TABLE IV

SPECTROSCOPIC DATA FOR REDUCTION PRODUCTS OF HARMAN DERIVATIVES

Compd	uv (mμ) in CH_3OH	δ (ppm), J in Hz[a]
4a[c]	224(ε28,400), 269(5500), 298(5800), 330(1300)	7.95(J = 5), 7.20(J = 5) ortho on pyridine ring; 5.00(m) vinyl; 4.14(4,m) aliphatic[b]
4b[c]	231(ε24,600), 265(4100), 302(5500), 335(1100)	8.10(J = 5), 7.17(J = 5) ortho on pyridine ring; 4.95(m) vinyl; 3.16(4,m) aliphatic
4c[c]	224(ε25,400), 272(5800), 296(6200), 330(1100)	8.02(J = 6), 7.20(J = 6) ortho on pyridine ring; 4.91(m) vinyl; 3.41(4,m) aliphatic[b]
4d[c]	230(ε17,800), 268(4000), 304(3300), 335(2200)	7.92(J = 6), 7.10(J = 6) ortho on pyridine ring; 4.97(m) vinyl; 3.20(4,m) aliphatic
5a	226(ε24,600), 272(5200), 300(5600), 331(1700)	7.90(J = 5), 7.11(J = 5) ortho on pyridine ring; 2.85(2,m), 2.01(2,m,) aliphatic[b]
6[c]	212(ε13,000), 265(5900), 310(2640)	7.97(J = 5), 6.93(J = 5) ortho on pyridine ring; 4.62(m) vinyl; 3.25(3), 2.12(3) aliphatic
7b	212(ε28,900), 250(7400), 300(4600)	6.90, 6.28, 6.18 aromatic; 2.78(5,m) aliphatic; 1.37(3,J = 7) $CHCH_3$
8[c]	210(ε14,800), 257(6300), 302(3000)	8.08(J = 5), 6.97(J = 5) ortho on pyridine ring; 4.72(m) vinyl; 2.43(4,m) aliphatic
10a[c]	Tailing 200–250	5.06(m) vinyl; no aromatic
10b[c]	Tailing 200–250	5.08(m) vinyl; no aromatic

[a] Me groups, NH's, and picrate absorption omitted. Spectrum in $CDCl_3$ unless otherwise noted. [b] Determined in DMSO-d_6 [c] The ir spectrum showed a sharp peak at 6.0 μ (KBr) due to the vinyl ether group.

was taken up in water and CH_2Cl_2. The org layer was resolved by liquid–liquid partition chromatography on diatomaceous earth with a heptane–methyl cellosolve solvent system. A ratio of 1:5 lower phase:diatomaceous earth was used and the recording spectrophotometer was set at 250 mμ. Concn of eluate from the second major peak (0.5 hold-back volume) afforded **12** as a colorless oil, which was unstable to air and heat, but could be stored for at least a month under N_2 at 5°. It had uv max 250 mμ (ε 5650), 290 (2820) sh, 340 (705); nmr δ 7.10 (m, 4, arom), 5.84 (broadened apparent s, 2, vinyl) ppm. Isomeric nonconjugated diene structures are ruled out for **12** because they would require 3 vinyl protons. *Anal.* ($C_{19}H_{26}N_2$): C, H, N.

Acknowledgment.—We wish to thank Mr. L. Brancone and staff for microanalyses, Mr. W. Fulmor and staff for spectra, and Mr. C. Pidacks and staff for partition chromatographic separations. We also thank Mr. R. Vessey and Mr. E. Markely for conducting the biological assays.

Synthesis of Some s-Triazoles with Potential Analgetic and Antiinflammatory Activities[1]

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A series of 5-alkyl-4-amino-s-triazole-3-thiols have been prepared. 4-Amino-5-ethyl-s-triazole-3-thiol showed moderate analgetic and antiinflammatory activities and a few derivatives showed weak analgetic and/or antiinflammatory activities, but of a lower order than the parent compound.

