fluoride, 7783-39-3; perfluoro-2,2-bis[2-(2,3-dichloropropyl)-4-propyltriazene]diisopropylmercury, 10408-00-1; silver difluoride, 7783-95-1.

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Studies on the Diazo-β-azomethine–v-triazine Equilibrium[1,2]

CARROLL TEMPLE, JR., C. L. KUSSNER, AND JOHN A. MONTGOMERY

Kettering-Meyer Laboratory, Southern Research Institute, Birmingham, Alabama 35205

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The nitrosation of some 3-[5- (or 4-) aminoimidazol-4- (or 5-) yl]-s-triazoles and 5-[5- (or 4-) aminoimidazol-4- (or 5-) yl]tetrazoles is described. The resulting diazoimidazole–v-triazine systems are used to study the effect of solvent and certain groups on the diazo-β-azomethine–v-triazine equilibrium. Structure assignments are based on data obtained from the infrared and proton magnetic resonance spectra.

The nitrosation of 5- (or 4-) aminoimidazole-4- (or 5-) carboxamide provided 5-diazoimidazole-4-carboxamide, which was readily converted to imidazo[4,5-*d*]-*v*-triazin-4(3H)-one (2-azahypoxanthine).[3a] Similarly 4-aminoimidazo[4,5-*d*]-*v*-triazine (2-azaadenine) was obtained directly from 5- (or 4-) aminoimidazole-4- (or 5-) carboxamidine.[4] Although other condensed *v*-triazines behave as the corresponding diazo isomers on reaction with nucleophiles,[5] the conversion of an imidazo[4,5-*d*]-*v*-triazine to a diazoimidazole is unreported.[6] In this paper the preparation of some diazoimidazole–*v*-triazine systems, and the effect of solvent and certain groups on the diazo-β-azomethine–*v*-triazine equilibrium is described.

6-(1-Benzylhydrazino)purine (**1**), prepared from 6-chloropurine and benzylhydrazine, was treated with diethoxymethyl acetate to give a mixture of **2** and **3** that was resolved. The latter (**3**) results from opening of the pyrimidine ring of **2** during the reaction.[7a] Treatment of either **2** or **3** with 11% methanolic hydrogen chloride provided the aminoimidazole **4**. Similarly, treatment of 9-benzyl-6-hydrazinopurine with phosgene resulted in cyclization and opening of the pyrimidine ring to give directly 5-(5-amino-1-benzylimidazol-4-yl)-*s*-triazol-3-ol (**12**). The preparation of the remaining aminoimidazoles (**5**, **10**, **11**, **14**, **15**, and **16**) has been reported.[7] The nitrosation reaction was carried out by the addition of sodium nitrite to a solution of the aminoimidazole in hydrochloric acid with the exception of **5**, which gave unidentified products by this method. A pure product was obtained, however, by the addition of the dihydrochloride of **5** to a solution of sodium nitrite. Although system **17** was prepared successfully on a small scale, the dried product from a large run exploded violently (see the Experimental Section). The properties of the new compounds are summarized in Table I.

Results and Discussion

The structure assignments, based on the infrared and proton magnetic resonance (pmr) spectra of solutions of the diazoimidazole–*v*-triazine systems, are presented in Table II. In the nitrosation of **5** two crops with identical ultraviolet spectra but different infrared spectra were obtained. In the first crop the presence of a strong diazo band at 2170 cm^{-1} and of only weak bands in the 1700–1500-cm^{-1} region of the infrared spectrum indicated that this material was mainly 3-[5- (or 4-) diazoimidazol-4- (or 5-) yl]-*s*-triazole (**6a**) (see Scheme I).[8] In contrast, the infrared spectrum of the second solid exhibited bands at 2145, 1670, and 1640 cm^{-1} indicating that this material was a mixture of **6a** and an isomeric *v*-triazine form, either **6b** or **6c**. The greater nucleophilicity of N-1 over N-4 of the *s*-triazole ring has been demonstrated by the cyclization of **5** with formamide to give *s*-triazolo[5,1-*i*]purine.[7] The cyclization to N-1 rather than N-4 has also been observed in other *s*-triazolo compounds.[9] Thus, the cyclization of **6a** should give mainly **6c** rather than **6b**. Additional evidence that ring closure to N-1 is favored over N-4 is provided by the preparation of **7a** (see below).

