CYCLOADDITION REACTIONS WITH AZABENZENES, XVIII[1] SYNTHESIS OF [2]PYRINDINES

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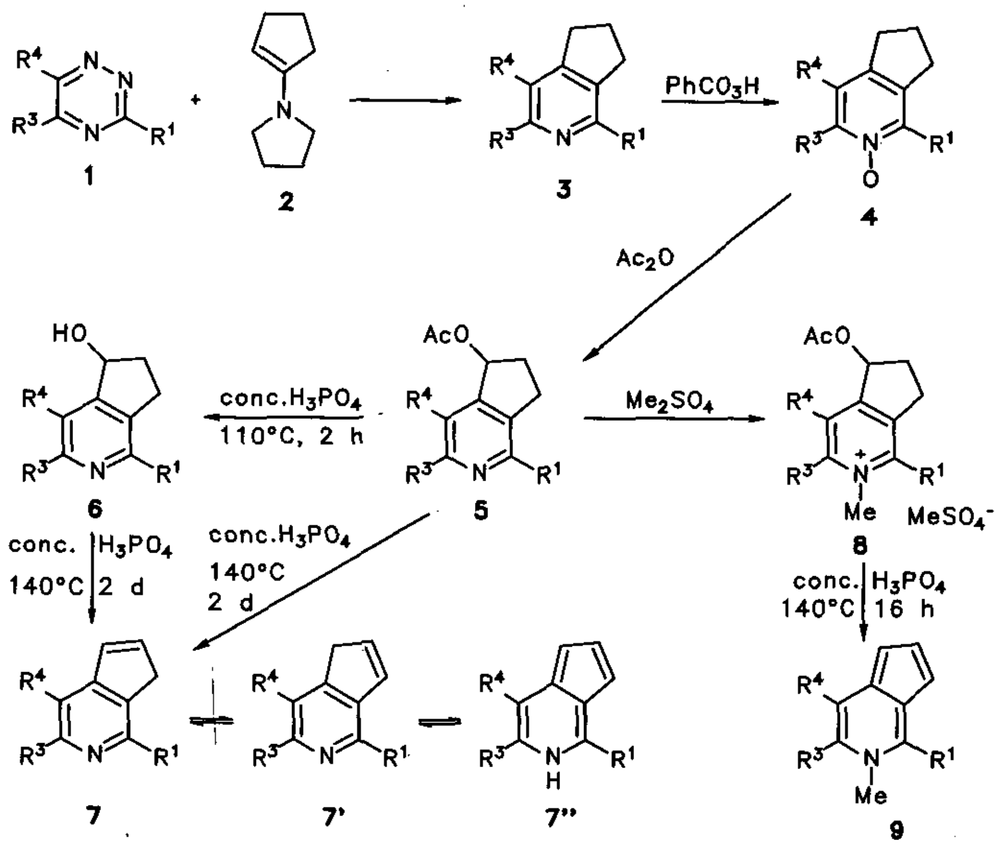
Abstract - The reaction of 1,2,4-triazines (1) and 1-cyclopentenylpyrrolidine (2) afforded 6,7-dihydro-5H-[2]-pyrindines (3) in good yields. Oxidation of 3 to the N-oxides (4), reaction of 4 with acetic anhydride to 5-acetoxy-6,7-dihydro-5H-[2]pyrindines (5) and elimination of acetic acid afforded [2]pyrindines (7). 2-Methyl-2H-[2]pyrindines (9) were also prepared.

Dedicated to Professor E. C. Taylor on the occasion of his 70th birthday

[2]Pyrindines (7) are not yet studied very intensively.[2] Better known are the 6,7-dihydro-5H-[2]pyrindines (3), because many alkaloids belong to this class of compounds.[3] Since we were interested in the 6,7-dihydro-5H-[2]pyrindine alkaloids and in 2H-[2]pyrindines (7"), we studied the synthesis of these compounds by Diels-Alder reaction with inverse electron demand of 1,2,4-triazines (1) with 1-cyclopentenylpyrrolidine (2). Reactions of 1 with 2 were already reported by Sauer et al.[4] and Boger et al.[5]

