

Table I. Triaryl Phosphorothionates Prepared by Phase-Transfer Catalysis

no.	Ar	yield, <sup>a</sup> %	mp, °C	lit. mp °C	mass spectrum	
					calcd	found
3a	C <sub>6</sub> H <sub>5</sub>	86	55	54 <sup>b</sup>		
3b	4H <sub>3</sub> C-C <sub>6</sub> H <sub>4</sub>	84	93-94	93-94 <sup>c</sup>		
3c	2,4(H <sub>3</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	76	63.0-64.5		426.1419	426.1428
3d	2naphthyl	83	94.5-96.0		492.0949	492.0957
3e	3,5(H <sub>3</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	80	92-94		426.1419	426.1438
3f	4Cl-C <sub>6</sub> H <sub>4</sub>	88	84-86	108.5 <sup>d</sup> 113 <sup>e</sup> 85-86 <sup>f</sup> 174 <sup>h</sup>	443.9310	443.9310
3g	4O <sub>2</sub> H-C <sub>6</sub> H <sub>4</sub>	82 <sup>g</sup>	177-179		477.0032	477.0029
3h	4NC-C <sub>6</sub> H <sub>4</sub>	88	158-159		417.0336	417.0336
3i	4Br-C <sub>6</sub> H <sub>4</sub>	86	96.0-97.5	88-99 <sup>i</sup>	575.7797	575.7799

<sup>a</sup> Yield of purified product after recrystallization from *n*-heptane; elemental analyses (C, H, N, P, S, Cl, Br) were submitted for review and agreed with the appropriate theoretical values. <sup>b</sup> Yamasaki, T. *Science Rep. Inst. Tohoku Univ.* 1954, 6, 172; *Chem. Abstr.* 1955, 49, 68581. <sup>c</sup> Beilstein 6 (3) 1372. <sup>d</sup> Mel'nikov, N. N.; Shevetsova, S.; Kagan, M. Y.; *Zh. Obshch. Khim.* 1960, 30, 2931; *Chem. Abstr.* 1961, 55, 9321a. <sup>e</sup> Kamai, G.; Koshkina, E. S. *Tr. Kazan. Khim.-Tekhnol. Inst.* 1955, 11: *Chem. Abstr.* 1956, 50, 6347a. <sup>f</sup> Mel'nikov, N. N.; Khokhlov, D. N. *Zh. Obshch. Khim.* 1953, 23, 1357; *Chem. Abstr.* 1954, 48, 9903e. <sup>g</sup> Recrystallized from acetone. <sup>h</sup> Ketelarr, J. A. A.; Gersmann, H. R. *J. Am. Chem. Soc.* 1950, 72, 5777.

Table II. Spectral Data of Triaryl Phosphorothionates

no.	IR, cm <sup>-1</sup>	<sup>1</sup> H NMR, ppm
3a	1587, 1185, 1158, 939, 798, 751, 685	7.35 (brs, 5 H)
3b	1493, 1181, 940, 923, 821, 748	2.33 (s, 3 H), 7.17 (s, 4 H)
3c	2880, 1477, 1242, 1180, 1098, 940, 902, 808, 763, 687	2.22 (s, 3 H), 2.24 (s, 3 H), 6.90 (d, 1 H, <i>J</i> = 7.5 Hz), 6.96 (brs, 1 H), 7.20 (d, 1 H, <i>J</i> = 7.5 Hz)
3d	1242, 1210, 1157, 981, 968, 946, 938, 875, 870, 741	7.43 (m, 3 H), 7.74 (s, 4 H)
3e	1281, 1125, 1018, 951, 854, 677	2.30 (s, 6 H), 6.87 (s, 3 H)
3f	1471, 1182, 1157, 1081, 921, 824, 786, 770	7.31 (dd, 2 H, <i>J</i> <sub>AB</sub> = 8.3, <i>J</i> <sub>BP</sub> = 1.5 Hz), 7.35 (d, 2 H, <i>J</i> <sub>AB</sub> = 8.3 Hz)
3g	1587, 1523, 1485, 1356, 1190, 1162, 930, 858, 800, 750	7.73 (dd, 2 H, <i>J</i> <sub>AB</sub> = 9.0, <i>J</i> <sub>BP</sub> = 1.5 Hz), 8.44 (d, 2 H, <i>J</i> <sub>AB</sub> = 9.0 Hz)
3h	1193, 1161, 923, 834	7.38 (dd, 2 H, <i>J</i> <sub>AB</sub> = 9.0, <i>J</i> <sub>BP</sub> = 2.0 Hz), 7.78 (d, 2 H, <i>J</i> <sub>AB</sub> = 9.0 Hz)
3i	1185, 1158, 925, 828, 798, 765, 670	7.13 (dd, 2 H, <i>J</i> <sub>AB</sub> = 9.0, <i>J</i> <sub>BP</sub> = 1.5 Hz), 7.54 (d, 2 H, <i>J</i> <sub>AB</sub> = 9.0 Hz)

