the concentration of ferric ion present, and can also account for the absence of any isomeric 1,3-dicarbazylcyclobutane.

Experimental Section[7]

Hydrolysis of N-Vinylcarbazole.—To a solution of 1 g (5×10^{-3} mole) of N-vinylcarbazole (Matheson Coleman and Bell, mp 67°) in 44 ml of 9:1 methanol–water, 0.01 g (2.5×10^{-5} mole) of ferric nitrate (Mallinckrodt, $Fe(NO_3)_3 \cdot 9H_2O$) was added. The mixture was stirred at room temperature and a white precipitate gradually appeared. At the end of 4 days, 0.7 g of white solid was collected. This material was identified as carbazole by melting point and mixture melting point determinations with known samples of carbazole, mp 238–241°, and by comparison of their infrared spectra. The mother liquor furnished acetaldehyde in about 50% yield based on the isolation of acetaldehyde 2,4-dinitrophenylhydrazone, mp 145–147°, lit.[8] mp 148°. Comparable results were obtained when the same molar concentrations of hydrochloric acid were used instead of ferric nitrate.

Formation of the Dimer.—To a solution of 2 g (0.01 mole) of N-vinylcarbazole in 88 ml of 9:1 methanol–water, 0.2 g (5×10^{-4} mole) of ferric nitrate was added. The mixture was stirred and a white precipitate was observed within 10 min. At the end of 1 hr, the solid was collected by filtration. The yield was 0.4 g (20%), mp 189–193°. Recrystallization from an ethanol–acetone (1:1) solution raised the melting point to 191–193.5°.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25; mol wt, 386.5. Found: C, 86.74; H, 5.80; N, 7.31; mol wt, 373 (Rast method), 386 (mass spectrum).

Acknowledgment.—We are indebted to Dr. G. Dudek of Harvard University and Mrs. G. Dudek of this department for the mass spectral and nmr analyses.

(7) Analysis was by Dr. M. S. Nagy, Massachusetts Institute of Technology, Cambridge, Mass. Melting points are not corrected. The nmr spectrum was recorded by using a Varian A-60 spectrometer, and mass spectral analysis was done by using a mass spectrophotometer, A.E.I. MS9.

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3-Hydroxy-4-Substituted 1,2,5-Thiadiazoles. A New Synthesis

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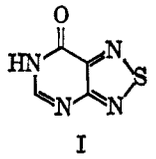
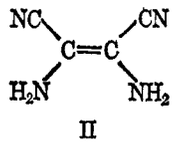
Received July 29, 1965

Although 2,1,3-benzothiadiazole bicyclic systems have been known since the last century,[1] 1,2,5-thiadiazoles were not described until 1957. The monocyclic system has been obtained by oxidation of 2,1,3-benzothiadiazole derivatives[2-4] to 1,2,5-thiadiazole-3,4-dicarboxylic acid and also by basic cleavage of 1,2,5-thiadiazolo[3,4-*d*]pyrimidin-7(6H)-one (I) to 4-amino-1,2,5-thiadiazole-3-carboxamide.[5]

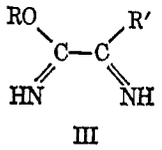
Carmack and associates have synthesized 3,4-dicyano-1,2,5-thiadiazole[6] by ring closure from thionyl chloride and hydrogen cyanide tetramer (II) and have developed a general synthesis from substituted oxalimidates (III).[7]



I



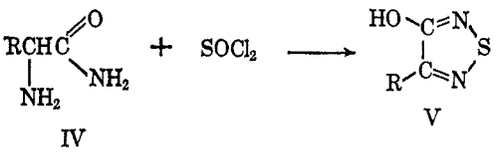
II



III

Two other interesting approaches have led to 3-cyano-4-hydroxy-1,2,5-thiadiazole,[8] obtained from the reaction of potassium cyanide and sulfur dioxide in the absence of hydroxylic solvents, and to 3-phenyl-1,2,5-thiadiazole,[9] formed by refluxing S_4N_4 with ethylbenzene.

α-Amino acid amides undergo condensation with 1,2-dicarbonyl compounds to give 2-hydroxypyrazines.[10] We are indebted to Dr. R. G. Jones of these laboratories for calling to our attention the fact that this demonstrated similarity of α-amino acid amides (IV) to aromatic vicinal diamines suggests a route for the direct synthesis of substituted monocyclic hydroxythiadiazoles[11] (V).