The chemistry of s-triazoles has been described by Kröger, *et al.*[2] In recent years there has been a growing interest in the pharmacology of s-triazole derivatives. Yale and Piala[3] have reported that 5-(*p*-aminophenyl)-s-triazole-3-thiol shows diuretic and natriuretic activity in rats when administered intraperitoneally. In connection with synthesis of condensed s-triazole heterocycles described elsewhere[4] we prepared a series of 5-alkyl(aryl)-4-amino-s-triazole-3-thiols. The zwitterionic character of this series of compounds prompted us to study their pharmacological properties.

Chemistry.—4-Amino-5-alkyl(aryl)-s-triazole-3-thiols were prepared according to published procedures.[2a,5] Most of the N- and S-substituted derivatives were synthesized starting from the Et analog **2**. Arylidene and alkylidene derivatives were obtained by condensing **2** with carbonyl compounds according to conventional methods.[2a,6] Compound **24** obtained by condensation of **2** with 2-methyl-2-thiocyanato-4-pentanone[7] according to the procedure of Mathes[8] gave on alkylation the monoalkyl derivative **37** showing that the mercapto group of the pyrimidine nucleus was unaffected.

S-Alkylations of **2** were carried out by treating with a wide variety of alkylating agents in the presence of calcd amounts of methanolic alkali or NaOEt. A Mannich reaction was carried out on the *N*-formyl derivative of **2** using piperidine to furnish the *S*-piperidinomethyl derivative **28**. Reaction with aromatic acid chlorides at low temperatures and an optimum pH value (6.5) gave *S*-aroyl derivatives. Performing the acylations at higher temperatures and lower pH gave exclusively the

(1) Contribution No. 204 from Ciba Research Centre.

(2) (a) H. Beyer and C. F. Kröger, *Justus Liebigs Ann. Chem.*, **637**, 135 (1960); (b) C. F. Kröger, E. Tenor, and H. Beyer, *ibid.*, **643**, 121 (1961).

(3) H. L. Yale and J. J. Piala, *J. Med. Chem.*, **9**, 42 (1966).

(4) T. George, R. Tahilramani, and D. A. Dabholkar, *Indian J. Chem.*, **7**, 959 (1969).

(5) E. Hoggarth, *J. Chem. Soc.*, 614 (1950).

(6) V. J. Mazzola, K. F. Bernandy, and R. W. Franck, *J. Org. Chem.*, **32**, 486 (1967).

(7) R. A. Mathes, F. D. Steward, and F. Swedish, Jr., *J. Amer. Chem. Soc.*, **70**, 1452 (1948).

(8) R. A. Mathes, *ibid.*, **75**, 1747 (1953).

N-aroyl derivative on account of S–N transacylation. Compound **2** reacted with Ac_2O, isocyanates, and *p*-toluenesulfonyl isocyanates to give the corresponding derivatives according to conventional methods. The synthesis of **39**, **40**, and **42** has been reported elsewhere.[4] Demarcapto compounds **43** and **44** were obtained according to the procedure described by Kröger, *et al.*[2b]

Pharmacological Testing and Results.—Antiinflammatory activity was determined in the rat by the carrageenin paw edema test.[9] The foot volume was measured by the method similar to that described by Winter and Nuss.[10] Analgetic activity was determined in 3 different tests: (a) AcOH writhing test[11] in the mouse, (b) tail-flick test[12] in the mouse, and (c) the Randall and Selitto test[13] in the rat. The ED_{50} and ED_{30} values were based on at least 3 logarithmically spaced doses per drug and calcd by the method of Bliss.[14] The results are summarized in Table I.

