(4 H, m, aromatic), 4.29 (2 H, s, >CCH_2O), 3.90 (3 H, s, H_3CO), 2.90 (3 H, s, OSO_2CH_3), 1.52 (6 H, s, >$C(CH_3)_2$).

Preparation of the π-Complexed Methanesulfonates. The π-complexed methanesulfonates were prepared by treatment of the noncomplexed methanesulfonates with chromium hexacarbonyl in a Strohmeier apparatus as described previously.[3] Melting points, analyses, and yields are recorded in Table II.

2-[π-(p-Chlorophenyl)chromium tricarbonyl]-2-methylpropyl methanesulfonate (6a-OMs): IR ($CHCl_3$) 3030, 1450 (aromatic), 1970, 1900 (C≡O), 1400, 1160 (OSO_2), 1380 cm^{-1} (>$C(CH_3)_2$); NMR ($CDCl_3$) δ 5.65–5.26 (4 H, complex m, aromatic), 4.00 (2 H, s, >CCH_2O), 2.93 (3 H, s, OSO_2CH_3), 1.29 (6 H, s, >$C(CH_3)_2$).

2-[π-(m-Anisyl)chromium tricarbonyl]-2-methylpropyl methanesulfonate (5a-OMs): IR ($CHCl_3$) 3030, 1530 (aromatic), 2800, 1250 (aromatic methoxyl), 1970, 1900 (C≡O), 1400, 1150 (OSO_2), 1380 cm^{-1} (>$C(CH_3)_2$); NMR [$(CD_3)_2CO$] δ 5.90–5.17 (4 H, complex m, aromatic), 4.17 (2 H, s, >CCH_2O), 3.33 (3 H, s, OCH_3), 3.01 (3 H, s, OSO_2CH_3), 1.44 (6 H, s, >$C(CH_3)_2$).

Products from the Acetolysis of 2-[π-(p-Chlorophenyl)-chromium tricarbonyl]-2-methylpropyl Methanesulfonate (6a-OMs). A 25-mL sample of 0.033 M **6a**-OMs and 0.05 M sodium acetate in oxygen-free, anhydrous acetic acid was heated under nitrogen at 100 °C for 20 h (11 half-lives), cooled, poured over ice, and extracted with three 20-mL portions of pentane. The combined extracts were washed with excess, cold, saturated aqueous sodium carbonate solution and with two portions of cold water and dried over anhydrous magnesium sulfate. When spotted on a thin-layer plate coated with silica gel and developed with 50/50 ether/pentane, three yellow spots were evident.

The yellow solution was decomplexed by using 1.5 g (2.7 mmol) of ceric ammonium nitrate in 30 mL of acetone and 20 mL of water.[2] The mixture was stirred until the yellow color had disappeared (1 h), and the ether–pentane layer was washed with water, filtered through anhydrous sodium sulfate, and concentrated to ~10 mL. A GLC analysis on a 12-ft Carbowax column showed three components having relative retention times (relative peak areas in parentheses) of 4.7 (34%), 6.1 (12%), and 21.8 (54%). The first and second components were identified as 3-(p-chlorophenyl)-2-methyl-1-propene (**8**) and 1-(p-chlorophenyl)-2-methyl-1-propene (**9**), respectively, by comparison of their IR and NMR spectra with those of authentic samples. The third component was identified as 3-(p-chlorophenyl)-2-methyl-2-propyl acetate (**10**) from the following spectral characteristics: IR (CCl_4) 3030, 1500 (aromatic), 2950, 2900 (CH), 1730 (C=O), 1380, 1360 (>$C(CH_3)_2$), 1235, 1020 cm^{-1} (C—O, acetate); NMR ($CDCl_3$) δ 7.29–7.1 (4 H, A_2B_2 q, aromatic), 3.0 (2 H, s, O>CCH_2–aryl), 1.9 (3 H, s, $OCOCH_3$), 1.4 (6 H, s, >$C(CH_3)_2$).

Kinetic Studies. The acetolysis rates were measured titrimetrically, with the ampule technique described previously,[1] on ~0.03 M solutions of the methanesulfonate in acetic acid buffered with 0.05–0.1 M sodium acetate and containing ~1% acetic anhydride. Oxygen-free solutions prepared as described previously[1] were employed with the complexes.

