sensitive to the nature of the solvent.[12] In this case a is 0.57.[12] On the other hand, a is only 0.14 for the allylic rearrangement of thionbenzoates. Apparently these thion esters rearrange by a mechanism which involves very little change in charge separation between the ground state and the transition state.

The effect of α- and γ-methyl groups on the rate of rearrangement of allyl thionbenzoate is also consistent with a small change in polarity in going to the transition state of the reaction. As is apparent from the data in Table II an α-methyl group increases rate by a factor of *ca.* 55 and a γ-methyl group increase rate by a factor of about 6. However, α- or γ-methyl groups are known to increase the reactivity of strongly electron-demanding reactions, such as the solvolysis of allyl chloride in formic acid,[19] by a factor of 10^3.

Experimental

Thiobenzoyl chloride was prepared as described by Staudinger.[17]

Allyl Thionbenzoate.—To a suspension of 1.0 g. of sodium hydride (51.6% NaH) in 20 ml. of ether was added 1.2 g. of allyl alcohol. After stirring for about 15 minutes, freshly distilled thiobenzoyl chloride[17] was added dropwise until a slight red color persisted. The ether solution was then washed with dilute sodium bicarbonate and dried over anhydrous potassium carbonate. Distillation gave 1.9 g. (52%) of a yellow oil, b.p. 84–86°(0.5 mm.). Characteristic infrared bands occurred at 1270(s), 1230(s), 1075(m), 1050(m) and 1030(m) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.37; H, 5.65. Found: C, 67.51; H, 5.53.

Crotyl thionbenzoate was prepared as described for allyl thionbenzoate from a sample of crotyl alcohol[20]; $n^{25}D$ 1.4260 (reported[20] $n^{25}D$ 1.4260). Rapid, short path distillation gave the thionester in 39% yield, b.p. 93–95° (0.3 mm.). The infrared spectrum showed characteristic bands at 1270(s), 1230(s), 1080(m), 1050(m), 1030(m) and 970(m) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.49; H, 6.35.

α-Methylallyl Thionbenzoate.—The sodium salt of 2.4 g. of α-methyl allyl alcohol[21] was prepared in 25 ml. of anhydrous tetrahydrofuran with 1.4 g. of 51.6% sodium hydride–oil dispersion. The stirred suspension of the salt was cooled to −20° and 4.2 g. of thiobenzoyl chloride[17] added dropwise. After 15 minutes, the dark brown mixture was poured into ether and washed with dilute aqueous sodium bicarbonate. After drying over potassium carbonate and removal of the solvent at reduced pressure, 4.2 g. of dark oil was obtained. Short path distillation gave 1.5 g. (23)% of the yellow ester, b.p. 80–85° (0.5 mm.). The infrared spectrum showed characteristic bands at 1270(s), 1330(s), 1070(m), 1050(m) and 1030(m) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.69; H, 6.59.

Allyl Thiolbenzoate.—To a slurry of 6.0 g. of potassium thiobenzoate[22] in 25 ml. of ether was added 3.6 g. of allyl bromide. After stirring for 3 days at room temperature the ether solution was washed with water and dilute aqueous sodium bicarbonate. Distillation gave 4.2 g. (79%) of the desired ester, b.p. 85–86° (0.5 mm.), $n^{25}D$ 1.5799. Characteristic infrared bands appeared at 1670, 1210 and 920 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.37; H, 5.65. Found: C, 67.39; H, 5.59.

Crotyl Thiolbenzoate.—Crotyl chloride (9.1 g.) was added to 16 g. of sodium thiobenzoate in 200 ml. of acetone. After standing overnight the solution was poured into water and extracted with several portions of ether. The ether solution was dried over magnesium sulfate and distilled. The yield of ester was 7.5 g. (38%), b.p. 98–100° (0.5 mm.), $n^{25}D$ 1.5755. Characteristic infrared bands appeared at 1670, 1210, 970 and 920 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}SO$: C, 68.71; H, 6.29. Found: C, 68.79; H, 6.29.

Solvents.—Acetic acid, acetonitrile, acetone and tetrahydrofuran were purified in the usual manner.[12] Chlorobenzene and cyclohexane were washed with concentrated sulfuric acid followed by water and aqueous sodium carbonate. These solvents were then dried with Linde type 4A Molecular Sieve and distilled.

