Carbonyl Stretching Frequencies and Transmission of Electronic Effects in 1-Phenyl-3-(5-aryl-2-furyl)propenones and 1-Phenyl-3-(5-aryl-2-thienyl)propenones

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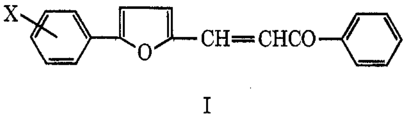
Received November 27, 1972

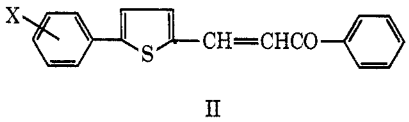
The s-cis and s-trans carbonyl stretching frequencies of a series of *trans*-1-phenyl-3-(5-aryl-2-furyl)propenones (I) and *trans*-1-phenyl-3-(5-aryl-2-thienyl)propenones (II) have been measured in carbon tetrachloride and chloroform solutions. Statistically significant linear free-energy relationships were obtained between ν(C=O) and σ^+ constants; poorer correlations using σ values were obtained in all cases. The data were also treated using the Swain–Lupton F and R constants, and poorer correlations than noted with σ^+ were obtained. The influence of the conformation on the transmission of electronic effects is discussed and compared with that in analogous systems. The parameters of the linear free-energy relationships for series I and II were compared with those for a series of *trans*-1-phenyl-3-arylpropenones (III). Using the slopes of ν(C=O) *vs.* σ^+ correlations in series I–III the transmissive factors for the furan and thiophene rings were calculated and related to data published earlier. The determined order of transmission for the intervening groups was furan > thiophene > benzene.

In preceding work[2–6] we have investigated, using linear free-energy relationships between the carbonyl stretching frequencies and substituent constants, the transmission of electronic effects and the influence of conformation on this transmission in a series of substituted chalcones and other α,β-unsaturated ketones. Furthermore, we used[7–10] the correlations between the carbonyl stretching frequencies and substituent constants for quantitative study of the transmission of electronic effects by the furan and thiophene bridges in several systems.

Continuing our investigations of linear free-energy relationships of α,β-unsaturated ketones and of transmission of electronic effects by various intervening groups, we have measured the carbonyl stretching frequencies of a series of *trans*-1-phenyl-3-(5-aryl-2-furyl)propenones (I) and *trans*-1-phenyl-3-(5-aryl-2-thienyl)propenones (II) and compared the results with those for a series of *trans*-1-phenyl-3-arylpropenones (III) (chalcones) reported earlier.[1,2]



I



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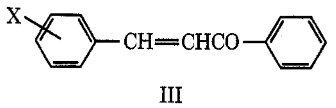

III

Results and Discussion

Carbonyl Stretching Frequencies.—The carbonyl stretching frequencies measured in CCl_4 and $CHCl_3$ solutions for a series of *trans*-1-phenyl-3-(5-aryl-2-furyl)propenones (I) and *trans*-1-phenyl-3-(5-aryl-2-thienyl)propenones (II) are listed in Tables I and II, respectively. The carbonyl region of the spectra of these compounds is similar in shape to that of the analogous region of the spectra of substituted chalcones.[2,3] On the basis of this analogy and the solvent

TABLE I

1-PHENYL-3-(5-ARYL-2-FURYL)PROPENONES (I)[a]

Compd	X	In CCl_4 $\nu_{s\text{-cis}}$	In CCl_4 $\nu_{s\text{-trans}}$	In $CHCl_3$ $\nu_{s\text{-cis}}$
1	4-OCH_3	1666.0	1642.5	1660.0
2	4-CH_3	1667.5	1644.5	1661.0
3	4-H	1668.5	1645.5	1662.0
4	4-Cl	1668.5	1646.5	1662.5
5	4-Br	1669.0	1647.0	1662.5
6	3-Cl	1669.5	1647.0	1663.5
7	3-Br	1670.0	1648.0	1663.5
8	3-NO_2	1670.5	1649.5	1664.0
9	4-NO_2	1671.5	*b*	1665.0

[a] Frequencies are given in cm^{-1}. [b] Not available because of low solubility of compound in CCl_4.

TABLE II

1-PHENYL-3-(5-ARYL-2-THIENYL)PROPENONES (II)[a]

Compd	X	In CCl_4 $\nu_{s\text{-cis}}$	In CCl_4 $\nu_{s\text{-trans}}$	In $CHCl_3$ $\nu_{s\text{-cis}}$	In $CHCl_3$ $\nu_{s\text{-trans}}$
10	4-OCH_3	1664.5	1645.0	1658.0	1633.0
11	4-CH_3	1665.0	1646.0	1658.5	1634.5
12	3-CH_3	1666.0	1647.0	1659.5	1636.0
13	4-H	1666.0	1647.0	1660.0	1636.0
14	4-Cl	1666.5	1647.0	1660.0	1636.5
15	4-Br	1667.0	1647.5	1660.5	1636.5
16	3-Cl	1667.5	1648.0	1661.0	1638.0
17	4-NO_2	1668.0	1649.5	1662.0	1639.0

[a] Frequencies are given in cm^{-1}.

