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Selected aryl aldehydes **I** were reacted with 1-benzosuberone to give the corresponding 2-arylidene-1-benzosuberones **II**. Condensation of these chalcones with urea and thiourea revealed the formation of the corresponding substituted pyrimidin-2-ones **III**, and pyrimidine-2-thiones **IV** respectively. The structure of all products was substantiated by chemical and spectral methods.

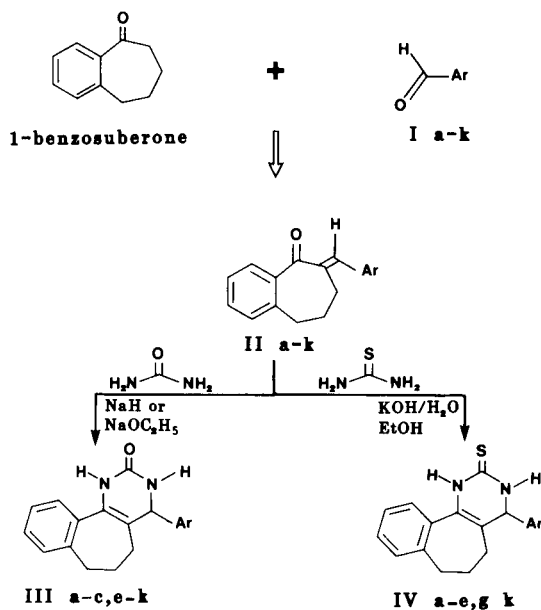
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The present work aims to investigate the reactions of urea and thiourea with new exocyclic α,β -unsaturated cyclic ketones and to establish the structure of the products by chemical and spectral methods. Thus, selected aromatic and heterocyclic aldehydes **Ia-k**, were condensed with 1-benzosuberone to give the corresponding 2-arylidene-1-benzosuberones **IIa-k**. The structure of these chalcones is evident from their chemical and spectral data (*cf.* Tables 1 and 2). The infrared spectra show two strong absorptions characteristic of α,β -unsaturated carbonyl compounds

[2a,3]. The electronic spectra show absorption bands attributed to the conjugated system of the *trans*-configuration of the α,β -unsaturated carbonyl compounds [4-8]. Additional support to the structure of compounds **II** comes from their nmr-spectra, which show multiplets in the region δ 1.80-3.26 ppm attributed to the $\text{CH}_2\text{CH}_2\text{CH}_2$ groups. Other signals stand for the vinyl and aromatic protons (*cf.* Table 1). The mass spectra of these chalcones lend further support to their structure. Thus, chalcones **IIg,i-k** revealed molecular ion peaks at *m/e* 238, 254, 251 and 249 respectively, which represented also their base peaks.

Condensation of the above 2-arylidene-1-benzosuberones **II** with urea using either sodium hydride or sodium ethoxide as a condensing catalyst led to the formation of the corresponding substituted pyrimidin-2-ones **III** (*cf.* scheme 1). The structures of these products were evident from their spectral and chemical data (*cf.* Tables 1 and 2). Thus, the infrared spectra show stretching vibrations which are characteristic of the C=O and the two N-H

Scheme 1



Compound	Ar	Compound	Ar
I-IVa	C_6H_5	g	$\text{C}_4\text{H}_3\text{O}$ (2-furyl)
b	<i>m</i> - $\text{OCH}_3\text{-C}_6\text{H}_4$	h	$\text{C}_4\text{H}_3\text{S}$ (2-thienyl)
c	<i>p</i> - $\text{OCH}_3\text{-C}_6\text{H}_4$	i	$\text{C}_4\text{H}_3\text{S}$ (3-thienyl)
d	<i>p</i> - $\text{Cl-C}_6\text{H}_4$	j	$\text{C}_5\text{H}_5\text{N}$ (2-N-methylpyrrolyl)
e	C_{10}H_7 (1-naphthyl)	k	$\text{C}_5\text{H}_4\text{N}$ (3-pyridinyl)
f	C_{10}H_7 (2-naphthyl)		