Kinetic Procedure.—All reactions were run in sealed ampoules in a thermostated oil-bath controlled to ±0.05°. At appropriate times samples were removed from the bath, cooled, and examined for absorption at 420 mμ with a Beckman DU spectrophotometer equipped with a photomultiplier. A slit width of 0.3 mm. was employed.

(19) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(20) W. G. Young, S. H. Sharman and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

(21) S. Winstein and W. G. Young, *ibid.*, **58**, 104 (1936).

(22) O. Kym, *Ber.*, **32**, 3533 (1899).

COMMUNICATIONS TO THE EDITOR

N-*GUAN*-STREPTOLIDYL GULOSAMINIDE, A DEGRADATION PRODUCT OF THE STREPTOTHRICIN ANTIBIOTIC GROUP

Sir:

Among the various hydrolytic degradation products of streptolin,[1] streptothricin[2] and probably other, similar antibiotics,[3] is found a water soluble amino acid (I) referred to in the past as Compound C[2] or Compound 5.[4] In this Communication we present evidence which defines the structure of I as N-*guan*-streptolidyl gulosaminide (II).

Cellulose and charcoal chromatography afforded I as a crystalline dihydrochloride, m.p. 215–220° dec., $[\alpha]D$ −22.4° (*c* 3.00, water) (Found: C, 34.57; H, 6.17; N, 16.20; Cl, 16.70). Aminoacid I gave positive Weber (blue) and ninhydrin tests, and negative Sakaguchi, Ehrlich and Elson–Morgan tests. Van Slyke analysis indicated two primary amino functions: C-methyl, O-methyl, N-methyl and α-amino acid groups were shown to be absent. Prolonged vigorous acid hydrolysis of I resulted in a mixture of streptolidine,[5] gulosamine and 1,6-anhydrogulosamine.[4,6] Substance I

(1) E. E. Smissman, R. W. Sharpe, B. F. Aycock, E. E. van Tamelen and W. H. Peterson, *J. Am. Chem. Soc.*, **75**, 2029 (1953).

(2) H. E. Carter, R. K. Clark, Jr., P. Kohn, J. W. Rothrock, W. R. Taylor, C. A. West, G. B. Whitfield and W. G. Jackson, *ibid.*, **76**, 566 (1954).

(3) *E.g.*, roseothricin: T. Goto, Y. Hirata, S. Hosoya, and N. Komatsu, *Bull. Chem. Soc., Japan*, **30**, no. 7, 729 (1957).

(4) E. E. van Tamelen, J. R. Dyer, H. E. Carter, J. V. Pierce and E. E. Daniels, *J. Am. Chem. Soc.*, **78**, 4817 (1956).

(5) H. E. Carter, *et. al.*, *J. Am. Chem. Soc.*, **83**, 4296 (1961).

(6) This observation is incompatible with the intermolecular ether formulation for I proposed by the Japanese school (ref. 3).

rapidly consumed approximately three moles of periodate, giving one mole of formaldehyde, two moles of ammonia, and between one and two moles of formic acid[7]; treatment of the periodate product with acidic 2,4-dinitrophenylhydrazine gave (in small yield) glyceraldehyde 2,4-dinitrophenylhydrazone.[6] The marked stability of I to acid is due to the fact that it is an N-glycoside of a 2-aminosugar.[8]

In respect to glycosidic attachment, a provisional choice among the guanidine nitrogens was made possible by quantitative Van Slyke nitrous acid deamination studies. The N,N'-diacetyl derivative of I (non-crystalline, purified by cellulose chromatography: Found: C, 43.87; H, 6.03; N-acetyl, 15.5) evolved nitrogen much more slowly than mono-N-(benzenesulfonyl)-streptolidine or any model 2-aminoimidazoline studied (Table I), suggesting the absence of a primary

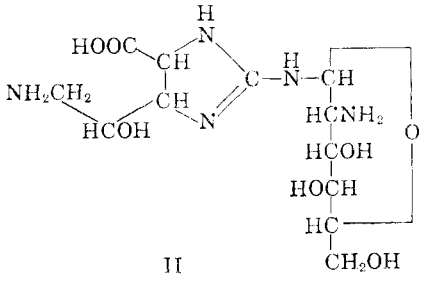
TABLE I

VAN SLYKE DETERMINATIONS ON GUANIDINES[a]

