^{13}C spectra of these 2-aminoamide–thionyl chloride products.[22] The 169–172 ppm chemical shift range could be consistent with structure **1**, if the products existed solely as the configurationally stable *E* isomer **1**-*E*. It appears unlikely, however, that the configurational preference of these compounds should be completely opposite that of the iminolactones **12–14**. On the basis of these ^{13}C spectra, the 2-aminoamide–thionyl chloride products should be reassigned the 1-oxo-1,2,5-thiadiazolidin-3-one structure (**2**) rather than the initially assigned 2-oxo-5-imino-1,2,3-oxathiazolidine structure (**1**).

Experimental Section

Spectra. Carbon-13 spectra were recorded on a Varian XL-100-15 NMR spectrometer, equipped with a Transform Technology FT attachment, operating at 25.16 MHz under conditions of full proton decoupling at a probe temperature of about 38 °C. Samples were observed in 12-mm o.d. tubes as saturated solutions (for solid compounds) or approximately 50% solutions (for liquid compounds) in $CDCl_3$ containing Me_4Si as internal standard. ^1H NMR spectra were also recorded on $CDCl_3$ solutions using a Varian XL-100-15 NMR spectrometer. Chemical shifts are relative to internal Me_4Si.

Materials. The 2-aminoamide–thionyl chloride products (**2a–d**) were prepared as previously described.[1] Compound **3a** was prepared according to the procedure of Chupp.[2] Compound **7** was prepared by the acetylation of *N*-methylaniline with acetyl chloride.[5] Compound **8**[6-8] was prepared from acetanilide by methylation using methyl fluorosulfonate. Compounds **9**,[9] **10**,[9] and **11**[10] were prepared by potassium hydroxide fusion of *N*-phenyl- (**15**),[9] *N*-*p*-tolyl- (**16**),[9] and *N*-benzyl-4-chlorobutanamide (**17**),[10] respectively. Compounds **12**,[11,12] **13**,[11] and **14**[11] were prepared from **15**, **16**, and **17**, respectively, upon treatment with silver tetrafluoroborate, according to the general procedure of Eschenmoser et al.[20] as applied by Schmir and Cunningham[12] for the preparation of **12**. All of the compounds had IR and ^1H NMR spectra in agreement with the assigned structures.

Acknowledgments. The authors thank the National Science Foundation for partial support of this work and Dr. W. S. Brey, Jr., Dr. L. W. Jaques, and Mr. P. I. Yang for recording the ^{13}C spectra reported in this paper. H. L. G. thanks the Proctor & Gamble Co. for a graduate fellowship (1974–1975).

Registry No.—**2a**, 61218-56-2; **2b**, 61218-57-3; **2c**, 61218-58-4; **2d**, 61218-59-5; **3a**, 52559-50-9; **7**, 579-10-2; **9**, 4641-57-0; **10**, 3063-79-4; **11**, 5291-77-0; **8**-*Z*, 31001-89-5; **12**-*Z*, 51229-48-2; **12**-*E*, 51229-49-3; **13**-*Z*, 61218-60-8; **13**-*E*, 61218-61-9; **14**-*Z*, 61218-62-0; **14**-*E*, 61218-63-1.

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(22) **Note Added in Proof.** A referee suggested that the failure to observe any sign of syn–anti isomerism in the ^{13}C NMR spectra of our 2-aminoamide–thionyl chloride products could be consistent with structure **1** if syn–anti isomerization is fast at room temperature and/or the concentration of the minor isomer is too low to be detected by ^{13}C NMR, which is less sensitive than ^1H NMR. However, the proton spectrum of the 2-aminoamide–thionyl chloride product (**1d** or **2d**) failed to show any additional signals even upon cooling to −50 °C.

Heteroaromatic 10-π-Electron Systems. New *s*-Triazolo-*as*-triazines with a Bridgehead Nitrogen Atom

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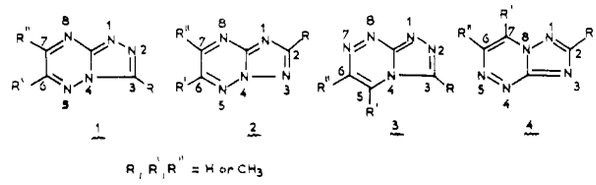
Received September 28, 1976

Four different polyazaindolizine systems of the *s*-triazolo-*as*-triazine type have been prepared either from 3-amino- or 3-hydrazino-*as*-triazines, or from 5-chloro-, 3,4-diamino-, or 3-hydrazino-*s*-triazoles.