Registry No. 1-OMs, 29240-45-7; **1a**-OMs, 31973-95-2; **2**-OMs, 29240-46-8; **2a**-OMs, 72938-23-9; **3**-OMs, 29240-47-9; **3a**-OMs, 31833-07-5; **4**-OMs, 29240-48-0; **4a**-OMs, 31833-08-6; **5**-OMs, 72925-77-0; **5a**-OMs, 72938-23-9; **6**-OMs, 72925-78-1; **6a**-OMs, 72926-38-6; **7**-OMs, 72925-79-2; **8**, 23063-65-2; **9**, 19366-15-5; **10**, 72925-80-5.

Transmission of Substituent Effects in Thiophenes. Infrared and Carbon-13 Nuclear Magnetic Resonance Studies

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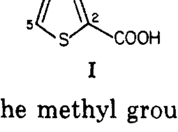
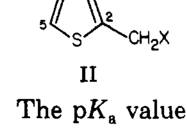
The carbon-13 NMR spectra in Me_2SO-d_6 and the infrared carbonyl stretching frequencies were determined for nine 4-(substituted methyl)-2-thiophene-2-carboxylic acids (I) and for nine 2-(substituted methyl)-4-thiophene carboxylic acids (II). Chemical shift assignments were made by employing chemical shift and intensity arguments and by interpretation of the proton-coupled spectra. The assignments in series I were supported by a lanthanide shift reagent study on Ia. Infrared carbonyl stretching frequencies were determined in chloroform and tetrachloromethane solutions. The infrared stretching frequency data were correlated reasonably well with σ_I constants, whereas the NMR data gave much poorer correlations with single-parameter approaches. The conclusions drawn from both the IR and NMR data are consistent with previously reported pK_a and carbon-13 NMR data which indicated unequal transmission of substituent effects in the two series. All of the data, pK_a, IR, and NMR, for transmission of substituent effects can be explained in terms of differences in the relative coplanarity of the two systems and its consequences on the π-inductive effect.

Reports have recently appeared describing the effect of substituents on the acidity and the carbon-13 chemical shifts in $CDCl_3$ of 4-methyl-2-thiophenecarboxylic acids (I) and 2-methyl-4-thiophenecarboxylic acids (II) substituted on the methyl group.[1] The pK_a values for both series were reasonably well correlated with σ_I values. Interestingly, the ρ value for series I was approximately 1.5 times larger than that for series II. Limited correlations were observed between the carbon-13 data and substituent constants. These results indicate that transmission of substituent effects is dramatically changed by reversing the location of the reaction site and the substituent in this



I



II

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Table I. Frequencies of C=O Stretching Vibration for Substituted 4-Methylthiophene-2-carboxylic Acids (I) and 2-Methylthiophene-4-carboxylic Acids (II) (in cm^{-1})

		CCl_4		CHCl_3
compd	X	ν(C=O) free	ν(C=O) bound	ν(C=O) bound
Ia	H	1733	1681	1694
Ib	OH	1734	1683	1699
Ic	OMe	1734	1682	1702
Id	SH	1734	1682	1698
Ie	OPh	1734	1683	1699
If	COOH	*a*	*a*	1712
Ig	SEt	1734	1682	1697
Ih	Br	1737	1685	1701
Ii	$\mathrm{SO_2Ph}$	*a*	*a*	1702
IIa	H	1738	1692	1702
IIb	OH	1739	1694	1711
IIc	OMe	1739	1690	1706
IId	SH	1739	1690	1705
IIe	OPh	1741	1691	1706
IIf	COOH	*a*	*a*	1718
IIg	SEt	1738	1686	1705
IIh	Br	1742	1693	1708
IIi	$\mathrm{SO_2Ph}$	*a*	*a*	1708

[a] The spectra were not recorded because of the low solubility of the compounds in tetrachloromethane.

system and is a similar result to a recent finding made in another heterocyclic system.[2] The greater sensitivity of series I to substituent effects has been suggested to arise from differences in the π-inductive effect.[1] Such a finding merits additional investigation and confirmation by employing other techniques for developing linear free-energy relationships. Consequently, we have examined the infrared carbonyl stretching frequencies and further studied the carbon-13 NMR chemical shifts for the compounds in series I and II, methods which we have found to be useful for examining the transmission of substituent effects in heterocyclic systems.[2,3]

Results and Discussion

Carbonyl Stretching Frequency Studies. The wavenumbers of the C=O stretching vibration for the series of substituted methylthiophenecarboxylic acids (I and II) were measured in tetrachloromethane and chloroform. The data are listed in Table I.