Scheme 2

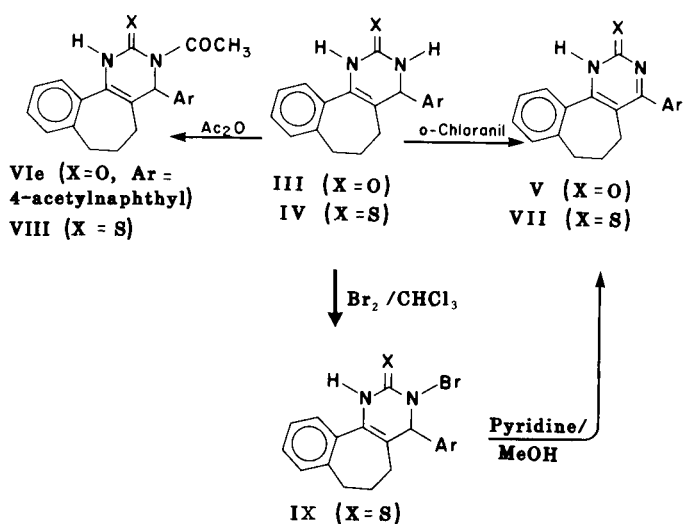


Table 1

The Infrared, Electronic and Nuclear Magnetic Resonance Spectral Data of Compounds **II-IX**

Compound	Infrared Spectra (Potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deuteriochloroform)	
	cm ⁻¹	ν	λ max (nm)	ϵ	δ	Assignment (No. of protons)
IIa	1664 (v s)	C=O	299	13410	1.95-3.03 (m)	(6) CH ₂ -CH ₂ -CH ₂
	1605 (s)		257	14245	7.15-7.85 (m)	(10) Ar-H + =CH
IIb	1594 (s)	C=C	235	15085		
	1663 (v s)	C=O	295	12375	1.92-2.98 (m)	(6) -CH ₂ -CH ₂ -CH ₂
IIc	1603 (s)		251	16500	3.80 (s)	(3) OCH ₃
	1590 (s)	C=C			6.75-7.83 (m)	(9) Ar-H + =CH
IId	1667 (s)	C=O	330	12590	1.93-2.97 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1595 (s)		250	21225	3.80 (s)	(3) OCH ₃
IIe	1585 (s)	C=C			6.79-7.77 (m)	(9) Ar-H + =CH
	1663 (s)	C=O	301	30450	1.90-2.98 (m)	(6) -CH ₂ -CH ₂ -CH ₂
IIe	1603 (s)		225 (sh)	32330	7.08-7.85 (m)	(9) Ar-H + =CH
	1590 (s)	C=C				
IIe	1663 (s)	C=O	310	8890	1.80-3.26 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1605 (s)		257	18520	7.54-8.66 (m)	(11) Ar-H
IIe		C=C				
	1595 (m)		221	71115	8.98 (s)	(1) =CH
IIe	1665 (s)	C=O	313	9935	1.86-3.32 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1605 (s)		250 (sh)	19535	7.56-8.58 (m)	(12) Ar-H + =CH
IIe		C=C				
	1590 (s)		233 (sh)	25500		
IIe	1660 (s)	C=O	340	15915	1.92-2.92 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1605 (s)		251	18505	6.43-7.82 (m)	(8) Ar-H + =CH
IIe		C=C				
	1590 (s)		224	27815		
IIh	1658 (s)	C=O	343	15400	1.93-2.90 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1600 (s)		266	10190	6.96-7.83 (m)	(8) Ar-H + =CH
IIh		C=C				
	1583 (v s)					
IIi	1662 (s)	C=O	317	11190	1.92-2.96 (m)	(6) CH ₂ -CH ₂ -CH ₂
	1604 (s)		256	11190	7.06-7.83 (m)	(8) Ar-H + =CH
IIi		C=C				
	1593 (s)					
IIj	1653 (s)	C=O	367	13280	1.93-2.92 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1600 (s)		260	12130	3.72 (s)	(3) N-CH ₃
IIj		C=C				
	1584 (v s)				6.12-7.75 (m)	(8) Ar-H + =CH
IIk	1663 (s)	C=O	287	14505	1.92-3.26 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1608 (s)		225	6790	7.52-9.14 (m)	(8) Ar-H
IIk		C=C				
	1595 (m)				9.30 (s)	(1) =CH
IIIa [a]	3330 (w)		284	4365	1.26-2.86 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3230 (m)	N-H			4.86 (s)	(1) H ₄
IIIa [a]	3080 (w-m)		222 (sh)	11320	6.92-8.50 (m)	(10) Ar-H + N-H
	1690 (s)	C=O			8.92 (s)	(1) N-H
IIIb [b]	3440 (w)		280	6030	1.50-2.80 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3330 (w)				4.00 (s)	(3) OCH ₃
IIIb [b]		N-H				
	3240 (m)		221	20420	5.20 (s)	(1) H ₄
IIIb [b]	3100 (w-m)				7.44-8.00 (m)	(9) Ar-H + N-H
	1690 (s)	C=O			8.86 (s)	(1) N-H

Table 1 (continued)