s-Triazolo-*as*-triazine heterocycles are among the least known in the polyazaindolizine series. In particular *s*-triazolo[2,3-*b*]-*as*-triazines **2** have never been described and only *s*-triazolo[4,3-*b*]-*as*-triazines **1**, *s*-triazolo[3,4-*c*]-as-triazines **3**, and *s*-triazolo[3,2-*c*]-*as*-triazines **4** substituted with phenyl, amino, hydroxy, or mercapto groups are known.[1-8] The synthesis and properties of unsubstituted and methyl-substituted *s*-triazolo-*as*-triazines **1–4** (Chart I) were of interest in con-

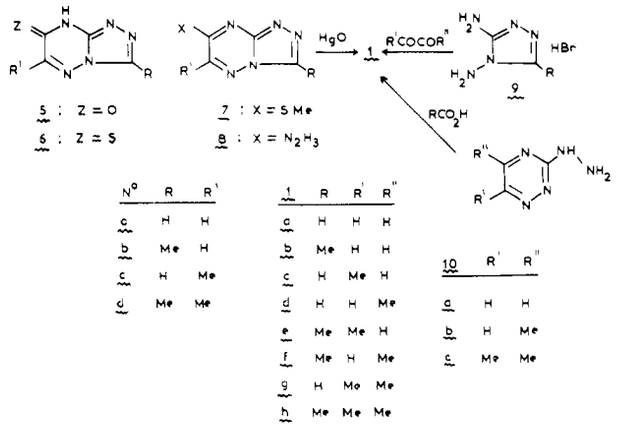
Chart I



junction with our previous investigations in the *as*-triazine[1] and azaindolizine[9] series.

Several routes to each system **1–4** were investigated. Unsubstituted and methyl-substituted *s*-triazolo[4,3-*b*]-*as*-triazines **1** have been obtained from the known 7-oxo-*s*-triazolo[4,3-*b*]-*as*-triazines **5**[3] using a multistep synthesis. The preparation involved successive thionylation of the carbonyl group, methylation at the sulfur atom, replacement of the methylthio group with hydrazine, and oxidation of the 7-hydrazino derivative with mercuric oxide (Chart II). Furthermore, it was found that a methyl group could be introduced into the 7 position upon treatment of compound **1** (R″ = H) with methylmagnesium iodide in tetrahydrofuran and diethyl ether. Under the reaction conditions the intermediate 7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazines are rather unstable and decompose easily to **1** (R″ = Me) except in the case of **1b** and **1c**, where controlled reaction conditions allowed their isolation.

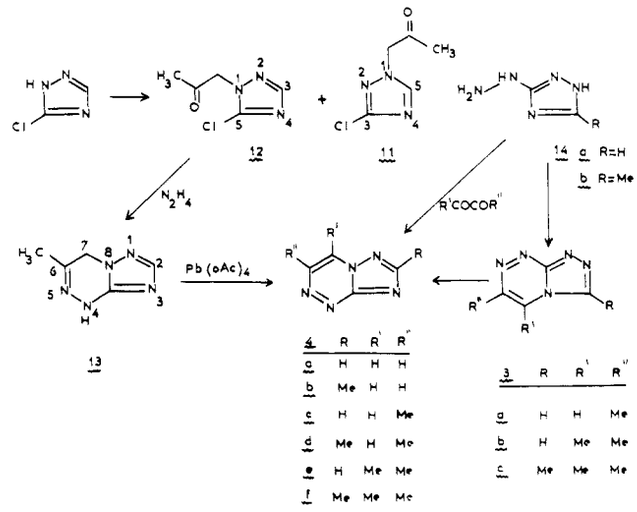
Chart II



3,4-Diamino-*s*-triazole hydrobromide (**9**) reacted with α-dicarbonyl compounds in acetic acid to afford the corresponding compounds **1**. Thus diacetyl yields **1g** whereas methylglyoxal gives only one of the two possible positional isomers; this was identified as **1c** already obtained from **5c** via **6c, 7c,** and **8c**. Cyclization of 3-hydrazino-*as*-triazines **10** with carboxylic acids or otho esters may result in the formation of two isomeric *s*-triazolo-*as*-triazines, **1** or **3**, depending on the nuclear nitrogen involved[1] in the cyclization step. However, only isomer **1** was obtained when condensing **10a–c** with formic acid, acetic acid, or triethyl orthoformate, regardless of the conditions used. This exclusive ring closure mode of 3-hydrazino-*as*-triazines can be explained by the enhanced nucleophilicity of N-2 as compared to N-4.[11]

