[CONTRIBUTION NO. 2012 FROM THE KODAK RESEARCH LABORATORIES]

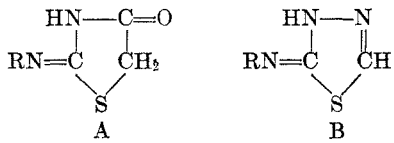
The Synthesis of Polyazaindenes and Related Compounds

G. A. REYNOLDS AND J. A. VANALLAN

Received April 1, 1959

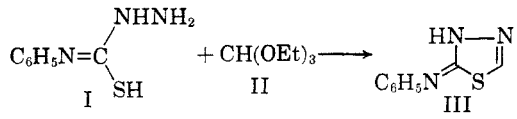
The reactions of the 2-hydrazino derivatives of pyridine, quinoline, benzothiazole, benzoxazole, benzoselenazole, and benzimidazole with orthoesters, aliphatic acids, aromatic esters, nitrous acid, phenylisothiocyanate, and phenylisocyanate which, in most cases, form ring-closed products, were investigated. The reaction of phenylthiosemicarbazide and orthoesters was also studied. Some heterocyclic compounds substituted in the 2-position with chlorine were treated with arylhydrazides in phenol to give ring-closed products. The ultraviolet spectra of the materials are discussed.

In continuation of the study of ring systems related to the iminothiazolidine A,[1] attention was turned to the action of orthoesters on 4-phenylthiosemicarbazide with the intention of obtaining compounds of the type B.



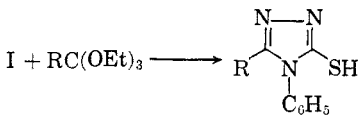
A B

The reaction of equimolecular portions of phenylthiosemicarbazide (I) with triethyl orthoformate (II) in boiling xylene proceeded as expected to give 2-phenylimino-1,3,4-thiadiazole (III), which had been obtained previously by ring closure of I with formic acid.[2] However, triethyl orthoacetate (IV)



I II III

and triethyl orthopropionate (V) rather surprisingly reacted with I to give 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole (VI) and 5-ethyl-3-mercapto-4-phenyl-1,2,4-triazole (VII), respectively, in good yield.



VI. R = CH_3
VII. R = C_2H_5

Thus, in these latter two cases, ring closure occurred through the anilino group rather than through the sulfur atom. A somewhat analogous case was found by Marckwald and Bott.[3] Benzoylphenylthiosemicarbazide and acetyl chloride gave 2-anilino-5-phenyl-1,3,4-thiadiazole but substitution of benzoyl chloride for acetyl chloride produced 4,5-diphenyl-3-mercapto-1,2,4-triazole.

These mercapto compounds are easily soluble in dilute sodium hydroxide. Methyl *p*-toluenesulfonate forms a salt with VI from which the free base, 5-methyl-2-methylmercapto-1-phenyl-1,3,4-thiadiazole (VIa), may be obtained. Sodium chloroacetate reacts with VII to give 5-methyl-2-carboxymethylmercapto-1-phenyl-1,3,4-thiadiazole (VIIa).

Lawson and Morley[4] have shown conclusively that 2-mercaptoimidazoles exist almost exclusively as the thione tautomers and that the absorption at 260 mμ in 2-mercaptoimidazoles is due mainly to contributions from the thione form. They have also shown that the absorption of the *S*-methyl derivative of 2-mercaptoimidazoles occurs at slightly lower wave lengths and with a much reduced intensity.

Spectroscopic examination of VIa, VII, and VIIa shows an interesting parallel in the light-absorption of these compounds to those of Lawson and Morley, as shown in Table I.

TABLE I

COMPARISON OF THE LIGHT-ABSORPTION OF 2-MERCAPTOIMIDAZOLES AND OF 2-MERCAPTO-1,3,4-THIADIAZOLES

	λ_{max}(mμ)	ε	Solvent
2-Mercapto-4(5)-methylimidazole	263	14,700	EtOH
4(5)-Methyl-2-methylmercaptoimidazole	250	3,400	EtOH
VII	258	11,000	MeOH
VIa	245	2,620	MeOH
VIIa	245	3,075	MeOH

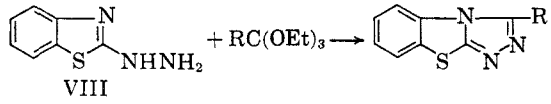
These results indicate that VII exists predominantly in the thione form and that alkylation occurs on the sulfur atom.

The ultraviolet absorption spectrum of III (λ_{max} 243 and 285 mμ) (ε= 5,800 and 16,200) is very different from that of VII and serves as a basis for distinguishing these isomers.

The behavior of 2-hydrazinobenzothiazole (VIII), a substance which is formally analogous to I, with II, IV, and V was next examined. Ring closure through the sulfur group is not possible in VIII, and the reaction proceeds readily, as expected, to give 8-thia-1,2,3a-triazacyclopent[a]indene (IXa), its 3-methyl (IXb), and 3-ethyl (IXc) derivatives,

(1) J. A. VanAllan, *J. Org. Chem.*, 21, 24 (1956).
(2) G. Pulvermaker, *Ber.*, 27, 617 (1894).
(3) W. Marckwald and A. Bott, *Ber.*, 29, 2914 (1896).
(4) A. Lawson and H. V. Morley, *J. Chem. Soc.*, 1103 (1956).