Reaction of the 1,2,4-triazines (1a-p) with 2 afforded the 6,7-dihydro-5H-[2]pyrindines (3a-p) in yields between 55% and 86%. Oxidation of 3a-l with perbenzoic acid gave 6,7-dihydro-5H-[2]pyrindine 2-oxides (4a-l) in yields between 54% and 95%. Heating 4a-k with acetic anhydride led to the isolation of 5-acetoxy-6,7-dihydro-5H-[2]pyrindines (5a-k) in yields between 17 and 59%. Hydrolysis of 5a-d and 5g-i with H_3PO_4 and 5e with KOH afforded the 5-hydroxy-6,7-dihydro-5H-[2]pyrindines (6a-e) and (6g-i). Treatment of 5a-c or 6a-c with conc. phosphoric acid for 2 days at 140°C gave [2]pyrin-



1,3-9	a	b	c	d	e	f	g	h	i	j	k
R^1	Ph	H	4-Tol	H	4-Tol	Ph	CO_2Me	CO_2Me	4-ClPh	H	4-Tol
R^3	Ph	H	H	Ph	H	H	Ph	Ph	CO_2Me	2-Furyl	CO_2Me
R^4	Ph	Ph	Ph	Ph	H	H	H	Ph	CO_2Me	2-Furyl	CO_2Me

1,3,4	l	m	n	o	p
R^1	Me	4-Tol	4-Tol	CO_2Me	SMe
R^3	Ph	Ph	4-Tol	H	CO_2Me
R^4	Ph	Ph	4-Tol	Ph	CO_2Me

dines (7a-c). Only the 5H- (7') and 7H-tautomer (7) could be detected by nmr spectroscopy, but no 2H-tautomer (7").

Alkylation of 5a-f with dimethyl sulfate afforded the 5-acetoxy-6,7-dihydro-2-methyl-5H-[2]pyridinium salts (8a-f). 8b-f were transformed into the 2-methyl-2H-[2]pyrindines (9b-f), when treated with conc. phosphoric acid. All compounds were characterized by their spectra and by elemental analysis.

EXPERIMENTAL

6,7-Dihydro-5H-[2]pyrindines (3a-p): Compound(2)(3.43 g, 25 mmol) was added dropwise to 1a-p (10 mmol) (neat or in 25 ml of methylene chloride) under nitrogen. The mixture was stirred for 16 h and evaporated. The residue was purified by column chromatography on silica gel with methylene chloride for 3a,c,d,g,l-n, ethyl acetate for 3b,h-k,o,p, or ether for 3e,f.

6,7-Dihydro-5H-[2]pyrindine N-oxides (4a-l): To 3a-n (10 mmol) in methylene chloride (20 ml) perbenzoic acid (20 ml) in methylene chloride (20 ml) was added. The mixture was stirred for 24 h at room temperature. To 3a,g,h,k,m,n perbenzoic acid (10 mmol) was added, and the mixture stirred for further 24 h. The methylene chloride solution of 3a,i,m,n with perbenzoic acid was heated for 5 h to reflux. The solution was washed with saturated sodium bicarbonate solution (2 x 20 ml), dried over magnesium sulfate and evaporated. The residue was purified by column chromatography on aluminum oxide with methylene chloride for 4a, chloroform for 4c,d,l, methanol for 4b, or ether for 4i. In cases of 3m and 3n, the starting material was recovered.

5-Acetoxy-6,7-dihydro-5H-[2]pyrindines (5a-k): 4a-k (10 mmol) were heated in acetic anhydride (5 ml) for 3 h to 80°C. After removal of the acetic anhydride, the residue was dissolved in ether (20 ml), washed with saturated sodium bicarbonate solution (10 ml), and dried over magnesium sulfate. Compounds (5a,g,h) were isolated by addition of hexane. In all other cases, the etheral extract was evaporated, and the residue was purified by column chromatography on silica gel with ether for 5b,e,f,i,j, chloroform for 5c,d, or methylene chloride for 5k.