Based on the behavior of homologous "azaindolizine" systems[1,10,11] we expected *s*-triazolo[3,4-*c*]-*as* triazines **3** to isomerize easily to compounds **4** through fission of bond N-4–C-5 and Dimroth rearrangement, contrary to system **1**. Hence an unequivocal synthesis of **4** was carried out (Chart III). Reaction of 3-chloro-*s*-triazole with chloroacetone affords two isomeric 1-acetonyl-3- or -5-chloro-*s*-triazoles **11** and **12**. These compounds have been identified by comparison of their fragmentations under electron impact with those of recently studied[12] 1-methyl-3- or -5-chloro-*s*-triazoles. Thus the molecular ions of **11** and **12** fragment mostly into ketene and the

Chart III



4	R	R′	R″
a	H	H	H
b	Me	H	H
c	H	H	Me
d	Me	H	Me
e	H	Me	Me
f	Me	Me	Me

3	R	R′	R″
a	H	H	Me
b	H	Me	Me
c	Me	Me	Me

1-methyl-3- or -5-chloro-*s*-triazoles ion, respectively. These ions have characteristic fragmentation patterns.[12] The action of hydrazine on **12** leads to 6-methyl-4,7-dihydro-*s*-triazolo[3,2-*c*]-*as*-triazine (**13**). This compound was dehydrogenated to **4c** with lead tetraacetate under conditions which preclude any rearrangement.

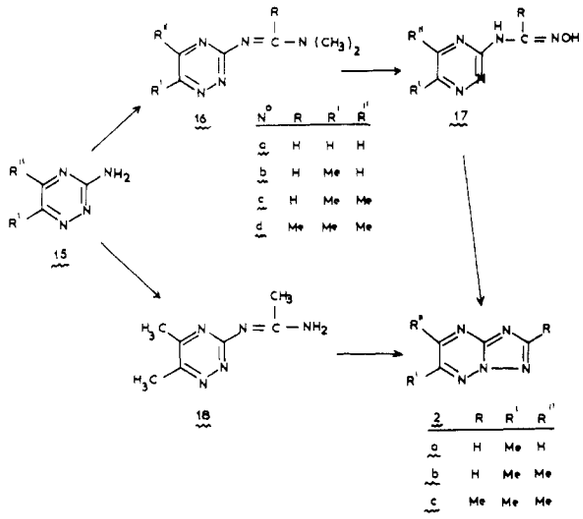
Condensations of 3-hydrazino-*s*-triazoles **14** with α-dicarbonyl compounds are not unequivocal syntheses of either **3** or **4**. The transformation may involve cyclization either at the N-2 or N-4 atom of the *s*-triazole ring. The situation is further complicated by the possible occurrence of the Dimroth rearrangement of **3** to **4** as stated before. Under controlled reaction conditions the reaction of diacetyl and **14a** or **14b** in ethanol leads to only one product in each case. However, if the temperature is increased or a longer reaction time used the former product is transformed into an isomeric compound. Moreover, a fast and complete conversion is also achieved if the initial product is treated with an aqueous solution of sodium hydroxide at room temperature. These results suggest that the thermodynamically more stable products are **4e** and **4f**[10] (Chart III). Methylglyoxal and **14a** afforded one product to which structure **3a** was assigned since it rearranges easily to **4c** obtainable also from **13**. Compound **14b** and methylglyoxal gave only **4d**. Similarly, even under controlled reaction conditions, glyoxal gives only one product to which the structure **4a** (or **4b**) is assigned by analogy.

The last *s*-triazolo-*as*-triazine system of interest, namely, the previously unknown *s*-triazolo[2,3-*b*]-*as*-triazines **2**, were obtained from 3-amino-*as*-triazine derivatives using two methods known to effect cyclization in related systems.[13–16]

Treatment of 3-amino-*as*-triazines **15** with *N,N*-dimethylformamide or *N,N*-dimethylacetamide acetal yielded the corresponding amidines **16** (Chart IV). These compounds react with hydroxylamine to give the amidoximes **17**. These, except **17a**, when treated with phosphorus oxychloride led in each case to only one *s*-triazolo-*as*-triazine different in every aspect from the corresponding *s*-triazolo[3,2-*c*]-*as*-triazine **4** already prepared from **14**. Therefore, the structure of the cyclization products must be **2**. This is consistent with the higher nucleophilic character of the ring nitrogen atom N-2 (as compared to N-4) as observed in the cyclization of 3-hydrazino-*as*-triazines. In contrast, attempts to cyclize **17a** using phosphorus oxychloride or lead tetraacetate were unsuccessful; polyphosphoric acid hydrolyzed the amidoxime to 3-formylamino-*as*-triazine.

