β-(2,6-Bishydroxymethylphenyl)ethanol (7m).—A solution of 1.1 g. of **7m** in 50 ml. of dry tetrahydrofuran was added dropwise with vigorous stirring to a suspension of 1.1 g. of lithium aluminum hydride in 250 ml. of dry tetrahydrofuran. The mixture then was refluxed for 14 hr. and the excess hydride was destroyed by the addition of magnesium sulfate hydrate. The mixture was filtered, the residue was washed with tetrahydofuran, and the combined filtrates were evaporated under reduced pressure. Crystallization of the residue from ethyl acetate gave 0.61 g. of triol **7m**, m.p. 95–96°. Recrystallization gave the raised m.p. 98–99° (lit.[15] m.p. 105° for monohydrate); infrared spectrum (Nujol): 3.0–3.2 μ (broad, OH), no C=O absorption.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.75; H, 7.71.

Erythrocentaurin (2).—A mixture of 210 mg. of triol **7m** and 2.1 g. of active manganese dioxide in 240 ml. of ether was stirred vigorously for 18 hr., filtered, and evaporated under reduced pressure. Crystallization of the residue, 145 mg., from ether yielded erythrocentaurin (**2**), m.p. 138–139°; infrared spectrum (KBr): 5.83 and 5.92 μ (lactone and aldehyde C=O). Infrared spectral, melting point, and mixture melting point comparison showed the material to be identical with the natural product.[27]

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.37; H, 4.70.

Acknowledgment.—The technical assistance by Messrs. Ronald G. Lewis, Thomas E. Wollner, Lloyd M. Woerner, and Miss Patricia G. Gettys is acknowledged gratefully herewith.

1,2,4-Triazoles. VIII. *s*-Triazolo[2,3-*a*]pyrazine Derivatives[1a]

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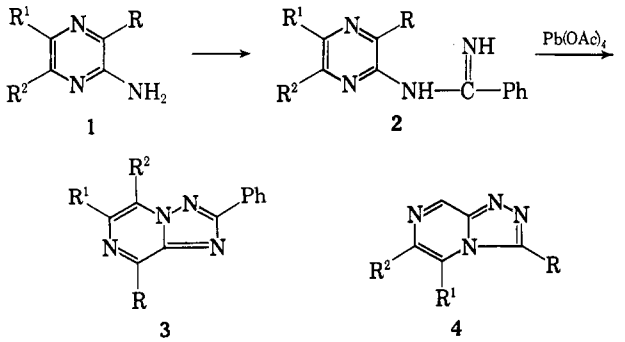
Cyclization of N-2-pyrazinylbenzamidines (**2**) with lead tetraacetate led to 2-phenyl-*s*-triazolo[2,3-*a*]pyrazine derivatives (**3**). Aliphatic cyanides would not form amidines with the 2-aminopyrazines (**1**) used, this being the limiting factor in the reaction scheme. Ultraviolet spectral data for the *s*-triazolo[4,3-*a*]pyrazines (**4**) and the *s*-triazolo[2,3-*a*]pyrazine systems are reported and compared with those of similar systems.

Of the two possible ways of effecting fusion of an *s*-triazole nucleus with a pyrazine nucleus, one, the *s*-triazolo[4,3-*a*]pyrazine system, has been reported on in an earlier communication.[2] We now wish to describe the synthesis of several examples of the isomeric *s*-triazolo[2,3-*a*]pyrazine system. The synthesis of this nucleus can be achieved most efficiently by starting with a preformed pyrazine ring and bringing about a ring closure to form the *s*-triazole nucleus, rather than the reverse procedure of forming the pyrazine nucleus by a suitable cyclization reaction.