With tetrachloromethane solutions, two absorption bands occur in the C=O stretching region. The higher wavenumber band (in the region of 1742–1733 cm^{-1}) was assigned to the C=O stretching vibration of the free carboxylic acid groups. The lower wavenumber absorption (in the 1694–1681-cm^{-1} region) was assigned to the carbonyl stretching vibration of the carboxylic acid groups bonded by an intermolecular hydrogen bond of the type C=O···HO (probably a cyclic dimeric association) which is common in the case of carboxylic acids. This observation was also supported by the change in the relative intensities of the two carbonyl bands on lowering the concentrations of solutions. On the other hand, in chloroform solutions only one carbonyl stretching band was observed in the 1711–1697-cm^{-1} region for both series of compounds. The previously reported order of acidity for compounds I and II is also in agreement with somewhat higher Δν values ($\Delta\nu = \nu_{\mathrm{free}} - \nu_{\mathrm{bound}}$) determined in tetrachloromethane for series I which indicates stronger intermolecular hydrogen bonds. On comparison of the above-mentioned wavenumber regions, it can be concluded that in chloroform solutions hydrogen bonding between the carboxylic groups and chloroform molecules is preferred to self-association of the acids. In chloroform solutions, there is no evidence for the presence of two possible conformations of the carboxylic group with respect to the thiophene ring sulfur atom. However, the absorption bands in tetrachloromethane are much broader than in chloroform, which suggests the overlapping of two bands belonging to O–S cis and O–S trans conformers. In tetrachloromethane solution the influence of the substituents on the C=O stretching wavenumbers is rather small; moreover, in this solvent not all the spectra have been measured due to the low solubility of some compounds. In chloroform solution the carbonyl stretching frequencies are more sensitive to substituent effects and can be correlated moderately well with σ_{I} substituent constants (see Table II).

Table II. Results of Regression Analysis for Correlations of C=O Stretching Frequencies with σ_{I} Substituent Constants

series	r^{a}	ρ^{b}	ν^{c}	s^{d}	n^{e}	omitted[f]
I^{g}	0.915	12.61	1694.4	0.5	7	COOH, OMe
II^{g}	0.968	9.75	1702.5	0.5	7	COOH, OH
I^{h}	0.919	12.87	1694.5	0.5	7	COOH, OMe
II^{h}	0.970	9.90	1702.5	0.5	7	COOH, OH

[a] Correlation coefficient. [b] Slope. [c] Intercept. [d] Standard deviation. [e] Number of compounds used in correlation. [f] Excluded due to large deviation from the line of the other points. [g] σ_{I} values taken from ref 7; for EtS and $\mathrm{PhSO_2}$ substituents the σ_{I} values of the MeS and $\mathrm{MeSO_2}$ groups, respectively, were used. [h] σ_{I} values are the same as those employed in ref 1.