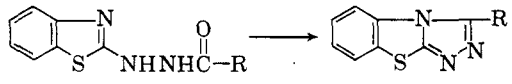
respectively, in good yield. The cyclization of VIII to IXa may also be effected with formic acid or with $CH_3COCH(OEt)_2$. Refluxing VIII with acetic



VIII

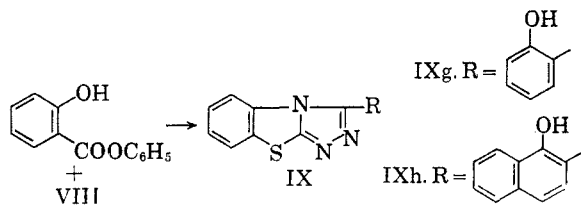
IXa. R = H
IXb. R = CH_3
IXc. R = C_2H_5

acid, propionic acid, or other higher aliphatic acids in attempts to obtain IXb and IXc resulted only in the formation of the corresponding acyl derivatives of the hydrazine. It was then found that the acyl derivatives of the hydrazines could be cyclized by refluxing them in phenol.[5] This reaction affords a convenient route to the higher alkyl derivatives of IXa, for which the necessary orthoesters are not readily available. Several 3-alkyl derivatives were prepared in this manner. In one example, a dibasic

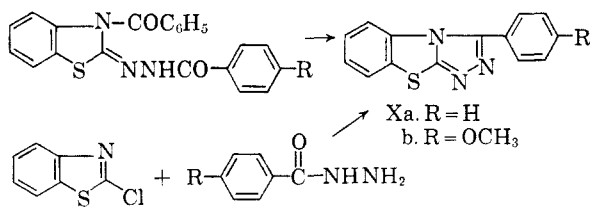


IXd. R = C_3H_7
IXe. R = i-C_3H_7
IXf. R = n-C_5H_{11}

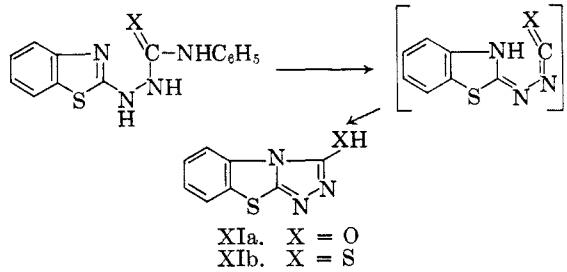
acid was reacted with VIII. As an excess of the acid could not be employed as the solvent, phenol was used, thus yielding the ring-closed material directly. Phenyl salicylate reacts readily with VIII in trichlorobenzene to give 3-(2-hydroxyphenyl) - 8 - thia - 1,2,3a - triazacyclopent[a]indene (IXg).



In a similar manner, phenyl 1-hydroxy-2-naphthoate gives the corresponding 1-hydroxy-2-naphthyl derivative, IXh. Phenyl benzoate failed to form a hydrazide with VIII. Equimolecular proportions of benzoyl chloride and VIII in the presence of pyridine gave a poor yield of 2,x-dibenzoylhydrazinobenzothiazole. Two molecular equivalents of benzoyl chloride to one of VIII under the same conditions gave a quantitative yield of the dibenzoyl compound which was cyclized in refluxing phenol to Xa. Alternatively, 2-chlorobenzothiazole and benzhydrazide react smoothly in boiling phenol to give Xa, and 4-methoxybenzhydrazide gave the methoxy derivative, Xb.



When heated either with or without a solvent, 1-(2-benzothiazolyl)-4-phenylsemicarbazide readily undergoes ring closure, with the loss of anilin to give 3-hydroxy-8-thia-1,2,3a-triazacyclopent[a]indene (XIa). In a similar fashion, 1-(2-benzothiazolyl)-4-phenylthiosemicarbazide under the same conditions gives 3-mercapto-8-thia-1,2,3a-triazacyclopent[a]indene (XIb). Both of these latter



XIa. X = O
XIb. X = S

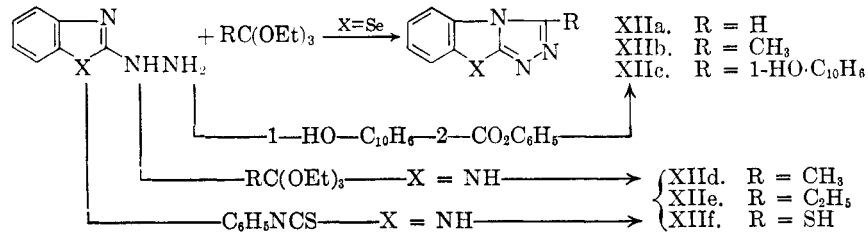
substances are soluble in dilute alkali and can be precipitated therefrom with acetic acid. Although XIa and XIb have been represented here in the enol and thiol forms, the absence of a hydroxy band in the infrared spectrum of XIa indicated that the oxygen in this substance is double-bonded and, by analogy, XIb may have a double-bonded sulfur rather than a mercapto group in position 3.

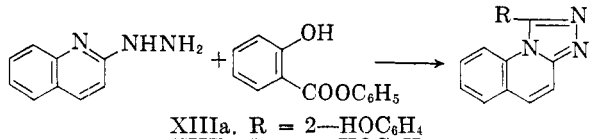
The cyclization proceeds equally well if the sulfur atom of VIII is replaced by selenium or nitrogen. For example, 2-benzoselenazolylhydrazine reacts with triethylorthoformate to give 8-selena-1,2,3a-triazacyclopent[a]indene (XIIa), and 2-benzimidazolylhydrazine with triethyl orthoacetate gives 3 - methyl - 1,2,3a,8 - tetrazacyclopent[a]indene (XIId). Other derivatives were prepared as noted in the diagram.