phenyl) phosphorothionate had been reported in the literature on three occasions; however, each reference contains a different melting point, so this material was also fully characterized.

### Experimental Section

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. Infrared spectra were determined with a Beckman Microlab MX-250 spectrophotometer as KBr disks; absorbance positions are reported in reciprocal centimeters (cm<sup>-1</sup>). Proton magnetic resonance spectra were re-

corded on a Varian EM-390 spectrometer as solutions in chloroform-*d* unless otherwise stated. High-resolution mass spectra were recorded on a MAT instrument. Elemental analyses were determined by the General Electric Research and Development Center analytical services group.

**Preparation of Triphenyl Phosphorothionate: Typical Example.** A 500-mL round-bottomed flask equipped with a reflux condenser, mechanical stirrer, and addition funnel was charged with phenol (56.4 g, 0.6 mol) and sodium hydroxide solution, (24.0 g, 1.2 mol in 150 mL of water). To this solution was added Aliquot 336 (2.25 g) and 150 mL of dichloromethane. The solution was stirred rapidly while thiophosphoryl chloride (33.9 g, 0.2 mol) was added dropwise from the addition funnel over a period of 0.25 h. The solution was stirred at room temperature for 2 h and then the contents of the flask poured into a separatory funnel. The phases were separated and the aqueous layer extracted with two 100-mL portions of dichloromethane. The combined organic extracts were washed with brine and then dried over anhydrous magnesium sulfate. The solution was filtered and concentrated and the oil taken up in 100 mL of hot *n*-heptane whereupon crystals of pure thiophosphate formed, 48.8 g, (86%); mp 55 °C.

### Literature Cited

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## Heterocycles. 11. Synthesis of Substituted Benzo[*h*]quinazolines

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2-Arylidene-1-tetralones (I) were condensed with benzamidine or guanidine to give the corresponding substituted benzo[*h*]quinazolines II and III, respectively. The structures of all products were established by chemical and spectroscopic methods.

Aryl aldehydes were previously reacted with 1-tetralones (1) to yield 2-arylidene-1-tetralones (I). These were condensed with benzamidine to produce the corresponding 4-aryl-2-phenylbenzo[*h*]hexahydroquinazolines (IIa-i) (cf. Scheme 1). The structures of the products are different from those previously mentioned (2) and were substantiated by spectral and chemical