Compound	Infrared Spectra (Potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deuteriochloroform)	
	cm ⁻¹	ν	λ max (nm)	ϵ	δ	Assignment (No. of protons)
IIIc [b]	3400 (w)		283	6920	1.40-2.92 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3330 (w)	N-H			4.02 (s)	(3) OCH ₃
	3220 (m)		228	18490	5.22 (s)	(1) H _a
	3080 (w-m)				7.32-8.06 (m)	(9) Ar-H + N-H
	1685 (v s)	C=O			8.96 (s)	(1) N-H
IIIe [b]	3400 (w)		282	10865	1.52-2.84 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3330 (w)		224	66665	6.16 (s)	(1) H _a
		N-H				
	3220 (m)				7.60-8.60 (m)	(12) Ar-H + N-H
	3090 (m)				9.10 (s)	(1) N-H
IIIf [c]	1685 (s)	C=O				
	3440 (w)		274	8690	1.46-3.00 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3340 (w)	N-H	222	62560	5.86 (s)	(1) H _a
	3240 (m)				7.72-8.72 (m)	(12) Ar-H + N-H
	3090 (w-m)				9.30 (s)	(1) N-H
IIIg [b]	1695 (v s)	C=O				
	3420 (w)		279	6010	1.66-2.70 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3320 (w)	N-H	225	19120	5.06 (s)	(1) H _a
	3220 (w)				5.85-7.36 (m)	(8) Ar-H + N-H
	3080 (w-m)				8.95 (s)	(1) N-H
IIIh [b]	1680 (s)	C=O				
	3430 (w)		283	4630	1.66-2.86 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3330 (w)	N-H	228	15430	5.64 (s)	(1) H _a
	3220 (m)				7.50-8.10 (m)	(8) Ar-H + N-H
	3080 (w-m)				9.10 (s)	(1) N-H
IIIi [b]	1685 (s)	C=O				
	3420 (w)		281	4475	1.62-2.84 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3330 (w)	N-H	226	14530	5.42 (s)	(1) H _a
	3230 (m)				7.64-8.22 (m)	(8) Ar-H + N-H
	3090 (w-m)				8.96 (s)	(1) N-H
IIIj [b]	1690 (s)	C=O				
	3380 (m)		280	5085	1.66-2.84 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3200 (m)	N-H	224	18415	3.92 (s)	(3) N-CH ₃
	3080 (m)				5.46 (s)	(1) H _a
	1675 (s)	C=O			6.38-8.00 (m)	(8) Ar-H + N-H
IIIk [b]					8.92 (s)	(1) N-H
	3480 (w-m)		283	4470	1.64-2.84 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3280 (w)	N-H	262	5615	5.32 (s)	(1) H _a
	3190 (w)		227	15865	7.52-8.44 (m)	(9) Ar-H + N-H
	3080 (w-m)				9.06 (s)	(1) N-H
IVa [b]	1650 (s)	C=O				
	3230 (m)	N-H	301	34405	1.56-2.96 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1570 (s)	amide II	265	83540	5.26 (s)	(1) H _a
	1490 (s)	C=C	231	87225	7.24-8.12 (m)	(9) Ar-H
	1206 (s)	amide I			9.46 (s)	(1) N-H
IVb [b]					10.30 (s)	(1) N-H
	3130 (m)	N-H	295	7585	1.66-3.02 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1575 (s)	amide II	266	18730	3.96 (s)	(3) OCH ₃
	1490 (s)	C=C	224	20590	5.16 (s)	(1) H _a
	1210 (s)	amide I			7.16-8.02 (m)	(8) Ar-H
				9.40 (s)	(1) N-H	
				10.26 (s)	(1) N-H	

Table 1 (continued)