TABLE I

PHARMACOLOGICAL ACTIVITIES OF SOME *s*-TRIAZOLES

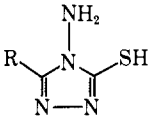
No.	Anti-inflammatory activity[a] (rat)	Analgetic activity[b] AcOH writhing test (mouse) ED_{50}, mg/kg po	Analgetic activity[b] Tail-flick test (mouse) ED_{30}, mg/kg po	Analgetic activity[b] Randall and Selitto test (rat) ED_{50}, mg/kg po
2	1	15	105	92
3	0.25	0	0	0
5	±	0	0	0
9	0.75	0	0	0
15	0.5	39	93	
16	0.5	0	0	0
19	0	41	0	0
27	0	24		65
31	0	14	118	0
35	0.25	0	0	0
39	±	0	0	0
40	±	0	0	0
43	0.25	0	0	0

[a] Carrageenin paw edema test po. Inactive at 100 mg/kg (0); border line activity (±); activity equiv to phenylbutazone 1. [b] Inactive at 100 mg/kg po (0); acetyl salicylic acid gave values 37, 251, and 50 in the respective analgetic tests.

Among the 5-alkyl-4-amino-*s*-triazole-3-thiols tested, **2** showed maximum analgetic and antiinflammatory activity. The analgetic activity was superior to that of acetylsalicylic acid in the Randall and Sellito test while the antiinflammatory activity was equal to that of phenylbutazone. Compounds **3** and **9** showed weak to moderate degree of antiinflammatory activity, respectively, but were devoid of analgetic properties. Compounds **2**, **3**, and **9** were inactive in the cotton pellet granuloma test.[15] Compound **15**, the acetonylidene derivative of **2**, showed a low degree of analgetic and antiinflammatory activity. The cycloalkylidene derivative **16** showed moderate antiinflammatory activity but no analgetic activity. All other alkylidene and arylidene derivatives of the 3-alkyl-4-amino-*s*-triazole-3-thiols were inactive. Compound **27** obtained by S-alkylation of **2**, was moderately analgetic but was devoid of antiinflammatory activity. The *S*-benzoyl derivative **31** showed the same activity pattern as **27**. The *n*-butylurea derivative **35** obtained from **2** showed weak antiinflammatory activity but no analgetic activity. The demercapto compound **43** showed some antiinflammatory activity, whereas the demarcapto analog **44**, obtained from **2**, showed no activity. All other compounds listed in Tables II–VI showed no antiinflammatory or analgetic activities.

TABLE II

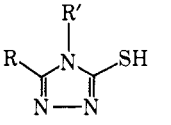
5-ALKYL-4-AMINO-*s*-TRIAZOLE-3-THIOLS

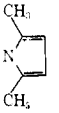
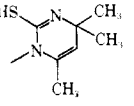
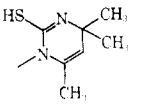


No.	R	Mp, °C	Formula	Analyses	Yield, %
1	CH_3	235	$C_3H_6N_4S$	C, H	67
2	C_2H_5	152	$C_4H_8N_4S$	C, H	65
3	$(CH_2)_2CH_3$	108	$C_5H_{10}N_4S$	C, H, N	57
4	$(CH_2)_3CH_3$	90	$C_6H_{12}N_4S$	C, H	51
5	$(CH_2)_4CH_3$	105	$C_7H_{14}N_4S$	C, H	47
6	$CH_2CH(CH_3)_2$	60	$C_6H_{12}N_4S$	C, H	46
7	CH_2OCH_3	105	$C_4H_8N_4OS$	C, H	49
8	Δ	181	$C_5H_8N_4S$	C, H	39
9	CF_3	142	$C_5H_8N_4S$	C, H	27
10	CF_2CF_3	144	$C_4H_3F_5N_4S$	C, H, N	31
11	$CF_2CF_2CF_3$	170	$C_5H_3F_7N_4S$	C, H, N	34
12	C_6H_5	223	$C_8H_8N_4S$	C, H	56
13	3,4,5-$C_6H_2(OMe)_3$	240	$C_{11}H_{14}N_4O_3S$	C, H	41

