Jan-Feb 1986 Heterocycles. Part VIII. Synthesis of New Substituted Benz[g]indazoles N. R. El-Rayyes* and A. Al-Jawhary

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Aryl aldehydes I reacted with α -tetralone to give the corresponding 2-arylidene-1-tetralone II. Condensation of the latter chalcones with hydrazine, methylhydrazine and phenylhydrazine produced the corresponding benzo[g]indazoles III, V and VI respectively. Acetylation of the 2H-benz[g]indazole derivatives III gave the corresponding 2-acetylated compounds IV. The structure of all products was elucidated by chemical and spectroscopic methods.

J. Heterocyclic Chem., 23, 135 (1986).

The reaction of hydrazines with different chalcones was investigated [1-3]. The present work describes the reaction of hydrazine and its derivatives with exocyclic α,β -unsaturated cyclic ketones. It intends also to establish the structure of the products by both chemical and spectral methods. Thus different aromatic and heterocyclic aldehydes Ia-i, were condensed with 1-tetralone to give the corresponding 2-arylidene-1-tetralones IIa-i. The structure of these chalcones is evident from their spectral data (cf. Table 1). The infrared spectra show two strong absorption bands which are characteristic for α,β -unsaturated carbonyl compounds [4a]. The electronic spectra show absorp-

tion bands attributed to the conjugated system of the $trans-\alpha,\beta$ -unsaturated carbonyl compounds [5-7]. Most of the cyclic compounds appear to belong to the trans-configuration [8,9]. The nmr-spectra reveals further support to their structures and reveal multiplets in the region δ 2.40-3.40 ppm which stand for the CH_2 - CH_2 groups. Other signals are attributed to the vinylic and aromatic protons (cf. Table 1). The mass spectra of the above chalcones are also in favour of their structure. Those of IIa,f,g and h show molecular ion peaks at m/e 234 (86.34%), m/e 269 (39.65%), m/e 236 (19.85%) and m/e 240 (100%) respectively.

Table 1

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

	Infrared Spectra (potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deute		
Compound	cm ⁻¹	ν	λ max (nm)	ϵ	δ	(No. of protons)	J in Hz
IΙa	1590 (s)		305	14350	2.86-3.18 (m)	(4) -CH ₂ -CH ₂ -	
	1605 (s)	C=C	275	10240	7.88 (s)	(1) = CH	
	1660 (s)	C=O	225	9945	7.20-8.20 (m)	(9) Ar-H	
IIb	1600 (s)	C=C	335	6100	2.85-3.18 (m)	(4) -CH ₂ -CH ₂ -	
	1665 (s)	C=O	250	6230	3.80 (s)	(3) OCH ₃	
	.,				7.82 (s)	(1) = CH	
					6.86-8.14	(8) Ar-H	
Hc	1588 (s)		326	39120	2.38 (s)	(3) -CH ₃	
	1600 (w)	C=C	270	15520	2.82-3.20 (m)	(4) -CH ₂ -CH ₂ -	
	1650 (s)	C=O	242	11175	7.87 (s)	(1) = CH	
	` '				7.17-8.18 (m)	(8) Ar-H	
IId	1595 (s)	C=C	310	35610	2.88-3.20 (m)	(4) -CH ₂ -CH ₂ -	
	1668 (s)	C=O	273	16060	7.84 (s)	(1) = CH	
					7.27-8.30 (m)	(8) Ar-H	
He	1600 (s)	C=C	310	14470	2.86-3.19 (m)	(4) -CH ₂ -CH ₂ -	
	1670 (s)	C=O	272	8265	7.84 (s)	(1) = CH	
	()		240	5425	7.24-8.23 (m)	(8) Ar-H	
IIf	1590 (s)		321	24630	2.90-3.14 (m)	(4) -CH ₂ -CH ₂ -	
	1605 (m)	C=C	295	33590	7.79 (s)	(1) = CH	
	1665 (s)	C=O	227	24630	7.20-8.19 (m)	(8) Ar-H	
IIg	1600 (s)	C=C	394	27800	2.40-3.20 (m)	(4) -CH ₂ -CH ₂ -	
8	1652 (s)	C=0	265	10000	3.73 (s)	(3) N-CH ₃	
	(-)		225	7000	6.20-8.17 (m)	(8) Ar-H $+ = CH$	
IIh	1600 (m)	C=C	352	20030	3.0-3.22 (m)	(4) -CH ₂ -CH ₂ -	
	1662 (s)	C=0	269	11815	7.08-8.08 (m)	(8) Ar-H $+ = CH$	
Hi	1600 (s)	C=C	353	17660	2.86-3.40 (m)	(4) -CH ₂ -CH ₂ -	
	1665 (s)	C=0	260	7850	6.52-8.16 (m)	(8) Ar-H $+ = CH$	

