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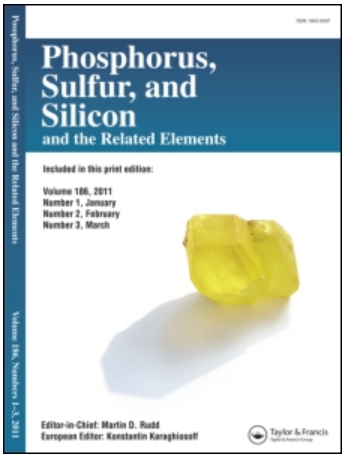

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SYNTHESIS OF SOME NEW FUSED SPIROHETEROCYCLIC SYSTEMS RELATED TO THIAZOLOPYRANS, THIAZOLOTHIOPYRANS AND THIAZOLOPYRIDINES

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SYNTHESIS OF SOME NEW FUSED SPIROHETEROCYCLIC SYSTEMS RELATED TO THIAZOLOPYRANS, THIAZOLOTHIOPYRANS AND THIAZOLOPYRIDINES

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1-Oxa-4-thiaspiro[4.4]nonan-2-one and/or 1-oxa-4-thiaspiro[4.5]decan-2-one were reacted with aniline to give the corresponding spirothiazolidinones(**1a, b**). Reaction of **1a, b** with chalcones yielded 2-(α-aracylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.4]nonan-3-one and 2-(α-aracylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.5]decan-4-one (**2a–h**). Compounds **2a–h** were reacted with acetic anhydride, phosphorus pentasulfide and ammonium acetate to give spirothiazolopyrans **3a–h**, spirothiazolothiopyrans **4a–h** and spirothiazolodihyropyridines **5a–h** respectively. All the synthesized spiroheterocycles derivatives were identified by conventional methods (IR, ^{1}H-NMR) and elemental analyses.

Key words: Spirothiazolopyrans, spirothiazolothiopyrans, spirothiazolodihydropyridines, spiroheterocycles, NMR.

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INTRODUCTION

Thiazolidinones derivatives have considerable commercial importance as drugs.[1] Spiro compounds showed optical activity, biological activity and photochromic properties.[2–8] To date no previous authors have reported the synthesis of spirothiazolidinones fused with pyrans, thiopyrans and pyridines, from this point of view and in continuation to our previous work.[9–19] We report herein the synthesis of spirothiazolopyrans, spirothiazolothiopyrans and spirothiazolopyridines.

RESULTS AND DISCUSSIONS

1-Thia-4-phenyl-4-azaspiro[4.4]nonan-3-one (**1a**) and 1-thia-4-phenyl-4-azaspiro[4.5]decan-3-one (**1b**) were prepared by the reaction of aniline with 1-oxa-4-thiaspiro[4.4]nonan-2-one and 1-oxa-4-thiaspiro[4.5]decan-2-one respectively.[9] Reaction of compounds **1a, b** with chalcones namely benzalacetophenone, 4-chlorobenzalacetophenone, 4-methoxybenzalacetophenone and 4-nitrobenzalacetophenone in a mixture of ethanol and pyridine afforded 2-(substituted-α-phenacylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.4]nonan-4-one and/or 2-(substituted-α-phenacylbenzyl)-4-phenlyl-1-thia-4-azaspiro[4.5]decan-3-one (**3a–h**) (Scheme I). The structure