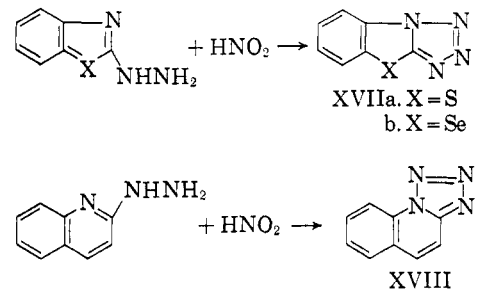
2-Quinolylhydrazine, which may be considered analogous to VIII in that the sulfur atom has been replaced by the ·CH=CH· group, was next examined with respect to its behavior with orthoesters, phenyl salicylate, and phenyl isocyanate. In each case, a product entirely analogous to those just described was obtained. The reaction of 2-quinolylhydrazine with phenyl salicylate to give 1 - (2 - hydroxyphenyl) - 2,3,9b - triazabenz[e]-indene (XIIIa) will serve to illustrate the course of the reaction. 2-Quinolylbenzhydrazide is readily cyclized to 1-phenyl-2,3,9b-triazabenz[e]indene by refluxing in phenol.[6]

(5) Refluxing the acylhydrazines in pyridine and pyridine hydrochloride, xylene and p-toluenesulfonic acid, or various other solvents, and an acid catalyst failed to bring about ring closure.

(6) The reaction of 2-quinolylhydrazine with formic acid, nitrous acid, and phenyl isothiocyanate was investigated by W. Marckwald and E. Meyer, *Ber.*, **33**, 1892 (1900), and the expected azabenz-[e]indenes were obtained in each case.

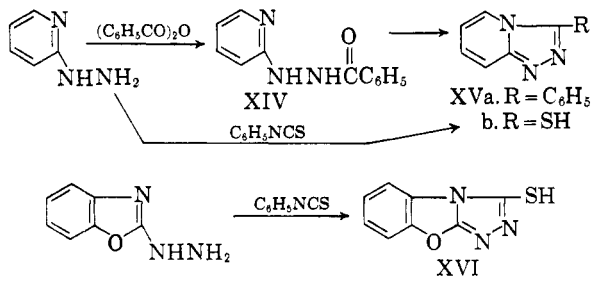






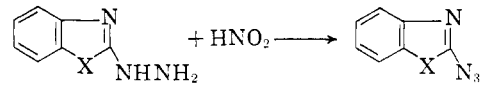
In a similar fashion, 2-pyridylhydrazine was converted to 2-(2-pyridyl)benzhydrazide (XIV) with benzoic anhydride in alcohol. 3-Phenyl-1,2,3a-diazaindene (XVa) was obtained in excellent yield by refluxing XIV in phenol for several hours.

Phenyl isothiocyanate reacts with 2-pyridylhydrazine and 2-benzoxazolylhydrazine to give 3-mercapto-1,2,3a-triazaindene (XVb), which has been synthesized by different methods,[7,8] and 3-mercapto - 8 - oxo - 1,2,3a - triazacyclopent[a]indene (XVI), respectively. Knott and Williams[9] have disclosed the preparation of XVb and XVI by the treatment of the heterocyclic hydrazine with carbon disulfide.



2 - Benzothiazolylhydrazine, 2 - benzoselenazolylhydrazine, and 2-quinolylhydrazine, on treatment with nitrous acid, give 8-thia-1,2,3,3a-tetrazacyclopent[a]indene (XVIIa), 8-selena-1,2,3,-3a-tetrazocyclopent[a]indene (XVIIb), and 1,2,3,-9b-tetrazabenz[e]indene (XVIII), respectively. The reaction of 2-chloroquinoline with sodium azide in aqueous ethanol also gives XVIII. These latter three substances were made to determine the effect of replacing the three carbon atoms of IXa and of XIIa and the one carbon atom of XIIIc with nitrogen on the ultraviolet absorption spectra of these compounds, which will be discussed in the next section. These tetraza compounds are exceptional in that they do not form quaternary salts, while those compounds containing the triaza system readily form crystalline metho-*p*-toluenesulfonates which may serve as convenient derivatives. The greater symmetry and consequent greater diffusion of the charge in the tetraza series is probably responsible for the nonformation of quaternary salts in the tetraza series.

The behavior of 2-hydrazinobenzimidazole, 1-(β-hydroxyethyl)-2-hydrazinobenzimidazole and 2-hydrazinobenzoxazole is unusual in that nitrous acid converts them to 2-azidobenzimidazole (XIXa), 1 - β - hydroxyethyl - 2 - azidobenzimidazole (XIXb), and 2-azidobenzoxazole (XIXa), respectively. The presence of the azido group is confirmed by a strong band at 4.64 μ, which is characteristic of the azido group. These latter



materials are extremely sensitive to light and turn from white to black after a few minutes' exposure to a sunlamp.

The cyclizations of the various hydrazides described take place at very different rates, depending on whether ring closure takes place at a heterocyclic atom which is located in a five- or a six-membered ring. For example, 2-quinolylbenzhydrazide is readily cyclized by several hours' heating in phenol or by heating above its melting

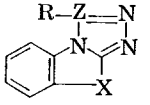
(7) W. H. Mills and H. Schindler, *J. Chem. Soc.*, **123**, 312 (1923).

(8) D. S. Tarbell, C. W. Todd, M. C. Paulson, E. G. Lindstrom, and V. P. Wystrach, *J. Am. Chem. Soc.*, **70**, 1381 (1948).

(9) E. B. Knott and L. A. Williams, U. S. Patent **2,861,-076** (1958).