No significant change occurred in the solid-state infrared spectral of the two crops described above over a period of 2 months. Both solids, however, coupled with 2-naphthol in glacial acetic acid to give good yields of the same naphthylazoimidazole (*via* **6a**). In contrast, the infrared spectrum of the sodium salt of **6** was transparent in the diazo absorption region, and showed bands at 1685 and 1640 cm^{-1}, indicating that this solid exists as the sodium salt of **6c**. Furthermore, neutralization of an aqueous solution of the salt deposited a mixture containing mainly **6a**.

In a trifluoroacetic acid (CF_3COOH) solution of **6** only one form was detected by the pmr spectrum. That this form is the diazo compound **6a** (protonated) was established by the presence of a strong diazo band at 2235 cm^{-1} in the infrared spectrum of the solution

(1) This investigation was supported by funds from the C. F. Kettering Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Contract No. PH43-64-51.

(2) A preliminary report of part of this work has appeared: C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *Chem. Ind.* (London), 2197 (1966).

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(7) (a) C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *J. Org. Chem.*, **30**, 3601 (1965); (b) C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *J. Org. Chem.*, **31**, 2210 (1966).

(8) Only representative NH tautomers of **6**, **9**, and **15** are shown. In addition, numerous resonance structures can be written for the diazoimidazoles, but for convenience the negative charge is depicted as being localized in the imidazole ring of **6a** and **7a**, and in the triazole or tetrazole ring of **8a**, **9a**, **13a**, **17a**, **18a**, and **19a**.

(9) (a) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. Van Allen, *J. Org. Chem.*, **24**, 787 (1959); (b) G. W. Miller and F. L. Rose, *J. Chem. Soc.*, 5642 (1963).

TABLE I

Compd	Yield, %	Mp, °C (recrystn solv)[a]	Ultraviolet absorption spectra at pH 1 (λ_{max}), mμ ($\epsilon \times 10^{-3}$)	Infrared absorption spectra, selected bands, cm^{-1}	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1	38[b]	183–185 dec[c] (A)	284 (20.0)	1665, 1600, 1545, 1515	$C_{14}H_{18}N_6O$[b]	58.73	6.33		58.58	6.15	
					$C_{12}H_{12}N_6$	59.98	5.03	34.98	60.16	4.92	35.10
2	67[d]	245–247 dec[c] (B)	245 (6.77), 303 (3.86)	1680, 1650, 1615, 1590	$C_{13}H_{10}N_6$	62.38	4.03	33.59	61.90	4.61	33.50
3	15	225–227 dec[e]	269 (14.0)	1660, 1550, 1495	$C_{13}H_{12}N_6O$	58.20	4.50	31.33	58.20	4.24	30.87
4	80,[f] 65[g]	193–194	257 (7.06)	1620, 1590, 1560, 1490	$C_{12}H_{12}N_6$	59.98	5.03	34.98	59.92	5.06	34.87
6	67	260–270 exptl	251 (3.47), 314 (6.66)[h]	2170, 1440, 1365, 1305[i]	$C_6H_5N_7$	37.27	1.86	60.87	37.05	2.05	60.87
				2145, 1670, 1640, 1320[j]					36.91	2.09	60.63
			251 (3.57), 313 (6.75)[k]	1670, 1640, 1540, 1515	$C_7H_9N_7OS$[k]	35.15	3.77	41.00	35.07	3.76	40.97
			252 (3.61), 314 (7.15)[l]	1685, 1640, 1500	$C_6H_4N_7O \cdot Na$[m]	29.86	2.01	48.75	30.03	2.06	49.68
7	77	123–124 dec (C)	285 (4.90), 327 (8.56)	2170, 1600, 1580, 1490	$C_{12}H_9N_7$	57.40	3.58	39.00	57.41	3.67	39.28
8	85	170–173 dec (D)	225 (25.5), 285 (5.07)	1640, 1530, 1490	$C_{12}H_9N_7$	57.40	3.58	39.00	57.47	3.85	39.45
9	83	>260 exptl (E)	287 (4.82), 327 (3.69)	1670, 1630, 1570, 1520	$C_{12}H_9N_7O$	53.95	3.37	36.70	53.89	3.43	36.94
12	71	>260 (A)	269 (12.3)	1695, 1650, 1620, 1595	$C_{12}H_{13}ClN_6O$[n]	49.20	4.45	28.70	49.06	4.65	28.31
					$C_{12}H_{12}N_6O$	56.25	4.68	32.80	56.06	4.42	32.67
13	96	120–122[o] (D)	257 (4.72), 304 (4.34)	1680, 1530, 1500	$C_{12}H_9N_7$	57.40	3.58	39.00	57.30	3.79	38.83
17	80	220–225 exptl (F)	245 (4.22), 320 (8.81)	2205, 2160, 1615, 1510	$C_4H_2N_8$	29.65	1.24	69.10	29.72	1.22	68.81
18	74	>147 exptl (D)	232 (16.6), 308 (5.58)	1635, 1605, 1520, 1500	$C_{11}H_8N_8$	52.40	3.17	44.40	52.60	3.62	44.05
19	58	>160 exptl (D)	255 (5.50), 321 (7.32)	2215, 1590, 1515, 1500	$C_{11}H_8N_8$	52.40	3.17	44.40	52.11	3.06	44.86