3-Amino-*as*-triazines **15** reacted with acetonitrile in the presence of aluminum chloride to afford triazinylacetamidines similar to **18**. However, the compounds are fairly unstable and

Chart IV



did not undergo oxidative cyclization to **2** with the exception of compound **18**. The latter when treated with lead tetraacetate in benzene gave **2c** obtainable also from the amidoxime **17d**.

Experimental Section

NMR spectra were determined on a Varian HA-100 spectrometer and are listed in Table I. Mass spectra were recorded on a JEOL JMS D100 instrument.

The following starting materials were obtained according to procedures described in the literature: 3,4-diamino-*s*-triazoles,[8] 7-oxo-*s*-triazolo[4,3-*b*]-*as*-triazines,[1] 3-hydrazino-*as*-triazines,[17] 3-chloro-*s*-triazoles,[12] and 3-hydrazino-*s*-triazoles.[18,19] Details concerning the purification and characterization of new compounds are reported in Table II.

***s*-Triazolo[4,3-*b*]-*as*-triazines 1. A.** A suspension of **5** (0.03 mol) and phosphorus pentasulfide (5 g) in 200 ml of acetonitrile was heated for 1 h. After evaporation to dryness the residue was poured in 30 ml of hot water and the precipitate of **6** was removed by filtration.

A stirred solution of **6** (0.02 mol) in 20 ml of 4% aqueous sodium hydroxide and 1.5 ml of methyl iodide was allowed to stand at room temperature for 30 min. The organic product was then extracted with chloroform and the extracts evaporated to dryness giving compound **7**.

A solution of **7** (0.01 mol) and hydrazine hydrate (0.02 mol) in 45 ml of ethanol was refluxed for 1 h. After cooling, **8** precipitated and was removed by filtration. Mercuric oxide (10 g) was added to 150 ml of absolute ethanol in which 0.01 mol of finely powdered **8** had been suspended. The mixture was stirred and refluxed for 24 h. The solid phase was filtered and the filtrate concentrated to dryness, leaving the corresponding compound **1**.

B. A solution of **1b** (R″ = H) (0.004 mol) in 30 ml of tetrahydrofuran was slowly added at room temperature to a solution of methylmagnesium iodide (0.012 mol) in diethyl ether (50 ml). The solution was refluxed for 6 h and, after cooling, a saturated solution of ammonium chloride in water was added. The product of reaction was extracted with chloroform. After evaporation a solid was obtained and purified through crystallization. Thus, 3,7-dimethyl-7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazine (or its tautomer) was obtained from **1b**: mp 128–129 °C (from benzene–ethyl acetate); yield 48%; mass spectrum M^+ *m/e* 151; NMR ($CDCl_3$) δ 1.48 (d, Me-7), 2.40 (s, Me-3), 4.38 (m, H-7), 7.08 (d, H-6), J_{H_6,H_7} = 2, J_{Me_7,H_7} = 7 Hz.

Anal. Calcd for $C_6H_9N_5$: C, 47.67; H, 6.00; N, 46.33. Found: C, 47.28; H, 6.03; N, 46.42.

6,7-Dimethyl-7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazine (or its tautomer) was obtained from **1c**: mp 136–137 °C (from benzene–ethyl acetate); yield 52%; mass spectrum M^+ *m/e* 151; NMR ($CDCl_3$) δ 1.43 (d, Me-7), 2.11 (s, Me-6), 4.25 (q, H-7), 7.95 (s, H-3), $J_{Me\text{-}7,H\text{-}7}$ = 7 Hz.

Anal. Calcd for $C_6H_9N_5$: C, 47.67; H, 6.00; N, 46.33. Found: C, 47.32; H, 5.94; N, 46.25.

On the contrary, if the crude products obtained from **1a, 1b, 1c,** and **1e** are chromatographed on neutral alumina, only the compounds **1d, 1f, 1g,** and **1h** are obtained, respectively (Table II).