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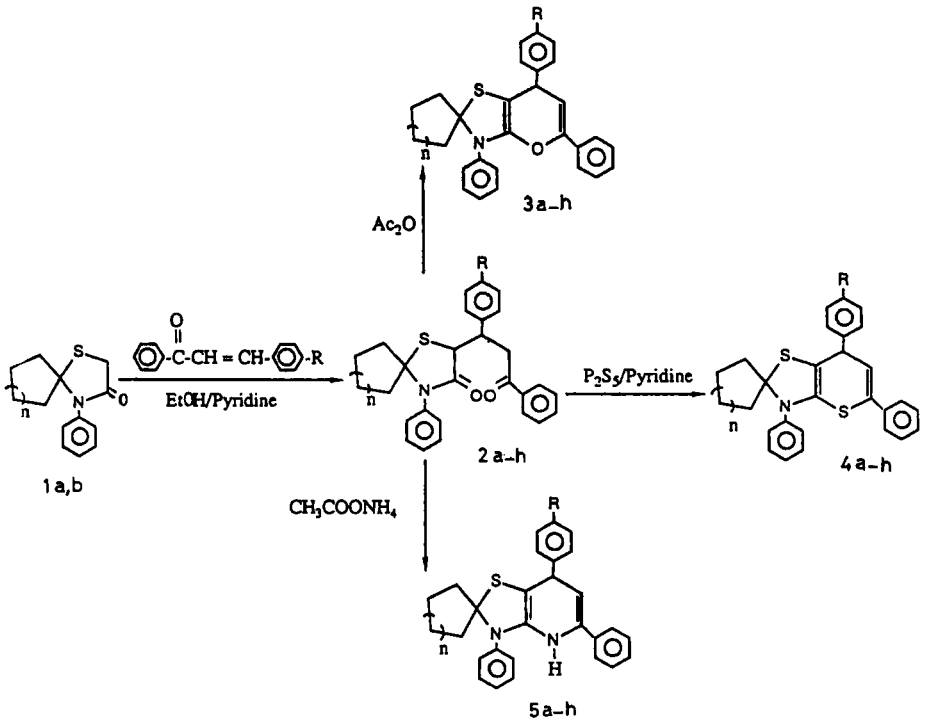

n = 1,2; R = H,Cl ,OCH_3, NO_2

SCHEME I

of compounds **3a–h** was established from their elemental analyses and spectroscopic data (Table I). The IR spectrum of **2a** showed characteristic absorption at 3050 cm^{-1} corresponding to the stretching vibrations of CH aromatic residue, 2920 cm^{-1} for CH aliphatic residue, 1675 cm^{-1} for carbonyl group stretching vibrations, 1400–1000 cm^{-1} for C—N stretching vibrations and 740 cm^{-1} for C—S. The ^{1}H-NMR spectrum of **2a** (DMSO-d_6) showed the following signals: δ1.30–1.70 (4H, m, two methylene groups of the cyclopentane moiety), 1.90–2.20 (4H, m, two methylene groups of cyclopentane moiety), 3.80 (2H, d, methylene group alpha to the carbonyl group), 4.10 (1H, q, the methine proton at benzylic carbon), 5.50 (the proton at C-5 of thiazole ring and 6.70–8.30 (15H, complex aromatic protons). Reaction of compounds **2a–h** with acetic anhydride afforded the spirothiazolopyrans **3a–h** in good yields (Scheme I, Table II). The structures of **3a–h** were confirmed on the basis of elemental analyses and spectroscopic data (Table II). The IR spectrum of **3a** showed characteristic absorption bands at 3040 cm^{-1} corresponding to the aromatic CH, 2830 cm^{-1} for CH aliphatic, 1600–1580 cm^{-1} for the aromatic rings, 720 cm^{-1} for C—S bond and no absorption bands for any carbonyl groups. The ^{1}H-NMR spectrum of **3a** ($CDCl_3$) showed the following signals: δ1.30–1.70 (4H, m, two methylene groups of the cyclopentane ring), 1.90–2.20 (4H, m, two methylene groups of the cyclopentane ring) and 6.90–8.20 ppm (17H, complex, the aromatic protons together with the proton at C-4 of pyran ring). Reaction of spiro

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TABLE I

Physical data of 2-(substituted-α-phenacylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.4]nonan-3-one and 2-(substituted-α-phenacylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.5]decan-3-one (**2a–h**)

Compd. No.	n	R	Yield %	Molecular Formula (solvent of crystalization)	M.P °C	IR (KBr) cm^{-1}	^{1}H-NMR (solvent) δ (TMS) ppm
2a	1	H	76	$C_{28}H_{27}NO_2S$ (ethanol)	185-186	3050(CH arom), 2940(CH aliph), 1675(C=O), 1400-1000(C-N),740(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.20 (4H,m),3.80(2H,d),4.10(1H.q),5.50 (1H,d),6.70-8.30(15H, complex).
2b	1	Cl	71	$C_{28}H_{26}NO_2SCl$ (ethano/water3:1)	107-108	3080(CH arom),2840(CH aliph),1675(C=O),1400-1000(C-N),1090(C-Cl), 770(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.20 (4H,m),3.70(2H,d),4.00(1H.q),5.30 (1H,d),6.80-8.90(14H,complex).
2c	1	OCH_3	70	$C_{29}H_{29}NO_3S$ (ethanol)	85-86	3050(CH arom),2940(CH aliph),1670(C=O),1400-1000(C-N),750(C-S).	(DMSO-d_6) 1.29-1.70(4H,m),1.90-2.20 (4H,m),3.70(2H,d),3.20(3H,s),4.10 (1H,q),5.20(1H,d), 6.80-8.40 (14H,complex).
2d	1	NO_2	70	$C_{28}H_{26}N_2O_4S$ (ethanol)	140-141	3050(CH arom),2940(CH aliph),1715(C=O),1510 (NO_2),750(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.20 (4H,m),3.75(2H,d),4.15(1H,q),5.20 (1H,d),6.80-8.40(14H,complex).