Compound	Infrared Spectra (Potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deuteriochloroform)	
	cm ⁻¹	ν	λ max (nm)	ϵ	δ	Assignment (No. of protons)
IVc [d]	3310 (w-m)		294	7405	1.66-2.92 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3210 (m)	N-H	260	17665	3.96 (s)	(3) OCH ₃
	3110 (w)		242	16810	5.18 (s)	(1) H _a
	1575 (s)	amide II	225	16240	7.18-8.06 (m)	(8) Ar-H
	1518 (s)				8.50 (s)	(1) N-H
	1483 (s)	C=C				
	1195 (s)	amide I			9.22 (s)	(1) N-H
IVd [d]	3300 (w-m)		290	8515	1.66-2.86 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3200 (m)	N-H	265	20220	5.24 (s)	(1) H _a
	3100 (w)				7.40-8.06 (m)	(8) Ar-H
	1577 (s)	amide II	232	24725	8.66 (s)	(1) N-H
	1490 (s)	C=C			9.40 (s)	(1) N-H
	1195 (s)	amide I				
IVe [b]	3200 (m)	N-H	324	5025	1.52-2.98 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1563 (s)	amide II	295	12185	6.16 (s)	(1) H _a
	1485 (s)	C=C	271	19850	7.52-8.58 (m)	(11) Ar-H
	1205 (s)	amide I			9.46 (s)	(1) N-H
					10.42 (s)	(1) N-H
IVg [b]	3190 (m)	N-H	292	8640	1.60-2.86 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1573 (s)	amide II	263	16295	5.26 (s)	(1) H _a
	1500 (s)	C=C	243	16000	6.60-8.04 (m)	(7) Ar-H
	1210 (s)	amide I	229	15555	9.32 (s)	(1) N-H
					10.26 (s)	(1) N-H
IVh [b]	3200 (m)	N-H	291	8300	1.58-2.98 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1570 (s)	amide II	252	19430	5.52 (s)	(1) H _a
	1490 (s)	C=C	235	20085	7.38-8.08 (m)	(7) Ar-H
	1207 (s)	amide I			9.44 (s)	(1) N-H
					10.30 (s)	(1) N-H
IVi [b]	3200 (m)	N-H	293	7090	1.58-3.02 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1575 (s)	amide II	265	16100	5.32 (s)	(1) H _a
	1500 (s)	C=C	241	17980	7.50-8.06 (m)	(7) Ar-H
	1210 (s)	amide I			9.42 (s)	(1) N-H
					10.26 (s)	(1) N-H
IVj [b]	3210 (m)	N-H	291	10235	1.56-3.00 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1565 (s)	amide II	262	19055	3.86 (s)	(3) N-CH ₃
	1485 (s)	C=C	226	17850	3.96 (s)	(1) H _a
	1210 (s)	amide I			5.36-8.00 (m)	(7) Ar-H
					9.30 (s)	(1) N-H
				10.24 (s)	(1) N-H	
IVk [b]	3195	N-H	298	5830	1.58-2.86 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1573 (s)	amide II	226	14880	5.30 (s)	(1) H _a
	1480 (s)	C=C	235	14475	7.56-9.10 (m)	(8) Ar-H
	1213 (s)	amide I			9.46 (s)	(1) N-H
					10.36 (s)	(1) N-H
Vc [b]	3450 (br)		340	14285	1.92-3.12 (m)	(6) -CH ₂ -CH ₂ -CH ₂
		N-H				
	3080 (w)		267	11040	4.06 (s)	(3) OCH ₃
	1635 (s)	C=O	216 (sh)	19805	7.46-8.32 (m)	(9) Ar-H + N-H
	1610 (m)	C=N				
1570 (w-m)	C=C					
Vf	3450 (br)		339	13155	2.20-3.32 (m)	(6) -CH ₂ -CH ₂ -CH ₂
		N-H				
	3060 (w)		278 (sh)	11545	8.06-9.00 (m)	(12) Ar-H + N-H
	1640 (v s)	C=O	256 (sh)	15300		
	1610 (w)	C=N	240 (sh)	19730		
	1590 (m)	C=C				

Table 1 (continued)

Compound	Infrared Spectra (Potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deuteriochloroform)	
	cm ⁻¹	ν	λ max (nm)	ϵ	δ	Assignment (No. of protons)
VIe [c]	3450 (br)	N-H	291 (sh)	6630	1.66-2.84 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3030 (w)		279	9550	2.32 (s)	(3) N-COCH ₃
	1740 (s)		250	11935	2.90 (s)	(3) Ar-COCH ₃
	1710 (s)	C=O			7.50 (s)	(1) H ₄
	1695 (s)				7.70-9.06 (m)	(11) Ar-H + N-H
VIIb	3450 (br)	N-H	294	6335	1.66-3.00 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	1545 (s)	amide II	254	12040	3.98 (s)	(3) OCH ₃
	1500 (m)	C=C			7.12-8.26 (m)	(8) Ar-H
	1265 (s)	amide I			10.40 (s)	(1) N-H
VIIIi	3450 (br)	N-H	311	9005	—	—
	1540 (s)	amide II	255	23085		
	1510 (s)	C=C				
	1280 (s)	amide I				
VIIIc [c]	3450 (br)	NH	331	9835	1.46-2.60 (s)	(6) -CH ₂ -CH ₂ -CH ₂
	3150 (w)		266	15030	2.92 (s)	(3) N-COCH ₃
	1695 (s)	C=O	239	17070	3.50 (s)	(3) OCH ₃
	1515 (s)	amide II	222	19295	6.50 (s)	(1) H ₄
	1490 (w)	C=C			7.16-8.16 (m)	(8) Ar-H
	1200 (m)	amide I			8.66 (s)	(1) N-H
VIII d [c]	3440 (br)	N-H	330	10215	1.80-2.86 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3160 (w)		264 (sh)	13095	2.92 (s)	(3) N-COCH ₃
	1700 (s)	C=O	243	20290	6.46 (s)	(1) H ₄
	1520 (s)	amide II			7.72-8.20 (m)	(8) Ar-H
	1490 (m)	C=C			8.88 (s)	(1) N-H
	1205 (m)	amide I				
IXc [b]	3310 (w)	N-H	341	13835	1.94-3.06 (m)	(6) -CH ₂ -CH ₂ -CH ₂
	3070 (w)		272 (sh)	20850	4.06 (s)	(3) OCH ₃
	1740 (m-s)	C=O	257	25090	5.06 (s)	(1) H ₄
	1570 (m)	C=C			7.44-8.28 (m)	(9) Ar-H + N-H