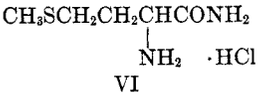


IV V

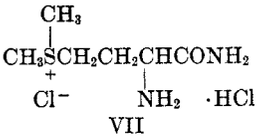
The initial experiments were carried out in chloroform with thionyl chloride and alaninamide hydrochloride. Very low yields of a product were isolated that had the characteristics expected of 3-hydroxy-4-methyl-1,2,5-thiadiazole. Improved results were obtained when the α-amino acid amides were allowed to react with thionylaniline[12] in pyridine. A number of 3-hydroxy-4-substituted 1,2,5-thiadiazoles were thus prepared in yields usually ranging from 20 to 60% (Table I).

The stable aromatic character of the ring system is demonstrated by the marked phenolic properties of the hydroxyl function.[8] The pK_a values determined were generally in the range 6.4–7.3.

A large-scale preparation of methioninamide (VI),[10,13] without purification of the ester intermediate, allowed the isolation of a methylsulfonium chloride by-product (VII) in about 30% yield.



VI



VII

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(6) D. Shew, *Dissertation Abstr.*, **20**, 1593 (1959).

(7) R. Y. Wen, *ibid.*, **23**, 4121 (1963).

(8) J. M. Ross and W. C. Smith, *J. Am. Chem. Soc.*, **86**, 2861 (1964).

(9) V. Bertini and P. Pino, *Angew. Chem.*, **77**, 262 (1965).

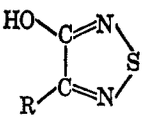
(10) R. G. Jones, *J. Am. Chem. Soc.*, **71**, 78 (1949).

(11) Personal communications with Dr. Carmack, of Indiana University, indicate that he has prepared the 1,2,5-thiadiazole in the same manner.

(12) A. Michaelis, *Ann.*, **274**, 173 (1893); *Ber.*, **24**, 745 (1891).

(13) The α-amino acid esters were prepared according to the procedure of T. Curtius and F. Goebel, *J. Prakt. Chem.*, [2] **37**, 150 (1888). The α-amino acid amides were prepared as methioninamide described in ref 10.

TABLE I



Compd	R	Yield pure, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	pK_a'
VIII	CH_2=CH	54	92–94	$C_4H_4N_2OS$	37.48	3.14	21.86	37.30	3.24	20.98	6.80
IX	$CH_3SCH_2CH_2$	57	65	$C_5H_8N_2OS_2$	34.07	4.57	15.89	33.85	4.60	15.94	7.0
X	CH_3	22	146	$C_3H_4N_2OS$	31.02	3.47		31.21	3.23		7.10
XI	$(CH_3)_2CH$	42	84–85	$C_5H_8N_2OS$	41.64	5.59	19.43	41.86	5.79	19.67	7.25
XII	C_6H_4	56	165–166	$C_8H_6N_2OS$	53.91	3.39	15.72	54.23	3.78	15.68	6.98
XIII	$C_6H_4CH_2$	45	139–140	$C_9H_8N_2OS$	56.22	4.19		56.02	4.35		7.1

Methioninamide methylsulfonium chloride hydrochloride (VII) was allowed to react with thionyl chloride in chloroform. The resulting product was 3-hydroxy-4-vinyl-1,2,5-thiadiazole, dimethyl sulfide having been eliminated during the reaction. Methioninamide hydrochloride yielded the expected methylmercaptoethylhydroxythiadiazole without complication.

Experimental Section[14]

3-Hydroxy-4-methyl-1,2,5-thiadiazole (X). Method A.—To 10 g of alaninamide hydrochloride[13] suspended in 200 ml of chloroform was added 150 ml of thionyl chloride. The well-stirred reaction mixture was heated to reflux for 48 hr. The reaction was concentrated *in vacuo* to a brown solid, which was then taken up in 600 ml of chloroform. The solution was washed with two 150-ml portions of water and extracted with two 150-ml portions of 10% sodium hydroxide solution. The basic extracts were cooled to 0°, made acidic with concentrated hydrochloric acid, and extracted with four 200-ml portions of chloroform. The latter solution was washed with water, followed by brine, dried over magnesium sulfate, and concentrated *in vacuo*. A yield of 150 mg (1.2%) of product was obtained as a yellow solid. It was sublimed at 75° (0.3 mm), mp 143°.