On comparison of the regression coefficients for correlations of the C=O stretching frequencies with σ_{I} for I and II, it can be observed that the inductive effects are transmitted in system I more efficiently than in series II, which is in good agreement with the previous observation using correlations between the $\mathrm{p}K_{\mathrm{a}}$ values and σ_{I} constants. The ratio of regression coefficients $\rho_{\mathrm{I}}/\rho_{\mathrm{II}} = 1.3$ for (C=O) vs. σ_{I} correlation is close to the ratio $\rho_{\mathrm{I}}/\rho_{\mathrm{II}} = 1.5$ obtained by using the $\mathrm{p}K_{\mathrm{a}}$ vs. σ_{I} correlation. The carbonyl stretching frequencies for series I are lower than that for series II, which is consistent with the order of the carbonyl stretching frequencies determined by Gronowitz and Rosenberg[4] for 2- and 3-thiophenecarboxylic acids which has been suggested to result from the higher electron-releasing effect of the thiophene ring at position 2 compared with position 3. This suggestion is seemingly in contradiction with the higher acid strength of the 2-carboxylic acids in comparison with the 3-carboxylic acids. The higher acidity of the 2-carboxylic acids than that of their 3-carboxylic isomers in five-membered-ring heterocyclic systems has been explained in terms of the inductive effect of the proximate heteroatom.[5] While there can be little doubt about the importance of the heteroatom's inductive effect on the 2-carbon or about the electron distribution in the five-membered-ring heterocyclic system, it seems that another factor which appears to have been previously overlooked may contribute to the understanding of these results. Namely, the higher carbonyl stretching frequency of the 3- or 4-thiophenecarboxylic acids can be satisfactorily explained as a result of the fact that such a carboxyl function cannot achieve the same degree of coplanarity that a 2-carboxyl group can because the 3-carboxyl function is flanked by two, not one, ortholike protons. By use

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Table III. Carbon-13 NMR Shifts (δ) for Series I

X	COOH	CH_2	C(2)	C(3)	C(4)	C(5)	other
H	162.5	15.2	133.9	134.6	137.9	128.3	
OH	162.5	58.5	134.2	132.4	144.5	127.8	
OMe	162.4	57.4	134.5	132.7	140.0	129.8	68.6
SH	162.4	22.2	134.4	133.5	142.7	128.7	
OPh	162.3	64.3	134.7	132.7	138.6	130.4	157.7, C(1′); 114.5, C(2′); 129.1, C(3′); 120.5, C(4′)
COOH	162.5	35.1	133.9	134.6	135.5	130.1	171.5
SEt	162.5	29.1	134.4	133.8	139.9	129.4	25.0, 14.4
Br	162.2	27.8	135.1	133.7	139.0	131.8	
SO_2Ph	162.2	55.5	134.3	134.5	137.9	133.6	129.1, C(1′); 127.6, C(2′); 128.9, C(3′); 133.7, C(4′)

Table IV. Carbon-13 NMR Shifts (δ) for Series II

X	COOH	CH_2	C(2)	C(3)	C(4)	C(5)	other
H	163.2	14.9	140.0	125.0	133.7	131.1	
OH	163.2	58.1	147.3	123.8	133.3	131.8	
OMe	163.0	57.2	141.9	126.2	133.3	133.0	67.9
SH	163.0	22.2	146.0	125.2	133.3	132.0	
OPh	163.0	63.9	140.4	127.0	133.4	133.4	157.4, C(1′); 114.7, C(2′); 129.3, C(3); 120.9, C(4)
COOH	163.1	34.7	137.2	126.8	133.1	132.2	171.0
SEt	163.0	29.0	143.5	126.0	133.3	132.3	24.8, 14.3
Br	162.7	27.5	141.6	128.4	133.5	134.4	
SO_2Ph	162.7	55.2	137.5	138.9	133.3*	134.6	130.3, C(1′); 127.8‡, C(2′); 128.9‡, C(3′); 133.7*, C(4′)

of this argument, the greater acidity of the 2-carboxylic acids can be understood in terms of a combination of σ- and π-inductive effects, the latter being enhanced by greater coplanarity for the 2-carboxylic acid series. This approach can be used to explain the greater transmission of inductive substituent effects in series I in comparison with those of II. The more coplanar compounds I provide a more efficient arrangement for π-inductive transmission via the π electrons of the ring and carboxylic acid group and thus result in a larger ρ value in the Hammett correlations (as was previously observed[1]).