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TABLE I (*Continued*)

Compd. No.	n	R	Yield %	Molecular Formula (solvent of crystalization)	M.P °C	IR (KBr) cm^{-1}	^{1}H-NMR (solvent) δ (TMS) ppm
2e	2	H	60	$C_{29}H_{29}NO_2S$ (ethanol/water 4:1)	120-121	3080(CH arom),2840(CH aliph), 1680,1700(C=O), 710(C-S).	(DMSO-d_6) 1.30-1.60(6H, complex), 1.70-2.10(4H,m), 3.60(2H,d), 4.10 (1H,q),5.00(1H,d), 6.90-8.30 (15H, complex).
2f	2	Cl	65	$C_{29}H_{28}NO_2SCl$ (ethanol/water 2:1)	123-124	3050(CH arom),2860(CH aliph),1700(C=O),1090 (C-Cl),730(C-S).	(DMSO-d_6) 1.30-1.60(6H, complex) 1.70-2.10(4H,m), 3.60(2H,d),4.10 (1H,q),5.20(1H,d), 6.85-8.40 (14H, complex).
2g	2	OCH_3	67	$C_{30}H_{31}O_3NS$ (ethanol)	85-87	3060(CH arom),2860(CH aliph),1700(C=O), 710 (C-S).	(DMSO-d_6) 1.30-1.60(6H, complex), 1.70-2.10(4H,m),3.60(2H,d),3.20 (3H,s),4.10(1H,q),5.20(1H,d), 6.70-8.40(14h, complex).
2h	2	NO_2	60	$C_{29}H_{28}N_2O_4S$ (ethanol)	163-165	3040(CH arom),2860(CH aliph), 1690,1710(C=O), 710(C-S).	(DMSO-d_6) 1.30-1.60(6H,m), 1.70-2.10(4H,m), 3.70(2H,d),4.10 (1H,),4.10(1H,d), 6.90-8.40 (14H, complex).

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TABLE II

Physical data of spirothiazolopyrans (3a–h), and spirothiazolothiopyrans (4a–h) and spirothiazolodihydropyridines (5a–h)

Compd. No.	n	R	Yield %	Molecular Formula (solvent of crystalization)	M.P. °C	IR (KBr) cm^{-1}	^{1}H-NMR (solvent), δ(TMS)
3a	1	H	50	$C_{28}H_{25}NOS$ (ethanol)	150-151	3040(CH arom),2830(CH aliph), 1600,1580(C=C arom),720(C-S).	($CDCl_3$) 1.30-1.70(4H,m),1.90-2.20(4H,m), 6.90-8.20(17H, complex).
3b	1	Cl	55	$C_{28}H_{24}NOSCl$ (ethanol)	168-170	3050(CH arom),2840(CH aliph), 1600,1580(C=C arom),1090 (C-Cl),730(C-S).	($CDCl_3$) 1.30-1.70(4H,m),1.90-2.20(4H,m), 6.90-8.20(16H, complex).
3c	1	OCH_3	60	$C_{29}H_{27}NO_2S$ (ethanol)	120-121	3040(CH arom),2855(CH aliph), 1600,1585(C=C arom),720(C-S).	($CDCl_3$) 1.30-1.70(4H,m),1.90-2.10(4H,m), 3.20(3H,s),7.00-8.15(16H, complex).
3d	1	NO_2	61	$C_{28}H_{24}N_2O_3S$ (ethanol)	150-151	3020(CH arom),2840(CH aliph), 1600,1585(C=C arom),1510 (NO_2),730(C-S).	($CDCl_3$) 1.30-1.70(4H,m),1.90-2.10(4H,m), 7.00-8.15(16H, complex).
3e	2	H	60	$C_{29}H_{27}NOS$ (ethanol/water 1:1)	154-156	3050(CH arom),2850(CH aliph), 1600,1580(C=C arom),720(C-S).	(DMSO-d_6) 1.30-1.60(6H,m),1.70-2.20 (4H,m),7.00-8.20(17H, complex).
3f	2	Cl	65	$C_{29}H_{26}NOSCl$ (ethanol/water 1:2)	170-171	3040(CH arom),2850(CH aliph), 1600,1580(C=C arom),1090 (C-C),720(C-S).	(DMSO-d_6) 1.30-1.60(6H,m),1.70-2.20 (4H,m),6.80-8.10(16H, complex).