[a] Perdeuteriobenzene. [b] DMSO-d₆. [c] Deuteriotrifluoroacetic Acid. [d] Perdeuterio-1,4-dioxane.

groups [9a,10 and 11]. The electronic spectra of these pyrimidones show absorption maxima which can be ascribed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of their chromophores [11]. Their nmr spectra show four main sets of chemical shifts. The -CH₂-CH₂-CH₂- moieties were characterised by 6H multiplets in the range δ 1.26-2.92 ppm. The singlets in the region δ 4.86-6.16 ppm stand for the benzylic hydrogens (H₄). The multiplets in the range δ 5.85-8.60 ppm are ascribed to the Ar-H and the N-H protons at position 1. The more deshielded N-H protons at position 3 were represented by singlets in the range δ 8.86-9.10 ppm, which disappear upon treatment with deuterium oxide. The mass spectra lend further support to the structure of the pyrimidones **III**. Thus, compounds **IIIb,c,e,g,h,j,k** show molecular ion peaks at m/e 320 (78.13%), 320 (90.73%), 304 (74.61%), 280 (79.38%), 296 (100%), 293 (100%), and 291 (53.91%) respectively. All the above spectra showed prominent peaks corresponding to $[M-1]^+$ ions.

Condensation of the chalcones **II** with thiourea revealed the formation of the corresponding substituted pyrimidine-2-thiones **IV** (*cf.* Scheme 1). The structures of these products were evident from their spectral data (*cf.* Table 1). The infrared spectra showed absorption bands ascribed to the N-H and C=S groups [9b,13,14]. The electronic spectra agree well with the proposed structure and show absorptions at higher wavelengths and intensities than the corresponding pyrimidones **III**. The nmr-spectra show chemical shifts which stand for the different protons of these thiones. Thus, the N-H groups at positions 1 and 3 showed two singlets ascribed to H₁ and H₃ of the thiones. The mass spectra of the thiones **IVa,b,d,e,i-k** showed signals which can be ascribed to their molecular ions.

Further insight concerning the structure of the pyrimidones **III** and the pyrimidine-thiones **IV** can be gleaned out from their chemical behaviour (*cf.* Scheme 2). Thus, dehydrogenation of **IIIc,f** with *o*-chloranil led to the for-