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[2] A. Perjéssy, *Chem. Zvesti*, **23**, 905 (1969).

[3] N. S. Silver and D. W. Boykin, Jr., *J. Org. Chem.*, **35**, 759 (1970).

[4] A. Perjéssy, *Chem. Zvesti*, **23**, 441 (1969).

[5] W. F. Winecoff, III, and D. W. Boykin, Jr., *J. Org. Chem.*, **37**, 674 (1972).

[6] P. J. Duke and D. W. Boykin, Jr., *ibid.*, **37**, 1436 (1972).

[7] A. Perjéssy, P. Hrnčiar, and A. Krutošíková, *Tetrahedron*, **28**, 1025 (1972).

[8] A. Perjéssy, P. Hrnčiar, and R. Frimm, *Collect. Czech. Chem. Commun.*, **28**, 3781 (1972).

[9] A. Perjéssy, P. Hrnčiar, and R. Sokolová, *ibid.*, in press.

[10] A. Perjéssy, P. Hrnčiar, R. Frimm, and Ľ. Fišera, *Tetrahedron*, **28**, 3781 (1972).

sensitivity of the bands (see below) we assign the intense, higher frequency band to the C=O stretching mode of the s-cis conformer ($\nu_{\text{s-cis}}$) and the lower frequency band of much weaker intensity to the C=O stretching mode of the s-trans conformer ($\nu_{\text{s-trans}}$) (see Tables I and II). As was the case for chalcones,[2,3,11] the s-cis conformation, as assessed from band intensities, predominates in the equilibrium mixture. Since the s-trans carbonyl stretching frequencies of chalcones measured in $CHCl_3$ have not been reported previously, we include them in Table III for the sake of comparison with data of compounds of series I and II. In the spectra of 1-phenyl-3-(5-aryl-2-thienyl)-propenones (II) in $CHCl_3$ both the $\nu_{\text{s-cis}}$ and $\nu_{\text{s-trans}}$ bands appear. However, in the case of 1-phenyl-3-(5-aryl-2-furyl)propenones (I) in $CHCl_3$ only the s-cis band is clearly observable. In some cases on the lower frequency side of the $\nu_{\text{s-cis}}$ band a small pronounced shoulder occurs, probably corresponding to the carbonyl band of the s-trans conformer. This may be due to a low concentration of the s-trans conformer in the equilibrium mixture or to the overlapping of the weak $\nu_{\text{s-trans}}$ band with the higher frequency wing of an intense ν(C=C) band in the 1600 cm^{-1} region. For these reasons this report describes for series I in $CHCl_3$ only the s-cis carbonyl stretching frequencies.

TABLE III

1-PHENYL-3-ARYLPROPENONES (III) IN $CHCl_3$

Compd	X	$\nu_{\text{s-trans}}$, cm^{-1}
18	4-$N(CH_3)_2$	1627.0
19	4-OCH_3	1635.0
20	4-CH_3	1639.5
21	4-H	1643.5
22	4-F	1643.0
23	4-Cl	1644.0
24	3-Cl	1645.0
25	4-CN	1646.0
26	3-NO_2	1646.0
27	4-NO_2	1648.0

Comparison of the $\nu_{\text{s-cis}}$ frequencies of compounds in series I with those of series II (see Tables I and II) shows that exchange of the furan ring for the thiophene ring causes a frequency decrease of 1.5–3.5 cm^{-1} in both solvents. This is similar to the case of 1-phenyl-3-(2-furyl)propenones and 1-phenyl-3-(2-thienyl)-propenes[12] as well as of other unsaturated carbonyl compounds[7-10] containing furan and thiophene rings, respectively. On the other hand, the $\nu_{\text{s-trans}}$ frequencies of compounds of series II are 0.5–2.5 cm^{-1} higher than those of series I.

When comparing the data from Tables I and II with that for chalcones III[2,3] (see Table III), we found that the insertion of the furan or thiophene intervening group in the chalcone system produces a significant decrease in both the $\nu_{\text{s-cis}}$ and $\nu_{\text{s-trans}}$ frequency similar to the other previously described cases.[7-10]

In passing from CCl_4 to $CHCl_3$ we observe a decrease of 6.0–6.5 cm^{-1} in the $\nu_{\text{s-cis}}$ frequency of compounds in both series I and II. However, in the case of the $\nu_{\text{s-trans}}$ frequency the same decrease is 10.0–12.0 cm^{-1}. This is similar to the chalcones III,[2,3] where the CCl_4–$CHCl_3$ solvent effect is roughly two times more efficient for $\nu_{\text{s-trans}}$ frequency than for $\nu_{\text{s-cis}}$ frequency. Hayes and Timmons[11] found that the carbonyl bands of s-trans conformers of several α,β-unsaturated ketones were more solvent sensitive than those of corresponding s-cis conformers.