[a] A, ethanol; B, ethyl acetate–petroleum ether (bp 85–105°); C, triturated with ether; D, tetrahydrofuran–petroleum ether; E, N,N-dimethylformamide–water; F, dioxane–petroleum ether. [b] Ethanolate. [c] Presoftening. [d] Crude yield. [e] Taken from 200°. [f] Prepared from **3**. [g] Prepared from **2**. [h] Solvent contains 0.8% dimethyl sulfoxide, 9.2% ethanol, and 90% 0.1 *N* HCl. [i] First crop. [j] Second crop. [k] 1:1 dimethyl sulfoxide complex. Calcd for S: 13.40. Found for S: 13.46. [l] Dissolved in water. [m] Sodium salt monohydrate. [n] Hydrochloride. Calcd for Cl: 12.12. Found for Cl: 12.00. [o] Solidified and remelted at 148–149° dec.

TABLE II

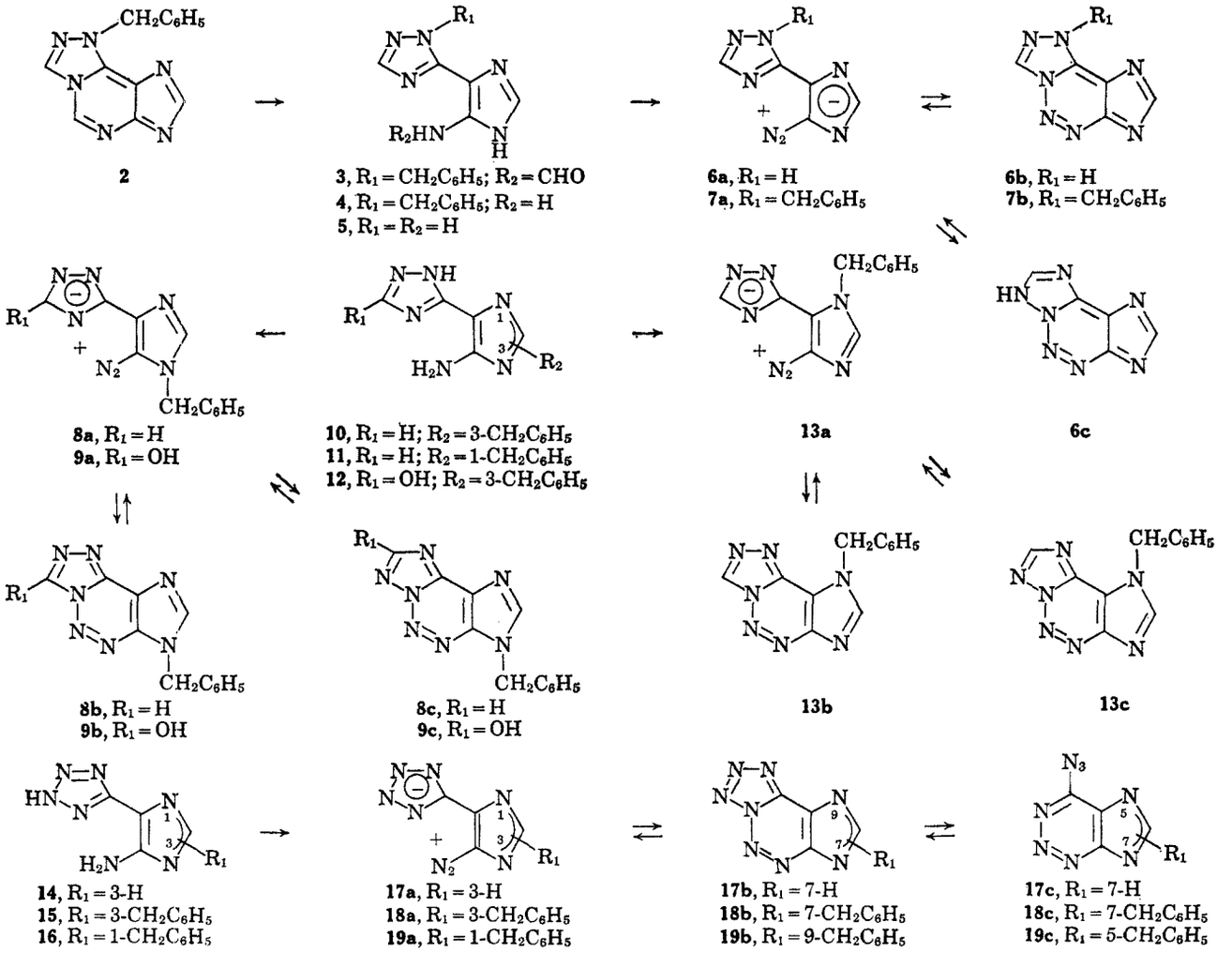
INFRARED AND PMR SPECTRAL ASSIGNMENTS

System	Solvent[a]	Concn, % (w/v)	σ (cm^{-1})[b]	Chemical shift (τ), ppm: *v*-Triazine CH	*v*-Triazine C_6H_5	*v*-Triazine CH_2	Diazoimidazole CH	Diazoimidazole C_6H_5	Diazoimidazole CH_2
6	A	5	...[c]	1.13, 1.18					
	B	10		1.00, 1.18					
	C	10	2235				0.97, 1.70		
	5A + 1C	4.2		1.19, 1.25			1.08, 1.72		
	5A + 2C	3.6		1.25, 1.32			1.15, 1.73		
	5A + 3C[d]	3.1		1.33, 1.37			1.23, 1.82		