C. A solution of 3,4-diamino-*s*-triazole hydrobromide (0.9 g) and the α-dicarbonyl compound (0.005 mol) in acetic acid (5 ml) was allowed to stand at room temperature for 3 h. After evaporation 20 ml of water was added and the solution neutralized with sodium bicarbonate. The product was extracted with chloroform and the residue after evaporation purified by crystallization.

D. Compound **10** (0.02 mol) in 5 ml of formic or acetic acid was cyclized after 40 min of reflux. The same results were obtained from a solution of **10** in ethyl orthoformate (10 ml) and ethanol (35 ml) after 24 h of reflux.

***s*-Triazolo[3,4-*c*]-*as*-triazines 3 and *s*-Triazolo[3,2-*c*]-*as*-triazines 4. A.** A solution of 3-chloro-*s*-triazole (1.0 g) and chloroacetone (11 g) in 30 ml of 1-butanol was refluxed for 8 h, then evaporated to dryness. Water (30 ml) was added and the solution neutralized with 5% aqueous sodium bicarbonate. After extraction with chloroform and evaporation the isomers **11** and **12** were separated by chromatography on a column of alumina (eluent petroleum ether–benzene, 1:1, R_f **11** > R_f **12**).

Compound **11** in 48% yield: mp 90–91 °C (from benzene–hexane); mass spectrum M^+ *m/e* 159 and 161; NMR ($CDCl_3$) δ 2.26 (s, CH_3), 5.05 (s, CH_2), 8.11 (s, H_5).

Anal. Calcd for $C_5H_6N_3OCl$: C, 37.61; H, 3.76; N, 26.33; Cl, 22.25. Found: C, 37.66; H, 3.84; N, 26.36; Cl, 22.09.

Compound **12** in 32% yield: mp 128–130 °C (from benzene–hexane); mass spectrum M^+ *m/e* 159 and 161; NMR ($CDCl_3$) δ 2.26 (s, CH_3), 5.05 (s, CH_2), 7.96 (s, H_3).

Anal. Calcd for $C_5H_6N_3OCl$: C, 37.61; H, 3.76; N, 26.33; Cl, 22.25. Found: C, 37.53; H, 3.81; N, 26.27; Cl, 22.12.

A solution of **12** (0.10 g) and hydrazine hydrate (1.25 g) in methanol (5 ml) was heated at 150 °C in a sealed tube for 5 h. The residue was triturated with 10 ml of ether and the hydrochloride of **13** precipitated and was filtered off and crystallized: mp 177–178 °C (from methanol); yield 50%; NMR (Me_2SO-d_6) δ 1.90 (s, CH_3), 4.73 (s, CH_2), 7.70 (s, H_2).

The hydrochloride of **13** (2.0 g) was dissolved in 50 ml of water at 50 °C. The solution was neutralized with sodium bicarbonate. An extraction with chloroform yielded **13**: mp 112–113 °C (from benzene–ethyl acetate); yield 85%; mass spectrum M^+ *m/e* 137; NMR ($CDCl_3$) δ 2.05 (s, CH_3), 4.75 (s, CH_2), 7.73 (s, H_2).

Anal. Calcd for $C_5H_7N_5$: C, 43.79; H, 5.14; N, 51.07. Found: C, 43.81; H, 5.12; N, 51.02.

Lead tetraacetate (0.7 g) was added to a solution of **13** (0.1 g) in anhydrous benzene (20 ml) and the stirred mixture was refluxed for 30 min. The hot filtrate was neutralized with sodium bicarbonate. The product (**4c**) was extracted with chloroform and chromatographed on a column of alumina (eluent benzene–chloroform, 3:2): mp 80–81 °C; mass spectrum M^+ *m/e* 135.

Anal. Calcd for $C_5H_5N_5$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.22; H, 3.45; N, 51.42.