Table 2
 Yields, Melting Points and Elemental Analyses of Compounds II-IX

Compound No.	Yield (%)	Mp °C	Formula	Calcd. %					Found %				
				C	H	N	Cl (Br)	S	C	H	N	Cl (Br)	S
IIa	85	77-78	C ₁₈ H ₁₆ O	87.06	6.49	—	—	—	87.02	6.51	—	—	—
IIb	80	117-118.5	C ₁₉ H ₁₈ O ₂	81.99	6.51	—	—	—	81.87	6.47	—	—	—
IIc	81	106-107	C ₁₉ H ₁₈ O ₂	81.99	6.52	—	—	—	82.42	6.53	—	—	—
IId	75	87-88	C ₁₈ H ₁₅ ClO	76.46	5.35	—	12.54	—	76.18	5.52	—	12.41	—
IIe	73	94-96	C ₂₂ H ₁₈ O	88.56	6.08	—	—	—	88.82	6.11	—	—	—
IIf	70	142-143	C ₂₂ H ₁₈ O	88.56	6.08	—	—	—	88.52	6.02	—	—	—
IIg	79	123-124	C ₁₆ H ₁₄ O ₂	80.65	5.92	—	—	—	80.69	5.81	—	—	—
IIh	80	138.5-140	C ₁₆ H ₁₄ OS	75.56	5.55	—	—	12.60	75.76	5.52	—	—	12.77
IIi	84	147-149	C ₁₆ H ₁₄ OS	75.56	5.55	—	—	12.60	75.51	5.53	—	—	12.71
IIj	73	128-130	C ₁₇ H ₁₇ NO	81.24	6.82	5.57	—	—	81.14	6.85	5.53	—	—
IIk	79	95-97	C ₁₇ H ₁₅ NO	81.90	6.06	5.62	—	—	81.94	6.08	5.68	—	—
IIIa	72	189-191	C ₁₉ H ₁₈ N ₂ O	78.59	6.25	9.65	—	—	78.52	6.15	9.61	—	—
IIIb	75	205-207 [a]	C ₂₀ H ₂₀ N ₂ O ₂	74.98	6.29	8.74	—	—	74.87	6.35	8.71	—	—
IIIc	78	208-210	C ₂₀ H ₂₀ N ₂ O ₂	74.98	6.29	8.74	—	—	74.88	6.37	8.78	—	—
IIIe	85	234-236 [a]	C ₂₃ H ₂₀ N ₂ O	81.15	5.92	8.23	—	—	81.38	6.07	7.98	—	—
IIIf	75	223-224 [a]	C ₂₃ H ₂₀ N ₂ O	81.15	5.92	8.23	—	—	81.09	5.89	8.20	—	—
IIIg	75	213-214	C ₁₇ H ₁₆ N ₂ O ₂	72.84	5.75	9.99	—	—	72.85	5.78	9.86	—	—
IIIh	84	193-195 [a]	C ₁₇ H ₁₆ N ₂ OS	68.89	5.44	9.45	—	10.80	68.78	5.35	9.40	—	10.71
IIIi	77	185-187 [a]	C ₁₇ H ₁₆ N ₂ OS	68.89	5.44	9.45	—	10.80	68.81	5.39	9.37	—	10.75
IIIj	83	210-212 [a]	C ₁₈ H ₁₉ N ₃ O	73.70	6.53	14.32	—	—	73.62	6.47	14.30	—	—
IIIk	75	208-210 [a]	C ₁₈ H ₁₇ N ₃ O	74.21	5.88	14.42	—	—	74.10	5.81	14.39	—	—
IVa	80	255-256.5 [a]	C ₁₉ H ₁₈ N ₂ S	74.47	5.92	9.14	—	10.46	74.30	6.01	9.05	—	10.46
IVb	84	229-231 [a]	C ₂₀ H ₂₀ N ₂ OS	71.40	5.99	8.33	—	9.53	71.27	6.01	8.28	—	9.55
IVc	86	208-210 [a]	C ₂₀ H ₂₀ N ₂ OS	71.40	5.99	8.33	—	9.53	71.53	6.08	8.36	—	9.52
IVd	85	227-228 [a]	C ₁₉ H ₁₇ ClN ₂ S	66.95	5.03	8.22	10.40	9.41	66.78	5.10	8.24	10.30	9.24
IVe	80	221-222 [a]	C ₂₃ H ₂₀ N ₂ S	77.49	5.65	7.86	—	8.99	77.40	5.72	7.90	—	8.94
IVg	80	258-259 [a]	C ₁₇ H ₁₆ N ₂ OS	68.89	5.44	9.45	—	10.82	68.77	5.32	9.56	—	10.66
IVh	78	250-252 [a]	C ₁₇ H ₁₆ N ₂ S ₂	65.35	5.16	8.97	—	20.52	65.48	5.26	9.00	—	20.34
IVi	88	254-255 [a]	C ₁₇ H ₁₆ N ₂ S ₂	65.35	5.16	8.97	—	20.52	65.13	5.30	8.86	—	20.28
IVj	70	220-222 [a]	C ₁₈ H ₁₉ N ₃ S	69.87	6.19	13.58	—	10.36	69.85	6.22	13.47	—	10.20
IVk	72	222-224 [a]	C ₁₈ H ₁₇ N ₃ S	70.33	5.57	13.67	—	10.43	70.24	5.70	13.59	—	10.35
Vc	80	249-251	C ₂₀ H ₁₈ N ₂ O ₂	75.45	5.70	8.80	—	—	75.39	5.61	8.72	—	—
Vf	70	262-264 [a]	C ₂₃ H ₁₈ N ₂ O	81.63	5.36	8.28	—	—	81.51	5.19	8.18	—	—
VIe	75	186-187	C ₂₇ H ₂₄ N ₂ O ₃	76.40	5.70	6.60	—	—	77.14	5.74	6.68	—	—
VIIb	72	150-152 [a]	C ₂₀ H ₁₈ N ₂ OS	71.83	5.42	8.38	—	9.59	71.79	5.40	8.31	—	9.55
VIIi	76	194-195	C ₁₇ H ₁₄ N ₂ S ₂	65.77	4.55	9.02	—	20.66	65.68	4.50	9.00	—	20.57
VIIIe	85	182-183	C ₂₂ H ₂₂ N ₂ O ₂ S	69.81	5.86	7.40	—	8.47	69.71	5.93	7.42	—	8.41
VIIIId	72	186-186.5	C ₂₁ H ₁₉ ClN ₂ OS	65.87	5.00	7.32	9.26	8.37	65.78	5.06	7.39	9.50	8.30
IXc	81	196-198 [a]	C ₂₀ H ₁₉ BrN ₂ O ₂	60.16	4.80	7.02	20.0	—	60.07	4.56	7.00	19.95	—