An adaptation of the method[3] used to obtain derivatives of the *s*-triazolo[2,3-*a*]pyridine ring system was used in this study. Suitably substituted 2-aminopyrazines[4] (**1**) such as the 3,6-dimethyl, 5,6-dimethyl, and 5,6-diphenyl derivatives were condensed with benzonitrile in the presence of aluminum chloride to form the appropriate N-2-pyrazinylbenzamidine (**2**), which with lead tetraacetate underwent oxidative ring closure to the corresponding 2-phenyl-*s*-triazolo[2,3-*a*]pyrazine (**3**). It was found that amidine formation occurred only with the aryl cyanides and in no case was the yield greater than 56%. Even with alkyl cyanides such as trichloroacetonitrile, where the cyano group has greatly increased electrophilic character, the only product isolated was that formed by self-condensation of the nitrile, namely 2,4,6-tri(trichloromethyl)-*s*-triazine.[5] As various substituted 2-aminopyridines have been converted into the corresponding N-2-pyridylamidines in good yield with alkyl cyanides and aluminum chloride,[3b] one can attribute the lack of amidine formation with alkyl cyanides in the pyrazine series to the lower basicity of the 2-aminopyrazine derivatives. Thus, 2-aminopyridine with a pK_a value of 6.86 and aniline, pK_a 4.58, are much stronger bases[6] than 2-aminopyrazine, pK_a 3.14, and there are numerous examples in the literature, largely from the work of Oxley and Short,[7] that substantiate this reasoning. It is interesting that the amidine derived from 2-amino-5,6-diphenylpyrazine (**1**, R = H; $R^1 = R^2$ = Ph) was formed in best yield (56%), whereas that derived from 2-amino-3,6-dimethylpyrazine (**1**, R = R^2 = CH_3; R^1 = H) was formed in only 18% yield. This can be attributed to the greater stability of the amidine derived from the former amine under the alkaline conditions used in the isolation procedure, as 2-amino-5,6-diphenylpyrazine would be expected to be a slightly weaker base than the dimethyl compounds. This decomposition of the amidines under reaction work-up conditions was more noticeable in the pyridine series where low temperatures were required to suppress the hydrolysis.[3b]



(1) (a) Part VII: K. T. Potts, *J. Org. Chem.*, **28**, 543 (1963). (b) This research was partially supported by a grant (to G. M. B.) from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the said fund and also to the Public Health Service for partial support (K. T. P.) from Public Health Service Grant CA-05973, National Cancer Institute.

(2) P. J. Nelson and K. T. Potts, *J. Org. Chem.*, **27**, 3243 (1962).

(3) (a) J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 727, 4506 (1957); (b) H. R. Burton and K. T. Potts, unpublished results.

(4) A. E. Erickson and P. E. Spoerri, *J. Am. Chem. Soc.*, **68**, 400 (1946).

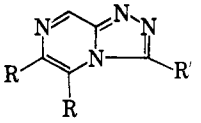
(5) T. R. Norton, *ibid.*, **72**, 3527 (1950).

(6) A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948).

(7) P. Oxley, M. W. Partridge, and W. F. Short, *ibid.*, 1110 (1947); 303 (1948).