5-Hydroxy-6,7-dihydro-5H-[2]pyrindines (6a-d, g-i): 5a-d, g-i (2 mmol) were heated in conc. phosphoric acid (4 ml) under nitrogen for 2 h to 100°C. The mixture was neutralized with 6 N NaOH, diluted with water (10 ml), and extracted with ether (3 x 20 ml). The organic phases were dried over magnesium sulfate, evaporated, and the residues were purified by column chromatography on silica gel with ether for 6a,h, ether then ethyl acetate for 6i, ethyl acetate for 6b, or methylene chloride for 6d,g. Compound 6c separated on addition of water and was isolated by filtration.

5-Hydroxy-6,7-dihydro-1-(4-tolyl)-5H-[2]pyrindine (6e): To 5e (1 mmol) in methanol (5 ml) KOH (33.6 mg, 6 mmol) in methanol (10 ml) was added with stirring. After 20 h at room temperature, the mixture was evaporated, and the residue was chromatographed on silica gel column. Compound (5e) was eluted with ether, and 6e with ethyl acetate.

5-Acetoxy-2-methyl-6,7-dihydro-5H-[2]pyridinium methosulfates (8a-f): 5a-f (2.0 mmol) in dry toluene (20 ml) were stirred with dimethyl sulfate (2.0 mmol) for 1 week at room temperature. The precipitate was filtered and washed with toluene.

2-Methyl-2H-[2]pyrindines (9b-f): Compounds (8b-f) (1,0 mmol) were heated in conc. phosphoric acid (3 ml) under nitrogen for 16 h at 140°C. The mixture was poured to ice under nitrogen, and ether (25 ml) was added to the mixture. The aqueous layer was made alkaline with 6 N NaOH until pH 10. The mixture was diluted with water (30 ml) and extracted with ether (3 x 35 ml). The organic phases were dried over magnesium sulfate and evaporated.

5H- (7') and 7H-[2]Pyrindines (7a-c): Compounds (5a-c, 6a-c) (2.5 mmol) were heated with conc. phosphoric acid (5 ml) under nitrogen for 2 days at 140°C. The mixture was diluted with water (20 ml), neutralized with 5 N NaOH, and extracted with methylene chloride (3 x 25 ml). The organic phases were dried with magnesium sulfate, evaporated and purified by column chromatography on silica gel with methylene chloride for 7/7'a, ether for 7/7'b, or chloroform for 7/7'c.

No.	yield	mp (°C)	^{1}H-nmr, 60-MHz, $CDCl_3$, δ-values	formula	calcd /found C	H	N
3a	82%	176-178 ether	1.96 (2H, quin, J=7 Hz), 2.78 (2H, t, J=7 Hz), 3.15 (2H, t, J=7 Hz), 7.21 (13H, m), 7.85 (2H, m)	$C_{26}H_{21}N$	89.88 89.81	6.09 6.10	4.03 4.09
3b	68%	59 ether	2.08 (2H, quin, J=7 Hz), 3.00 (4H, t, J=7 Hz), 7.38 (5H, s), 8.37 (2H, s)	$C_{14}H_{13}N$	86.12 86.10	6.71 6.64	7.17 7.14
3c	78%	130-132 CH_2Cl_2	1.98 (2H, quin, J=7 Hz), 2.38 (3H, s), 3.04 (4H, m), 7.25 (2H, d, J=8 Hz), 7.46 (5H, m), 7.70 (2H, d, J=8 Hz), 8.52 (1H, s)	$C_{21}H_{19}N$	88.38 88.43	6.71 6.84	4.91 4.94
3d	86%	104-105 CH_2Cl_2	2.05 (2H, quin, J=7 Hz), 2.92 (4H, m), 7.25 (10H, m), 8.62 (1H, s)	$C_{20}H_{17}N$	88.25 88.61	6.32 6.26	5.16 5.19
3e	67%	42 ether/ n-hexane	1.96 (2H, quin, J=7 Hz), 2.35 (3H, s), 2.95 (4H, m), 7.05 (1H, d, J=5 Hz), 7.08-7.10 (4H, m), 8.44 (1H, d, J=5 Hz)	$C_{15}H_{15}N$	86.08 85.80	7.22 7.20	6.69 6.64
3f	60%	54 ether/ n-hexane	2.02 (2H, quin, J=7 Hz), 3.00 (4H, m), 7.10 (1H, d, J=5 Hz), 7.28-7.88 (5H, m), 8.46 (1H, d, J=5 Hz)	$C_{14}H_{13}N$	86.12 86.23	6.71 6.69	7.17 7.13
3g	55%	101 ether	2.10 (2H, quin, J=7 Hz), 2.95 (2H, t, J=7 Hz), 3.26 (2H, t, J=7 Hz), 3.96 (3H, s), 7.36 (3H, m), 7.65 (1H, s), 7.93 (2H, m)	$C_{16}H_{15}NO_2$	75.87 75.99	5.97 5.95	5.53 5.51
3h	70%	136-137 136-137[4]	2.03 (2H, quin, J=7 Hz), 2.76 (2H, t, J=7 Hz), 3.36 (2H, t, J=7 Hz), 3.93 (3H, s), 7.13 (10H, m)				
3i	88%	128-130 ether	2.15 (2H, quin, J=7 Hz), 3.15 (4H, t, J=7 Hz), 3.93 (3H, s), 3.96 (3H, s), 7.36 (2H, d, J=8 Hz), 7.70 (2H, d, J=8 Hz)	$C_{18}H_{16}ClNO_4$	62.52 62.68	4.66 4.46	4.05 3.96