[a] Melting was accompanied by decomposition.

mation of the corresponding 2(1*H*)-pyrimidones **Vc,f** respectively [15]. On the other hand, treatment of **IIIc** with bromine in chloroform led to the formation of the *N*-bromo-2(1*H*)-pyrimidone **IXc** which upon dehydrobromination with pyridine gave the corresponding 2(1*H*)-pyrimidone **Vc** [11]. The structure of compounds **Vc,f** and **IXc** can be predicted on the basis of their spectral and chemical analyses (*cf.* Tables 1 and 2). Thus, the infrared spectra

of **Vc,f** revealed strong bands at 1635, 1610 and 3450 cm⁻¹ characteristic of the C=O, C=N and N-H groups respectively [11,16]. The uv spectra show absorptions at longer wavelengths than that of their precursors **IIIc,f**, due to extend conjugation [11,17]. The nmr spectra were void of the two chemical shifts ascribed to the benzylic hydrogen (H₄) and the N-H proton (H₃), indicating their elimination upon dehydrogenation.

On the other hand, the infrared spectrum of **IXc** show absorptions characteristic of the N-H and C=O groups [2b]. The nmr-spectrum showed (1H) singlet characteristic of the benzylic proton (H₄), and was void of the signal which stand for the N-H(H₃), due to its substitution by the bromine.

Upon dehydrogenation of compounds **IVb,i** they afforded the corresponding dehydrogenated 2(1H)-pyrimidinethiones **VIIIb,i** (cf. Scheme 2). The structure of compounds **VIIIb,i** can be established from their spectral and chemical analyses (cf. Tables 1 and 2). Thus, the infrared spectra showed absorption bands which can be ascribed to N-H and C=S groups [18]. The electronic and nmr-spectra showed similar behaviour to those of compounds **V**.

On the other hand, acetylation of compounds **IIIe**, **IVc,d** revealed the formation of the *N*-acetylated products **VIe** and **VIIIc,d** respectively. Their structure is evident from their spectral and chemical data (cf. Tables 1 and 2). The infrared spectra showed absorption bands which can be ascribed to N-H, C=O, and C=S groups respectively. The nmr-spectra revealed (3H) singlets representing the N-COCH₃ protons, whereas the (1H) singlets of the N-H groups at position 3 (H₃) have disappeared, indicating the substitution of these hydrogens by acetyl groups.

It can be assumed at this respect that the formation of the above pyrimidones **III** and pyrimidinethiones **IV** seems to proceed by the Michael addition of the urea or thiourea to the chalcones **II** followed by the cyclization of the intermediate addition product [12]. The occurrence of these condensations is in good agreement with the proposed (*E*)-configuration of the chalcones **II**.

EXPERIMENTAL

Melting points (uncorrected) were measured using an electrothermal melting point apparatus, electronic and infrared spectra were run on Pye Unicam SP8-100 and Perkin-Elmer 580B, respectively. The nmr and mass spectra were carried out using Varian T 60 A and Varian MAT 311A, respectively. Microanalyses were determined by Professor H. Malissa and G. Reuter, Analytical Laboratories, German Federal Republic.

Preparation of 2-Arylidene-1-benzosuberones **IIa-k**. General Procedure.