Carbon-13 NMR Studies. The assignments of the carbon-13 spectra for the substituted 4-methylthiophene-2-carboxylic acids (I) were accomplished by using chemical shift and signal-intensity arguments and by interpretation of the coupled spectra[6] and are in good agreement with the previous report.[1] The assignment of the signal appearing in the 162-ppm region to the carboxyl carbon is consistent with reported values for this function. The methylene carbon ranged from 22 to 58 ppm as the substituent X was varied. Its position was in accord with previously observed values in similar systems and was readily characterized by its multiplicity (triplet) in the coupled spectra. The aromatic carbon pair C(2) and C(4) could be differentiated from the other thiophene ring pair C(3) and C(5) by signal intensity. The signals for the low-intensity pair, arising from carbons C(2) and C(4), could be easily assigned by inspection of the coupled spectrum since C(4) appears as a triplet due to coupling to the methylene protons whereas C(2) appears as a broad singlet. Differentiation of the signals for C(3) and C(5) was more difficult. Substituent chemical shift arguments suggest that the signal for C(5) should appear upfield from that of C(3). The assignment based upon chemical shift arguments was supported by a lanthanide shift reagent study with 4-methylthiophene-2-carboxylic acid. If it is assumed that the complex occurs primarily at the carboxyl function, C(3) should experience the greater shift on incremental addition of a lanthanide reagent. Complexing with sulfur was found to be undetectable by carrying out a control study using 3-methylthiophene. The observed shifts for C(3) and C(5) of 4-methylthiophenecarboxylic acid, extrapolated to a 1:1 molar ratio of lanthanide and thiophene, were 7 and 4 ppm, respectively. The assignments of the carbon resonances in the second series, 2-substituted thiophene-4 carboxylic acids II, were analogous to that described above for series I. However, in this case unambiguous assignment of C(3) and C(5) was readily made on the basis of the observed coupling of the methylene protons with C(3) and the absence of such coupling with C(5). The chemical shift assignments are found in Tables III and IV.

Table V. Correlation of Chemical Shifts of Series II vs. I

carbon						
ser II	ser I	r^a	ρ^b	i^c	s^d	n^e
CH_2	CH_2	0.999	0.996	−0.120	0.125	9
C(2)	C(4)	0.955	1.230	−29.98	0.989	9
C(3)	C(5)	0.969	0.866	13.76	0.394	9
C(4)	C(2)	0.365	0.447	113.59	0.167	9
C(3)	C(3)	0.372	0.700	32.84	1.503	9
C(5)	C(5)	0.920	0.604	54.21	0.452	9

^{a} Correlation coefficient. ^{b} Slope. ^{c} Intercept. ^{d} Standard deviation. ^{e} Number of compounds used in correlation.

For comparison of the effect of substituents in the two series I and II, carbon-13 shift data for corresponding carbons from the two series were plotted against each other. The plot of the two sets of methylene chemical shifts gave an excellent straight line ($r = 0.999$) with a slope of 0.996. Also, plotting chemical shift data for C(2) series II vs. those of C(4) series I and the data for C(3) series II vs. those of C(5) series I along with the respective C(5)–C(5) plot gave reasonable correlations. The results of these comparisons are shown in Table V. It is important to note that neither the plot of C(4) series II data vs. C(2) series I data nor the plot of the two C(3) data sets gave a correlation, consistent with the IR and pK_a data, which clearly indicates that substituent effects are not transferred equally to the carboxyl-bearing carbons.

Attempts were made to correlate the carbon-13 chemical shift data with σ_I; however, of all carbons in both series only C(5) in series II gave a correlation coefficient greater than 0.9 ($r = 0.913$) when all compounds were included in

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(7) (a) O. Exner, "Advances in Linear Free Energy Relationships", Plenum Press, London and New York, 1972, p 37; (b) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, 85, 907 (1963).

the correlations. Consequently, it was concluded that the carbon-13 chemical shifts could not be satisfactorily correlated with a single-parameter expression.

Experimental Section

The syntheses of the compounds employed in this study have been previously described.[8]

The infrared spectra were recorded on a Perkin-Elmer 567 spectrophotometer in the region of 1800–1600 cm^{-1} with tetrachloromethane and dried chloroform as solvents. For measurement, NaCl cells with path lengths of 0.01, 0.1, 0.5, and 1 cm were used. Uniform concentrations for all compounds were chosen to give an absorption of 70–75%. The C=O stretching frequencies were determined with an accuracy of ± 1 cm^{-1}.