	5A + 4C	2.8		1.35, 1.37			1.30, 1.89		
	1A + 1C	2.5					1.35, 1.95		
	D	<4	...[c]	1.31, 1.31					
7	A	10	2160				1.77, 2.22	2.67	3.98
	C	10	...[c]	1.41, 1.68	2.63	4.09			
	E	10	2165				1.88, 2.20	2.69	3.98
8	A	<10	...[c]	0.92, 1.17	2.62	4.15			
	C	10	2200				0.67, 1.27	2.42	4.12
	1A + 1C	10		1.24, 1.37	2.61	4.16			
	E	<10	...[c]	1.20, 1.33	2.73	4.20			
9	A	10	...[c]	0.97	2.58	4.20			
	C	10	2185				1.47	2.37	4.20
13	A	10	...[c]	0.98, 1.13	2.53	4.15			
	C	10	2230				1.22, 2.05	2.55	4.00
	1A + 1C[e]	10		1.31, 1.38	2.60	4.16	1.25, 1.64	2.60	3.92
	E	<10	...[c]	1.27, 1.36	2.63	4.13			
17	A	10	2165				2.12		
	C	10	2245				1.63 (2.85)		
	1A + 1C	9					1.80		
18	A	10	...[c]	0.73	2.57	4.07			
	C	10	2200				1.23	2.35	4.10
19	A	10	2218				1.14	2.58	4.00
	C	10	2235				1.90	2.52	3.95
	E	10	2210				1.87	2.69	4.07

[a] A, dimethyl sulfoxide-d_6; B, N,N-dimethylformamide; C, trifluoroacetic acid; D, methoxyethanol; E, acetic acid. [b] Wavenumber of the infrared absorption band assigned to the diazo group. [c] No diazo band detected. [d] K [**6a**]/[**6b**] = 0.83. [e] K [**13a**]/[**13b**] = 0.32.