TABLE III

DERIVATIVES OF 5-ALKYL-4-AMINO-*s*-TRIAZOLE-3-THIOLS



No.	R	R'	Mp, °C	Formula	Analyses	Yield, %
14	Et	N=CHCH$_3$	170	$C_6H_{10}N_4S$	C, H	59
15	Et	N=C(CH$_3$)$_2$	195	$C_7H_{12}N_4S$	C, H, N	66
16	Et	N=C$_5$H$_8$	168	$C_9H_{14}N_4S$	C, H	71
17	Et	N=CHC$_6$H$_3$-2-Cl-5-NO$_2$	236	$C_{11}H_{10}ClN_5O_2S$	C, H, N	80
18	Et	N=CH-*p*-C$_6$H$_4$F	165	$C_{11}H_{11}FN_4S$	C, H	82
19	Et	N=CH-*p*-C$_6$H$_4$OCH$_3$	188	$C_{12}H_{14}N_4OS$	C, H	76
20	Et	N=CH-*p*-C$_5$H$_4$N	260	$C_{10}H_{11}N_5S$	C, H	72
21	Et	N=CHOC$_2$H$_5$	90	$C_7H_{12}N_4OS$	C, H	67
22	Et		200	$C_8H_{10}N_4S$	C, H	26
23	Et		157	$C_{10}H_{14}N_4S$	C, H	75
24	Et		260	$C_{11}H_{17}N_5S_2$	C, H	94
25	CF_3		251	$C_{10}H_{12}F_3N_5S_2$	C, H, N	84

Antiinflammatory drugs such as acetylsalicyclic acid, phenylbutazone, and indomethacin also exhibit anal-

(9) C. A. Winter, E. A. Risley, and G. W. Nuss, *Proc. Soc. Exp. Biol. Med.*, **111**, 544 (1962).

(10) C. A. Winter and G. W. Nuss, *Arthritis Rheum.*, **9**, 394 (1966).

(11) H. I. Chernov, M. M. Blatter, P. S. Bernard, D. E. Wilson, and A. J. Plummer, *Proc. Soc. Exp. Biol. Med.*, **125**, 747 (1967).

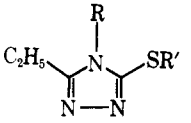
(12) F. E. D'Amour and D. L. Smith, *J. Pharmacol. Exp. Ther.*, **72**, 74 (1941).

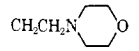
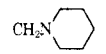
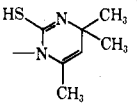
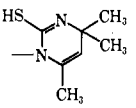
(13) L. O. Randall and J. J. Selitto, *Arch. Int. Pharmacodyn.*, **171**, 409 (1957).

(14) C. I. Bliss, "The Statistics of Bioassay," Academic Press, New York, N. Y., 1952, p 445.

(15) R. Meier, W. Schuler, and P. A. DeSaulles, *Experientia*, **6**, 469 (1950).

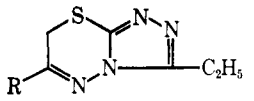
TABLE IV
ACYL AND ALKYL DERIVATIVES OF 4-AMINO-5-ETHYL-s-TRIAZOLE-3-THIOL

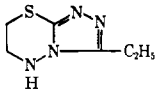


No.	R	R′	Mp, °C	Formula[a]	Yield, %
26	NH_2	$CH_2C_6H_5$	143	$C_{11}H_{14}N_4S$[b]	26
27	NH_2	$CH_2CH_2N(C_2H_5)_2$	85	$C_{10}H_{21}N_5S$	53
28	NH_2		109	$C_{10}H_{19}N_5OS$	46
29	NHCHO		123	$C_{11}H_{19}N_5OS$	38
30	NH_2	$CH_2C{\equiv}CH$	90	$C_7H_{12}N_4S$	43
31	NH_2	COC_6H_5	109	$C_{11}H_{12}N_4OS$	32
32	$N{=}C(CH_3)_2$	COC_6H_5	154	$C_{14}H_{16}N_4OS$	26
33	$N(COCH_3)_2$	H	83	$C_8H_{12}N_4O_2S$	46
34	$NHCOCH_3$	H	205	$C_6H_{10}N_4OS$	85
35	$NHCONHC_4H_9$	H	180	$C_9H_{17}N_5OS$	52
36	$NHCONHSO_2$-p-$C_6H_4CH_3$	H	215	$C_{12}H_{15}N_5O_3S_2$	56
37		C_4H_9	153	$C_{15}H_{25}N_5S_2$	66
38		$COCH_3$	240	$C_{13}H_{19}N_5OS_2$	69

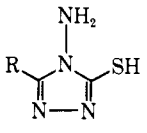
[a] All compds were analyzed for C, H. [b] Also N anal.