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TABLE II (*Continued*)

Compd. No.	n	R	Yield %	Molecular Formula (solvent of crystalization)	M.P. °C	IR (KBr) cm^{-1}	^{1}H-NMR (solvent), δ(TMS)
3g	2	OCH_3	70	$C_{30}H_{29}NO_2S$ (ethanol)	148-150	3040(CH arom),2850(CH aliph), 1600,1580(C=C arom),730(C-S).	(DMSO-d_6) 1.25-1.60(6H,m),1.80-2.10 (4H,m),3.20(3H,s),7.00-8.10(16H,complex)
3h	2	NO_2	65	$C_{29}H_{26}N_2O_3S$ (ethanol/water 1:1)	160-161	3050(CH arom),2820(CH aliph), 1600,1580(C=C arom),1510(NO_2) 730(C-S).	(DMSO-d_6) 1.30-1.70(6H,m),1.80-2.10 (4H,m),7.00-8.20(16H, complex).
4a	1	H	65	$C_{28}H_{25}NS_2$ (ethanol/water 1:1)	160-161	3030(CH arom),2850(CH aliph), 1600,1580(C=C arom),710(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.10 (4H,m),6.90-8.20(17H, complex).
4b	1	Cl	68	$C_{28}H_{24}NS_2C$ (ethanol)	174-175	3030(CH arom),2820(CH aliph), 1600,1585(C=C arom),1090 (C-Cl),730(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.80-2.20 (4H,m),7.00-8.20(16H, complex).
4c	1	OCH_3	62	$C_{29}H_{27}NOS_2$ (ethanol)	130-132	3050(CH arom),2830(CH aliph), 1600,1580(C=C arom),1510 (C-C),730(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.80-2.20 (4H,m),3.20(3H,s),7.00-8.20(16H, complex).
4d	1	NO_2	67	$C_{28}H_{24}N_2O_2S_2$ (ethanol/water 1:2)	175-176	3050(CH arom),2830(CH aliph), 1600,1580(C=C arom),1510 (NO_2),730(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.80-2.10 (4H,m),7.00-8.20(16H, complex).
4e	2	H	68	$C_{29}H_{27}NS_2$ (ethanol)	140-141	3050(CH arom),2900(CH aliph), 1600,1580(C=C arom),730(C-S).	(DMSO-d_6) 1.25-1.65(6H,m),1.80-2.10 (4H,m),6.80-8.10(17H, complex).
4f	2	Cl	70	$C_{29}H_{26}NS_2Cl$ (ethanol)	149-150	3050(CH arom),2900(CH aliph), 1600,1580(C=C arom),1090 (C-Cl),740(C-S).	(DMSO-d_6) 1.25-1.65(6H,m),1.80-2.20 (4H,m),6.70-8.10(16H, complex).