(see Table II). In contrast only one *v*-triazine form, **6c**, was found in either dimethyl sulfoxide-d^6 (DMSO-d_6) or 2-methoxyethanol solutions of **6**. In both of these solutions none of the diazo form was detected by the pmr spectra when the temperature was increased to about 95°. After the addition of CF_3COOH to the DMSO-d_6 solution, however, both the diazo and *v*-triazine forms of **6** could be observed by the pmr spectrum. Furthermore, addition of the acid in increments showed a corresponding increase in the amount of the diazo form, which was the only form observed when the ratio of DMSO-d_6 to CF_3COOH was 1:1. Also the mobile nature of this equilibrium was demonstrated by the reaction of 2-naphthol with a DMSO solution of

SCHEME I



6 to give the corresponding naphthylazoimidazole. A second product was obtained from this reaction that analyzed for a 1:1 complex between DMSO and the *v*-triazine **6c**. The latter was indicated by the presence of bands at 1670 and 1640 cm^{-1}, and the absence of diazo absorption bands in the infrared spectrum.

The diazoimidazole (**7a**), resulting from the nitrosation of 2-benzyl-3-[5- (or 4-) aminoimidazol-4 (or 5-) yl]-*s*-triazole (**4**), can undergo cyclization to N-4 of the *s*-triazole ring to give **7b**, but cyclization to N-1 is blocked by the benzyl group. Although the benzyl group could result in stabilization of the *v*-triazine **7b** (see below), the infrared spectrum of the isolated product indicated that the diazoimidazole **7a** was the major isomer present. In addition **7a** was the only isomer detected by the infrared and pmr spectra of either a DMSO-d_6 or acetic acid (CH_3COOH) solution of **7**. These data indicate that cyclization to N-4 of the *s*-triazole ring is highly unfavorable, supporting the assignment of the structure **6c** rather then **6b** to the cyclization product from **6a**. Unexpectedly, only the *v*-triazine from **7b** (protonated) was detected in a CF_3COOH solution of **7**. The difference in structure of **6** and **7** in this medium could be due to a change in the major site of protonation. Apparently, protonation of the *s*-triazole ring of **6** results in diazoimidazole stabilization, whereas protonation of the imidazole ring of **7** results in *v*-triazine stabilization.

The nitrosation of the amino-N-benzylimidazoles **10**, **11**, and **12**, respectively, gave mainly the *v*-triazines **8c**, **13c**, and **9c**, identified by the absence of diazo absorption in the solid-state infrared spectra. Similarly only the *v*-triazine form of these compounds was detected in DMSO-d_6, 1:1 DMSO-d_6–CF_3COOH, and CH_3COOH solutions. The stability of the *v*-triazine form is attributed to the electron release of the N-benzyl group. In CF_3COOH, however, only the diazoimidazoles (protonated) **8a**, **9a**, and **13a** were observed. The reaction of **9** and **13** with 2-naphthol in CH_3COOH provided the corresponding naphthylazoimidazoles. The coupling of **8** with 2-naphthol in this medium was unsuccessful; however, this reaction was successful in CF_3COOH.

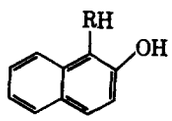
Next, the products from the nitrosation of the aminoimidazoles **14**, **15**, and **16** were examined. These systems contain a tetrazole ring, and ring closure of the diazoimidazole can give only one *v*-triazine form (see Scheme I).[8] In this form, however, either the *v*-triazine ring can reopen to give a diazoimidazole or the tetrazole ring can open to give a 4-azidoimidazol[4,5-*d*]-*v*-triazine (6-azido-2-azapurine). The solid-state infrared spectrum of **17** exhibited bands at 2205 and 2160 cm^{-1}, which could be due either to a doublet of the diazo absorption band of **17a** or to a mixture of the diazo **17a** and azido **17c** isomers. The reaction of **17** with 2-naphthol in CH_3COOH and in DMSO provided

the same naphthylazoimidazole. In addition only the diazoimidazole **17c** was detected in either DMSO-d_6 or 1:1 DMSO-d_6–CF_3COOH solutions of **17**. In the former solvent the assignment of structure is based on the presence of a diazo absorption band at 2245 cm^{-1} in the infrared spectrum of the solution. The pmr spectrum of a CF_3COOH solution of **17**, however, showed two imidazole CH peaks. The low-field peak (τ 1.63, 80%) is consistent with the diazoimidazole **17a**, but the material associated with the high-field peak (τ 2.85, 20%) is unidentified. Although the latter may be due to **17c**, the position of the CH peak is higher than that observed in 6-azidopurines.[7b] The recovery of **17** from a CF_3COOH solution showed that decomposition had not occurred.