No.	yield	mp (°C)	^{1}H-nmr, 60-MHz, $CDCl_3$, -values	formula	calcd /found C	H	N
3j	70%	96 CH_2Cl_2/ n-hexane	2.07 (2H, quin, J=7 Hz), 2.88 (2H, t, J=7 Hz), 3.00 (2H, t, J=7 Hz), 5.93-6.56 (4H, m), 7.37-7.57 (2H, m), 8.49 (1H, s)	$C_{16}H_{13}NO_2$	76.48 76.68	5.22 5.24	5.57 5.47
3k	68%	104 ether	2.03 (2H, quin, J=7 Hz), 2.33 (3H, s), 3.06 (4H, t, J=7 Hz), 3.86 (3H, s), 3.90 (3H, s), 7.13 (2H, d, J=8 Hz), 7.60 (2H, d, J=8 Hz)	$C_{19}H_{19}NO_4$	70.14 70.23	5.89 5.94	4.30 4.34
3l	78%	112-113 CH_2Cl_2	2.04 (2H, quin, J=7 Hz), 2.06 (3H, s), 2.87 (4H, m), 7.14 (10H, m)	$C_{21}H_{19}N$	88.38 88.43	6.71 6.84	4.91 4.94
3m	83%	157-158 CH_2Cl_2	2.02 (2H, quin, J=7 Hz), 2.43 (3H, s), 2.81 (2H, t, J=7 Hz), 3.20 (2H, t, J=7 Hz), 7.20 (12H, m), 7.82 (2H, d, J=8 Hz)	$C_{27}H_{23}N$	89.71 89.38	6.41 6.22	3.88 3.85
3n	77%	130-131 CH_2Cl_2	1.97 (2H, quin, J=7 Hz), 2.22 (3H, s), 2.30 (3H, s), 2.35 (3H, s), 2.75 (2H, t, J=7 Hz), 3.16 (2H, t, J=7 Hz), 7.12 (10H, m), 7.82 (2H, d, J=8 Hz)	$C_{29}H_{27}N$	89.42 89.50	6.99 6.92	3.59 3.54
3o	60%	129-130 ether	2.10 (2H, quin, J=7 Hz), 3.04 (2H, t, J=7 Hz), 3.44 (2H, t, J=7 Hz), 4.04 (3H, s), 7.47 (5H, s), 8.57 (1H, s)	$C_{16}H_{15}NO_2$	75.87 76.02	5.97 6.03	5.53 5.55
3p	61%	69-70 ether	2.13 (2H, quin, J=7 Hz), 2.60 (3H, s), 2.83 (2H, t, J=7 Hz), 3.13 (2H, t, J=7 Hz), 3.86 (3H, s), 3.93 (3H, s)	$C_{13}H_{15}NO_4S$	55.50 55.49	5.37 5.46	4.98 4.93
4a	48%	209-210 CH_2Cl_2	1.98 (2H, m), 2.80 (4H, m), 7.18 (15H, m)	$C_{26}H_{21}NO$	85.92 86.16	5.82 5.87	3.85 3.83
4b	95%	74-75 ether	2.12 (2H, quin, J=7 Hz), 2.95 (4H, t, J=7 Hz), 7.41 (5H, m), 8.80 (2H, s)	$C_{14}H_{13}NO$	79.60 79.73	6.20 6.09	6.63 6.61

