Heterocycles. Part XII. Synthesis of New Benzo[6,7]cyclohepta[1,2-*d*]pyrimidine

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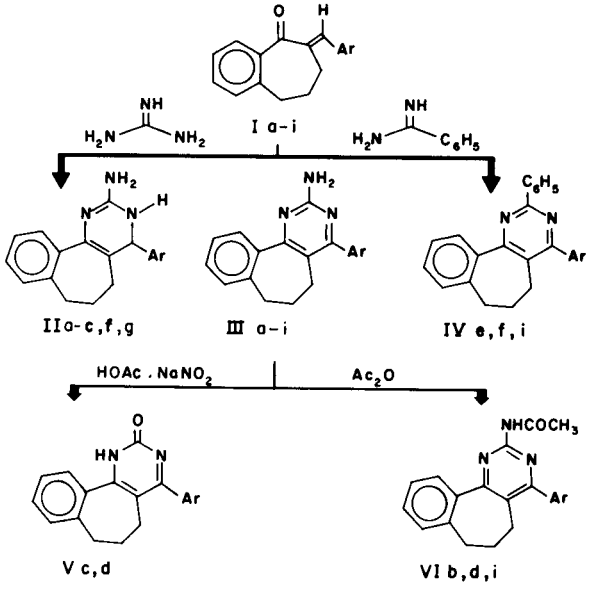
Received December 6, 1986

Selected 2-arylidene-1-benzosuberones **I** were condensed with guanidine hydrochloride to give the corresponding substituted 2-aminopyrimidines **II** and **III** respectively. Condensation of chalcones **I** with benzamidine hydrochloride revealed the formation of the corresponding substituted 2-phenylpyrimidines **IV**. The structure of all products was substantiated by chemical and spectroscopic methods.

J. Heterocyclic Chem., **24**, 1141 (1987).

The present investigation describes the reactions of guanidine and benzamidine hydrochlorides with exocyclic α,β-unsaturated cyclic ketones [2] and the establishment of the structure of the products by chemical and spectral methods. Thus, selected 2-arylidene-1-benzosuberones **Ia-i**, were condensed with guanidine using different reaction conditions [3,4]. The condensation with guanidine carbonate for relatively short periods led exclusively to the formation of 2-amino-3,4-dihydropyrimidines **IIa-c,f,g**.



Compound	Ar
II-Va	C_6H_5
b	*p*-OCH_3-C_6H_4
c	*p*-Cl-C_6H_4
d	$C_{10}H_{17}$ (1'-naphthyl)
e	C_4H_3O (2'-furyl)
f	C_4H_3S (2'-thienyl)
g	C_4H_3S (3'-thienyl)
h	C_5H_6N (2'-*N*-Methylpyrrolyl)
i	C_5H_4N (3'-Pyridyl)
VIb	3'-acetyl-4'-methoxyphenyl
d	4'-acetylnaphthyl
i	3'-pyridyl

On the other hand, the condensation with the liberated free guanidine gave predominantly the corresponding substituted 2-aminopyrimidines **IIIa-i** [5], together, in some cases, with minor amounts of the substituted 2-amino-3,4-dihydropyrimidines (**IIc,f** and **g**) (*cf.* Scheme 1). Condensation of the chalcones with guanidine hydrochloride for long periods led to the formation of the pyrimidines **III** as sole products. The structure of the dihydropyrimidines **II** can be established from their spectral and chemical analyses (*cf.* Tables 1,2). Thus, the infrared spectra of compounds **IIa-c,f,g** show major absorptions (in potassium bromide) which can be attributed to N-H, C=N [6,7a]. A similar infrared absorption pattern was obtained when the spectrum was run in dimethylsulfoxide. The shoulder which appears in the region 1680-1690 cm^{-1} can be attributed to the C=C-NH-C=N chromophore of the 1,4-dihydropyrimidine tautomer, and indicates that this tautomer is present only in small amounts in the solid form or in aprotic polar solvents [6,8]. The electronic spectra display an $n \rightarrow \pi^*$ transition for the chromophore C=C-N=C-NH which appears as a medium intensity band in the 274-278 nm region [7b,9]. The nmr revealed broad signals in the range of δ 5.00-3.63 ppm (NH_2, N-H) which disappeared upon deuteration. The spectrum showed singlets in the range of δ 5.25-4.92 ppm characteristic of H_4 in addition to the multiplets of the methylene and aryl protons (*cf.* Table 1). The mass spectra of compounds **IIc,f** show molecular ion peaks at m/e 324 (29.44%) and 295 (100%) respectively, in addition to prominent $[M-1]^+$ and $[M-2]^+$ ion peaks. The structure of the products **III** was established from their spectroscopic and chemical analyses (*cf.* Tables 1,2). Thus, the infrared spectra of compounds **III** (*cf.* Table 1) show stretching frequencies which are characteristic of the NH_2, C=N and the C=C groups of the pyrimidine nucleus [10-14]. Additional support to the structure of compounds **III** comes from their nmr-spectra (*cf.* Table 1), which show three main sets of chemical shifts. The ($-CH_2-CH_2-CH_2-$) grouping was characterised by (6H)-multiplets in the range δ 3.20-1.40 ppm. The singlets in the region δ 7.00-5.40 ppm