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF THE CYCLOPENT[e]INDENES[a]



$\lambda m\mu(\epsilon \times 10^{-3})$. X = S, Z = C

R = H	R = CH_3	R = C_2H_5	R = n-C_3H_7	R = n-C_5H_{11}	R = i-C_3H_7	R = OH	R = SH	R = $OCCH_3$	R = C_6H_5	4—$CH_3OC_6H_4$
212(24.4)	213(22.0)	213(23.4)	213(23.2)	214(30.0)	214(21.5)	218(30.0)	212(31.5)	214(21.0)	214(21.2)	214(22.0)
220(22.0)	220(38.6)	221(21.7)	270(24.3)	220(24.3)	221(23.0)	232(12.3)	...	232(14.0)	246(15.0)	255(15.7)
225(23.8)	225(37.0)	223(21.5)	226(21.8)	225(22.9)	225(23.5)	254(5.8)	254(5.5)	238(12.8)	294(6.3)	294(8.8)
~244(10.6)	~244(10.4)	~244(10.5)	~243(10.3)	~243(10.5)	~244(10.5)	...	...	255(6.2)		
282(2.7)	282(4.6)	282(2.7)	282(2.9)	282(2.9)	286(3.6)	286(3.5)	274(7.6)	288(3.7)		
289(2.8)	289(4.8)	290(2.8)	290(3.0)	290(3.0)	291(3.4)	292(3.3)	311(11.5)	294(3.5)		

X = Se, Z = C		X = NH, Z = C		X = S, Z = N	X = Se, Z = N	X = O, Z = C
R = H	R = CH_3	R = CH_3	R = C_2H_5	R = H	R = H	R = SH
214(18.8)	214(23.4)	214(60.0)	214(61.0)		228(23.3)	
229(20.0)	229(17.8)			222(21.0)		
~244(12.0)	~244(11.0)	~232(19.5)	~232(20.0)	~240(10.0)	~240(15.0)	
283(2.6)	283(2.0)	288(4.9)	288(5.5)	282(6.7)	286(3.5)	250(9.1)
292(2.8)	292(2.1)	293(5.0)	294(5.6)	292(6.8)	295(3.9)	290(7.9)

[a] The absorption spectra were measured using methanol as a solvent.

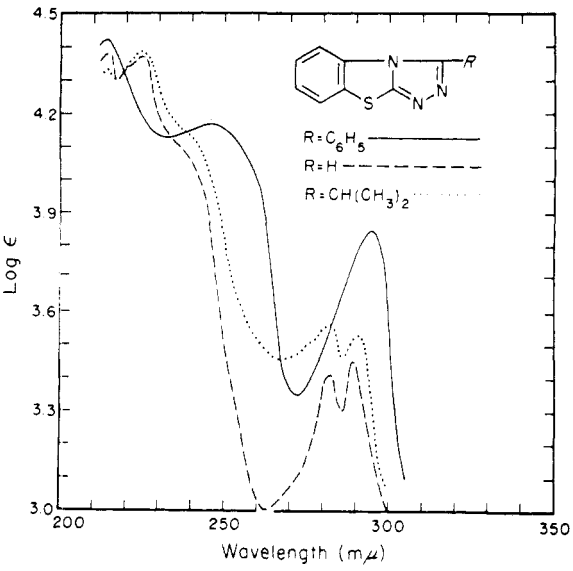


Fig. 1. Ultraviolet absorption spectra of cyclopent[a]indenes in methanol

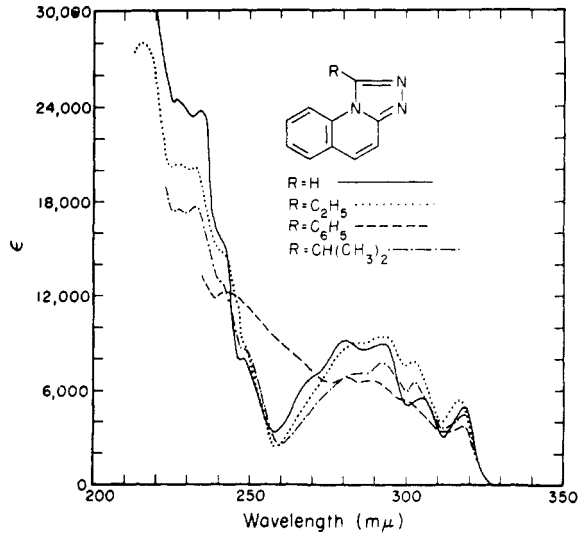


Fig. 2. Ultraviolet absorption spectra of the 2,3,9b-triazabenz[g]indenes in methanol

point, while benzothiazolylbenzhydrazide is not ring-closed unless it is refluxed in phenol for about 24 hr. This also applies to the other hydrazides which were cyclized.

DISCUSSION OF THE ULTRAVIOLET ABSORPTION SPECTRA

The ultraviolet absorption spectra of the alkyl cyclopent[a]indenes IXa → IXf are practically identical, indicating that there is no steric interference of the 3-alkyl group with the hydrogen atom in the 4-position. The shape of the absorption spectrum is reminiscent of benzimidazole,[10] which has peaks at 244(5,500), 272(5,100), and 279(5,400) mμ. The 244-mμ peak of benzimidazole occurs only as a shoulder in the alkyl cyclopent[a]indenes, while the 272-mμ and 279-mμ bands of benzimidazole have been shifted to longer wave lengths by about 10 mμ, but the absorbency remains about the same. The spectra of the aryl cyclopent[a]indenes Xa and Xb show a single peak in the 214-mμ region, a definite peak at 246 mμ for Xa and at 255 mμ for Xb, and both have a single peak at 294 mμ. The longer wave-length bands show increased absorbency over the alkyl derivative (Table II and Fig. 1). The selenium analogues, XIIa and XIIb, show a bathochromic shift of about 5 mμ in the 225-mμ region of their spectra over that of their corresponding sulfur derivative, while the nitrogen analogues, XIId and XIIe, are exceptional in the high absorbency of the 214 mμ band ($\epsilon \approx$ 60,000) and the disappearance of the 229-mμ band. The spectra of the tetrazaindenes, XVIIa and XVIIb, are quite similar to those of XIIa. The spectra of the hydroxy compound, XIa, and those of the mercapto derivative, XIb, show a bathochromic shift and a hyperchromic effect in keeping with their respective auxochromic properties, the sulfur atom, as is known, being the more powerful auxochrome.