No.	yield	mp (^{o}C)	^{1}H-nmr, 60-MHz, $CDCl_3$, δ-values	formula	calcd /found C	H	N
4c	82%	177-178 CH_2Cl_2	2.07 (2H, quin, J=7 Hz), 2.44 (3H, s), 2.94 (4H, m), 7.39 (9H, m), 8.30 (1H, s)	$C_{21}H_{19}NO$	83.69 83.72	6.35 6.33	4.65 4.60
4d	89%	199-200 CH_2Cl_2	2.10 (2H, quin, J=7 Hz), 2.86 (4H, m), 7.07 (10H, m), 8.28 (1H, s)	$C_{20}H_{17}NO$	83.59 83.86	5.96 6.04	4.87 4.89
4e	75%	131-132 $MeCO_2Et$	2.07 (2H, quin, J=7 Hz), 2.40 (3H, s), 2.84 (4H, m); 6.95-7.53 (5H, m), 8.15 (1H, d, J=7 Hz)	$C_{15}H_{15}NO$	79.97 79.96	6.71 6.65	6.25 6.11
4f	77%	110 ether/ CH_2Cl_2	2.07 (2H, quin, J=7 Hz), 2.86 (4H, m), 7.06 (1H, d, J=7 Hz), 7.49 (5H, s), 8.17 (1H, d, J=7 Hz)	$C_{14}H_{13}NO$	79.59 79.67	6.20 6.28	6.63 6.37
4g	43%	149-151 CH_2Cl_2/ether	2.16 (2H, quin, J=7 Hz), 2.93 (4H, t, J=7 Hz), 3.96 (3H, s), 7.33 (4H, m), 7.73 (2H, m)	$C_{16}H_{15}NO_3$	71.36 71.55	5.54 5.63	4.06 5.20
4h	50%	170-172 ether	2.10 (2H, quin, J=7 Hz), 2.75 (2H, t, J=7 Hz), 3.03 (2H, t, J=7 Hz), 4.00 (3H, s), 7.05 (10H, m)	$C_{22}H_{19}NO_3$	76.50 76.60	5.54 5.60	4.06 4.04
4i	54%	179-180 methanol	2.11 (2H, quin, J=7 Hz), 2.86 (2H, t, J=7 Hz), 3.28 (2H, t, J=7 Hz), 3.90 (3H, s), 3.97 (3H, s), 7.46 (4H, s)	$C_{18}H_{16}ClNO_5$	59.76 59.49	4.46 4.58	3.87 3.87
4j	50%	161-163 $MeCO_2Et$	2.12 (2H, quin, J=7 Hz), 2.94 (4H, m), 5.97 (1H, d, J=7 Hz), 6.40 (2H, m), 7.09 (1H, d, J=7 Hz), 7.42 (2H, m), 8.16 (1H, s)	$C_{16}H_{13}NO_3$	71.90 71.68	4.90 5.01	5.24 5.19
4k	56%	122-124 CH_2Cl_2/ether	2.10 (2H, quin, J=7 Hz), 2.40 (3H, s), 2.83 (2H, t, J=7 Hz), 3.26 (2H, t, J=7 Hz), 3.90 (3H, s), 4.00 (3H, s), 7.30 (4H, m)	$C_{19}H_{19}NO_5$	66.85 66.99	5.61 5.66	4.10 3.99
4l	66%	175-176 CH_2Cl_2	2.08 (2H, quin, J=7 Hz), 2.53 (3H, s), 2.89 (4H, m), 7.09 (10H, m)	$C_{21}H_{19}NO$	83.69 83.57	6.35 6.14	4.65 4.61