Table 1

The Infrared, Electronic and Nuclear Magnetic Resonance of Compounds **II-VI**

Compound	Infrared Spectra (Potassium Bromide) cm^{-1}	ν	Electronic Spectra (Ethanol) λ max (nm)	ϵ	NMR δ	Assignment No. of Protons
IIa [a]	3450 (m)		278	3785	1.20-3.00 (m)	(6) $-CH_2-CH_2-CH_2$
	3350 (m)	NH + NH_2	218 sh	19155	5.00 (br)	(3) NH + NH_2
	3060 (w)					
	3030 (w)				5.24 (s)	(1) H_4
	1690 sh	C=C-NH-C=N			7.40-8.26 (m)	(9) Ar-H
	1645 (s)	C=C-N=C-NH				
	1630 (s)					
	1540 (s)	C=C				
	1490 (m)					
IIb [a]	3450 (m)		274	6250	1.22-2.90 (m)	(6) $CH_2-CH_2-CH_2$
	3360 (m)	N-H + NH_2	230	20600	3.90 (s)	(3) OCH_3
	3080 (w)					
	1685 sh	C=C-NH-C=N			4.56 (br)	(3) NH + NH_2
	1645 (s)	C=C-N=C-NH			5.10 (s)	(1) N_4
	1625 (s)				7.02-8.10 (m)	(8) Ar-H
	1555 (s)	C=C				
	1515 (m)					
IIc [a]	3430 (m)		277	4155	1.32-2.80 (m)	(6) $CH_2-CH_2-CH_2$
	3340 (m)	N-H + NH_2	225	24780	3.66 (br)	(3) NH + NH_2
	3060 (w)					
	3020 (w)				5.20 (s)	(1) H_4
	1685 sh	C=C-NH-C=N			7.32-8.12 (m)	(8) Ar-H
	1640 (s)	C=C-N=C-NH				
	1625 (s)					
	1545 (s)	C=C				
	1490 (s)					
IIf [a]	3440 (m)		276	4440	1.43-2.40 (m)	(6) $-CH_2-CH_2-CH_2$
	3345 (m)	NH + NH_2	227	20330	3.63 (br)	(3) NH + NH_2
	3070 (w)					
	3020 (w)				5.25 (s)	(1) H_4
	1680 sh	C=C-NH-C=N			6.83-7.63 (m)	(7) Ar-H
	1640 (s)	C=C-N=C-NH				
	1625 (s)					
	1544 (s)	C=C				
	1485 (m)					
IIg [a]	3440 (m)		274	4200	1.30-2.16 (m)	(6) $-CH_2-CH_2-CH_2$
	3340 (m)	NH + NH_2	226	18080	3.86 (br)	(3) NH + NH_2
	3080 (w)					
	3020 (w)				4.92 (s)	(1) H_4
	1680 sh	C=C-NH-C=N			6.80-7.56 (m)	(7) Ar-H
	1640 (s)	C=C-N=C-NH				
	1625 (s)					
	1545 (s)	C=C				
	1480 (m)					
IIIa [b]	3500 (w)		321	8380	1.40-2.72 (m)	(6) $-CH_2-CH_2-CH_2$
	3300 (m)	N-H	238	19600	6.00 (s)	(2) NH_2
	3175 (m)					
	1630 (s)	C=N			7.26-8.66 (m)	(9) Ar-H
	1550 (s)					
	1495 (w)	C=C				
	1465 (m)					