Table 1 continued

	Infrared Spectra (potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deute		
Compound	cm ⁻¹	ν	λ max (nm)	€	δ	Assignment (No. of protons)	J in Hz
IIIa	1600 (s)	G. N	295	9315	1.30-3.68 (m)	(5) -CH ₂ -CH ₂ -CH	
	1675 (s)	C=N	240	12050	4.80 (d)	(1) H ₃	12
	3340 (s)	NH			5.81 (br)	(1) NH	
					7.02-8.0 (m)	(9) Ar-H	
IIIb	1607 (s)	C=N	294	13115	1.60-3.28 (m)	(5) -CH ₂ -CH ₂ -CH	
	3335 (s)	NH	224	20340	3.76 (s)	(1) NH	
					3.82 (s)	(3) OCH ₃	
					4.47 (d)	(1) H ₃	12
					6.87-8.0 (m)	(8) Ar-H	
IIIc	1590 (s)	~	360	7435	1.88-3.24 (m)	(5) -CH _o -CH _o -CH	
	, ,	C=N			2.36 (s)	(3) CH ₂	
	1605 (s)				3.72 (s)	(1) NH	
	3330 (s)	NH			4.52 (d)	(l) H,	12
	. ,				7.08-8.0 (m)	(8) Ar-H	

The above exocyclic α,β -unsaturated carbonyl compounds IIa-h were condensed with hydrazine hydrate to yield the corresponding 2H-benz[g]-3-arylhexahydroindazoles IIIa-h (cf. Scheme 1). The structures of these pro-

Compound	Ar	Compound	Ar		
I–VI a b c d e	C ₆ H ₅ p-OCH ₃ -C ₆ H ₄ p-CH ₃ -C ₆ H ₄ p-NO ₂ -C ₆ H ₄ p-Cl-C ₆ H ₄	f g h i	m-Cl-C ₆ H ₄ C ₅ H ₈ N C ₄ H ₃ S C ₄ H ₃ O		

ducts were substantiated from their spectral and chemical properties (cf. Tables 1 and 2). Thus, their infrared spectra show stretching vibrations which are characteristic for C=N and N-H groups [1,4b]. The electronic spectra of the benzindazoles III show absorption maxima which can be ascribed to $\pi \to \pi^*$ and $\pi \to \pi^*$ transitions. The latter can

be correlated to the Ar-C=N-N-H chromophores [1,10].

The nmr spectra of compounds III show four main sets of chemical shifts. The (-CH₂-CH₂-CH-) moieties were represented by multiplets in the region δ 1.60-4.20 ppm. The doublet that appeared in the region δ 4.80-4.47 ppm stands for the H₃ (J = 12 Hz). The N-H protons were represented by one signal, in the range δ 3.72-5.81 ppm, which disappears upon treatment with deuterium oxide. The aromatic hydrogens showed multiplets in the range δ 6.87-8.0 ppm.

The mass spectra is also in favour of their structure. Thus compounds IIIa,h,g show three peaks at m/e 278 (100%) and m/e 254 (100%) and m/e 249 (100%) which represents both their parent and base peaks. The most prominent peaks of the IIIa and h were shown at m/e 277 (54.31%) and m/e 253 (46.13%) and represent the [M-1]⁺ ions

Further insight concerning the structure of the 2H-benz-[g]indazoles may be gleaned out from their chemical reactivity. Thus, their acetylation lead to the formation of the corresponding 2-acetylbenz[g]-3-arylhexahydroindazoles IVb-h.

The structure of these products was also established by chemical and spectral analyses (cf. Tables 1,2). The infrared spectra of compounds IV show stretching bands in the regions 1595-1620 cm⁻¹ and 1665-1690 cm⁻¹ attributed to C=N and C=O respectively [1]. The electronic spectra revealed absorption maxima which can be assigned to the $\pi \to \pi^*$ of the N-acetylated chromophore [10]. The nmr spectra were void of the signals representing the N-H proton. Instead, 3H singlets representing the protons of the N-acetyl group appeared in the range δ 2.08-2.96 ppm. Other protons in these compounds were represented by different chemical shifts (cf. Table 1). The mass spectra of IVg shows a molecular ion peak at m/e 291 (63,63%) and a base peak at m/e 56 (100%) corresponding to the ion $[C_2H_2NO]^+$.