Similarly, **19** existed mainly as the diazoimidazole **19a** in the solid state and in DMSO-d_6, CH_3COOH, and CF_3COOH solutions. Compound **18** was found to exist mainly as the *v*-triazine **18b** in the solid state and in a DMSO-d_6 solution, and as the diazoimidazole **18a** in trifluoroacetic acid.

TABLE III

VISIBLE SPECTRA OF (NAPHTHYLAZO)IMIDAZOLES[a]



R	λ_{max}, mμ 0.1 *N* HCl	pH 7	0.1 *N* NaOH
...[b]	474		508
6a	476	...[c]	493
8a	487	...[c]	523
9a	549	545	534
13a	...[c]	...[c]	497
17a	...[c]	467	492
18a	...[c]	467	512
19a	...[c]	467	503

[a] Naphthyl derivatives of **6a**, **8a**, **9a**, and **13a** were dissolved in 8% methanolic dimethyl sulfoxide, and of **17a**, **18a**, **19a** in a minimum amount of 0.1 *N* NaOH. The resulting solutions were then diluted with the appropriate solvent to give a concentration of 10–15 mg/l. [b] Naphthyl derivative of 5-diazoimidazole-4-carboxamide. See ref 3b. [c] These curves showed broad peaks with multiple shoulders.

Experimental Section

The ultraviolet spectra were determined with a Cary Model 14 recording spectrophotometer; the solid-state infrared spectra were determined in pressed potassium bromide disks with a Perkin-Elmer Model 521 spectrophotometer. The infrared spectra of solutions were run in fixed-thickness cells equipped with windows of Irtran-2 for solutions in dimethyl sulfoxide or trifluoroacetic acid, and with windows of silver chloride for solutions in acetic acid. The pmr spectra were obtained on Varian A-60 or A-60A spectrometers, using tetramethylsilane as an internal reference. Probe temperature was about 40°. The melting points were determined on a Kofler Heizbank apparatus and are corrected. The yields and properties of the products are summarized in Table I.

6-(1-Benzylhydrazino)purine (1).—A solution of 6-chloropurine (2.0 g) in ethanol (40 ml) containing benzylhydrazine dihydrochloride (2.6 g) and triethylamine (4 ml) was refluxed for 4 hr and evaporated to dryness *in vacuo*, and the resulting residue was dissolved in hot water (100 ml). After filtration the warm filtrate deposited a small amount of oil, which was separated by decantation. The solution was then cooled to deposit a yellow solid, which was recrystallized from ethanol to give the ethanolate of **1**. A 25-mg sample was dried *in vacuo* over P_2O_5 at 78° to give the anhydrous compound. See Table I.

1-Benzyl-*s*-triazolo[3,4-*i*]purine (2) and N-[5- (or 4-) (1-Benzyl-*s*-triazol-5-yl)imidazol-4- (or 5-) yl]formamide (3).—A solution of **1** (4.0 g) in diethoxymethyl acetate (25 ml) was stirred at room temperature for 20 hr. Compound **3** deposited from the reaction, and was collected by filtration and dried *in vacuo* over P_2O_5 at 78° for 7 hr (see Table I).

The filtrate was evaporated to dryness *in vacuo*, and the resulting solid was washed with petroleum ether and dried *in vacuo* over P_2O_5 to give crude **2**, yield 2.8 g (67%). A portion of this sample was recrystallized from ethyl acetate–petroleum ether (bp 80–105°) then dried *in vacuo* over P_2O_5 at 110° for 4 hr to give pure **2** (see Table I).

2-Benzyl-3-[5- (or 4-)aminoimidazol-4- (or 5-) yl]-*s*-triazole (4).—A solution of **3** (188 mg) in 11% methanolic hydrogen chloride (10 ml) was stirred at room temperature for 18 hr, and evaporated to dryness *in vacuo*. The resulting residue was dissolved in H_2O, and the solution was neutralized with 1 *N* ammonium hydroxide. The solid of **4** that deposited was collected by filtration and dried *in vacuo* over P_2O_5 at 78° for 2 hr. A similar treatment of **2** also provided **4** (see Table I).