Table 1 (continued)

Compound	Infrared Spectra (Potassium Bromide) cm^{-1}	ν	Electronic Spectra (Ethanol) λ max (nm)	ε	NMR δ	Assignment No. of Protons
IIIb [a]	3450 (m)		323	10140	1.92-3.20 (m)	(6) -CH_2-CH_2-CH_2
	3310 (m)	N-H	240	17600	4.00 (s)	(3) OCH_3
	3200 (m)		213 sh	21670	6.84 (s)	(2) NH_2
	1630 (s)	C=N			7.32-8.26 (m)	(8) Ar-H
	1545 (s)					
	1512 (m)	C=C				
	1465 (m)					
IIIc [c]	3500 (w)		325	8405	1.52-3.00 (m)	(6) -CH_2-CH_2-CH_2
	3310 (m)	N-H	245	20215	5.64 (s)	(2) NH_2
	3190 (m)		214 sh	24330	7.72-8.46 (m)	(8) Ar-H
	1625 (s)	C=N				
	1550 (s)					
	1495 (m)	C=C				
	1465 (m)					
IIId [b]	3500 (w)		319	10000	1.46-2.86 (m)	(6) -CH_2-CH_2-CH_2
	3290 (m)	N-H	276	8280	6.10 (s)	(2) NH_2
	3160 (m)				7.30-9.00 (m)	(11) Ar-H
	1625 (s)	C=N				
	1555 (s)					
	1540 (s)	C=C				
	1460 (m)					
IIIe [b]	3460 (w)		339	11360	1.66-3.06 (m)	(6) -CH_2-CH_2-CH_2
	3320 (m)	N-H	271	10130	5.52 (s)	(2) NH_2
	3180 (m)		246	14740	6.60-8.80 (m)	(7) Ar-H
	1645 (s)	C=N	211 sh	18560		
	1540 (vs)	C=C				
	1470 (vs)					
IIIf [b]	3500 (m)		339	11960	1.66-2.86 (m)	(6) -CH_2-CH_2-CH_2
	3290 (m)	N-H	251	17830	5.40 (s)	(2) NH_2
	3140 (m)		220	18740	7.06-8.72 (m)	(7) Ar-H
	1630 (s)	C=N				
	1545 (vs)					
	1470 (m)	C=C				
	1460 (m)					
IIIg [b]	3500 (m)		327	9260	1.62-2.76 (m)	(6) -CH_2-CH_2-CH_2
	3290 (m)	N-H	245	20540	5.54 (s)	(2) NH_2
	3165 (m)		218	19300	7.16-8.70 (m)	(7) Ar-H
	1620 (s)	C=N				
	1550 (s)	C=C				
	1465 (ms)					
IIIh [a]	3450 (w)		340	62700	1.92-3.18 (m)	(6) -CH_2-CH_2-CH_2
	3320 (m)	N-H	296 sh	39680	4.00 (s)	(3) N-CH_3
	3190 (m)		284 sh	42855	6.84 (s)	(2) NH_2
	1635 (s)	C=N	247 sh	108730	6.40-8.52 (m)	(7) Ar-H
	1555 (s)					
	1540 (s)	C=C				
	1485 (m)					
IIIi [a]	3320 (m)	N-H	326	8460	1.92-3.12 (m)	(6) -CH_2-CH_2-CH_2
	3150 (m)		238	17310	7.00 (s)	(2) NH_2
	1650 (s)	C=N	215 sh	24420	7.60-9.60 (m)	(8) Ar-H
	1550 (s)					
	1540 (s)	C=C				
	1475 (m)					

Table 1 (continued)