Table 1 continued

	Infrared Spectra (potassium bromide)		Electronic Spectra (Ethanol)		NMR (Deute		
Compound	cm ⁻¹	ν	λ max (nm)	ϵ	δ	Assignment (No. of protons)	J in Hz
IIId	1600 (s)	C=N	285	15190	_		
IIIe	3330 (s) 1608 (m)	NH C=N	300	11690	1.72-3.20 (m)	(5) -CH ₂ -CH ₂ -CH	
1116	3360 (s)	NH	240	4350	3.72 (s)	(1) NH	
	5500 (S)	MII	223	7885	4.50 (d)	(1) H ₃	12
			223	1000	7.20-8.0 (m)	(8) Ar-H	
IIIf	1598 (s)		243	5420	— (m)	-	
1111	1675 (m)	C=N					
	3300 (m)	NH				•	
IIIg	1600 (w)		295	5000	1.20-3.57 (m)	(5) -CH ₂ -CH ₂ -CH	
8	1615 (m)	C=N	225	6365	3.69 (s)	(3) N-CH ₃	
	,				4.70 (s)	(1) N-H	
	3300 (s)	NH			4.60 (d)	(1) H_3	12
	``				6.0-8.0 (m)	(7) Ar-H	
IIIh	1585 (s)	C. N	300	15630	1.70-4.20 (m)	(5) -CH ₂ -CH ₂ -CH	
	1605 (s)	C=N	237	12715	3.76 (s)	(1) NH	
	3340 (s)	NH			4.74 (d)	(1) H ₃	12
					6.96-7.90 (m)	(7) Ar-H	
IVb	1505 ()		285	10165	2.0-3.44 (m)	(5) -CH ₂ -CH ₂ -CH	
IVD	1595 (w) 1615 (w)	C=N	225	10780	2.96 (s)	(3) COCH ₃	
	1690 (s)	C=0	220	10100	3.74 (s)	(3) OCH ₃	
	1090 (8)	C=0			4.90 (d)	(1) H ₃	10
					6.74-8.0 (m)	(8) Ar-H	
IVc	1615 (w)	C=N	291	11795	1.90-3.40 (m)	(5) -CH ₂ -CH ₂ -CH	
1.0	1672 (s)	C=0			2.33 (s)	(3) COCH ₃	
	1012 (5)				2.34 (s)	(3) CH ₃	10
					4.92 (d)	(1) H_3	
					7.0-8.0 (m)	(8) Ar-H	
IVd	1610 (m)	C=N	289	19700	2.00-3.10 (m)	(5) -CH ₂ -CH ₂ -CH	
	1670 (s)	C=0			2.40 (s)	(3) COCH ₃	
					5.05 (d)	$(1) H_3$	10
					7.20-8.25 (m)	(8) Ar-H	
IVe	1620 (m)	C=N	290	3857	1.90-3.40 (m)	(5) -CH ₂ -CH ₂ -CH	
	1665 (s)	C=O			2.40 (s)	(3) COCH ₃	10
					4.92 (d)	(1) H ₃ (8) Ar-H	10
1376	1600 ()	C=N	295	3190	7.05-8.25 (m) 1.28-3.0 (m)	(5) -CH ₂ -CH ₂ -CH	
IVf	1600 (m) 1680 (s)	C=0	293	3190	2.08 (s)	(3) COCH ₃	
	1000 (s)	C=0			4.80 (d)	(1) H ₃	10
					7.0-8.01 (m)	(8) Ar-H	
IVg	1610 (m)	C=N	290	6600	1.43-3.60 (m)	(5) -CH ₂ -CH ₂ -CH	
• ' ' ' '	1670 (s)	C=O	220	7200	2.33 (s)	(3) COCH ₃	
					3.70 (s)	(3) N-CH ₃	
					5.00 (d)	(1) H_3	10
					6.07-8.03 (m)	(7) Ar-H	
IVh	1615 (w)	C=N	285	10500	2.03-3.60 (m)	(5) -CH ₂ -CH ₂ -CH	
	1670 (s)	C=O		9880	2.37 (s)	(3) COCH ₃	
					5.27 (d)	$(1) H_3$	10
					6.15-8.0 (m)	(7) Ar-H	
Va	1585 (s)	C=N	310	5250	1.70-3.44 (m)	(5) -CH ₂ -CH ₂ -CH	
	1600 (m)	C=N			2.80 (s)	(3) N-CH ₃	10
					3.66 (d)	(1) H ₃	12
			010	10000	7.16-8.0 (m)	(9) Ar-H (5) -CH ₂ -CH ₂ -CH	
Vb	1585 (s)	C N	313	18030	1.60-3.20 (m) 2.80 (s)	(3) N-CH ₂ -CH ₂ -CH	
	1610 (s)	C=N	227	12180	2.60 (s) 3.64 (d)	(1) H ₃	12
					3.80 (s)	(3) OCH ₃	
					6.88-8.0 (m)	(8) Ar-H	
					0.00 0.0 (m)	<u> </u>	