Preparation of System 6.—A solution of sodium nitrite (23.4 g) in water (625 ml) containing 1.1 *N* HCl (100 ml) was cooled in an ice bath, and a solution of the dihydrochloride of **5** (25.0 g) in H_2O (500 ml) was added in a steady stream with stirring. The ice bath was removed and after 10 min the dark material (0.6 g) that deposited from the reaction mixture was removed by filtration. The clear, yellow filtrate was again cooled in an ice bath, and solid sodium nitrite (16.0 g) was added. The ice bath was removed and the mixture was allowed to stand at room temperature for 30 min. The solid that deposited was collected by filtration, washed with cold water, and dried *in vacuo* over P_2O_5 to give 1.7 g of **6**. The stoppered filtrate was refrigerated at 5° for 18 hr and the second crop that deposited was collected by filtration, washed with water, and dried *in vacuo* over P_2O_5 at 56° for 18 hr to give 10.5 g of **6** (see Table I).

A solution of **6** (500 mg) in 1 *N* NaOH (3.0 ml) was stirred at room temperature for 2.5 hr, and the solid (90 mg) that deposited was removed by filtration. One-half of the filtrate was neutralized with 1 *N* HCl. After standing for 18 hr the solution deposited 195 mg of **6**. The other half of the filtrate was evaporated to dryness under reduced pressure, and the resulting residue was dried *in vacuo* over P_2O_5 at 78° to give 215 mg of the sodium salt monohydrate of **6** (see Table I).

General Procedure for the Nitrosation of Aminoimidazoles.—A mixture of the aminoimidazole (2.1 mmoles) and 1.1 *N* HCl (2.0 ml) in water (10 ml) was cooled in an ice bath, and sodium nitrite (3.0 mmoles) was added with stirring. After 1 hr the ice bath was removed, and the mixture was stirred at room temperature. Compounds **13**, **18**, and **19** were collected by filtration after 4 hr, and compounds **7**, **8**, and **9** after 20 hr (see Table I).

5-(5-Amino-1-benzylimidazol-4-yl)-*s*-triazol-3-ol (12).—Phosgene gas was passed into a suspension of 9-benzyl-6-hydrazino-9H-purine (2.0 g) in water (35 ml) containing concentrated hydrochloric acid (0.8 ml) for 1.5 hr. Next, nitrogen was bubbled through the mixture for 1.5 hr. The solid was collected by filtration and recrystallized from ethanol to give 1.5 g of the hydrochloride of **12** in two crops. From the aqueous filtrate an additional 240 mg of the hydrochloride was obtained. Neutralization of a solution of the hydrochloride (655 mg) in 1 *N* sodium hydroxide with 1 *N* hydrochloric acid deposited the free base (510 mg) of **12** (see Table I).

Preparation of System 17.—*Caution: When the transfer of the dried reaction product from 5.0 g of the aminoimidazole was attempted, a very loud explosion occurred. The operator received numerous cuts and suffered from impaired hearing for several months.* A suspension of **14** (350 mg) in water (8 ml) containing 1.1 *N* hydrochloric acid (2.2 ml) was cooled in an ice bath, and sodium nitrite (220 mg) was added with stirring. After 30 min the ice bath was removed and after 4 hr the solid was collected by filtration, washed with water (5 ml) and ethanol (10 ml), and dried *in vacuo* over P_2O_5 to give 300 mg of **17** (see Table I).

Preparation of Naphthylazoimidazoles.—Each of the systems (0.5 g) was added with stirring to a solution of 2-naphthol (2 g) in glacial acetic acid (100 ml). To obtain coupling with **8**, trifluoroacetic acid rather than acetic acid was used as the solvent. After 18 hr at room temperature the naphthylazoimidazoles of **6**, **9**, **13**, **17**, **18**, and **19** were collected by filtration, washed with

ether, and dried *in vacuo* over P_2O_5. The azo derivative of **8** was isolated by evaporation of the trifluoroacetic acid solution, and washing of the resulting residue with ethanol and ether. In addition, **6** and **17** coupled with 2-naphthol in dimethyl sulfoxide to provide the azo derivative. In the reaction of **6** a precipitate was isolated that analyzed for a 1:1 complex of **6** and dimethyl sulfoxide (see Table I). All the azo derivatives were identified by the absence of a diazo absorption band in the infrared spectra, and the presence of a band near 500 mμ in the visible spectra (see Table III).