Compound	Infrared Spectra (Potassium Bromide) cm^{-1}	ν	Electronic Spectra (Ethanol) λ max (nm)	ϵ	NMR δ	Assignment No. of Protons
IVe [a]	1590 (m)	C=N	320	5605	2.20-2.90 (m)	(6) $-CH_2-CH_2-CH_2$
	1533 (s)		266	15455	6.50-8.70 (m)	(12) Ar-H
	1410 (m)	C=C				
	1385 (m)					
IVf [a]	1590 (m)	C=N	320	4935	2.38-2.88 (m)	(6) $-CH_2-CH_2-CH_2$
	1540 (s)		263	13865	7.15-8.70 (m)	(12) Ar-H
	1530 (s)	C=C				
	1390 (m)					
IVi [a]	1590 (m)	C=N	292	3665	2.20-2.90 (m)	(6) $-CH_2-CH_2-CH_2$
	1570 (wm)		259	14665	7.10-9.10 (m)	(13) Ar-H
	1540 (s)					
	1530 (s)	C=C				
	1420 (m)					
	1390 (s)					
Vc [c]	3450 (br)	N-H	333	10000	2.00-3.46 (m)	(6) $-CH_2-CH_2-CH_2$
	3060 (w)		260	11475	7.86-9.00 (m)	(9) Ar-H + N-H
	1633 (s)	C=O				
	1605 (m)	C=N				
	1580 (m)	C=C				
Vd [c]	3450 (br)	N-H	332	10385	2.06-3.58 (m)	(6) $-CH_2-CH_2-CH_2$
	3060 (w)		270	11990	7.78-9.12 (m)	(12) Ar-H + N-H
	1635 (vs)	C=O				
	1605 (m)	C=N				
	1580 (m)	C=C				
VIb [d]	3440 (br)	N-H	304	13820	2.00-3.20 (m)	(6) $-CH_2-CH_2-CH_2$
	1730 (s)	C=O	255	17090	2.32 (s)	(3) $Ar-COCH_3$
	1710 (s)	C=O				
	1610 (m)	C=N			2.52 (s)	(3) $N-COCH_3$
	1550 (s)	C=C			4.16 (s)	(3) OCH_3
	1520 (s)				7.40-8.60 (m)	(8) Ar-H + N-H
VId [d]	3450 (br)		291	13650	1.80-3.06 (m)	(6) $-CH_2-CH_2-CH_2$
	3230 (w)	N-H	238	26260	1.56 (s)	(3) $Ar-COCH_3$
	3130 (w)					
	3070 (w)				2.80 (s)	(3) $N-COCH_3$
	1675 (s)	C=O			7.66-8.80 (m)	(11) Ar-H + N-H
	1685 (s)	C=O				
	1610 (m)	C=N				
	1560 (m)	C=C				
	1545 (s)					
VIi [d]	3460 (br)		300	4170	1.86-3.06 (m)	(6) $-CH_2-CH_2-CH_2$
	3210 (w)	N-H	241	10215	2.74 (s)	(3) $N-COCH_3$
	3110 (w)					
	3070 (w)				7.54-9.60 (m)	(9) Ar-H + N-H
	1685 (vs)	C=O				
	1608 (m)	C=N				
	1585 (s)					
	1550 (s)	C=C				
	1525 (s)					

[a] DMSO-d_6. [b] Benzene. [c] Deuteriotrifluoroacetic acid. [d] Deuteriochloroform.