Table 1 continued

	Infrared (•	Electronic Spectra (Ethanol)		NMR (Deute		
Compound	cm ⁻¹	•	,	•	δ	Assignment (No. of protons)	J in Hz
Compound	cm -	ν	λ max (nm)	ϵ	O	(140. or protons)	J 111 112
$V_{\mathbf{c}}$	1585 (s)	G N	_		1.70-3.36 (m)	(5) -CH ₂ -CH ₂ -CH	
	1610 (s)	C=N			2.84 (s)	(3) Ar-CH ₃	
					2.88 (s)	(3) N-CH ₃	
					3.74 (d)	(1) H ₃	12
					7.24-8.08 (m)	(8) Ar-H	
Vd	1585 (w)	a .v	300	13890	2.60-3.40 (m)	(5) -CH ₂ -CH ₂ -CH	
	1600 (w)	C=N			3.10 (s)	(3) N-CH ₃	
					3.84 (d)	(1) H ₃	12
					7.20-8.28 (m)	(8) Ar-H	
Ve	1585 (m)	0. N	315	7110	1.60-3.86 (m)	(5) -CH ₂ -CH ₂ -CH	
	1610 (m)	C=N			2.80 (s)	(3) N-CH ₃	
					7.19-8.0 (m)	(8) Ar-H	
Vf	1585 (s)	0 N	312	16585	1.70-3.60 (m)	(5) -CH ₂ -CH ₂ -CH	
	1595 (m)	C=N	239	1520	2.80 (s)	(3) N-CH ₃	
			215	7200	3.80 (d)	(1) H ₃	12
					7.19-8.0 (m)	(8) Ar-H	
Vg	1587 (m)	C=N	312	10195	1.70-3.80 (m)	(5) CH ₂ -CH ₂ -CH	
	1605 (m)	C=11	225	14510	2.90 (s)	(3) N-CH ₃	
					6.40-7.99 (m)	(7) Ar-H	
Vh	1585 (s)	C=N	311	16100	1.70-3.47 (m)	(5) -CH ₂ -CH ₂ -CH	
	1610 (s)	C-N	237	9715	2.88 (s)	(3) N-CH ₃	
					3.95 (d)	(1) H ₃	12
					6.92-8.0 (m)	(7) Ar-H	
VIa	1600 (s)	C=N	345	21360	2.0-3.44 (m)	(5) -CH ₂ -CH ₂ -CH	
					4.62 (d)	$(1) H_3$	12
****					6.80-8.12 (m)	(14) Ar-H	
VIb	1600 (s)	C=N	345	17380	1.80-3.44 (m)	(5) -CH ₂ -CH ₂ -CH	
			246	6475	3.74 (s)	(3) OCH ₃	
					4.74 (d)	$(1) H_3$	12
377	1600 ()	. N	n.=		6.84-8.10 (m)	(13) Ar-H	
VIc	1600 (s)	C=N	347	41600	1.90-3.40 (m)	(5) -CH ₂ -CH ₂ -CH	
			247	28205	2.34 (s)	(3) Ar-CH ₃	
					4.58 (d)	(1) H ₃	12
371.1	1500 ()	C N	000		6.80-8.12 (m)	(13) Ar-H	
VId	1598 (s)	C=N	330	17945	-	_	
VIe	1598 (s)	CN	295	18390		(-)	
VIC	1390 (S)	C=N	340	16150	1.94-3.25 (m)	(5) -CH ₂ -CH ₂ -CH	
			246	8970	4.60 (d)	(1) H_3	12
VIf	1600 (-)	CN	242	0070	7.0-8.16 (m)	(13) Ar-H	
V 11	1600 (s)	C=N	343	9270	1.80-3.32 (m)	(5) CH ₂ -CH ₂ -CH	
					4.50 (d)	(1) H_3	12
Vlg	1600 (s)	C=N	251	10065	6.79-8.04 (m)	(13) Ar-H	
Vig	1000 (s)	C=N	351	12865	1.10-3.77 (m)	(5) CH ₂ -CH ₂ -CH	
			300 (sh)	6095	3.60 (s)	(3) N-CH ₃	
			252	11850	4.73 (d)	(1) H ₃	12
VIh	1600 (s)	C=N	230	13540	5.90-8.0 (m)	(12) Ar-H	
* 111	1000 (s)	C=IV	339	17635	1.90-3.56 (m)	5) CH ₂ -CH ₂ -CH	
			224	15570	4.86 (d) 6.84-8.14 (m)	(1) H ₃	12
					0.04-0.14 (m)	(12) Ar-H	