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meso Ionic Compounds. II. Derivatives of the *s*-Triazole Series

K. T. POTTS,[1] S. K. ROY, AND D. P. JONES

Departments of Chemistry, University of Louisville, Louisville, Kentucky 40208 and Rensselear Polytechnic Institute, Troy, New York 12181

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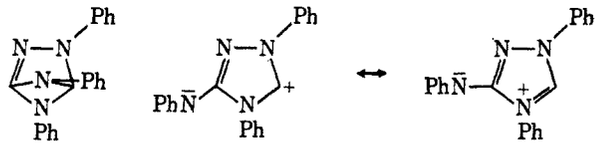
Further examples of *meso* ionic compounds containing the *s*-triazole nucleus are reported and exceptions to the cyclization procedures leading to these products are noted. These *meso* ionic compounds do not take part in 1,3-dipolar addition reactions. Convenient routes to *s*-triazolium salts are also described.

In studies of the chemistry of the *s*-triazole ring system,[2] our attention was drawn to a series of products to which unlikely structures had been assigned in the early literature. In an earlier, preliminary communication,[1c] we showed that some of these products were best regarded as *meso* ionic compounds, of which the most often quoted example is the sydnone system,[3] and we now describe further examples of these products as well as exceptions to the cyclization procedures used in their synthesis. Related ring closures leading to *s*-triazolium salts are also described.

On the basis of dipole moment data, Schonberg[4a] and Warren[4b] suggested that the bridged-ring *endo*-triazolines obtained by Busch and co-workers[5] did not exist as such but rather as zwitterions. Thus the large dipole moment (7.2 D.) of the nitric acid precipitant "nitron" (**1**) suggested a zwitterion structure, of which **2** and **3** are two possible canonical forms.



1 **2** **3**

In an early review of the sydnones, Baker and Ollis[6] suggested that these *endo*-triazolines were analogous to the sydnones and that they could be represented as *meso* ionic compounds. Our earlier work established the *meso* ionic nature of these products and showed that they belonged to the *s*-triazole system and not the alternative, isomeric 1,3,4-oxadiazole or thiadiazole ring systems. The correct skeletal arrangement of the atoms was shown by the synthesis of many of these products using ring closures at different portions of the molecule in such a way that skeletal rearrangements were precluded. This was found to be true in all cases except one, and the detailed experimental study needed to establish the behavior of this particular reaction system is described in detail below. The ring systems were also degraded to products that confirmed the assigned structures.

This was illustrated by the synthesis, among others, of *anhydro*-5-hydroxy-2,3,4-triphenyl-*s*-triazolium hydroxide (**6**, $R_1 = R_2 = R_3 = Ph$; X = O), originally represented as 2,3,4-triphenyl-3,4-endoxytriazoline (**4**, $R_1 = R_2 = R_3 = Ph$) by the action of phosgene on N-amino-N,N′-diphenylbenzamidine (**5**, $R_1 = R_2 = R_3 = Ph$), and also by the ring closure of 1-benzoyl-1,4-diphenylsemicarbazide (**7**, $R_1 = R_2 = R_3 = Ph$; X = O) with sodium ethoxide. The latter cyclization could not be effected with acidic cyclodehydration agents or by heat; with acetic acid–acetic anhydride the product isolated was shown to be 1-benzoyl-2,2-diacetyl-1-phenylhydrazine. This structure was confirmed by its synthesis using standard procedures and the formation of this product can be readily attributed to thermal decomposition of 1-benzoyl-1-phenylthiosemicarbazide to 1-benzoyl-1-phenylhydrazine followed by acetylation with acetic anhydride. The corresponding cyclization of 1-benzoyl-1,4-diphenylthiosemicarbazide (**7**, $R_1 = R_2 = R_3 = Ph$; X = S) to the analogous *anhydro*-5-mercapto-2,3,4-triphenyl-*s*-triazolium hydroxide (**6**, $R_1 = R_2 = R_3 = Ph$; X = S) occurred with such great ease that the intermediate benzoyl compound was not isolated on treatment of 1,4-diphenylthiosemicarbazide with benzoyl chloride. The formation of this *meso* ionic compound by the action of thiophosgene on N-amino-N,N′-diphenylbenzamidine was also an extremely facile reaction. These ready cyclizations were characteristic of the sul-

(1) (a) 1,2,4-Triazoles. XVII. (b) Support of this work by the U. S. Atomic Energy Commission, Contract AT-(40-1)-3016, is gratefully acknowledged. (c) Presented in part as a preliminary communication: K. T. Potts, S. K. Roy, and D. P. Jones, *J. Heterocyclic Chem.*, **2**, 105 (1965).

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(3) For recent reviews, see F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964); Y. Noel, *Bull. Soc. Chim. France*, 173 (1964).

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