Table 2

Yields, Melting Points and Elemental Analysis of Compounds **II-VI**

Compound No.	Yield (%)	Mp °C	Formula	Calcd. % C	H	N	Cl	S	Found % C	H	N	Cl	S
IIa	85	166-168	$C_{19}H_{19}N_3$	78.86	6.62	14.52	–	–	78.80	6.52	14.58	–	–
IIb	75	190-192	$C_{20}H_{21}N_3O$	75.21	6.63	13.16	–	–	75.18	6.66	13.18	–	–
IIc	81	182-183	$C_{19}H_{18}ClN_3$	70.47	5.60	12.98	10.95	–	70.62	5.50	13.09	10.77	–
IIf	78	172-173	$C_{17}H_{17}N_3S$	69.12	5.80	14.22	–	10.85	69.06	5.81	14.32	–	10.70
IIg	83	174-176	$C_{17}H_{17}N_3S$	69.12	5.80	14.22	–	10.85	69.09	5.91	14.18	–	10.70
IIIa	76	190-192	$C_{19}H_{17}N_3$	79.41	5.96	14.62	–	–	79.38	5.90	14.63	–	–
IIIb	82	235-237	$C_{20}H_{19}N_3O$	75.69	6.03	13.24	–	–	75.54	6.04	13.15	–	–
IIIc	75	227-229	$C_{19}H_{16}ClN_3$	70.92	5.01	13.06	11.02	–	70.90	5.05	13.02	11.00	–
IIId	90	200-201	$C_{23}H_{19}N_3$	81.87	5.68	12.45	–	–	81.82	5.61	12.39	–	–
IIIe	85	168-169	$C_{17}H_{15}N_3O$	73.63	5.45	15.15	–	–	73.33	5.36	14.88	–	–
IIIf	73	138-139	$C_{17}H_{15}N_3S$	69.60	5.15	14.32	–	10.93	69.58	5.10	14.29	–	10.88
IIIg	80	186-188	$C_{17}H_{15}N_3S$	69.60	5.15	14.32	–	10.93	69.73	5.23	14.39	–	10.86
IIIh	85	148-149	$C_{18}H_{18}N_4$	74.46	6.25	19.29	–	–	74.07	6.21	19.15	–	–
IIIi	82	228-230	$C_{18}H_{16}N_4$	74.98	5.59	19.43	–	–	74.91	5.61	19.35	–	–
IVe	77	98-99	$C_{23}H_{18}N_2O$	81.63	5.36	8.28	–	–	81.77	5.41	8.32	–	–
IVf	80	152-154	$C_{23}H_{18}N_2S$	77.93	5.12	7.90	–	9.04	77.85	5.08	7.89	–	9.03
IVi	86	161-162	$C_{24}H_{19}N_3$	82.49	5.48	12.02	–	–	82.60	5.41	12.07	–	–
Vc	82	293-295	$C_{19}H_{15}ClN_2O$	70.70	4.68	8.68	10.98	–	70.56	4.62	8.70	10.93	–
Vd	75	295-297	$C_{23}H_{18}N_2O$	81.63	5.36	8.28	–	–	81.58	5.32	8.30	–	–
VIb	77	172-173	$C_{24}H_{23}N_3O_3$	71.80	5.77	10.47	–	–	71.48	5.88	10.38	–	–
VId	85	154-156	$C_{27}H_{23}N_3O_2$	76.94	5.50	9.97	–	–	76.82	5.64	10.21	–	–
VIi	85	178-180	$C_{20}H_{18}N_4O$	72.71	5.49	16.96	–	–	72.23	5.64	16.84	–	–

stand for the NH_2 groups which disappear upon deuteration. The multiplets in the region δ 9.60-6.40 ppm are ascribed to the aromatic protons [5,10]. The electronic spectra of these pyrimidines show absorption bands in the region 340-321 nm reflecting their extended conjugation and are ascribed to the ^{1}La and ^{1}Lb bands of the substituted 2-aminopyrimidines [14,15]. The mass spectra lend further support to the structure of the pyrimidines **III**. Thus, compounds **IIIa,b,c,d,e,f** and **g** show molecular ion peaks at m/e 287 (100%), 317 (9.69%), 321 (1.01%), 337 (98.20%), 277 (100%), 293 (100%) and 293 (5.67%) respectively. All the above spectra reflect the aromatic character of compounds **III** and support the aminopyrimidine rather than the iminopyrimidine structure.

Condensation of the chalcones **Ie,f,i** with benzamidine hydrochloride revealed the formation of the 2-phenylpyrimidines **IVe,f,i** (*cf.* Scheme 1). The structure of compounds **IV** is evident from their chemical and spectral data (*cf.* Tables 1,2). Thus, the infrared spectra show absorptions corresponding to C=N and C=C groups in the pyrimidine system. The nmr of these compounds show multiplets which can be ascribed to the methylene and aryl protons. Further insight concerning the structure of compounds **IV** can be gleaned out from their electronic spectra, which show absorption maxima correlated to the substituted pyrimidine systems [17]. The mass spectra lend further support to their structure. Thus, compounds **IVe,f,i** revealed molecular ion peaks at m/e 338 (100%), 354 (100%) and 349 (77.83%) respectively.