The condensation of the chalcones II with methyl and phenyl hydrazines revealed the formation of 2-methyl and 2-phenylbenz[g]-3-arylhexahydroindazoles Va-i and VIa-h respectively. The structure of these products was established by chemical and spectral analyses (cf. Tables 1,2). The infrared spectra show stretching vibrations which stand for C=N in the systems [1,4b]. The electronic spectra of these systems show absorption maxima ascribed to the π

 $\rightarrow \pi^*$ transition of the chromophores Ar-C=N-N-R [1,10]. It can be envisaged that the N-phenyl substituent of the indazoles VI showed red shifts, which is in good agreement with previous observations [1,10]. The nmr spectra of compounds V were characterized by 3H singlets in the range δ 2.80-3.10 ppm, which stand for the N-CH₃ group of the indazole system. On the other hand, the spectra of all compounds V and VI revealed doublets (J = 12 Hz) which can

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

Compound	Yield	Мр				Calcd.%					Found %		
No.	(%)	°C	Formula	C	H	N	Cl	S	C	H	N	Cl	S
**	00	107	C II O	07.15	6.00				97.05	5.97			
IIa	82	107	C ₁₇ H ₁₄ O	87.15	6.02			_	87.05 82.09	6.00	_	_	_
IIb	85	109	$C_{18}H_{16}O_2$	81.79	6.10	_	_		82.09 87.12	6.35			_
He	79	125	C ₁₈ H ₁₆ O	87.06	4.49	 5 01	_	_	72.91	4.59	- 4.91	_	_
IId	75	185	C ₁₇ H ₁₃ NO ₃	73.11	4.69	5.01	_	_	72.91 75.92	4.69		— 13.07	_
IIe	87	141	C ₁₇ H ₁₃ ClO	75.98	4.87	_	13.19				_		
IIf	81	111	C ₁₇ H ₁₃ ClO	75.98	4.87	<u> </u>	13.19	_	75.95 80.84	5.01	 5.78	13.20	
IIg	90	126-127	C ₁₆ H ₁₅ NO	80.98	6.37	5.90	_	— 13.34	74.81	6.14 4.96		_	13.60
IIh	80	92	C ₁₅ H ₁₂ OS	74.96	5.03	_					_		13.00
IIi	87	73	$C_{15}H_{12}O_2$	80.33	5.39	_	_	_	80.21	5.31		_	_
IIIa	90	83	C ₁₇ H ₁₆ N ₂	82.22	6.49	11.28			81.93	6.29	11.29		
Шь	92	147	$C_{18}H_{18}N_2O$	77.63	6.51	10.06	_	_	77.73 82.31	6.34 6.86	9.83 10.55		_
IIIc	92	126	$C_{18}H_{18}N_2$	82.40	6.91	10.67							
IIIq	87	241-242	$C_{17}H_{15}N_3O_2$	69.61	5.15	14.32	10.50		69.50	5.04	13.97	10.50	
IIIe	88	175	C ₁₇ H ₁₅ ClN ₂	72.21	5.34	9.90	12.53		72.18	5.25	9.70	12.50	
IIIf	85	100	$C_{17}H_{15}ClN_2$	72.21	5.34	9.90	12.53		72.08	5.49	9.77	12.51	
IIIg	93	80	$C_{16}H_{17}N_3$	76.46	6.81	16.71	_	10.60	76.31	6.56	16.68	_	
IIIh	90	105	$C_{15}H_{14}N_2S$	70.76	5.54	11.01		12.60	70.87	5.43	11.30	12.51	
IVb	88	144-145	$C_{20}H_{20}N_2O_2$	74.97	6.29	8.74			74.86	6.21	8.56		
IVc	85	80	$C_{20}H_{20}N_2O$	78.91	6.62	9.20			78.90	6.59	8.92		