B. A stirred solution of 3-hydrazino-*s*-triazole hydrochloride (0.05 mol) and α-dicarbonyl compound (0.07 mol) in 10 ml of ethanol was

Table I. NMR Spectra of *s*-Triazolo-*as*-triazines 1–4[a]

No.	R	R′	R″
1a	9.13	8.61 d (J = 1.5 Hz)	8.45 d
1b	2.83	8.56 d (J = 1.5 Hz)	8.47 d
1c	8.99	2.72	8.49
1d	9.00	8.26	2.75
1e	2.76	2.72	8.43
1f	2.78	8.29	2.72
1g	8.88	2.64	2.67
1h	2.72	2.63	2.65
2a	8.59	2.78	8.67
2b	8.55	2.75	2.70
2c	2.61	2.70	2.67
3a	8.78	3.00	8.43
3b	8.62	2.90 q (J = 0.6 Hz)	2.93 q
3c	2.73	2.93	2.93
4a	7.83	6.94 d (J = 2.4 Hz)	6.16 d
4b	2.34	6.94 d (J = 2.4 Hz)	6.12 d
4c	7.80	2.22	6.05
4d	2.36	2.16	6.00
4e	7.80	2.10	2.07
4f	2.43	2.10	2.07

[a] Chemical shifts in parts per million (Me_4Si as internal standard); solvent $CDCl_3$.

Table II. Purification and Characterization of New Compounds[a]

Registry no.	Compd	Mp, °C	Method of prepn	Yield, %	Crystn solvent	M^+ MS	Mol formula
275-01-4	**1a**	165–166	I A	56	Benzene and ethyl acetate	121	$C_4H_3N_5$
61139-68-2	**1b**	186–187	I A	62	Benzene and ethyl acetate	135	$C_5H_5N_5$
61139-69-3	**1c**	139–140	I A	55	Benzene and *n*-hexane	135	$C_5H_5N_5$
			I B	60			
61139-70-6	**1d**	234–235	I C	65	Benzene and ethanol	135	$C_5H_5N_5$
			I D	41			
			I D[a]	85			
61139-71-7	**1e**	136–137	I A	72	Benzene and ethyl acetate	149	$C_6H_7N_5$
61139-72-8	**1f**	215–216	I B	65	Benzene and ethanol	149	$C_6H_7N_5$
			I D	32			
			I B	62			
61139-73-9	**1g**	123–124	I C	38	Benzene and ethyl acetate	149	$C_6H_7N_5$
			I D	41			
			I D[a]	53			
61139-74-0	**1h**	173–174	I B	60	Benzene and ethyl acetate	163	$C_7H_9N_5$
			I D	54			
61139-75-1	**2a**	146–148	III A	25	Benzene and ethyl acetate	135	$C_5H_5N_5$
61139-76-2	**2b**	122–124	III A	31	Benzene and ethanol	149	$C_6H_7N_5$
61139-77-3	**2c**	86–87	III A	50	Benzene and *n*-hexane	163	$C_7H_9N_5$
			III B	75			
61139-78-4	**3a**	137–138	II B	45	Benzene and ethyl acetate	135	$C_5H_5N_5$
61139-79-5	**3b**	114–115	II B	42	Benzene and ethyl acetate	149	$C_6H_7N_5$
61139-80-8	**3c**	144–145	II B	48	Benzene and ethyl acetate	163	$C_7H_9N_5$
452-28-8	**4a**	176–177	II B	42	Benzene and ethyl acetate	121	$C_4H_5N_5$
61139-81-8	**4b**	189–190	II B	62	Benzene and ethyl acetate	135	$C_5H_5N_5$
61139-82-0	**4c**	80–81	II A	28	Benzene and ethanol	135	$C_5H_5N_5$
			II B	31			
61139-83-0	**4d**	169–170	II B	35	Benzene and ethyl acetate	149	$C_6H_7N_5$
61139-84-2	**4e**	148–149	II B	33	Benzene and ethanol	149	$C_6H_7N_5$
61139-85-3	**4f**	162–163	II B	37	Benzene and ethyl acetate	163	$C_7H_9N_5$
21119-72-2	**6a**	205 dec		85	Water	153	$C_4H_3N_5S$
61139-86-4	**6b**	225 dec		85	Water	167	$C_5H_5N_5S$
14742-98-4	**6c**	248–250		85	Water	167	$C_5H_5N_5S$
14894-20-3	**6d**	237–238		85	Water	181	$C_6H_7N_5S$
61139-87-5	**7a**	219–220		90	Benzene and ethyl acetate	164	$C_5H_5N_5S$
61139-88-6	**7b**	199–200		90	Benzene and ethanol	181	$C_6H_7N_5S$
25623-90-9	**7c**	171–172		90	Benzene and petroleum ether	181	$C_6H_7N_5S$
61139-89-7	**7d**	198–199		90	Benzene and ethyl acetate	195	$C_7H_9N_5S$
21119-77-7	**8a**	236–237		70	Water–ethanol	151	$C_4H_5N_7$
61139-90-0	**8b**	252–253		70	Water–ethanol	165	$C_5H_7N_7$
14742-99-5	**8c**	247–248		70	Methanol	165	$C_5H_7N_7$
14894-21-4	**8d**	242–243		70	Water–ethanol	179	$C_6H_9N_7H_2O$
61139-91-1	**16a**	72–75		51	Benzene and *n*-hexane	151	$C_6H_9N_5$
61139-92-2	**16b**	102–104		40	Benzene and *n*-hexane	165	$C_7H_{11}N_5$
61139-93-3	**16c**	94–95		92	Benzene and *n*-hexane	179	$C_8H_{13}N_5$
61139-94-4	**16d**	84–86		92	Benzene and *n*-hexane	193	$C_9H_{15}N_5$
61139-95-5	**17a**	161–162		31	Water and ethanol	139	$C_4H_5N_5O$
61139-96-6	**17b**	210–211		37	Water and ethanol	153	$C_5H_7N_5O$
61139-97-7	**17c**	226–227		78	Water and ethanol	167	$C_6H_9N_5O$
61139-98-8	**17d**	208–209		55	Water and ethanol	181	$C_7H_{11}N_5O$
61139-99-9	**18**	133–134		30	Benzene and *n*-hexane	165	$C_7H_{11}N_5$