Additional support to the structure of compounds **II** and **III** comes from their chemical reactions (*cf.* Scheme 1). Thus, compounds **II** were dehydrogenated using either *o*-chloranil or the parent chalcone to give the pyrimidines **III**. On the other hand, compounds **IIIc,d** were treated with nitrous acid to give the substituted 2(1*H*)-pyrimidinones **Vc,d**. These show resemblance to the products obtained by the reaction between urea and chalcones **Ic,d** previously reported [2]. The structure of these products was evident from their spectra [2] (*cf.* Table 1). Thus, the nmr-spectra of compounds **V** show a (6H)-multiplet of the methylene protons at δ 3.52-2.03 ppm and another multiplet (Ar-H + NH) at δ 9.06-7.82 ppm. Their infrared spectra show a strong band at 1635 cm^{-1} (ν C=O) together with two medium bands at 1605 and 1580 cm^{-1} (ν C=N and ν C=C) respectively as well as broad and weak bands at 3450 and 3060 cm^{-1} (ν N-H bonded) [18]. The electronic spectra of these compounds show intense bands at 333 and 270 nm.

Acetylation of compounds **IIIb,d,i** with acetic anhydride gave the mono-**VIi** and the di-acetylated derivatives **VIb,d** (*cf.* Scheme 1). The infrared spectra (*cf.* Table 1) show absorption bands characteristic of the N-H, C=O and C=C groups. The nmr-spectra of compounds **VI** show (3H)-singlets in the range δ 2.80-2.52 ppm which can be ascribed to N-$COCH_3$ group. The two additional acetyl

groups of **VIb,d** were identified by singlets at δ 2.32 ppm and δ 1.56 ppm respectively. The electronic spectra of these compounds show two maxima in the ranges (304-291 nm) and (255-238 nm) characteristic of their chromophores [19]. The mass spectra of compounds **VIb,d** show molecular ion peaks at m/e 401 (29.09%) and 421 (1.83%) respectively. Both spectra show prominent peaks corresponding to $[M\text{-}COCH_3]^+$ and $[M\text{-}NCOCH_3]^+$ ions at m/e 358 (16.24%), 344 (100%), and 378 (44.69%), 364 (6.27%) for **VIb,d** respectively.

It can be argued in this respect that the 3,4-dihydropyrimidines **II** result from the Michael addition of the guanidine to the chalcones **I**, followed by cyclization of the addition products. Consequently, the pyrimidines **III** are produced from the dehydrogenation of their dihydroprecursors [3,8]. The formation of the pyrimidines **IV** can be assumed to follow the same pattern [3].

EXPERIMENTAL

Melting points (uncorrected) were measured using a Bock monoscope M (thermal microscope), electronic and infrared spectra were run on Pye Unicam SP8-100 and Perkin Elmer 580B, respectively. The nmr spectra were carried out using Varian T-60 A and Bruker 300-AM with TMS as an internal standard with deuterium lock. The mass spectra were measured on Varian MAT 311A. Microanalyses were determined by Professors H. Malissa & G. Reuter, Analytical Laboratories, German Federal Republic.

Condensation of Guanidine Hydrochloride with 2-Arylidene-1-benzosuberones **1**. General Procedure. Method (A).

To a solution of 0.05 mole (4.50 g) of guanidine carbonate dissolved in 10 ml of distilled water was added 0.05 mole (2.0 g) of sodium hydroxide in 10 ml of aqueous ethanol. To this solution was then added in portions, 0.01 mole of chalcone **I** dissolved in 60 ml of ethanol. The solution was refluxed for about two hours and was then concentrated under vacuum and cooled. The analytically pure product formed was filtered, washed with distilled water and then with petroleum ether to give 2-amino-4-aryl-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidines **IIa-c,f,g**.

Method (B).

To a solution of 0.1 mole (10 g) of guanidine hydrochloride in 60 ml of ethanol was added 0.1 mole (4 g) of sodium hydroxide. The solution was stirred for 10-15 minutes and the precipitated sodium chloride was filtered. The filtrate was then added to an ethanolic solution of 0.02 mole of the chalcone **I**. The resulting solution was refluxed for about 6 hours, ethanol was distilled off and water was added. The aqueous solution was acidified with 1*M* hydrochloric acid and the precipitated material was filtered and then washed with distilled water. The product was then washed with warm ethanol and the insoluble residue was crystallized from ethanol to give 2-amino-4-arylbenzo[6,7]cyclohepta[1,2-*d*]pyrimidines **IIIa-i**. The filtrate was concentrated and cooled to give a product which was filtered and crystallized from ethanol/water solution to give the 2-amino-4-aryl-3,4,6,7-tetrahydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidines **IIc-f** and **g**.