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4g	2	OCH_3	73	$C_{30}H_{29}NOS_2$ (ethanol/water 1:1)	130-13	3050(CH arom),2920(CH aliph), 1600,1580(C=C arom),740(C-S).	(DMSO-d_6) 1.25-1.65(6H,m),1.80-2.10 (4H,m),3.20(3H,s),6.70-8.10(16H, complex).
4h	2	NO_2	72	$C_{29}H_{26}N_2O_2S_2$ (ethanol)	140-142	3045(CH arom),2900(CH aliph), 1600,1580(C=C arom),1510 (NO_2),730(C-S).	(DMSO-d_6) 1.30-1.60(6H,m),1.80-2.10 (4H,m),6.70-8.10(16H, complex).
5a	1	H	61	$C_{28}H_{26}N_2S$ (ethanol)	160-162	3150(NH),3050(CH arom),2940 (CH aliph),1600,1580(C=C arom),730(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.20 (4H,m),6.70-8.20(16H,complex),10.25 (1H,s).
5b	1	Cl	56	$C_{28}H_{25}N_2SCl$ (ethanol)	130-132	3150(NH),3050(CH arom),2920 (CH aliph),1600,1580(C=C arom),730(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.20 (4H,m),6.7-8.20(16H, complex),10.20 (1H,s).
5c	1	OCH_3	60	$C_{29}H_{28}N_2OS$ (ethanol)	80-82	3150(NH),3050(CH arom),2900 (CH aliph),1600,1580(C=C arom), 730(C-S).	(DMSO-d_6) 1.30-1.70(4H,m),1.90-2.10 (4H,m),6.80-8.10(16H,complex),10.20 (1H,s).
5d	1	NO_2	62	$C_{28}H_{25}N_2O_2S$ (ethanol/water 1:1)	150-152	3150(NH),3050(CH arom),2900 CH aliph),1600,1580(C=C arom),1510(NO_2),720(C-S).	(DMSO-d_6) 1.35-1.70(4H,m),1.90-2.10 (4H,m),6.80-8.10(16H, complex),10.20 (1H,s).
5e	2	H	50	$C_{29}H_{28}N_2S$ (ethanol)	120-122	3150(NH),3050(CH arom),2900 (CH aliph),1600,1580(C=C arom),730(C-S).	(DMSO-d_6) 1.25-1.65(6H,m),1.80-2.10 (4H,m),6.80-8.10(17H,complex),10.20 (1H,s).

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TABLE II (*Continued*)

Compd. No.	n	R	Yield %	Molecular Formula (solvent of crystalization)	M.P. °C	IR (KBr) cm^{-1}	^{1}H-NMR (solvent), δ(TMS)
5f	2	Cl	55	$C_{29}H_{27}N_2S$ (ethanol)	100-102	3150(NH),3050(CH arom),2910 (CH aliph),1600,1580(C=C arom),1090(C-Cl),730(C-S).	(DMSO-d_6) 1.25-1.65(6H,m),1.80-2.20 (4H,m),6.70-8.10(16H, complex),10.20 (1H,s).
5g	2	OCH_3	66	$C_{30}H_{30}N_2OS$ (ethanol)	110-112	3150(NH),3060(CH arom),2940 (CH aliph),1600,1580(C=C arom),720(C-S).	(DMSO-d_6) 1.25-1.70(6H,m),1.80-2.10 (4H,m),6.70-8.10(16H, complex),10.20 (1H,s).
5h	2	NO_2	60	$C_{29}H_{27}N_2O_2S$ (ethanol)	160-162	3150(NH),3050(CH arom),2940 (CH aliph),1600,1580(C=C arom),1520(NO_2),730(C-S).	(DMSO-d_6) 1.30-1.60(6H,m),1.80-2.10 (4H,m),6.65-8.10(16H, complex),10.20 (1H,s).

derivatives **2a–h** with phosphorus pentasulfide in pyridine afforded spirothiazolothiopyran derivatives **4a–h** in good yields. The structure assignment of the prepared compounds **4a–h** was elucidated by their elemental and spectral analyses (Table II). The IR spectrum of **4a** showed characteristic absorption bands at 3030 cm^{-1} corresponding to the stretching vibrations of CH aromatic, 2850 cm^{-1} for the CH aliphatic, 1600, 1580 cm^{-1} for the aromatic rings and 710 cm^{-1} for the stretching vibrations of C—S bond. The ^{1}H-NMR spectrum of **4a** (DMSO-d_6) showed the following signals: δ1.30–1.70 (4H, m, two methylene groups of cyclopentane ring), 1.90–2.20 (4H, m, two methylene groups of cyclopentane ring), 6.90–8.20 (17H, complex, aromatic and the proton of C-4 at thiopyran ring). Reaction of spiro derivatives **2a–h** with ammonium acetate yielded spirothiazolodihydropyridine derivatives **5a–h** in good yields. All the prepared compounds were identified by conventional methods such as elemental and spectral analyses (IR and ^{1}H-NMR spectra). The physical properties and spectral analysis have been given in Table II. The ^{1}H-NMR spectrum of **5a** showed characteristic strong at

