Yield: 40%, m.p. 300-301 °C. IR(KBr): 3424(NH), 1624(C=O) cm^{-1}. ^1H NMR (DMSO-d_6) 11.80 (s, 2H, NH_2, deuter.); 8.05-7.10 (m, 13H, aromatic); 2.9 (s, 3H, CH_3). MS: m/z(%), 390 (M^+,1), 235 ($(M-CH_3-C_6H_4-SO_2)^+$, 100)

Anal. Calcd. for $C_{22}H_{18}N_2O_3S$: N, 7.17. Found: N, 7.16.

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