TABLE I

ULTRAVIOLET ABSORPTION DATA OF s-TRIAZOLO[4,3-a]PYRAZINE DERIVATIVES

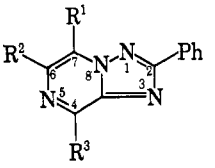


R	R¹	Solvent[a]	λmax, mμ (log ε)									
H	H	E	206 (4.46)		253 (sh) (3.31)	262 (sh) (3.37)	269 (sh) (3.40)		292 (3.57)			
H	CH_3	C[b]	214 (4.11)	231 (sh) (3.08)		257 (3.14)	270 (sh) (3.05)	298 (3.10)	308 (3.09)	322 (2.98)	338 (2.64)	
		E	211.5 (4.38)		255 (sh) (3.24)	262 (3.27)	270 (3.26)		299.5 (3.48)			
H	C_2H_5	C	212 (4.47)	219 (sh) (4.41)		260 (3.41)	268 (sh) (3.35)	290 (sh) (3.39)	299 (3.42)	308 (3.42)	322 (3.30)	339 (2.94)
CH_3	H	C	213 (4.50)	218 (sh) (4.42)	231 (sh) (3.36)	261 (sh) (3.45)	278 (sh) (3.51)	292 (sh) (3.59)	299 (3.61)	307.5 (sh) (3.57)	321 (sh) (3.28)	
CH_3	CH_3	C	217 (4.49)	223 (sh) (4.39)	263 (sh) (3.35)	269 (sh) (3.38)	280 (3.39)	302 (sh) (3.53)	309 (3.56)	319 (sh) (3.50)	333 (sh) (3.23)	
CH_3	C_2H_5	C	217.5 (4.53)	224 (4.46)	260 (sh) (3.37)	272 (sh) (3.41)	280.5 (3.43)	304 (sh) (3.56)	310 (3.58)	318 (sh) (3.53)	333 (sh) (3.22)	
Ph	H	C	205 (4.56)	229 (sh) (3.58)		253 (4.33)			321 (3.71)			
Ph	CH_3	C	205 (4.59)			251 (4.39)		315.5 (3.63)	325 (sh) (3.61)	336 (sh) (3.37)		
Ph	C_2H_5	C	205		250.5 (4.33)			316 (3.59)	324 (sh) (3.58)	340.5 (sh) (3.37)		
Ph	Ph	E	207.5 (4.83)	223 (sh) (4.35)	254 (4.31)			318 (sh) (3.71)				

[a] E = 95% ethanol; C = cyclohexane. [b] This compound was not sufficiently soluble in cyclohexane for accurate determination of log ε values.

TABLE II

ULTRAVIOLET ABSORPTION DATA OF 2-PHENYL-s-TRIAZOLO[2,3-a]PYRAZINE DERIVATIVES[a]



R	R¹	R²	λmax, mμ (log ε)						
H	CH_3	CH_3	205	249 (4.65)	258 (4.62)	281 (sh) (3.91)	294 (3.82)	301 (sh) (3.78)	315 (3.55)
CH_3	CH_3	H	205	247 (4.61)	255 (sh) (4.59)	278 (sh) (4.01)	286 (sh) (3.91)	303 (sh) (3.54)	
H	Ph	Ph	204 (4.66)	220 (sh) (4.31)			268.5 (4.69)	292 (4.16)	

[a] All spectra were determined in cyclohexane solution.

Attempts to form the N-2-pyrazinylalkylamidines *via* the imino ester route[8] which was employed in the pyridine series[3b] were unsuccessful. 2-Amino-3,6-dimethylpyrazine was heated with ethyl acetimidate hydrochloride under a variety of conditions but the amine was always recovered. The failure of this method can likewise be attributed to the weakly basic character of the 2-aminopyrazine.[6]

In our previous paper on the s-triazolo[4,3-a]pyrazine system, attempts were made to prepare 3,5,6-triphenyl-s-triazolo[4,3-a]pyrazine (**4**, R = R¹ = R² = Ph) by the cyclization of N-benzoyl-2,3-diphenyl-6-hydrazinopyrazine with phosphoryl chloride. A product having all the spectral characteristics expected for this compound was obtained but in extremely poor yield. We have now found that this ring closure can be effected in nearly quantitative yield by using polyphosphoric acid at 150° as the condensation medium. Details are reported in the Experimental.

Ultraviolet Absorption Spectra of the s-Triazolopyrazines.—Table I lists the spectral data for members of the s-triazolo[4,3-a]pyrazine series examined and Table II lists those of the s-triazolo[2,3-a]pyrazine series. s-Triazolo[4,3-a]pyrazine has three main absorption bands at 206, 253, and 292 mμ in its spectrum (Fig. 1) which is very similar to that of 3-methyl-s-triazolo[4,3-a]pyridine and s-triazolo[4,3-a]pyrimidine (Fig. 1). These spectra indicate that the replacement of a —CH= group in the pyridine ring of the s-triazolo-

(8) A. Pinner, *Ber.*, **16**, 352, 1643 (1883); **17**, 179 (1884); I. D. Lamb and A. C. White, *J. Chem. Soc.*, 1253 (1939); A. Dornow and H. Theidel, *Chem. Ber.*, **88**, 1267 (1955).