TABLE V
CONDENSED SYSTEMS DERIVED FROM
4-AMINO-5-ETHYL-s-TRIAZOLE-3-THIOL



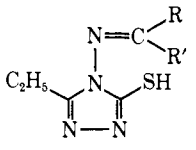
No.	R	Mp, °C	Formula[a]	Yield, %
39	H	225	$C_6H_8N_4S \cdot HBr$	84
40	C_6H_5	159	$C_{12}H_{12}N_4S$	57
41	OC_5H_4N	148	$C_{11}H_{11}N_5S$	35
42		180	$C_6H_{10}N_4S$	47

[a] All compds were analyzed for C, H, N.



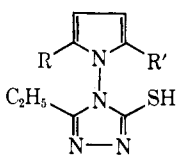
I

2, R = C_2H_5
9, R = CF_3
12, R = C_6H_5
13, R = 3, 4, 5, $C_6H_2(OCH_3)_3$



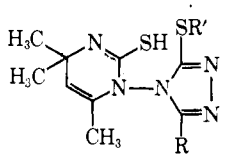
II

14, R = CH_3; R′ = H
15, R = CH_3; R′ = CH_3
18, R = C_6H_5; R′ = H
21, R = OC_2H_5; R′ = H



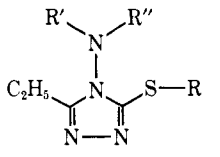
III

22, R = R′ = H
23, R = R′ = CH_3

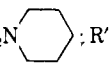


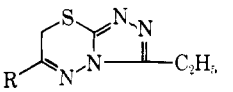
IV

24, R = C_2H_5; R′ = H
25, R = CF_3; R′ = H
37, R = C_2H_5; R′ = Bu
38, R = C_2H_5; R′ = $COCH_3$



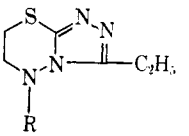
V

26, R = $CH_2C_6H_5$; R′ = R″ = H
27, R = $CH_2CH_2N(C_2H_5)_2$; R′ = R″ = H
29, R =  ; R′ = H; R″ = CHO
31, R = COC_6H_5; R′ = H; R″ = H
33, R = H; R′ = R″ = $COCH_3$
34, R = H; R′ = H; R″ = $COCH_3$
35, R = H; R′ = H; R″ = CONHBu
36, R = H; R′ = H; R″ = $CONHSO_2$-p-$C_6H_4CH_3$



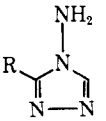
VI

39, R = H(HBr)
40, R = C_6H_5



VII

42, R = H



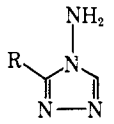
VIII

43, R = CF_3
44, R = C_2H_5

getic activity. However, no such apparent parallelism was observed with compounds of the present series.

TABLE VI

3-ALKYL-4-AMINO-s-TRIAZOLES



No.	R	Mp, °C	Formula[a]	Yield, %
43	CF_3	260	$C_3H_3F_3N_3$	44
44	C_2H_5	100	$C_4H_8N_4$	51

[a] C, H anal.

Experimental Section[16]

5-Alkyl-4-amino-s-triazole-3-thiols (1–8) were prepd according to the procedure of Beyer and Kröger.[2a]

4-Amino-5-perfluoroalkyl-s-triazole-3-thiols (9–11).—In a typical prepn, thiocarbohydrazide (15 g) was refluxed with excess CF_3COOH (45 ml) for 2 hr. The residue, obtained on evapn of excess of reagent under reduced pressure, crystd on trituration with Et_2O. Recrystn from Et_2O yielded 7 g of 4-amino-5-trifluoromethyl-s-triazole-3-thiol (**9**), mp 142°.