Carbon NMR spectra were obtained by employing a JEOL FX-60Q Fourier transform NMR spectrometer operating at a frequency of 15.04 MHz. Data were accumulated on a Texas Instruments 980B computer using 8192 data points over a 4-kHz spectral width to yield a data-point resolution of 0.99 Hz. For noise-decoupled spectra, samples were irradiated by using a pulse width corresponding to 45°, and a 5-s pulse-repetition time was used. For the proton-coupled spectra, a gated pulse sequence was used to obtain NOE intensification of the signals. The NMR samples were prepared by weight as 0.1 M solutions with commercial NMR grade dimethyl-d_6 sulfoxide. The signals are referenced to Me_4Si by giving the most intense solvent signal the value of 39.6 ppm.

The linear free-energy statistical treatment of the data was carried out as previously described.[9]

The lanthanide shift reagent studies on Ia were carried out in $CDCl_3$, for solubility reasons, by using tris(6,6,7,7,8,8,8-heptafluoro-2,2,3,5-tetramethyl-3,5-octanedionato)europium. Shift data were collected at 0, 0.05, 0.1, 0.2, and 0.3 molar equiv of the lanthanide with respect to Ia, and the data reported are a result of extrapolation to a 1:1 complex. The control study with 3-methylthiophene was carried out in the same manner, and no change (less than 0.1 ppm for a 1:1 complex) in chemical shift for any carbon was observed.

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Registry No. Ia, 14282-78-1; Ib, 14282-65-6; Ic, 54796-49-5; Id, 61854-93-1; Ie, 61854-92-0; If, 61854-96-4; Ig, 61854-94-2; Ih, 54796-50-8; Ii, 61854-95-3; IIa, 19156-50-4; IIb, 25744-99-4; IIc, 61854-98-6; IId, 61855-00-3; IIe, 61854-99-7; IIf, 61855-03-6; IIg, 61855-01-4; IIh, 61854-97-5; IIi, 61855-02-5.

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Evidence for Bicyclic Oxonium Ions in the Nitrous Acid Deamination of Benzyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosides[1]

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The nitrous acid deamination of conformationally rigid benzyl amino-4,6-*O*-benzylidenedeoxy-D-hexopyranosides was studied: benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**5**) and benzyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (**4**) in aqueous dioxane both gave some benzyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**2**). Thus, a trans-diaxial arrangement of hydroxyl and amino groups in the ground state does not appear to be an absolute requirement for epoxide formation, although such an arrangement clearly is most conducive to this reaction, as a comparison of yields showed. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (**7**) under similar conditions gave, by elimination, benzyl 4,6-*O*-benzylidene-α-D-*erythro*-hexopyrano-3-uloside (**8**) and, by benzyloxy migration, 2-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (**11**). Contrary to expectation, the same products, **8** and **11**, were isolated from the deamination of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**10**) and its α-D-mannopyranoside analogue (**7**). A bicyclic oxonium ion is postulated as an intermediate for the deamination of the α-D-gluco isomer. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**13**), with nitrous acid, gave benzyl 4,6-*O*-benzylidene-2-deoxy-β-D-*erythro*-hexopyrano-3-uloside (**14**). Here also, a bicyclic oxonium ion appears to be involved. All products isolated in this or earlier work from the deamination of 2-amino-4,6-*O*-benzylidene-D-glucopyranosides can be explained by mechanisms involving bicyclic oxonium ion intermediates. Such intermediates are apparently not involved in the deamination of the manno or altro analogues.

Nitrous acid deamination was used early to study structures of 2-amino-2-deoxy-D-glucose[2,3] and its analogues. Deamination reactions of various amino sugars were reviewed by Williams.[4] Inversion and rearrangement products were reported.[5-9] Nitrous acid deamination was used to cleave hydrolysis-resistant glycosidic linkages[10] by a technique valuable in the elucidation of the structure of heparin.[10-14] Hydrazinolysis followed by nitrous acid deamination of α_1-acid glycoprotein gave acidic and neutral mono- and oligosaccharides.[15]

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[1] (a) From the M.S. thesis of Wai-Pan Chan, University of the Pacific, Stockton, CA, 1974. (b) A preliminary version was presented at the 172nd National Meeting of the American Chemical Society, San Francisco, CA, 1976, No. CARB 6. (c) Partial support by the Research Corp. is gratefully acknowledged.

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