Equimolar amounts of the aldehydes (0.1 mole) and 1-benzosuberone (0.1 mole) in ethanol (70 ml) were treated with an ethanolic solution of sodium hydroxide (2.0 g/30 ml ethanol), and the resulting mixture was stirred on cold for 3-4 hours. The precipitated product was filtered off and crystallized from ethanol. Thus, the aldehydes **Ia-k** were condensed with 1-benzosuberone to give 2-benzylidene-**IIa**, 2-(*m*-methoxybenzylidene)-**IIb**, 2-(*p*-methoxybenzylidene)-**IIc**, 2-(*p*-chlorobenzylidene)-**IId**, 2-(1'-naphthylidene)-**IIe**, 2-(2'-naphthylidene)-**IIIf**, 2-(2'-furylidene)-**IIg**, 2-(2'-thienylidene)-**IIh**, 2-(3'-thienylidene)-**IIi**, 2-(2'-*N*-methylpyrrolylidene)-**IIj**, and 2-(3'-pyridinylidene)-**IIk**-1-benzosuberones.

Condensation of Urea with 2-arylidene-1-benzosuberones. General Procedure.

a) Sodium hydride Method.

To 0.01 mole of the 2-arylidene-1-benzosuberone (**II**) and 0.03 mole of urea dissolved in 50 ml of dry benzene was added about 1 g of sodium hydride (0.042 mole). A few drops of methanol were added to initiate the reaction and the mixture was stirred on cold for 20 hours. Benzene was distilled off, water was added and the aqueous solution neutralized with 1*M*-hydrochloric acid. The precipitated product was filtered off, washed with distilled water and crystallized from benzene/acetone to give 4-aryl-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidin-2(1*H*)-ones **IIIa-c,e-k**.

b) Sodium Ethoxide Method.

A mixture of 0.01 mole of the 2-arylidene-1-benzosuberone (**II**) and 0.03 mole of urea in 50 ml of absolute ethanol was added to sodium ethoxide (1.4 g sodium metal in 30 ml of ethanol) and the mixture was refluxed for 15-20 hours. Ethanol was distilled off and water was added to the residue. The aqueous solution was then neutralized with 1*M*-hydrochloric acid, the precipitated product was filtered off and crystallized from benzene/acetone.

Condensation of Thiourea with 2-Arylidene-1-benzosuberone. General Procedure.

To 0.01 mole of the 2-arylidene-1-benzosuberone (**II**) and 0.02 mole of thiourea in 50 ml of absolute ethanol was added 0.05 mole of potassium hydroxide (2.8 g/3 ml of water). The mixture was refluxed for 8 hours, after which ethanol was distilled off. The residue was dissolved in water and aqueous solution neutralized with 1*M*-hydrochloric acid. The precipitated product was filtered off and crystallized from benzene/acetone to give 4-aryl-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidine-2(1*H*)-thiones **IVa-e,g-k**.

Dehydrogenation of Compounds **III** and **IV** with *o*-Chloranil. General Procedure.

The pyrimidone derivatives **IIIc,f** or the pyrimidine-thiones **IVb,i** were dissolved in tetrahydrofuran. An equimolar amount of *o*-chloranil was added gradually and the solution stirred by room temperature for 3 hours for **IIIc,f** or 24 hours for **IVb,i**. The precipitated products **Ve** and **Vf** were filtered off and crystallized from ethanol and benzene/acetone to give 4-aryl-6,7-dihydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidin-2(1*H*)-ones **Vc,f** respectively.

In case of compounds **IVb,i**, the solvent was concentrated and the material was poured into petroleum ether (bp 30-50°). The precipitated products were crystallized from benzene/hexane and ethanol to give 4-aryl-6,7-dihydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidine-2(1*H*)-thiones **VIIIb,i** respectively.

Acetylation of Compounds **IIIe** and **IVc,d**. General Procedure.

To about 0.5 g of each of compounds **IIIe** or **IVc,d** was added 3-5 ml of acetic anhydride and the solution was refluxed on a heating mantle for 3 hours. The products which precipitated on the addition of about 10 ml of 1:1 aqueous ethanol solution were crystallized from benzene for **VIe** or ethanol for **VIIIc,d** to give 3-acetyl-4-(4'-acetyl-1'-naphthyl)-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidin-2(1*H*)-one (**VIe**) and 3-acetyl-4-aryl-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidine-2(1*H*)-thiones **VIIIc,d** respectively.

Bromination of Compound **IIIc**.

To a solution of 1.0 g of **IIIc** in 20 ml of chloroform was added 0.4 ml of bromine in 5 ml of chloroform. The mixture was refluxed for 3 hours and allowed to stand overnight [11]. Concentration of the solution and cooling brought about precipitation of the product, 3-bromo-4-(4'-methoxyphenyl)-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidin-2(1*H*)-one **IXc**, crystallized from ethanol.

Dehydrobromination of **IXc**.

To 0.5 g of **IXc** dissolved in 2 ml of methanol was added 3 ml of pyridine and the solution was heated for 1.5 hours [11]. Concentration and cooling of the solution caused precipitation of the product **Vc**.

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