TABLE III

Antibacterial screening of compunds **3a–h–5a–h** (inhibition zones mm)

Compound No.	Staphylococcus aureus DSM 346	Escherichia coli DSM 423
3a	23	31
3b	25	52
3c	85	50
3e	27	60
3f	55	21
3g	-ve	50
3h	22	57
4a	26	87
4b	54	91
4c	-ve	52
4d	25	22
4e	60	27
4f	24	51
4h	-ve	55
5a	-ve	25
5b	27	60
5c	85	31
5d	50	-ve
5e	20	23
5f	48	29
5h	87	-ve

DSM = Deutsche Sammlumg von Mikroogramifmer (German Collection of Microorganisms).

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3150 cm^{-1} for stretching vibrations of NH group of dihydropyridine ring, 3050 cm^{-1} for aromatic CH, 2940 cm^{-1} for aiphatic CH stretching vibrations, 1600, 1580 cm^{-1} for aromatic ring and 730 cm^{-1} for C—S stretching vibrations. The ^{1}H-NMR spectrum of **5a** (DMSO-d_6) showed the following signals: δ1.30–1.70 (4H, m, two methylene groups of cyclopentane ring), 1.90–2.20 (4H, m, two methylene groups of cyclopentane ring), 6.70–8.20 (16H, complex, the aromatic protons and the proton of C-4 of dihydropyridine ring) and 10.25 ppm (1H, s, the NH proton of the dihydropyridine moiety).

Antimicrobial Activity

The antibacterial activity of the newly synthesized compounds was tested against the following organisms *Staphylococcus aureus DSM 346*, *Escherichia coli*, *DSM 423* using the agar cup diffusion technique.[20] Results of biological testing are shown in Table III. The data showed that most of the synthesized compounds exhibited remarkable effects.

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EXPERIMENTAL

The time required for completion of the reaction was monitored by thin layer chromatography (TLC). Melting points were determined in open glass capillaries and are uncorrected. IR-spectra were recorded on a Pye-Unicam SP 200 G spectrophotometer ^{1}H-NMR spectra were meausred on EM 360 90 MHz NMR spectrophotometer. Microanalyses were determined on a Perkin Elmer 240 C microanalyser. Mass spectra were performed on a Finnigan 4023 quadrupole system equipped with a Model 4500 source upgrade.

Preparation of 1-oxa-4-thiaspiro[4.4]nonan-2-one and 1-oxa-4-thiaspiro[4.5]decan-2-one

These compounds were prepared according to our reported procedure.[9]

Preparation of 1-thia-4-phenyl-4-azaspiro[4.4]nonan-3-one (**1a**) *and 1-thia-4-phenyl-4-azaspiro[4.5]-decan-3-one* (**1b**)

These compounds were prepared according to our previous method.[9]

Synthesis of 2-(substituted-α-phenacylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.4]nonan-3-one and 2-(substituted-α-phenacylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.5]decan-3-one **2a–h**

General procedure: A mixture of 4-phenyl-1-thia-4-azaspiro[4.4]nonan-3-one (**1a**) and/or 4-phenyl-1-thia-4-azaspiro[4.5]decan-3-one (**1b**) (0.01 mole) and benzalacetophenone (or substituted benzalacetophenone) (0.01 mole) in 50 ml absolute ethanol and 5 ml pyridine was refluxed for 6 hrs, then the reaction mixture was cooled to room temperature whereby the products were precipitated, filtered and crystallized from the proper solvents (Table I).

2-(α-Phenacylbenzyl)-4-phenyl-1-thia-4-azaspiro[4.4]nonan-3-one (**2a**)

A mixture of **1a** (2.33 g, 0.01 mole) and benzalacetophenone (2.08 g, 0.01 mole) in absolute 50 ml and pyridine (5 ml) was allowed to react according to the above general procedure to give 3.35 g (70%) of **2a**. The product was crystallized from ethanol: m.p. 185–187°C, IR (KBr): 3050 (CH arom), 2940 (CH aliph), 1675 (C=O), 1400–1000 (C=N) and 740 cm^{-1} (C—S); ^{1}H-NMR (DMSO-d_6): δ1.30–1.70 (4H, m) 1.90–2.20 (4H, m), 3.80 (2H, d), 4.10 (1H, q), 5.50 (1H, d), 6.70–8.30 ppm (15H, complex); MS, m/e (% relative intensity) 441(70), 232(100), 210(60), 205(60), 201(80), 119(50), 105(45), 77(42), 71(40).