IVd	87	180-182	$C_{19}H_{17}N_3O_3$	68.04	5.11	12.53	10.01		67.91	5.09	12.40	10.60	
IVe	84	176-177	C ₁₉ H ₁₇ ClN ₂ O	70.26	5.27	8.62	10.91		70.70	5.24	8.49	10.69	
IVf	82	oil	$C_{19}H_{17}CIN_2O$	70.26	5.27	8.62	10.91		70.17	5.15	8.51	10.81	
IVg	90	115	$C_{18}H_{19}N_3O$	73.69	6.52	14.32		10.50	73.51	6.48	14.19		10.51
IVh	91	106	$C_{17}H_{16}N_2OS$	68.89	5.44	9.44		10.79	68.69	5.43	9.38		10.51
Va	87	137	$C_{18}H_{18}N_2$	82.40	6.91	10.67			82.49	6.90	10.60		
Vb	86	180-182	$C_{19}H_{20}N_{2}O$	78.05	6.89	9.58			77.94	6.87	9.57		
Vc	88	152-153	$C_{19}H_{20}N_{2}$	82.56	7.29	10.13			82.43	7.16	10.02		
Vd	84	233-235	$C_{18}^{17}H_{17}^{20}N_3O_2$	70.34	5.57	13.67			70.08	5.56	13.48		
Ve	81	195-196	$C_{18}H_{17}CIN_2$	72.84	5.77	9.43	11.94		72.81	5.73	9.37	11.91	
Vf	82	120-121	$C_{18}H_{17}CIN_2$	72.84	5.77	9.43	11.94		72.79	5.72	9.40	11.92	
Vg	89	96	$C_{17}H_{19}N_3$	76.94	7.21	15.83			76.76	7.18	15.64		
Vh	87	131-132	$C_{16}H_{16}N_{2}S$	71.60	6.01	10.43		11.94	71.48	5.95	10.39		11.83
Vi	80	85	$C_{16}^{16}H_{16}N_{2}O$	76.16	6.39	11.10			76.15	6.28	11.07		
VIa	80	157-158	$C_{23}H_{20}N_{2}$	85.15	6.21	8.63			85.03	6.14	8.61		
VIb	82	165-166	$C_{24}^{23}H_{22}N_{2}O$	81.32	6.25	7.90			81.32	6.19	7.79		
VIc	84	163-164	$C_{24}H_{22}N_2$	85.17	6.55	8.27			85.07	6.52	8.39		
VId	79	124-125	$C_{23}^{24}H_{19}^{22}N_3O_2$	74.77	5.18	11.37			74.61	5.28	11.15		
VIe	82	155-156	$C_{23}H_{19}CIN_2$	76.97	5.33	7.80	9.87		76.76	5.14	7.72	10.04	
VIf	81	160-161	$C_{23}H_{19}ClN_2$	76.97	5.33	7.80	9.87		76.68	5.35	8.05	10.03	
VIg	88	151-152	$C_{22}H_{21}N_3$	80.70	6.46	12.83			80.51	6.32	12.75		
VIh	87	159-160	$C_{21}^{22}H_{18}^{21}N_{2}^{3}S$	76.33	5.49	8.47		9.70	76.21	5.38	8.46		9.64

be assigned to the protons at position three (H₃) and two multiplets that can be ascribed to the aryl and (CH₂-CH₂-CH-) moieties.

The mass spectra lends further support to the structure of the latter compounds. Those of Va,f,h show molecular ion peaks at m/e 262 (100%), m/e 297 (22.62%) and m/e 268 (100%) respectively. It is apparent that the molecular ion peaks of Va,h represent also their base peaks. The base peak of Vf was represented by a signal at m/e 185 (100%) which stand for the ion [M-C₆H₄Cl]*. The mass spectra of compounds VIb,h showed signals at m/e 354 (100%) and m/e 330 (100%) which can be ascribed to both molecular ion and base peaks. It is worth mentioning that all the above compounds showed prominent peaks that

can be assigned to [M-1]+ ions.