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No.	yield	mp (^{o}C)	^{1}H-nmr, 60-MHz, $CDCl_3$, δ-values	formula	calcd /found		
					C	H	N
5a	59%	199-200 ether	1.70 (3H, s), 2.33 (2H, m), 3.29 (2H, m), 6.18 (1H, m), 7.34 (13H, m), 7.95 (2H, m)	$C_{28}H_{23}NO_2$	82.94 82.92	5.72 5.63	3.45 3.45
5b	48%	108-109 CH_2Cl_2/hexane	1.69 (3H, s), 2.50 (2H, m), 3.02 (2H, m), 6.36 (1H, m), 7.36 (5H, s), 8.44 (1H, s), 8.52 (1H, s)	$C_{16}H_{15}NO_2$	75.87 76.09	5.97 6.05	5.53 5.46
5c	48%	122-123 $CHCl_3$/hexane	1.72 (3H, s), 2.32 (2H, m), 2.40 (3H, s), 3.19 (2H, m), 6.38 (1H, m), 7.47 (9H, m), 8.55 (1H, s)	$C_{23}H_{21}NO_2$	80.44 80.51	6.16 6.12	4.08 4.10
5d	47%	218-220 $CHCl_3$	1.68 (3H, s), 2.43 (2H, m), 3.12 (2H, m), 6.22 (1H, m), 7.20 (10H, m), 8.68 (1H, s)	$C_{22}H_{19}NO_2$	80.25 80.34	5.78 5.80	4.25 4.36
5e	43%	106-197 ether	2.12 (3H, s), 2.41 (3H, s), 2.47 (2H, m), 3.14 (2H, m), 6.20 (1H, m), 7.15-7.79 (5H, m), 8.57 (1H, d, J=5 Hz)	$C_{17}H_{17}NO_2$	76.38 76.63	6.41 6.44	5.24 5.23
5f	42%	62-63 ether/hexane	2.11 (3H, s), 2.45 (2H, m), 3.18 (2H, m), 6.21 (1H, m), 7.24-7.90 (6H, m), 8.60 (1H, d, J=5 Hz)	$C_{16}H_{15}NO_2$	75.87 76.14	5.97 5.93	5.53 5.53
5g	50%	116-118 ether/hexane	2.10 (3H, s), 2.55 (2H, m), 3.40 (2H, m), 4.00 (3H, s), 6.20 (1H, m), 7.40 (3H, m), 7.93 (3H, m)	$C_{18}H_{17}NO_4$	69.44 69.56	5.50 5.57	4.50 4.45
5h	46%	115-117 ether	1.70 (3H, s), 2.43 (2H, m), 3.43 (2H, m), 4.06 (3H, s), 6.26 (1H, m), 7.26 (10H, m)	$C_{24}H_{21}NO_4$	74.40 74.73	5.46 5.51	3.62 3.62
5i	45%	110-112 CH_2Cl_2/hexane	2.07 (3H, s), 2.53 (2H, m), 3.18 (2H, m), 3.87 (3H, s), 3.97 (3H, s), 6.44 (1H, m), 7.58 (4H, m)	$C_{20}H_{18}ClNO_6$	59.49 59.22	4.49 4.43	3.47 3.52
5j	17%	124 ether/hexane	1.89 (3H, s), 2.48 (2H, m), 3.02 (2H, m), 5.91-6.55 (5H, m), 7.46 (2H, m), 8.60 (1H, s)	$C_{18}H_{15}NO_4$	69.89 69.98	4.89 5.03	4.53 4.43
5k	19%	116-117 ether/hexane	2.10 (3H, s), 2.43 (3H, s), 2.50 (2H, m), 3.26 (2H, m), 3.93 (3H, s), 4.00 (3H, s), 6.50 (1H, s), 7.30 (2H, d, J=8 Hz), 7.73 (2H, d, J=8 Hz)	$C_{21}H_{21}NO_6$	65.79 65.77	5.52 5.52	3.65 3.51