Table I. Spectrometric Data of Compounds II-V

IR (KBr)			UV (ethanol)		IR (KBr)			UV (ethanol)	
compd	$\nu$ , $\text{cm}^{-1}$	bond	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$	compd	$\nu$ , $\text{cm}^{-1}$	bond	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$
IIa	1590 (s)	C=C	250	21030	IVg	1590 (w)	C=N	260	6835
	1638 (m)	C=N	310	5735		1630 (br)	C=O	285	5580
	3200 (br)	NH				3000 (br)	NH	354	7670
IIIg	1610 (w)	C=C	226	19145	Vg			370	7670
	1630 (m)	C=N	297	4505		1660 (s)	C=O	226	7730
	3370 (m)	NH <sub>2</sub>	350	1735		3220 (m)	NH	262	7405
	3480 (m)							295	7250
							339	5395	
							349	5070	
NMR (CDCl <sub>3</sub> )					NMR (CDCl <sub>3</sub> )				
compd	$\delta$ , ppm	assignment	compd	$\delta$ , ppm	assignment				
IIa	2.0-3.40	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )	IIi	5.96	(br, 1, NH)				
	5.60	(s, 1, H <sub>4</sub> )		6.96-9.32	(m, 13, Ar-H)				
	6.0	(br, 1, NH)		2.18-3.25	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )				
	7.40-9.41	(m, 14 Ar-H)		4.64	(br, 1, NH)				
IIb	2.0-3.20	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )	IIIa	5.82	(s, 1, H <sub>4</sub> )				
	4.0	(s, 3, OCH <sub>3</sub> )		7.62-9.40	(m, 16, Ar-H)				
	5.60	(s, 1 H <sub>4</sub> )		1.70-3.20	(m, 4, CH <sub>2</sub> CH <sub>2</sub> )				
	6.02	(br, 1, NH)		7.30-7.75	(m, 9, Ar-H)				
IIc	7.30-8.81	(m, 13, Ar-H)	IIIb	11.85	(s, 2, NH <sub>2</sub> )				
	2.0-3.0	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )		2.18-3.70	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )				
	5.40	(s, 1, H <sub>4</sub> )		4.10	(s, 3, OCH <sub>3</sub> )				
	5.81	(br, 1, NH)		7.25-8.85	(m, 8, Ar-H)				
IId	7.41-9.0	(m, 13, Ar-H)	IIIc	12.0	(s, 2, NH <sub>2</sub> )				
	2.01-3.30	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )		3.05	(s, 4, CH <sub>2</sub> CH <sub>2</sub> )				
	5.51	(s, 1, H <sub>4</sub> )		7.33-8.30	(m, 8, Ar-H)				
	6.30	(br, 1, NH)		11.85	(s, 2, NH <sub>2</sub> )				
IIe	7.30-9.31	(m, 13, Ar-H)	IIId	1.45-3.05	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )				
	2.02-3.35	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )		6.80-7.4	(m, 8, Ar-H)				
	5.63	(s, 1, H <sub>4</sub> )		11.60	(s, 2, NH <sub>2</sub> )				
	6.08	(br, 1, NH)		3.40	(s, 4, CH <sub>2</sub> CH <sub>2</sub> )				
IIIf	6.74-8.92	(m, 12, Ar-H)	IIIe	7.42-8.60	(m, 7, Ar-H)				
	2.08-3.41	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )		12.0	(s, 2, NH <sub>2</sub> )				
	5.58	(s, 1, H <sub>4</sub> )		3.37	(s, 4, CH <sub>2</sub> CH <sub>2</sub> )				
	6.13	(br, 1, NH)		6.90-8.40	(m, 7, Ar-H)				
IIg	6.85-8.87	(m, 12, Ar-H)	IIIf	11.94	(s, 2, NH <sub>2</sub> )				
	2.20-3.41	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )		2.82-3.24	(m, 4, CH <sub>2</sub> CH <sub>2</sub> )				
	3.98	(s, 3, N-CH <sub>3</sub> )		3.98	(s, 3, N-CH <sub>3</sub> )				
	6.58	(br, 1, NH)		6.46-8.52	(m, 7, Ar-H)				
IIh	6.82-9.21	(m, 12, Ar-H)	IIIg	11.86	(s, 2, NH <sub>2</sub> )				
	2.13-3.52	(m, 4, CH <sub>2</sub> -CH <sub>2</sub> )		2.56	(s, 3, CH <sub>3</sub> )				
	5.63	(s, 1, H <sub>4</sub> )		3.07-4.0	(m, 4, CH <sub>2</sub> CH <sub>2</sub> )				
		7.30-8.30		(m, 8, Ar-H)					
				11.85	(s, 2, NH <sub>2</sub> )				

analyses (Table I). Thus, the infrared and the NMR spectra revealed the presence of the NH and Ar-CH moieties.