The spectra of the 2,3,9b-triazabenz[e]indenes are similar to those of the cyclopent[a]indenes. There is, however, a bathochromic shift of the entire spectrum and an increase of fine structure. The progressive lowering of the absorbency of the shorter wave-length bands as the substituent in the 1-position, R, as hydrogen, ethyl, and isopropyl is indicative of steric hindrance. The spectrum of 1-phenyl-2,3,9b-triazabenz[e]indene (XIIIg) is typical of a compound in which there is considerable steric interference, *i.e.*, a broadening of the maxima and decreased absorbency. The planarity of the phenyl group relative to the rest of the molecule is destroyed by its interference with the hydrogen in the 9-position (Fig. 2 and Table III). The spectra of the triazabenz[e]indenes are plotted by using molecular extinction coefficients, as this scale emphasizes the lowering of the absorbency due to steric hindrance.

In those cases where a number of compounds were prepared by the same method, a generalized procedure is given and the materials synthesized by this procedure are indicated by the appropriate letter in Tables IV, V, VI, VII, and VIII. The physical properties and analytical data for the compounds described in this paper are collected in these latter tables. Thus, 2-phenyl-1,3,4-thiadiazole (III), 5-methyl-(VI) and 5-ethyl-2-mercapto-1-phenyl-1,3,4-triazole (VII) were prepared according to the following procedure.

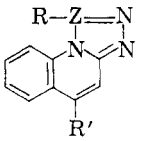
EXPERIMENTAL

Procedure A. A mixture of 0.1 mole of 4-phenylthiosemicarbazide and 0.11 mole of the orthoester in 60 ml. of xylene was heated to reflux. The alcohol which was formed was

(10) E. Steck, F. Nachod, G. Ewing, and N. Gorman, *J. Am. Chem. Soc.*, **70**, 3408 (1948).

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF THE 2,3,9b-TRIAZABENZ[e]INDENES



Z = C

λmμ

(ε × 10^{-3})

R = H	R = CH_3	R = H; R′ = CH_3	R = C_2H_5	R = $CH(CH_3)_2$	R = C_6H_5	R = OH	R = SH
216 (32.5)		220 (23.1)	216 (28)			214 (14.5)	216 (34)
226 (24.6)		230 (21.8)	226 (20.4)	226 (17.7)			
234 (24)		235 (22.4)	232 (20.1)	232 (17.8)		230 (21.9)	225 (26)
240∼(15.7)		242 (14.6)	240∼(15)	240∼(13)	242 (12.5)	236 (21.8)	240 (8.8)
248 (8.2)	248∼(8.9)	252 (9.5)	248∼(9.6)	249∼(8.5)	252 (9.5)	247 (20.4)	
						255 (19.0)	270∼(15)
280 (9.2)	283∼(8.9)	280 (8.0)	285 (8.8)	285 (7.4)	281 (6.9)	282 (2.8)	278 (22.3)
292 (9.2)	292 (9.5)	292 (8.2)	292 (9.5)	292 (7.9)	292 (6.8)	292 (3.5)	
305 (5.7)	302 (7.9)	304 (6.0)	302 (7.7)	302 (6.6)	303∼(5.5)	303 (4.1)	310 (7.2)
318 (5.2)	316 (5.7)	318 (5.6)	316 (5.7)	318 (4.8)	318 (4.1)	330 (6.0)	320 (7.6)

mμ (ε × 10^{-3})

R = SCH_2COOH	R = 4—$CH_3OC_6H_4$	Z = N
		209 (15.5)
215 (14.6)		
		236 (26.2)
		264 (8)
254 (6.5)		273 (10.8)
263 (6.7)		283 (7.9)
278 (3.4)		
297 (3.4)	288 (23.5)	
308 (3.9)	309 (17.3)	305 (2.8)
323 (3.8)	322 (13)	316 (3.3)

R = C_6H_5	R = SH
240 (11.5)	242 (12.5)
281 (9.4)	285 (10.2)
	340 (2.9)

R′ = hydrogen except where otherwise indicated.

TABLE IV

1,3,4-THIADIAZOLES AND 1,2,4-TRIAZOLES

	M.P., °C.	Empirical Formula	Calcd. C	Calcd. H	Found C	Found H	Solvent	Method of Prepn.	Yield, %
III	173							2	76
VI	220	$C_9H_9N_3S$	56.5	4.6	56.5	4.7	Xylene	A	68
	180[a]	$C_{17}H_{18}ON_3S$	54.2	4.8	54.1	5.1	Ethanol		92
VIa	120	$C_{10}H_{11}N_3S$	58.7	5.4	58.5	5.2	Toluene		79
VII	180	$C_{10}H_{11}N_3S$	58.5	5.4	58.4	5.4	Butanol	A	50
VIIa	189	$C_{12}H_{13}O_2N_3S$	54.9	5.0	54.5	5.1	Ethanol		91

[a] *p*-Toluenesulfonate salt.

removed continuously. When the theoretical amount of alcohol had been collected, the reaction was considered to be complete. The clear, faintly yellow residue was cooled. The precipitate which separated was collected by filtration, and recrystallized. The physical constants and analytical data are collected in the tables.

The conditions for the reaction of orthoesters with heterocyclic hydrazines are set forth in Procedure B.