Synthesis of spirothiazolopyrans (**3a–h**)

General procedure: A solution of the spiro derivatives (**2a–h**) (0.001 mole) in acetic anhydride (5 ml) was refluxed for ½ hr, then the reaction mixture was cooled to room temperature, diluted with 5 ml ether whereby the products were precipitated (Table II).

3',5',7'-Triphenylspiro cyclopentane-1,2'(3'H)pyrano[2,3-d]thiazole (**3a**)

A solution of **2a** (0.441 g, 0.001 mole) in 5 ml acetic anhydride (5 ml) was refluxed for ½ hr, according to the general procedure to yield 0.21 g (50% yield) of **3a**. The product was crystallized from ethanol, m.p. 150–152°C, IR (KBr): 3040 (CH arom), 2830 (CH aliph), 1600, 1580 (C=C arom) and 720 cm^{-1} (C—S); ^{1}H-NMR ($CDCl_3$), 1.30–1.70 (4H, m), 1.90–2.20 (4H, m), 6.90–8.20 (17H, complex); MS, m/e (% relative intensity) 423(100), 346(80), 232(70), 191(50), 114(50), 77(44).

Synthesis of spirothiazolothiopyrans (**4a–h**)

General procedure: A mixture of spiro derivatives **2a–h** (0.001 mole) and phosphorus pentasulfide (0.001 mole) in 5 ml pyridine was refluxed for ½ hr, then the reaction mixture was cooled to room temperature, poured into 50 ml cold water, extracted with chloroform and methylene chloride. The solvent extracts was washed with dilute hydrochloric acid and water, dried over calcium chloride. The solvents were removed to afford the title products (Table II).

3',5',7'-Triphenylspiro cyclopentane-1',2'(3'H)thiopyrano[2,3-d]thiazole (**4a**)

A mixture of **2a** (0.44 g, 0.001 mole) and phosphorus pentasulfide (0.23 g, 0.001 mole) in 5 ml pyridine was refluxed for ½ hr according to the general procedure to give 0.28 g (65% yield) of **4a**. The product was crystallized from ethanol/water (1:1), m.p. 160–162°C; IR (KBr) 3030 (CH arom), 2850 (CH alph.), 1600, 1580 (C=C arom) and 710 cm^{-1} (C—S); ^{1}H-NMR (DMSO-d_6) 1.30–1.70 (4H, m), 1.90–2.10 (4H, m), 6.90–8.20 (17H, complex); MS, m/e (% relative intensity) 439(100), 362(80), 248(70), 207(50), 119(45), 130(50), 77(42).

Synthesis of spirothiazolodihydropyridines (**5a–h**)

General procedure: A mixture of the spiro derivatives **2a–h** (0.001 mole) and ammonium acetate (0.001 mole) was fused at 200°C for ½ hr. The reaction mixture was cooled to room temperature, poured into 50 ml water, extracted with chloroform and methylene chloride. The solvent extracts was washed with dilute hydrochloric acid and water, dried over calcium chloride. The solvents were removed to yield the desired products (Table II).

4',7'-Dihydro-3',5',7'-triphenylspiro cyclopentane-1,2'(3'H)pyrido-[2,3-d]thiazole (**5a**)

A mixture of **2a** (0.44 g, 0.001 mole) and ammonium acetate (0.77 g, 0.001 mole) was fused at 200°C for ½ hr. The reaction mixture was worked up according to the above general procedure to afford 0.257 g (61% yield) of **5a**. The product was crystallized from ethanol, m.p. 160–162°C, IR (KBr) 3150 (NH), 3050 (CH arom), 2940 (CH alph), 1600, 1580 (C=C arom) and 730 (C—S); ^{1}H-NMR (DMSO-d_6); 1.30–1.70 (4H, m), 1.90–2.20 (4H, m), 6.70–8.20 (16H, complex), 10.25 (1H, s); MS, m/e (% relative intensity), 422(100), 345(80), 232(70), 191(50), 114(45), 77(40).

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