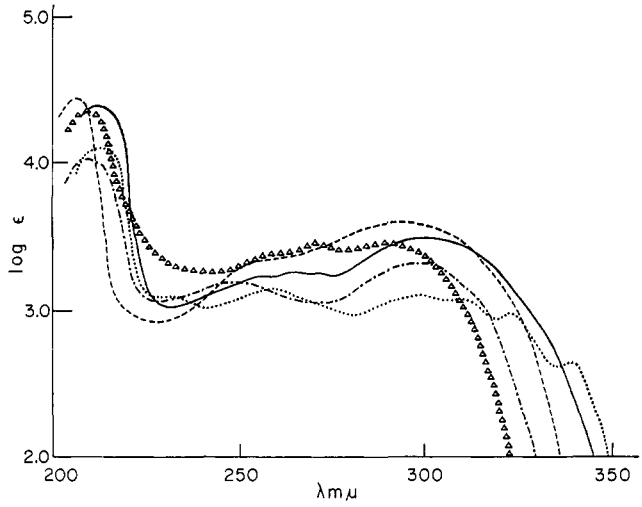


Fig. 1.—Absorption spectra of *s*-triazolo[4,3-*a*]pyrazine (– – – –), *s*-triazolo[4,3-*a*]pyrimidine (– · – ·), 3-methyl-*s*-triazolo[4,3-*a*]pyridine (ΔΔΔΔ), and 3-methyl-*s*-triazolo[4,3-*a*]-pyrazine (———), all in ethanol; 3-methyl-*s*-triazolo[4,3-*a*]pyrazine (· · · ·) in cyclohexane.

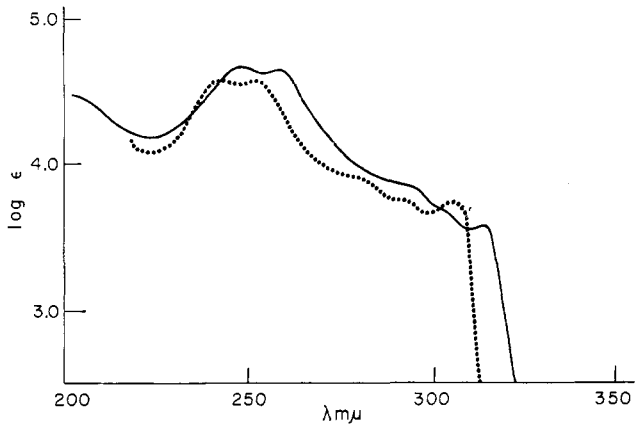


Fig. 2.—Absorption spectra of 6,7-dimethyl-2-phenyl-*s*-triazolo[2,3-*a*]pyrazine (———) and of 2-phenyl-*s*-triazolo[2,3-*a*]-pyridine (· · · ·) in cyclohexane.

[4,3-*a*]pyridine ring system with a nitrogen atom results in small shifts of the long wave-length band to longer wave length and the intermediate band to shorter wave length (pyrimidine and pyrazine systems) and much larger shifts when the two nitrogen atoms are adjacent (pyridazine). However, with the *s*-triazolo-[2,3-*a*]pyridine and *s*-triazolo[2,3-*a*]pyrimidine, important differences are apparent and a much greater shift of the long wave-length band occurred. Figure 2 shows the spectra of the 2-phenyl derivatives of the *s*-triazolo[2,3-*a*]pyridine and pyrazine systems. From these data, the absorptions in the 270–350-mμ region appear to consist of numerous $n \rightarrow \pi^*$ transitions which form a broad band due to multiple hydrogen bonding occurring in ethanol solution.

It is interesting to compare these data with the shifts observed[9] with the six-membered ring heterocycles themselves and with those reported by Bower[10] for the introduction of the nitrogen atom into the five-membered ring. These differences between the spectra of the *s*-triazolo[4,3-*a*] and -[2,3-*a*] series are extremely useful in establishing the structures of unknown products in these ring systems.

(9) S. F. Mason, *Quart. Rev.* (London), **15**, 330 (1961).
(10) J. D. Bower, *J. Chem. Soc.*, 4510 (1957).