No.	yield	mp (^{o}C)	^{1}H-nmr, 60-MHz, $CDCl_3$, δ-values	formula	calcd /found C	H	N
6a	91%	168-169	1.70 (1H, s), 2.25 (2H, m), 3.33 (2H, m), 5.25	$C_{26}H_{21}NO$	85.92	5.82	3.85
		CH_2Cl_2	(1H, m), 7.30 (13H, m), 7.85 (2H, m)		86.10	5.59	3.75
6b	79%	100 +)	2.12 (2H, m), 3.12 (3H, m), 5.23 (1H, m),	$C_{14}H_{13}NO$	79.59	6.20	6.63
		$MeCO_2Et$	7.25-7.88 (5H, m), 8.41 (2H, s)		79.52	6.25	6.63
6c	61%	213-214 *)	2.04 (2H, m), 2.39 (3H, s), 3.38 (3H, m),	$C_{21}H_{19}NO$	83.29	6.35	4.65
		methanol	5.07 (1H, m), 7.20-7.97 (9H, m), 8.59 (1H, s)		83.43	6.34	4.57
6d	89%	161-162	2.01 (2H, m), 2.10 (1H, s), 2.95 (2H, m),	$C_{20}H_{17}NO$	83.64	5.97	4.88
		CH_2Cl_2	5.15 (1H, m), 7.15 (10H, m), 8.50 (1H, s)		83.52	5.82	4.79
6e	72%	128-129	2.10 (2H, m), 2.47 (3H, s), 2.98 (2H, m), 3.72	$C_{15}H_{15}NO$	79.97	6.71	6.25
		ether	(1H, s), 5.15 (1H, t, J=7 Hz), 7.10-7.71 (5H, m),		79.71	6.73	6.11
			8.47 (1H, d, J=5 Hz)				
6g	21%	115-118 ")	1.98 (1H, dddd, J= 7; 8; 8,5; 13 Hz), 2.22 (1H, s),	$C_{16}H_{15}NO_3$	71.36	5.61	5.20
		ether	2.61 (1H, dddd, J=3.5; 7; 8; 13 Hz), 3.16 (1H, td,		71.12	5.72	5.13
			J=8; 18 Hz), 3.48 (1H, ddd, J=3.5; 8; 18 Hz), 4.00				
			(3H, s), 5.30 (1H, t, J=7 Hz), 7.45 (3H, m), 7.94				
			(1H, s), 8.04 (2H, m)				
6h	51%	89 *)	2.07 (2H, m), 3.27 (2H, m), 3.32 (1H, s), 3.88	$C_{22}H_{19}NO_3$	76.50	5.54	4.06
		ether	(3H, s), 4.84 (1H, m), 7.21 (5H, s), 7.29 (5H, s)		76.31	5.50	4.17
6i	45%	106 +)	2.03 (2H, m), 2.80 (1H, s), 3.21 (2H, m),	$C_{18}H_{16}ClNO_5$	59.76	4.46	3.87
		ether	3.93 (6H, s), 5.49 (1H, m), 7.42-8.02 (4H, m)		59.60	4.43	3.73
7a	95%	183-185	3.37, 3.78 (2H, t, J=2 Hz), 6.67, 6.79 (2H, m),	$C_{26}H_{19}NO$	90.40	5.54	4.06
		CH_2Cl_2	7.00-7.68 (13H, m), 7.89-8.20 (2H, m)		90.13	5.34	4.14
7b	34%	85-87	3.47, 3.71 (2H, m), 6.27, 6.84 (2H, m), 7.42, 7.47	$C_{14}H_{11}N$	87.01	5.74	7.25
		ether	(5H, s), 8.49, 8.64 (2H, s)		87.23	5.61	7.13