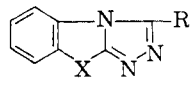
Procedure B. A mixture of 0.1 mole of the heterocyclic hydrazine and 0.11 mole of the orthoester in 60 ml. of xylene was refluxed for 3 to 4 hr. in a flask surmounted with an efficient fractionating column. The alcohol which was formed was continuously removed. When the theoretical amount of alcohol (0.3 mole) had been collected, the reaction was considered to be complete.

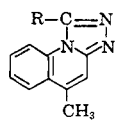
Procedure C gives the conditions for the condensation of *o*-hydroxyphenyl esters with the heterocyclic hydrazines.

Procedure C. A mixture of 0.1-molar quantities of the *o*-hydroxyphenyl ester and of the heterocyclic hydrazines in 50 ml. of 1,2,4-trichlorobenzene was refluxed. The water

TABLE V

CYCLOPENT[a]INDENES

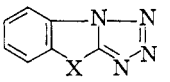


Notes	X = S R	M.P., °C.	Empirical Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Solvent	Method of Prepn.	Yield, %
					X = S							
	H	178	$C_8H_5N_3S$	54.8	2.8	24.3	54.8	2.7	24.3	H_2O or BuOH	B	76
a, b, c	CH_3	156	$C_9H_7N_3S$	57.1	3.7		57.1	3.7		H_2O	B and E	82, 70
	C_2H_5	126	$C_{10}H_9N_3S$	59.4	4.4		59.6	4.7		BuOH	B	77
d, e	*n*-C_3H_7	129	$C_{11}H_{11}N_3S$	60.8	5.1	19.4	60.7	4.9	19.1	CH_3CN	E	55
f	*i*-C_3H_7	b.p. 195–8/1 mm.	$C_{11}H_{11}N_3S$	60.8	5.1	19.4	60.2	4.8	18.8		E	40
g, h	*n*-C_5H_{11}	95	$C_{13}H_{15}N_3S$	63.6	6.0	17.2	63.6	6.0	17.3	CH_3CN	E	50
	C_6H_5	153	$C_{14}H_9N_3S$	67.0	3.6	12.8	66.9	3.7	13.1	EtOH	G	40
	p-$CH_3OC_6H_4$	145	$C_{15}H_{11}ON_3S$	64.2	3.9	14.9	63.9	4.1	15.4	EtOH	G	30
	OH	238	$C_8H_5ON_3S$	50.1	2.6		50.0	2.5		BuOH	D	63
i	CH_3CO_2	196	$C_{10}H_7O_2N_3S$	51.6	3.0		51.5	2.7		BuOH		88
	SH	250	$C_8H_5N_3S_2$	46.3	2.4	20.3	46.6	2.6	20.8	EtOH	D	63
	SCH_3	129	$C_9H_7N_3S$	49.0	3.2	19.0	49.5	4.0	19.7	EtOH		78
	2—HOC_6H_4	284	$C_{14}H_9ON_3S$	62.8	3.4		62.6	3.6		Trichlorobenzene	C	81
	1-HO-$C_{10}H_6$	259	$C_{18}H_{11}ON_3S$	68.0	3.5		68.3	3.0		BuOH	C	68
	SCH_2COOH	269	$C_{10}H_7O_2N_3S_2$	45.2	2.6	15.8	45.6	3.0	15.8	H_2O + DMF	H	70
	—$(CH_2)_4$—	>300	$C_{20}H_{16}N_6S_2$	59.5	4.0	20.8	58.7	4.4	20.6	DMF		65
					X = Se							
	H	165	$C_8H_5N_3Se$	43.1	2.3	18.9	43.7	2.3	19.3	EtOH	B	80
	CH_3	159	$C_9H_7N_3Se$	45.8	3.0	17.8	45.4	2.8	17.7	EtOH	B	70
	1—$HOC_{10}H_6$—	284	$C_{18}H_{11}ON_3Se$	59.2	3.0		58.9	3.0		$(Me)_2SO$ / EtOH ⟶	C	
	SCH_2COOH	250	$C_{10}H_7N_3SeSO_2$	38.5	2.3	13.5	39.1	2.3	13.7	H_2O + DMF	H	50
					X = NH							
	CH_3	231	$C_9H_8N_4$	62.8	4.7		63.2	5.1		BuOH	B	84
j		218	$C_{19}H_{19}O_3N_3S$	61.8	5.1		61.9	5.4		BuOH		87
	C_2H_5	260	$C_{10}H_9N_4$	64.9	4.9		64.2	5.6		BuOH	B	79
k		220	$C_{17}H_{18}O_3SN_4$	56.9	5.0		56.8	5.2		EtOH		91
l	SH	275 dec.	$C_8H_6N_4S$	50.5	3.2		50.4	3.0			D	59
					X = (CH=CH)							
	H	175	$C_{10}H_6N_2$	71.5	3.6		71.3	4.0		*i*-BuOH	5	
	CH_3	176	$C_{11}H_9N_3$	72.0	4.9		72.4	5.2		*i*-BuOH	B	78
	C_2H_5	123	$C_{12}H_{11}N_3$	73.1	5.6		73.5	5.7		Toluene	B	84
	$CH(CH_3)_2$	83–4	$C_{12}H_{13}N_3$	72.4	6.5		72.5	6.4		Ligroin	E	58
	OH	248	$C_{10}H_7ON_3$	65.0	3.8		65.0	3.7		BuOH	D	65
	SH	276									ref. (5)	
	C_6H_5	89	$C_{16}H_{11}N_3$	79.0	4.5		79.1	5.0		Benzene Ligroin		76
	2—HOC_6H_4	>290	$C_{16}H_{11}ON_3$	73.5	4.2		73.5	4.5		$(CH_3)_2SO$	C	87
	2—$HOC_{10}H_6$	289	$C_{20}H_{13}ON_3$	77.1	4.2		77.3	4.0		Trichlorobenzene	C	77
					X = O							
	SH	263	$C_8H_5ON_3$	60.2	3.2		59.9	3.5		EtOH	D	89
												