The reaction of the chalcones (I) with guanidine gave the corresponding 2-amino-4-aryl-5,6-dihydrobenzo[h]quinazolines (IIIa-i) (Scheme I). The structures of these products were deduced from their chemical and spectral analyses (Table I). The infrared spectra show absorption bands characteristic for the quinazoline system (3, 4, 5a, 6). The electronic spectra show three major maxima which can be ascribed to the <sup>1</sup>La and <sup>1</sup>Lb bands of the benzo[h]quinazolines (3, 6, 7). The NMR spectra show signals which can be attributed to the different types of protons ( $\delta$ ). The MS spectra of IIIe,f,j reveal molecular ion peaks at  $m/e$  263 (100%),  $m/e$  279 (38.63%), and  $m/e$  287 (79.64%), respectively. The base peaks of IIIe,f,j are found at  $m/e$  278 and  $m/e$  286 corresponding to  $(M - 1)^+$ . Chemical reactions lend further support to the structure of compounds III. Thus, treatment of IIIc,f with nitrous acid gave the corresponding 4-aryl-5,6-dihydro-benzo[h]-2-oxoquinazolines (IVc,f). Acetylation of IIIc,f with acetic anhydride gave the monoacetyl derivatives (Vc,f) (Scheme I). These show infrared (5b,c) and electronic spectra (3, 9) consistent with their structures (Table I).

#### Experimental Section

Microanalyses were performed by Prof. H. Malissa and G.

Table II. Melting Points and Yields of Compounds II-V

compd	mp, °C	yield, %	compd	mp, °C	yield, %
IIa	110	77	IIIc	222-223	80
IIb	199	80	IIId	173-174	78
IIc	143	82	IIIe	208-209	80
IId	154	81	IIIf	253-255	82
IIe	70	78	IIIg	156-157	81
IIIf	153	75	IIIj	193-194	78
IIg	95	79	IVc	295-296	82
IIh	115	80	IVf	275-276	80
IIi	105	78	Vc	207-208	90
IIIa	138-139	76	Vf	214-215	92
IIIb	182-183	77			

Reuter Analytisches Laboratorium BRD. Infrared spectra (KBr disk) were measured on Perkin-Elmer 580B infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded for solutions in deuteriochloroform with tetramethylsilane as an external standard on a Varian T60A spectrometer. Electronic spectra were taken for solutions in ethyl alcohol on a Pye Unicam SP8000 recording spectrometer. The mass spectra were carried out with Varian MAT 311 A. Melting points were determined by using a Bock-Monoscop M (thermal microscope).

**Reaction of the Chalcones I with Benzaniline or Guanidine. General Procedure.** A mixture of the  $\alpha,\beta$ -unsaturated

The reaction scheme shows the synthesis of 1,2,3,4-tetrahydronaphthalene-1-carbonitriles (IV and V) from 1,2,3,4-tetrahydronaphthalen-1-one (I a-j).
   
 1. **Starting material:** 1,2,3,4-tetrahydronaphthalen-1-one (I a-j), represented as a bicyclic ketone with a phenyl group (C<sub>6</sub>H<sub>5</sub>) at the 1-position.
   
 2. **Reaction 1:** I a-j reacts with phenylhydrazine (H<sub>2</sub>N-C(=NH)-C<sub>6</sub>H<sub>5</sub>) to form 1,2,3,4-tetrahydronaphthalene-1-carbonitriles (II a-i).
   
 3. **Reaction 2:** II a-i reacts with hydrazine hydrate (H<sub>2</sub>N-NH<sub>2</sub>) to form 1,2,3,4-tetrahydronaphthalene-1-carbonitriles (III a-g, j).
   
 4. **Reaction 3:** III a-g, j is converted to IV (1,2,3,4-tetrahydronaphthalene-1-carbonitrile) using NaNO<sub>2</sub>/HCl.
   
 5. **Reaction 4:** III a-g, j is converted to V (1,2,3,4-tetrahydronaphthalene-1-carbonitrile) using Ac<sub>2</sub>O.
   
 6. **Reaction 5:** III a-g, j is converted to V (1,2,3,4-tetrahydronaphthalene-1-carbonitrile) using Ac<sub>2</sub>O.
   
 7. **Reaction 6:** V is converted to IV (1,2,3,4-tetrahydronaphthalene-1-carbonitrile) using NaNO<sub>2</sub>/HCl.

Compound	Ar	Compound	Ar
I - Va	$C_6H_5$	I - Vg	$C_5H_5N$ (N-methyl- pyrrolyl)
b	$p-OCH_3-C_6H_4$	h	$C_5H_5N$ (4-pyridyl)
c	$p-Cl-C_6H_4$	i	$C_{10}H_7$
d	$m-Cl-C_6H_4$	j	$p-CH_3-C_6H_4$
e	$C_4H_2O$ (2-furyl)		
f	$C_6H_5$ (2-thienyl)		

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