5-Aryl-4-amino-s-triazole-3-thiols (12, 13) were prepd according to the procedure described by Hoggarth.[5]

4-Alkylidene(arylidene)amino-5-ethyl-s-triazole-3-thiols (14–19).—In a typical prepn of an arylidene derivative, **2** (2.88 g, 0.02 mole) and *p*-fluorobenzaldehyde (2.48 g, 0.02 mole) were refluxed together in EtOH (40 ml) for 2 hr. The cryst product, obtained on cooling, was filtered off and recrystd from MeOH to give 4.1 g of colorless cryst of **18**, mp 165°.

As a typical example of preparation of a cycloalkylidene derivative, **2** (2.88 g, 0.02 mole) was refluxed with excess cyclopentanone (30 ml) and concd HCl (0.5 ml) for 4 hr. Work-up as in previous experiment afforded 3 g of colorless crystals of **16**, mp 168°.

5-Ethyl-4-pyrrolo-s-triazole-3-thiol (22).—To a stirred suspension of **2** (2.88 g, 0.02 mole) in EtOH (75 ml) contg concd HCl (3 drops) was added 2,5-dimethoxytetrahydrofuran (2.88 g, 0.02 mole) and the mixt heated under reflux for 4 hr. Removal of the solvent and treatment of the residue with cold aq $NaHCO_3$ gave a solid which on recrystn from EtOH gave 1 g of colorless cryst, mp 200°.

5-Ethyl-4-(2,5-dimethyl)pyrrolyl-s-triazole-3-thiol (23).—Compd **2** (5.76 g, 0.04 mole) was refluxed with acetonylacetone (4.56 g, 0.04 mole) in EtOH (100 ml) contg concd HCl (8 drops) for 4 hr. Work-up as for **22** and recrystn from MeOH gave 6.5 g of colorless cryst, mp 157°.

1-[5-Ethyl-3-mercapto-s-triazol-4-yl]-2-mercapto-4,4,6-trimethyl-1,4-dihydropyrimidine (24).—A stirred mixt of **2** (5.76 g, 0.04 mole), 2-methyl-2-thiocyanato-4-pentanone (6.28, g, 0.04 mole), and concd HCl (3.5 ml) in EtOH (50 ml) was refluxed for 2 hr. The colorless cryst compd formed was filtered off and washed with dil $NaHCO_3$ and then with H_2O and EtOH. Recrystn from EtOH gave 8.5 g of colorless crystals, mp 260°.

1-[3-Acetylmercapto-5-ethyl-s-triazol-4-yl]-2-mercapto-4,4,6-trimethyl-1,4-dihydropyrimidine (38).—Compd **24** (5.68 g, 0.02 mole) was refluxed with Ac_2O (35 ml) for 2 hr. Removal of excess reagent and treatment of the residue successively with $NaHCO_3$, H_2O, and EtOH gave 4.5 g of colorless material after recrystn from CH_2Cl_2, mp 240°.

1-[3-Butylmercapto-5-ethyl-s-triazol-4-yl]-2-mercapto-4,4,6-trimethyl-1,4-dihydropyrimidine (37).—To a stirred soln of **24** (5.68 g, 0.02 mole) and BuBr (2.74 g, 0.02 mole) in EtOH (50 ml), methanolic NaOH (1 *N*, 28 ml) was added gradually and the mixt was refluxed for 2 hr. Evapn of solvent under reduced pressure gave an oily residue which was extd with CH_2Cl_2 and the ext dried (Na_2SO_4). Removal of solvent gave a residue which crystd on trituration with Et_2O. Recrystn from CH_2Cl_2–hexane gave 4.5 g of colorless crystals, mp 153°.

***S*-Benzyl-4-amino-5-ethyl-s-triazole-3-thiol** (26).—To a stirred ice-cold soln of **2** (1.44 g, 0.01 mole) in methanolic KOH (1 *N*, 12 ml) was added $PhCH_2Br$ (1.71 g, 0.01 mole) in EtOH (10 ml) maintaining a neutral soln by the addition of drops of 1 *N* methanolic KOH. After stirring for 2 hr, ice was added and the cryst product was sepd by filtration, washed with H_2O and EtOH, and recrystd from EtOH to give 5.5 g of colorless crystsls, mp 143°.