	H	222–3	$C_{11}H_9N_3$	72.2	4.9	22.9	71.9	5.0	23.0	H_2O	D	80
	SH	300									ref. 5	
	SCH_2COOH	230	$C_{13}H_{11}O_2N_3S$	57.2	4.0	15.4	57.6	4.1	15.2	H_2O-DMF		85

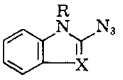
[a] Methyl *p*-toluenesulfonate salt, m.p. 170°(alc.). *Anal.* Calcd. for $C_{17}H_{17}O_3N_3S$: C, 54.5; H, 4.5. Found: C, 54.2; H, 5.0. [b] Also obtained by substituting $CH_3C(=NH)OCH(OEt)_2$ for triethyl orthoacetate. [c] The intermediate acetylhydrazinobenzothiazole melted at 214–215°. [d] Butyrylhydrazinobenzothiazole, m.p. 273–274°. [e] B. p. 198–202°/1 mm. [f] Isobutyrylhydrazinobenzothiazole, m.p. 230–231°. [g] Hexanoylhydrazinobenzothiazole, m.p. 240–241°. [h] B.p. 220–225°/1 mm. [i] Obtained by acetylation of the hydroxy compound with acetic anhydride containing sulfuric acid as a catalyst. [j] Methyl *p*-toluenesulfonate salt of the methyl derivative, m.p. 231°. [k] Methyl *p*-toluenesulfonate salt. [l] Purified by solution in dilute sodium hydroxide and reprecipitation with acetic acid.

TABLE VI

1,2,3,3a-TETRAZAINDENES AND AZIDES



Notes	M.P., °C	Empirical Formula	Calcd. C	H	N	S	Found C	H	N	S	Solvent	Method	Yield, %
						X = S							
[a]	110–1	$C_7H_4N_4S$	47.7	2.3	31.9	18.1	47.9	2.4	31.9	17.7	EtOH	F	98
						X = Se							
[a]	170 dec.	$C_7H_4N_4Se$	37.7	1.8	25.1		38.3	2.0	25.0		BuOH	F	96

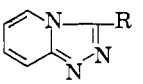


						X = N, R = H							
[b–d]	192 dec.	$C_7H_5N_5$	52.8	3.2	44.0		52.9	3.4	44.0		EtOH—H_2O	F	66
						X = N, R = CH_2CH_2OH							
	165 dec.	$C_9H_9N_5O$	53.2	4.4	34.5		53.3	4.6	33.8		H_2O	F	36
						X = O, R = H							
	67	$C_7H_4N_4O$	52.4	2.5			52.6	2.4			EtOH	F	72

[a] The IR curve showed no adsorption in the 4.6-μ region. [b] Strong band at 4.62 μ. [c] Adsorbed in the UV at 235 mμ (9,300) and 288 mμ (15,000). [d] Hydrazinobenzimidazole also gave results different from the other hydrazines when it reacted with formic acid. The product, m.p. 174°, analyzed as the formate salt of the hydrazine.

TABLE VII

1,2,3a-TRIAZAINDENES

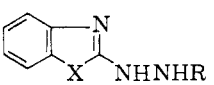


Notes	R	M.P., °C	Empirical Formula	Calcd. C	H	Found C	H	Solvent	Method	Yield, %
[a]	C_6H_5	175[c]	$C_{12}H_9N_3$	73.8	4.6	74.1	4.6	BuOH		89
	1—$HOC_{10}H_6$	239	$C_{16}H_{11}ON_3$	73.5	4.4	73.7	4.5	Trichlorobenzene	C	86
	SH	215	$C_6H_5SN_3$	47.0	3.3	47.4	3.5	BuOH	D	81
[b]		189	$C_6H_5ON_3$	63.1	5.3	63.0	5.4	BuOH	D	84

[a] 2-(2-Pyridyl)benzhydrazide, m.p. 202°, was refluxed in phenol as described in Procedure E. [b] Ring closure did not take place. This material is 1-phenyl-4-(2-pyridylsemicarbazide). [c] M.p. given as 176° in *J. Chem. Soc.*, 727 (1957).

TABLE VIII

AROYLHYDRAZIDES



Notes	R	M.P., °C	Empirical Formula	Calcd. C	H	Found C	H	Solvent
			X = S					
[a]	4—$CH_3OC_6H_4CO$	184	$C_{15}H_{13}O_2N_3S$	60.1	4.3	60.0	4.3	BuOH
[b]		257–8	$C_{22}H_{18}O_4N_3S$	58.5	4.0	58.4	4.2	EtOH
	$C_6H_5CH=CHCO$	258	$C_{16}H_{13}ON_3S$	65.2	4.3	65.6	4.9	
			X = (CH=CH)					
[d]	C_6H_5CO	204						
[c]		264 dec.	$C_{24}H_{23}O_4N_3$	64.2	5.1	64.2	5.0	H_2O
			X = O					
	C_6H_5NHCO	225	$C_{14}H_{12}O_2N_4$	62.6	4.4	62.8	4.5	BuOH

[a] Calcd.: N, 14.2. Found: 13.9. [b] Methyl *p*-toluenesulfonate salt of the 184° compound. [c] Methyl *p*-toluenesulfonate salt of 204° compound. [d] R. G. Fargher and R. Furness, *J. Chem Soc.*, **107**, 688 (1915).

which was formed distilled over first at 98–101°. The temperature at the stillhead then rose sharply and phenol distilled over at 180–190°. The reaction was considered complete when the stillhead temperature was 203°. Reaction was usually complete in about 2 hr. The product which had crystallized was collected by filtration and washed with alcohol and dried.