Experimental[11]

General Method of Preparation of N-2-Pyrazinylbenzamidines.—Equimolar quantities of the 2-aminopyrazine,[4] aluminum chloride, and benzonitrile were heated together at 180° for 2 hr. Water was added to the cooled reaction mixture, the resulting solution was made basic with aqueous sodium hydroxide solution, and the precipitated solid was collected, washed with cold water, and crystallized from petroleum ether (b.p. 60–80°), from which the amidines separated as colorless needles. Ether extraction of the filtrate gave no further product. N-(2,5-Dimethyl-6-pyrazinyl)benzamidine was obtained in 18% yield, m.p. 145–146°.

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.0; H, 6.2; N, 24.8. Found: C, 68.7; H, 6.1; N, 24.7.

The **picrate** crystallized from chloroform–petroleum ether as yellow needles, m.p. 153–154°.

Anal. Calcd. for $C_{19}H_{17}N_7O_7$: C, 50.1; H, 3.8; N, 21.5. Found: C, 50.3; H, 3.9; N, 21.2.

N-(2,3-Dimethyl-6-pyrazinyl)benzamidine was obtained in 37% yield and had m.p. 165–166°.

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.0; H, 6.2; N, 24.8. Found: C, 68.6; H, 6.2; N, 24.8.

N-(2,3-Diphenyl-6-pyrazinyl)benzamidine was obtained in 56% yield and had m.p. 187–188°.

Anal. Calcd. for $C_{23}H_{18}N_4$: C, 78.8; H, 5.2; N, 16.0. Found: C, 78.7; H, 5.2; N, 16.1.

The **picrate** crystallized from aqueous ethanol as fine yellow needles, m.p. 259–260° (dec.).

Anal. Calcd. for $C_{29}H_{21}N_7O_7$: C, 60.1; H, 3.7; N, 16.9. Found: C, 60.3; H, 3.9; N, 16.5.

Dehydrogenation of N-Pyrazinylbenzamidines.—A mixture of the amidine (0.005 mole), dry lead tetraacetate (3.5 g., 0.008 mole), and dry benzene (50 ml.) was heated under reflux for 30 min. The precipitated lead acetate was removed by filtration and the filtrate shaken with sodium hydroxide solution (100 ml. of 30% aqueous solution). The benzene solution was dried (anhydrous sodium sulfate) and then evaporated to dryness. The residue was recrystallized from the solvent specified below.

4,7-Dimethyl-2-phenyl-*s*-triazolo[2,3-*a*]pyrazine (0.63 g., 56%) crystallized from petroleum ether (b.p. 60–80°) as colorless needles, m.p. 103–104°.

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.6; H, 5.4; N, 25.0. Found: C, 69.5; H, 5.5; N, 24.8.

The **picrate** separated from benzene–petroleum ether as yellow needles, m.p. 216–217°.

Anal. Calcd. for $C_{19}H_{15}N_7O_7$: C, 50.3; H, 3.3; N, 21.6. Found: C, 50.0; H, 3.2; N, 21.3.

6,7-Dimethyl-2-phenyl-*s*-triazolo[2,3-*a*]pyrazine (0.57 g., 51%) crystallized from petroleum ether (b.p. 60–80°) as colorless needles, m.p. 133–134°.

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.6; H, 5.4; N, 25.0. Found: C, 69.3; H, 5.3; N, 24.8.

The **picrate** separated from benzene–petroleum ether as yellow needles, m.p. 192–193°.

Anal. Calcd. for $C_{19}H_{15}N_7O_7$: C, 50.3; H, 3.3; N, 21.6. Found: C, 50.5; H, 3.7; N, 21.4.

2,6,7-Triphenyl-*s*-triazolo[2,3-*a*]pyrazine (1.22 g., 70%) crystallized from ethanol as colorless needles, m.p. 238–239°.

Anal. Calcd. for $C_{23}H_{16}N_4$: C, 79.3; H, 4.6; N, 16.1. Found: C, 78.9; H, 4.8; N, 15.9.

All attempts to prepare a picrate or a methiodide derivative of this compound were unsuccessful.