No.	yield	mp (°C)	^{1}H-nmr, 60-MHz, $CDCl_3$, δ-values	formula	calcd /found C	H	N
7c	73%	156-158 ") $CHCl_3$	2.43 (3H, s), 3.59, 3.74 (2H, t, J=1.9 Hz), 6.66, 6.85 (1H, dt, J=5.6; 1.9 Hz), 7.12, 7.22 (1H, dt, J=5,6; 1.9 Hz), 7.30-7.85 (9H, m), 8.57, 8.66 (1H, s)	$C_{21}H_{17}N$	89.01 88.86	6.05 6.13	4.94 4.87
8a	12%	230-232 *)	2.29 (3H, s), 2.50 (2H, m), 3.35 (2H, m), 3.37 (3H, s), 3.94 (3H, s), 6.35 (1H, m), 7.31 (15H, m)	$C_{30}H_{29}NO_6S$	67.78 68.03	5.50 5.23	2.63 2.55
8b	92%	102-103 *) toluene	1.59 (3H, s), 2.52 (2H, m), 3.22 (2H, m), 3.37 (3H, s), 4.42 (3H, s), 6.02 (1H, m), 7.57 (5H, m), 9.00 (2H, s)	$C_{18}H_{21}NO_6S$	56.98 56.63	5.58 5.58	3.69 3.64
8c	79%	148-150 *) toluene	1.63 (3H, s), 2.12 (2H, m), 2.48 (3H, s), 2.85 (2H, m), 3.56 (3H, s), 4.20 (3H, s), 6.61 (1H, m), 7.46 (9H, m), 8.90 (1H, s)	$C_{25}H_{27}NO_6S$	63.95 63.60	5.80 5.74	2.98 2.92
8d	80%	106-107 *)	2.29 (3H, s), 2.58 (2H, m), 3.25 (2H, m), 3.38 (3H, s), 4.00 (3H, s), 6.28 (1H, m), 7.21 (10H, s), 9.26 (1H, s)	$C_{24}H_{25}NO_6S$	63.28 63.52	5.53 5.60	3.08 2.94
8e	81%	90-91 *)	2.11 (3H, s), 2.41 (3H, s), 2.75 (2H, m), 3.15 (2H, m), 3.37 (3H, s), 4.06 (3H, s), 6.32 (1H, m), 8.05 (1H, d, J=7 Hz), 9.05 (1H, d, J=7 Hz)	$C_{19}H_{23}NO_6S$	58.00 58.29	5.89 5.90	3.56 3.34
8f	82%	110-112 *)	2.12 (3H, s), 2.69 (4H, m), 3.37 (3H, s), 4.03 (3H, s), 6.37 (1H, m), 7.66 (5H, s), 8.10 (1H, d, J=7 Hz), 9.06 (1H, d, J=7 Hz)	$C_{18}H_{21}NO_6S$	56.98 56.75	5.58 5.41	3.69 3.40
9b	84%	101 ether	3.76 (3H, s), 6.54-6.84 (3H, m), 7.24-7.83 (7H, m)	$C_{15}H_{13}N$	86.92 86.59	6.32 6.13	6.76 6.49
9c	97%	130 toluene	2.44 (3H, s), 3.68 (3H, s), 6.33 (1H, m), 6.64 (1H, m), 7.02 (1H, s), 7.16-7.90 (10H, m)	$C_{22}H_{19}N$	88.85 88.58	6.44 6.31	4.71 4.56

No.	yield	mp (°C)	^1H-nmr, 60-MHz, $CDCl_3$, δ-values	formula	calcd /found C	H	N
9d	58%	146-148 ether	3.59 (3H, s), 6.25 (1H, m), 6.78 (1H, m) 7.00-7.45 (11H, m), 8.05 (1H, s)	$C_{21}H_{17}N$	89.01 88.86	6.05 5.88	4.71 4.72
9e	86%	87-88 ether	2.43 (3H, s), 3.55 (3H, s), 6.25 (1H, m), 6.50 (1H, m), 6.78-7.35 (7H, m)	$C_{16}H_{15}N$	86.84 86.87	6.83 6.57	6.33 6.17
9f	79%	104-105 ether	3.61 (3H, s), 6.11-6.65 (2H, m), 6.84-7.66 (8H, m)	$C_{15}H_{13}N$	86.92 86.64	6.32 6.18	6.76 6.53

*) [D_6]DMSO +) [D_6]acetone ") 300-MHz

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Received, 7th December, 1992