The hydroxy and mercapto derivatives were produced as follows.

Procedure D. A mixture of 0.1 mole of the isocyanate or isothiocyanate and heterocyclic hydrazine in 60 ml. of trichlorobenzene was refluxed for about 2.5 hr. After cooling to room temperature, the crystals which had separated were collected by filtration, washed well with benzene, and extracted twice with 400-ml. portions of warm 5% sodium hydroxide.

The extracts were combined and were acidified with acetic acid. The precipitate was collected by filtration, and crystallized from a suitable solvent.

Procedure E.[11] The procedure for cyclization with phenol is as follows. The heterocyclic hydrazine and a large excess of the appropriate aliphatic acid were refluxed 2 hr., cooled, and the acyl hydrazine collected by filtration. The acyl hydrazine was refluxed 2–20 hr. with 2.5 times its weight of phenol and the phenol was then removed by steam distillation. The residue was either recrystallized or first distilled *in vacuo* and then recrystallized.

Procedure F. Nitrous acid ring closure. The heterocyclic hydrazine was dissolved in 15 times its weight of 50% aqueous acetic acid, the solution cooled to 10–15°, and the calculated amount of sodium nitrite in a small amount of water was added. The tetraza compound usually separated at once, but the reaction mixture was allowed to stand in the cold for an hour before the product was collected.

Procedure G. The thiazaindenes substituted in the 3-position by an aromatic group were prepared in the following manner. A mixture of 0.1 mole each of 2-chlorobenzothiazole, arylhydrazide, and sodium phenoxide in 40–50 ml. of phenol was refluxed for 20 hr. The solvent was steam-distilled and the residue recrystallized from the appropriate solvent. Several runs made without sodium phenoxide resulted in slightly lower yields of the product.

Procedure H gives the conditions for the reaction of the mercapto compounds with sodium chloroacetate.

Procedure H. A mixture of 1 part each of mercapto compound and sodium chloroacetate in 10 parts of water was heated 15 min. on the steam bath, 1 part of sodium carbonate was added, and the heating was continued for 1 hr. After any insoluble material present had been filtered off, the filtrate was acidified with acetic acid and the product was collected and recrystallized.

2-Chlorobenzoselenazole. To 41 g. (0.19 mole) of 2-mercaptobenzoselenazole[12] was added 30 g. (0.22 mole) of sulfur monochloride in small portions, with stirring. When the exothermic reaction had subsided, external heat was applied until the frothing ceased; the mixture was then refluxed for 30 min. and allowed to stand at room temperature overnight. The dark tar was distilled to yield 36 g. of product, b.p. 135°/10 mm.

2-Hydrazinobenzoselenazole. A mixture of 36 g. (0.167 mole) of 2-chlorobenzoselenazole, 18.5 g. of hydrazine hydrate, and 10 ml. of water was heated on the steam bath for 1 hr. A solid began to separate almost at once and, after the reaction mixture was chilled, it was collected. Recrystallization from ethanol gave 25 g. of product, m.p. 226–227°.

Anal. Calcd. for $C_7H_7N_3Se$: C, 39.6; H, 3.3; N, 19.8. Found: C, 39.7; H, 3.0; N, 20.3.

1,2-Bis(8-thia-1,2,3a-triazacyclopent[a]inden-3-yl)ethane. A mixture of 33 g. (0.2 mole) of hydrazinobenzothiazole and 15 g. (0.1 mole) of adipic acid in 100 ml. of phenol was refluxed 4 hr. and the phenol removed by steam distillation. The solid residue was recrystallized, the yield and physical properties being indicated in Table V.

The methyl p-toluenesulfonate salts were prepared by heating equal weights of the compound to be quaternized and methyl *p*-toluenesulfonate for 5 hr. on the steam bath. The crystalline product was washed with acetone and crystallized from a suitable solvent.

2,x-Dibenzoylhydrazinobenzothiazole. A mixture of hydrazinobenzothiazole (8.2 g.; 0.05 mole) and 14 ml. of benzoyl chloride in 50 ml. of pyridine was allowed to stand for 2 hr. The mixture was poured into water and acidified with acetic acid. On standing overnight, the oily precipitate solidified. The product was collected by filtration and recrystallized from toluene to give 17 g. of product, m.p. 215°, yield 91%.

Anal. Calcd. for $C_{21}H_{16}O_2N_3S$: C, 67.2; H, 4.3; N, 11.2; S, 8.6. Found: C, 67.2; H, 4.1; N, 11.0; S, 8.8.

1,2,3,9a-Tetrazabenz[e]indene (XVIII). *Sodium azide method.* A mixture of 16.4 g. of 2-chloroquinoline and 8.0 g. of sodium azide in 60 ml. of 15% aqueous ethanol was refluxed for 6 hr. The solution was filtered while still hot. On chilling, 8.0 g. of XVIII, m.p. 153–154°, separated. A mixed melting point with an authentic sample of XVIII showed no depression of melting point.

Acknowledgment. We are indebted to D. Stewart and Thelma Davis, of the Chemistry Department, and E. R. Richardson, of the Physics Department, for the determination of the ultraviolet and infrared spectra.

ROCHESTER 4, N. Y.

(11) J. A. VanAllan, U. S. Patent 2,865,749 (1958).

(12) V. Ettal, M. Semonský, J. Kuňák, and A. Černý, *Chem. Listy*, 46, 749 (1952); *Chem. Abstr.*, 47, 12358 (1953).