Treatment of 2-Amino-3,6-dimethylpyrazine with Aliphatic Cyanides. A. Acetonitrile.—A mixture of the amine (0.62 g., 0.005 mole), aluminum chloride (0.8 g., 0.006 mole), and acetonitrile (2 ml.) was heated in a sealed tube at 160° for 2 hr. The reaction mixture was dissolved in water, basified with sodium hydroxide solution, and extracted with ether. Evaporation of the ether gave only the unreacted 2-aminopyrazine (0.42 g.).

(11) Ultraviolet absorption spectra were measured with an Optica CF-4 recording spectrophotometer (we are indebted to Drs. G. E. Lewis and R. A. Jones for assistance with these measurements), and infrared absorption spectra with a Perkin-Elmer Model 137 spectrophotometer or with a Grubb-Parsons DB1 spectrophotometer. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne.

TABLE III

ULTRAVIOLET ABSORPTION DATA OF SEVERAL FUSED *s*-TRIAZOLE SYSTEMS

	Solvent[a]	λ_{max}, mμ (log ε)							
3-Methyl-*s*-triazolo[4,3-*a*]pyridine	E	209 (4.38)	244 (sh) (3.14)	249 (sh) (3.26)	252 (sh) (3.30)	258 (3.39)	262 (3.41)	268 (3.47)	288 (3.47)
2-Methyl-*s*-triazolo[2,3-*a*]pyridine	C	217.5 (4.58)					273 (3.57)	281 (i) (3.52)	294 (i) (3.20)
s-Triazolo[4,3-*a*]pyrimidine	E	209 (4.04)	213 (sh) (3.98)				250 (3.20)	266 (sh) (3.08)	298 (3.31)
s-Triazolo[2,3-*a*]pyrimidine	E	208 (4.50)							273 (3.56)
s-Triazolo[4,3-*b*]pyridazine[c]	*b*			240 (4.22)					305 (3.81)
3-Phenyl-*s*-triazolo[4,3-*a*]pyridine	C		221 (4.23)	243 (4.16)				287.5 (3.97)	
2-Phenyl-*s*-triazolo[2,3-*a*]pyridine	C		244.5 (4.56)	252.5 (4.56)			281 (i) (3.88)	292.5 (i) (3.73)	306 (3.58)

[a] E = 95% ethanol; C = cyclohexane. [b] Solvent not given. [c] S. Takahayashi, *J. Pharm. Soc. Japan*, **76**, 765, 1296 (1956).

B. Trichloroacetonitrile.—A mixture of the amine (0.62 g., 0.005 mole), aluminum chloride (0.8 g., 0.006 mole), and trichloroacetonitrile (3 ml.) was heated in a sealed tube at 180° for 5 hr. Extraction of the resulting solid material with ethanol gave a colorless, crystalline product (0.91 g.) which separated from aqueous ethanol as colorless needles, m.p. 91–92°. This product was identified as 2,4,6-tri(trichloromethyl)-*s*-triazine (lit.[12] m.p. 91–92°) by no depression in the mixture melting point and by identical infrared spectra.

Anal. Calcd. for $C_6N_3Cl_9$: Cl, 16.6; N, 9.7. Found: Cl, 16.8; N, 9.4.

It was not possible to isolate any further products from the reaction mixture.

Attempted Reaction of 2-Amino-3,6-dimethylpyrazine with Ethyl Acetimidate Hydrochloride.—A mixture of the amine (0.6 g., 0.005 mole), ethyl acetimidate hydrochloride[13] (0.6 g., 0.005 mole), and ether was heated under reflux for 10 hr. The insoluble material was collected by filtration, and the filtrate evaporated to dryness. The residue (0.45 g.) consisted of unreacted 2-amino-3,6-dimethylpyrazine. The insoluble material was dissolved in water; the solution was made basic with aqueous sodium hydroxide. No further compounds were obtained by extracting this solution with ether. Condensation was not effected by changing the solvent to a more polar one with a higher boiling point or by the use of longer reaction periods.