[a] Satisfactory analytical data were obtained for all compounds listed.

allowed to stand for 2 h at room temperature (at −5 °C for glyoxal). Compound **3a** could be separated at this stage whereas **3b** was obtained after 16 h of refluxing. If, on the contrary, the solution was refluxed for at least 24 h the isomer **4** was obtained. After evaporation of the solvent the residue was dissolved in 50 ml of water and the solution neutralized with sodium bicarbonate. After extraction with chloroform the product was purified by column chromatography on alumina.

***s*-Triazolo[2,3-*b*]-*as*-triazines 2. A.** A solution of compound **15** (0.03 mol) and *N,N*-dimethylaminoformamide or -acetamide (0.03 mol) in 150 ml of toluene was refluxed for 4–6 h, then evaporated to dryness leaving the amidine **16.** To a solution of **16** (0.01 mol) and hydroxylamine hydrochloride (0.70 g) in 60 ml of methanol, 3 ml of methanolic sodium methoxide (0.5 M) was added and the resulting solution refluxed for 2 h. After cooling the amidoxime **17** was removed by filtration and crystallized. A hot solution of **17** (0.01 mol) in phosphorus oxychloride (4.5 ml) was refluxed for 10 min, cooled, poured on ice, and neutralized with aqueous sodium hydroxide (5 N). After extraction with chloroform and evaporation of the solvent, **2** was separated and chromatographed on a column of alumina (eluent chloroform).

Formamidoxine **17a** (0.5 g) was slowly added to 20 ml of polyphosphoric acid and the solution heated at 70 °C for 15 min. After cooling the mixture was poured on ice and the solution neutralized with sodium bicarbonate. 3-Formylamino-*as*-triazine was extracted with ethyl acetate and crystallized: mp 188–190 °C (from ethanol); yield 22%; mass spectrum M^+ *m/e* 124; NMR (Me_2SO-d_6) δ 8.61 (d, H_5), 9.15 (d, H_6), 9.36 (s, HCO), J_{H_5,H_6} = 2 Hz.

Anal. Calcd for $C_4H_4N_4O$: C, 38.71; H, 3.25; N, 45.15. Found: C, 38.68; H, 3.15; N, 44.98.

B. Aluminum chloride (1.33 g) was slowly added to a stirred mixture of **15c** (0.01 mol) and acetonitrile (0.7 g) at −5 °C. The mixture was then heated at 150 °C in a sealed tube for 1 h. Water (30 ml) was added and the resulting solution neutralized with sodium bicarbonate. The

acetamidine **18** was extracted with chloroform and after evaporation of the solvent the residue was chromatographed on a column of alumina (eluent benzene).

A stirred suspension of **18** (0.2 g) and lead tetraacetate (0.8 g) in 20 ml of anhydrous benzene was refluxed for 20 min. The hot solution was filtered and cooled and 20 ml of 30% aqueous sodium hydroxide was added. The product was extracted with chloroform, the solvent evaporated, and the separated compound **2c** purified by chromatography on alumina (eluent chloroform).

Acknowledgment. The authors wish to thank Professor M. Tisler for his comments and helpful discussions concerning the manuscript of this article.