Method B.—To 22 g of alaninamide, free base, suspended in 1500 ml of dry pyridine was added 121 g of thionylaniline.[12] The well-stirred reaction mixture was kept under a nitrogen atmosphere while being heated at 90° for 16 hr. The reaction was worked up as in the method A to yield 8.6 g of a rust-colored solid. The compound was purified by chromatography on silicic acid and Supercel: 6.56 g (22% yield), mp 144–146°, pK_a' = 7.10, mol wt 120 (calcd 116.1).

Methioninamide methylsulfonium chloride hydrochloride (VII) was obtained as a by-product, in about 30% yield, during the preparation of methioninamide (VIII), mp 168–172° from ethanol.

Anal. Calcd for $C_5H_{16}Cl_2N_2OS$: C, 30.63; H, 6.80; Cl, 30.12; N, 11.91; S, 13.61. Found: C, 30.56; H, 7.00; Cl, 29.88; N, 11.87; S, 13.80.

3-Hydroxy-4-Substituted 1,2,5-Thiadiazoles (Table I).—Compounds IX–XIII were prepared from thionylaniline and the appropriate α-amino acid amide. The 4-vinyl compound (VIII) was obtained as the only product isolated from the reaction starting with methioninamide methylsulfonium chloride hydrochloride (VII) and thionyl chloride. The molecular weight of each of the compounds in Table I was determined from the electrometric titration curve. The values found agreed with those calculated within the limits of experimental error.

Acknowledgment.—We are indebted to Messrs. W. L. Brown, G. M. Maciak, H. L. Hunter, A. Brown, D. Cline, and C. W. Ashbrook for elemental analyses and Mr. L. A. White for large-scale preparations of starting materials. In addition, we wish to thank Dr. H. Boaz and his group for the physicochemical measurements: Messrs. H. Howard and L. Huckstep. ultraviolet spectra; Mr. L. Spangle, titration; Messrs, P. Landis and J. Klemm, nmr; and Mr. D. Woolf and Miss M. Hofmann, infrared spectra.

(14) All melting points are corrected. Ultraviolet, infrared, and nmr spectra were obtained in ethanol, chloroform, and deuteriochloroform, respectively. Titrations were carried out in a 66% aqueous dimethylformamide system.

Dehydration of the Four Stereoisomers of 1-Decalol over Thoria, Silica–Alumina, and Silico–Phosphoric Catalysts[1]

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Received September 15, 1965

In the preceding paper of this series it was shown that the dehydration of 1-decalols over aluminas takes place preferentially through a *trans*-elimination reaction. Thus *cis,cis*-1-decalol formed about 89% 1,9-octalin and only 5% *cis*-1,2-octalin, while *cis,trans*-1-decalol yielded 4% of 1,9-octalin and 92% *cis*-1,2-octalin. A similar trend was obtained with *trans,cis*- and *trans,trans*-1-decalol.[1]

The present paper reports the dehydration of the four stereoisomers of 1-decalol over thoria and over acidic type catalysts, namely, silica–alumina and silico–phosphoric acid. The experiments were made in a micropulse reactor.[1]

Thoria.—Two sets of experiments were made, one using 30 mg and the other 500 mg of thoria (Table I). With the lesser amount of catalyst only *ca.* 3–13% of the decalols underwent dehydration to octalins, while with the 500 mg of thoria the dehydration amounted to from 26 to 61%, depending on the decalol used. The most resistant toward dehydration was the *trans,trans*-1-decalol, which is in agreement with a previous observation.[1] Part of the decalols underwent epimerization and dehydrogenation to *cis*- and *trans*-decalones.

The dehydration seems to proceed mainly *via* a *trans*-elimination reaction as evidenced by the formation of 1,9-octalin as the principal product from the dehydration of the *cis,cis*-1-decalol, and *cis*-1,2-octalin as the main olefin from the *cis,trans*-1-decalol. The stereospecificity of the dehydration of decalols in the presence of thoria was not so great, however, as in the

(1) Paper IX in the series of Dehydration of Alcohols. For the previous paper, see F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

(2) Taken from a Ph.D. dissertation submitted to the Graduate School, June 1965. Monsanto Co. Fellow, 1963–1964.