3,5,6-Triphenyl-*s*-triazolo[4,3-*a*]pyrazine.—Phosphorus pentoxide (35 g.) and orthophosphoric acid (17 ml.) were heated together on a steam bath for 3 hr. N-Benzoyl-2,3-diphenyl-6-hydrazinopyrazine[2] (3.8 g.) was added and the reaction mixture was heated at 150° for 3 hr. After cooling, water was added carefully and the solid material collected and recrystallized from ethanol. 3,5,6-Triphenyl-*s*-triazolo[4,3-*a*]pyrazine (3.0 g., 83%) separated as colorless needles, m.p. 240–241°.

Anal. Calcd. for $C_{23}H_{16}N_4$: C, 79.3; H, 4.6; N, 16.1. Found: C, 79.0; H, 4.6; N, 16.2.

(12) A. Weddige, *J. prakt. Chem.*, [2]**28**, 188 (1883).

(13) S. M. McElvain and J. W. Nelson, *J. Am. Chem. Soc.*, **64**, 1825 (1942).

Degradation of a C-Nor-D-homosapogenin

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Received April 10, 1964

The olefins **3** and **4**, produced by modified syntheses, were hydrogenated to a single compound, **5**. This sapogenin was converted to the unsaturated ketone **12a** and the lactone **11** by degradation of the side chain. Attempted ozonolysis of the pseudo-sapogenin **6** yielded in part the C-20 hydroxy derivatives **17** and **18**; these are postulated to have arisen from an epoxide intermediate (**15**).

The intricacies of the structural elucidation,[1] stereochemical determination,[2] and synthetic problems[3] presented by the C-nor-D-homo steroids and their more elaborate derivative alkaloids have stimulated a great deal of chemical research. A further incentive to these studies is provided by the strong hypotensive activity of some of these molecules, notably protoveratrine and its close relatives.[4] The intriguing aspects of these compounds led us to investigate a practicable route to some of their simpler analogs.[5] Three formally similar rearrangements recorded in the literature[6] provide an excellent method for synthesis of the basic skeleton starting from hecogenin, an abundantly available sapogenin. Projected degradation of the sapogenin side chain of the resultant C-nor-D-homo derivative would lead to molecules such as the unsaturated ketone **12**, in turn serving as intermediates to a variety of etiojervane derivatives.[7] These compounds would

(1) (a) L. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 867; (b) K. A. Jaeggi, E. Weiss, and T. Reichstein, *Helv. Chim. Acta*, **46**, 694 (1963), and references cited there.

(2) *Inter alia*, D. M. Bailey, D. P. G. Hamon, and W. S. Johnson, *Tetrahedron Letters*, 555 (1963); H. Mitsuhashi and Y. Shimizu, *Tetrahedron*, **19**, 1027 (1963); S. Okuda and K. Tsuda, *Chem. Ind.* (London), 512 (1961).

(3) P. W. Schiess, D. M. Bailey, and W. S. Johnson, *Tetrahedron Letters*, 549 (1963); R. A. Barnes and M. Sedlak, *J. Org. Chem.*, **27**, 4562 (1962).

(4) See L. C. Weaver, W. R. Jones, and S. M. Kupchan, *J. Pharm. Sci.* **51**, 1144 (1962), and references cited there.

(5) (a) H. Mitsuhashi, K. Shibata, T. Sato, and Y. Shimizu [*Chem. Pharm. Bull.* (Tokyo), **12**, 1 (1964)] have reported work along similar lines; (b) S. M. Kupchan and S. D. Levine [*J. Am. Chem. Soc.*, **86**, 701 (1964)] have recently described derivatives of this general type.

(6) (a) R. Hirschmann, C. S. Snoddy, Jr., C. F. Hiskey, and N. L. Wendler, *ibid.*, **76**, 4013 (1954); (b) J. Elks, G. H. Phillips, D. A. H. Taylor, and L. J. Wyman, *J. Chem. Soc.*, 1739 (1954); (c) R. Anliker, O. Rohr, and H. Heusser, *Helv. Chim. Acta*, **38**, 1171 (1955).

(7) The designation "etiojervane" will be used to describe 17aα-methyl-C-nor-D-homo-18-nor-5α,12α-androstane. *Cf.* J. Fried and A. Klingsberg, *J. Am. Chem. Soc.*, **75**, 4934 (1953), and ref. 5b.