It can be assumed that the formation of all the above indazole derivatives (III-VI) proceeds by the 1:2-addition of the hydrazines to the chalcones (II), followed by cyclization of the intermediate hydrazones [1-3,6,10-12]. The ease and high yield of these condensations are in good agreement with the proposed (E)-configuration of the chalcones II.

EXPERIMENTAL

Melting points were measured using a Bock-Monoscope M (thermal microscope), electronic and infrared spectra were run on Cary 17 and Perkin-Elmer 580B, respectively. The nmr and the mass spectra were carried out using Varian T60A and Varian MAT 311A, respectively. Micro-

analyses were determined by A. Bernhardt Microanalytical Laboratory, German Federal Republic.

Preparation of 2-Arylidene-1-tetralones IIa-i. General Procedure.

Equimolar amounts of the aldehydes (0.1 mole) and 1-tetralone (0.1 mole) in ethanol (100 ml) were treated with an aqueous solution of sodium hydroxide (5 g/10 ml water). Addition of the base was carried out during 20 minutes, and the mixture was stirred for further 3 hours. The precipitated product was filtered off and crystallized from hexane or cyclohexane. Thus, the aldehydes Ia-l were condensed with 1-tetralone to give 2-benzylidene-IIa, 2-p-methoxybenzylidene-IIb, 2-p-methylbenzylidene-IIc, 2-p-nitrobenzylidene-IId, 2-p-chlorobenzylidene-IIe, 2-m-chlorobenzylidene-IIf, 2-N-methylpyrrolylidene-IIg, 2-thienylidene-IIh and 2-furylidene-III 1-tetralones.

Condensation of the Hydrazines with 2-arylidene-1-tetralones II. General Procedure.

A mixture of the 2-arylidene-1-tetralone (0.01 mole) and hydrazine hydrate (0.02 mole) in ethanol (50 ml) was refluxed for 3 hours. The reaction mixture ws concentrated under reduced pressure and left to cool. The precipitated product was filtered off and crystallized from cyclohexane, to give:

2H-Benz[g]-3-arylhexahydroindazoles IIIa-h.

The reaction was repeated using methyl hydrazine or phenyl hydrazine to obtain 2-methylbenz[g]-3-arylhexahydroindazoles IVa-i and 2-phenylbenz[g]-3-arylhexahydroindazoles VIa-h respectively. These were also crystallized from cyclohexane.

Acetylation of the Indazole Derivatives III.

A mixture of the indazole derivatives (1 g) and acetic anhydride (5 ml)

were refluxed for 5 hours. The product was poured over ice, and the precipitated solid was filtered off. Crystallization from hexane gave the corresponding 2-acetylbenz[g]-3-arylhexahydroindazoles IVb-h.

Acknowledgement.

This research is part of Research Project SC028 supported by Research Council, Kuwait University.

REFERENCES AND NOTES

- [1] N. R. El-Rayyes, G. H. Hovakeemian and H. Hammoud, J. Chem. Eng. Data, 29, 225 (1984).
 - [2] N. R. El-Rayyes and A. J. Al-Johary, ibid., 30, 500 (1985).
 - [3] N. R. El-Rayyes and N. A. Al-Awadi, Synthesis, (in press).
- [4] L. J. Bellamy, "The Infrared Spectra Complex Molecules", Methuen, London, 1966, pp [a] 132, [b] 277.
- [5] H. S. French and L. Wiley, J. Am. Chem. Soc., 71, 3702 (1949).
 - [6] N. R. El-Rayyes, J. Heterocyclic Chem., 19, 415 (1982).
 - [7] H. J. Roth and F. Assadi, Arch. Pharm., 149, 303 (1970).
- [8] R. Baltzly, E. Lorz, P. B. Russel and F. M. Smith, J. Am. Chem. Soc., 77, 624 (1955).
- [9] A. E. Braude, F. Sondheimer and W. F. Forbes, *Nature*, 173, 117 (1954).
- [10] B. Laude and Le Quoc Khanh, Spectrochim. Acta, Part A, 31A, 1121 (1975).
- [11] N. R. El-Rayyes, G. H. Hovakeemian and H. Hammoud, Org. Magn. Reson., 21, 245 (1983).
 - [12] S. A. Busse and H. L. Gurewitsch, Ber., 63, 2209 (1930).