Compound	Moles of nitrogen evolved in hr. 0.25	1.0	3	10
2-Aminoimidazoline	0.26	1.02	1.87	...
2-Aminoimidazoline-4,5-dicarboxylic acid	0.88	1.87	2.44	...
Streptolidine·HCl[b]	0.33	1.29	2.00	2.22
N-Benzenesulfonyl streptolidine	0.23	0.52	1.17	1.45
N,N'-Diacetyl-N(*guan*)-streptolidylgulosaminide	0.06	0.05	0.20	0.28

[a] Values obtained with a normal Van Slyke apparatus, using sodium nitrite–glacial acetic acid at 25 ± 1°.
[b] Amount of nitrogen indicated in addition to that released by the non-guanidino primary amino group.

guanidino amino group in I, and therefore attachment of the aminosugar to the exocyclic nitrogen of the 2-aminoimidazoline moiety.[9,10]



II

(7) The release of the additional formic acid probably is the result of over-oxidation and to the acid-instability of the primary periodate product.

(8) In a simpler case, Dr. J. S. G. Cox (unpublished results, University of Wisconsin) demonstrated that N-(glucosyl)-guanidinoacetic acid is acid-hydrolyzed only slowly to the hexose and the guanidine components, but yet sensibly more rapidly than is N·*guan*-streptolidyl gulosaminide. The difference between these two systems may derive from the presence of a second, adjoining basic center in the latter case, which would be expected to inhibit acid cleavage of the glycosidic link.

(9) A like assignment was made by the Japanese workers (ref. 3), who depended upon the C=N stretching frequency of I and some model guanidines for their conclusions. Our own examination of this method, in which use was made of other representative guanidine models, demonstrated, however, that such exceptions to the working rules of the Japanese exist that deductions regarding alkyl substitution on guanidines, based on infrared spectral methods seem, at present, unjustified.

(10) Because of the positive rotations of streptolidine and α-D-gulosamine and the negative rotation of I, the β-configuration is tentatively assigned to the glycosidic linkage present in I.

Thus, structure II best accommodates the information available at the present time, and its incorporation into the complete formulas of streptothricin and streptolin is described in the accompanying Communication.[11]

(11) van Tamelen, *et al.*, **83**, 4295 (1961).

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THE STRENGTHS OF CYANOCARBON ACIDS AND AN H-ACIDITY SCALE FOR CONCENTRATED ACID SOLUTIONS

Sir:

The syntheses of a number of cyanocarbon acids have been reported previously from this laboratory.[1] These were shown to be unusually strong organic acids, and p*K*a's near 2 were reported. Further work now has proved them to be much stronger than originally thought and to possess an acid strength that is remarkable.

Reinterpretation of potentiometric titration curves shows the acids to be strong within the limitations of that method (p*K*a $< \sim 0.5$). Apparently the most feasible method of determining their strengths is to study their ultraviolet or visible spectra in solutions of strong mineral acids since the free anions usually have characteristic, strong electronic absorptions which should disappear on protonation. It has been found that a number of these acids do undergo reversible spectral changes characteristic of protonation in such solutions. The most promising approach to interpretation of the measured species concentration appears to be that of an "acidity function." Thus, this finding presents the possibility of determining the strengths of the cyanocarbon acids and simul-

TABLE I

IONIZATION CONSTANTS OF CYANOCARBON ACIDS, 25°

Cyanocarbon acid	p*K*a $HClO_4$	p*K*a H_2SO_4	λ_{max} (mμ) for longest wave-length band: Free anion	Protonated form
p-(Tricyanovinyl)-phenyl dicyanomethane	0.60	...	607	332
Methyl dicyanoacetate	−2.78	−2.93	235	<200
Hexacyanoheptatriene	−3.55	−3.90	645	347
Cyanoform	−5.13	−5.00	210	<200
Bis-(tricyanovinyl)-amine	−6.07	−5.98	467	366
Pentacyanopropene	<-8.5	...	395	?
Hexacyanoisobutylene pK_1	<-8.5	...	370	?
pK_2	(-2.9)[a]	...	336	370

[a] From a crude extrapolation of $-H_0 + \log (C_{A^-}/C_{HA})$ to zero concentration in $HClO_4$ and H_2SO_4.

(1) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).