Method (C).

To a solution of 0.01 mole of guanidine hydrochloride (1 g) and 0.02 mole of the 2-arylidene-1-benzosuberone **I** in 50 ml of ethanol was added 0.02 mole (1.2 g) of potassium hydroxide dissolved in 30 ml of ethanol. The solution was refluxed for 4 hours and the precipitate which formed on cooling was filtered, washed thoroughly with warm water and then with warm ethanol and crystallized from ethanol to give the condensed pyrimidines **IIIa-e**.

Condensation of Benzamidine Hydrochloride with 2-Arylidene-1-benzosuberones **I**. General Procedure.

To a mixture of 0.1 mole of benzamidine hydrochloride hydrate (31.32 g) and 0.2 mole of 2-arylidene-1-benzosuberone **I** in 100 ml of ethanol was added 0.2 mole of potassium hydroxide (11.2 g) dissolved in 30 ml of ethanol. The solution was refluxed for 5 hours followed by concentration. The product which formed on cooling was filtered, washed with warm water and then with warm ethanol. Concentration of the filtrate and crystallization of the residue from ethanol/water solution gave an additional crop of 4-Aryl-2-phenyl-6,7-dihydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]-pyrimidines **IVe,f** and **i**.

Dehydrogenation of the 3,4,6,7-Tetrahydro-5*H*-benzo[6,7]cyclohepta-[1,2-*d*]pyrimidines **II**. Method (A).

Equimolar amounts of **IIc,f** and *o*-chloranil were dissolved in tetrahydrofuran (1 g of **II** in 10 ml of THF). The solution was stirred at room temperature for 4 hours followed by concentration of the tetrahydrofuran and then the solution was poured into cold water. The precipitate which formed was filtered and crystallized from benzene/petroleum ether or ethanol to give the **IIIc,f** respectively.

Method (B).

To a solution of equimolar amounts of **IIb** and the chalcone **Ib** (0.35 and 0.31 g respectively) in ethanol (25 ml) was added 0.23 g of sodium hydroxide dissolved in 20 ml of ethanol. The solution was refluxed for 6 hours. Ethanol was distilled off and the precipitate which formed was washed with water, then twice with cold acetone to dissolve any contaminating chalcone, and the residue was crystallized from ethanol to give **IIIb**.

Conversion of the 2-Amino-4-aryl-6,7-dihydro-5*H*-benzo[6,7]cyclohepta-[1,2-*d*]pyrimidines **IIIc,d** into 4-Aryl-6,7-dihydro-5*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidin-2(1*H*)-ones **Vc,d**.

To about 1 g of **IIIc,d** dissolved in 15 ml of glacial acetic acid was added about 1.5 g of sodium nitrite dissolved in 10 ml of distilled water. The solution was then stirred on cold for 3-4 hours and then poured into cold distilled water. The precipitate formed was filtered, washed with distilled water and crystallized from benzene/hexane or ethanol to give compounds **Vc,d** respectively.

Acetylation of Compounds **III**.

To about 0.5 g of each of compounds **IIIb,d,i** was added 3-5 ml of acetic anhydride and the solution was refluxed for 4 hours and then cooled. The product was poured into 20 ml of 1:1 aqueous ethanol solution followed by extraction with ether, drying over magnesium sulphate and crystallization from benzene/hexane (for **VIb,i**) and ethanol/hexane (for **VId**) gave the corresponding 2-Acetamido-4-aryl-6,7-dihydro-5*H*-benzo-[6,7]cyclohepta[1,2-*d*]pyrimidines **Vb,d** and **i** respectively.

Acknowledgement.

This work is part of Research Project SC028 supported by Research Council, Kuwait University. H. M. Ramadan would like to thank the College of Graduate Studies for financial support.

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