Registry No.—**5a,** 874-40-8; **5b,** 875-84-3; **5c,** 19542-10-0; **5d,** 877-27-0; **9** (R = H), 23160-99-8; **9** (R = Me), 54557-76-5; **10a,** 28735-23-1; **10b,** 28735-26-4; **10c,** 19542-09-7; **11,** 61140-00-9; **12,** 61140-01-0; **13,** 61140-02-1; **13** HCl, 61140-03-2; **14a** HCl, 21126-64-7; **15a,** 1120-99-6; **15b,** 18915-36-1; **15c,** 17584-12-2; phosphorus pentasulfide, 1314-80-3; 3,7-dimethyl-7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazine, 61140-04-3; 6,7-dimethyl-7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazine, 61140-05-4; ethanedial, 107-22-2; 2-oxopropanal, 78-98-8; 2,3-butanedione, 431-03-8; 3-chloro-*s*-triazolo, 6818-99-1; chloroacetone, 78-95-5; *N,N*-dimethylformamide, 68-12-1; acetamide, 60-35-5; 3-formylamino-*as*-triazine, 61140-06-5.

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Phosphorus-Containing Cyclohexanes. Stereochemical Analysis of *cis*- and *trans*-2-Phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes

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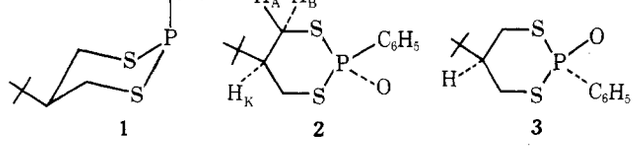
Received September 3, 1976

Assignments of configuration to *cis*- and *trans*-2-phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes (**2** and **3**) were accomplished through analysis of ^{1}H NMR spectral data and an LIS study with Eu(fod)$_3$. Cis diastereomer **2** was found to be conformationally heterogeneous with a considerable contribution made to the conformational equilibrium by the twist-boat conformer **4c**; the other major conformer was the chair structure with equatorial *tert*-butyl and axial phenyl groups. Complexation of **2** with Eu(fod)$_3$ had no significant influence on the conformational distribution. Trans diastereomer **3** adopted essentially one chair conformation with equatorial *tert*-butyl and phenyl substituents.

Although substituents attached to carbon or nitrogen atoms in saturated six-membered rings usually prefer an equatorial orientation, the same groups display this tendency to a much weaker degree when attached to other atoms such as sulfur,[1] phosphorus,[2-4] selenium,[5a] and arsenic;[5b] in fact, axial preferences are often encountered. This conformational novelty has stimulated much interest and study,[6] especially with regard to diverse phosphorus-containing cyclohexane systems.[2-4,7]

Previously, we reported[4a] that the more stable isomer (85% at 200 °C; ca. 97% at 25 °C) of 2-phenyl-5-*tert*-butyl-1,3,2-dithiaphosphorinane (**1**) possesses a cis configuration with the *P*-phenyl group axially disposed. In order to further support the stereochemical assignment, we converted **1** stereospecifically to cis 2-oxo derivative **2** and synthesized the trans diastereomer **3** for comparison. Stereochemical information on these compounds was obtained by ^{1}H NMR spectroscopy and ^{1}H NMR lanthanide-induced shift (LIS) studies. Our results, which yielded configurational assignments for **2** and **3,** as well as an analysis of their conformational behavior, are presented in this article.



1 2 3

Results and Discussion

Oxidation of **1** with hydrogen peroxide[8] (presumably stereospecific with retention[9]) afforded a single diastereomer (mp 105–106 °C); there was no evidence for the presence of the other possible isomer. Spectral and analytical data were consistent with **2.** The 100-MHz ^{1}H NMR spectrum of **2** exhibited a complex AA'BB'KX (X = ^{31}P) pattern which was treated as an A_2B_2KX approximation[10] to provide the parameters presented in Table I.[11] The nearly identical, middling values of J_{AK} and J_{BK} (e.g., 7.2 and 5.9 Hz) suggest that **2** is a mixture of conformational isomers in solution ($CDCl_3$ and C_6D_6); the axial and equatorial orientations of H_A, H_B, and H_K are interchanged, thereby averaging the ^{1}H NMR spectral parameters. This observation can be accommodated by a mixture of chair conformers (**4a** and **4b**), a twist-boat form (**4c**), or an equilibrium mixture of chair and boat forms.