***S*-(β-Diethylaminoethyl)-4-amino-5-ethyl-s-triazole-3-thiol** (27).—To a soln of NaOEt prepd from Na (1.01 g, 0.042 g-atom) in EtOH (50 ml) was added β-diethylaminoethyl chloride·HCl (3.78 g, 0.022 mole) and Ia (2.88 g, 0.02 mole). The mixt was refluxed for 4 hr and NaCl formed was filtered off. The filtrate on evapn under reduced pressure gave an oily residue which was treated with Et_2O and the Et_2O ext was dried (Na_2SO_4). Removal of the solvent gave a solid which on recrystn from Et_2O–petr ether melted at 85°; yield, 2.6 g.

***S*-[Piperidinomethyl]-4-formylamino-5-ethyl-s-triazole-3-thiol** (29).—5-Ethyl-4-formylamino-s-triazole-3-thiol was prepd by refluxing Ia with excess HCO_2H for 20 hr removing excess reagent under reduced pressure, and washing with H_2O and then EtOH. The compd (1.7 g, 0.01 mole), piperidine (0.93 g, 0.011 mole), formalin (0.8 ml), and EtOH (40 ml) were stirred together and heated under reflux for 4 hr. The ppt formed was filtered off, washed (H_2O), and recrystd from EtOH to afford colorless crystals; yield, 0.9 g, mp 123°.

***S*-(Benzoyl)-4-amino-5-ethyl-s-triazole-3-thiol** (31).—To a chilled, well-stirred soln of **2** (2.88 g, 0.02 mole) in methanolic KOH (1 *N*, 22 ml) was added dropwise BzCl (2.93 g, 0.02 mole) taking care to maintain the neutrality of the soln by the addition of drops of 1 *N* methanolic KOH during the addition of the BzCl and further stirring for 2 hr. At the end of 2 hr, crushed ice was added and the ppt formed was filtered off. It was dissolved in Et_2O and chilled to get colorless crystals (1.6 g), mp 109°.

4-[*N*,*N*-Diacetyl]amino-5-ethyl-s-triazole-3-thiol (33).—Compd **2** (2.88 g, 0.02 mole) was refluxed with Ac_2O (20 ml) for 4 hr. Removal of unreacted Ac_2O under reduced pressure and treatment with cold H_2O gave an oil which solidified on standing. Crystn from CH_2Cl_2 gave colorless needles; yield, 2.1 g, mp 82–83°.

4-(*N*-Acetyl)amino-5-ethyl-s-triazole-3-thiol (34).—Compd **33** (1 g) was heated with H_2O (5 ml) for 10 min, and then cooled. The solid obtained was crystd from $CHCl_3$ to give colorless crystals (0.7 g), mp 205°.

5-Ethyl-4-*p*-toluenesulfonylureido-s-triazole-3-thiol (36).—*p*-Toluenesulfonyl isocyanate (2.16 g, 0.011 mole) was added to a stirred suspension of **2** (2.88 g, 0.02 mole) in anhyd PhMe (30 ml) and refluxed for 4 hr. The ppt obtained on filtration was recrystd from EtOH to give colorless crystals (3.8 g), mp 215°.

4-Amino-5-trifluoromethyl-s-triazole (43).—Compd **9** (3 g) was refluxed with Raney Ni (W_2) in EtOH (200 ml) for 4 hr and filtered. The residue obtained on evapn of the filtrate was crystd from CH_2Cl_2–Et_2O to give 1.1 g of colorless crystals, mp 260°.

Acknowledgment.—Thanks are expressed to Dr. S. Selvavinayakam for microanalytical data.

(16) All melting points were taken in soft glass capillary tubes and are corrected. Ir spectra (Nujol) were taken on a Perkin-Elmer Model 237B spectrophotometer. Uv measurements were recorded on a Beckmann DB model spectrophotometer. These spectra agreed with the expected absorption bands. Where analyses are indicated only by the symbols of the elements, analytical results obtained for these elements were within ±0.3% of the theoretical values.