Linear Free-Energy Relationships.—In earlier work[2,3] we have treated statistically the linear free-energy relationships between the carbonyl stretching frequencies and σ as well as σ^+ constants for chalcones III. It was found[3] that the statistically most significant relationships were obtained using Brown and Okamoto's σ^+ values.

As expected, the $\nu_{\text{s-cis}}$ as well as the $\nu_{\text{s-trans}}$ frequencies of compounds in series I and II correlate well with substituent constants (see Table IV). For comparison we have included in Table IV the results of the statistical treatments for the chalcones III. Treatment of each of the 11 data sets with σ resulted in a poorer correlation than was obtained with σ^+. The correlation with σ^+ implies that in compounds of series I and II there operates a significant resonance interaction between the substituent and the carbonyl group even though it is separated by a large intervening group containing a double bond and a heterocyclic ring. The correlations for the $\nu_{\text{s-trans}}$ frequencies are in each case statistically more significant than those for the corresponding $\nu_{\text{s-cis}}$ frequencies.

The data were also treated employing the two-parameter approach described by Swain and Lupton.[13] We have previously noted that generally carbonyl stretching frequency data were correlated less satisfactorily by the two-parameter approach than by the use of σ^+ with the Hammett expression.[3,5] In each of the 11 data sets listed in the tables, correlations with σ^+ are superior to those employing the two-parameter method.[14] The values of % *R* for the 11 data sets do not vary within the calculated error.[14] The significance of % *R*[6,15] as well as the theoretical significance of the two-parameter approach has been questioned.[15] The results of the correlations of the 11 data sets recorded here lend support to the questioning of the utility of the Swain–Lupton approach.[15] In view of the poor correlations obtained in this work and the questions that have been raised about the approach, it seems inappropriate at this time to attempt to draw conclusions based upon the two-parameter linear free-energy relationship.

Influence of Conformation on Transmission.—Previous work has suggested that the effect of conformation on transmission in α,β-unsaturated ketones is largely a function of the relative coplanarity of the system.[2,5] It is expected that the steric requirements of I–III and consequently the relative coplanarity of the s-cis and s-trans isomers do not differ greatly from those previously studied. The observed $\rho_{\text{s-cis}}/\rho_{\text{s-trans}}$ ratios for I–III are generally in accord with those observed previously and support the expected view that steric factors are not particularly important.

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[11] W. P. Hayes and C. J. Timmons, *Spectrochim. Acta, Part A*, **24**, 323 (1968).

[12] S. V. Tsukerman, V. M. Nikitchenko, J. S. Rozum, and V. F. Lavrushin, *Khim. Geterotsikl. Soedin.*, 452 (1967).

[13] C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

[14] The results of the correlations with the Swain–Lupton approach are included in the microfilm edition of this journal.

[15] G. R. Wiley and S. I. Miller, *J. Org. Chem.*, **37**, 767 (1972).

TABLE IV

RESULTS OF STATISTICAL TREATMENT USING σ^+ CONSTANTS[a]

Series	Conformer	Solvent	n	ρ	s_ρ	i	s_i	s	r	$\bar{r}$
I	s-cis	CCl_4	9	3.32	0.19	1668.5	0.1	0.3	0.989	0.980
I	s-trans	CCl_4	8	4.74	0.27	1646.0	0.1	0.3	0.990	0.990
I	s-cis	$CHCl_3$	9	3.13	0.17	1662.2	0.1	0.2	0.990	0.987
II	s-cis	CCl_4	8	2.49	0.25	1666.2	0.0	0.3	0.970	0.971
II	s-trans	CCl_4	8	2.82	0.18	1647.0	0.0	0.2	0.989	0.990
II	s-cis	$CHCl_3$	8	2.72	0.23	1659.8	0.0	0.3	0.980	0.982
II	s-trans	$CHCl_3$	8	3.99	0.19	1636.0	0.0	0.2	0.993	0.989
III[b]	s-cis	CCl_4	10	5.62	0.48	1673.7	0.3	1.1	0.972	
III[b]	s-trans	CCl_4	10	7.20	0.34	1654.2	0.2	0.8	0.991	
III[c]	s-cis	$CHCl_3$	21	6.18	0.25	1666.7	0.0	0.6	0.985	
III	s-trans	$CHCl_3$	10	8.23	0.50	1641.9	0.0	1.2	0.985	

[a] n = number of points; ρ = slope; s_ρ = standard deviation of ρ; i = intercept; s_i = standard deviation of i; s = standard deviation; r = correlation coefficient; $\bar{r}$ = arithmetic mean of the correlation coefficients for series I and III and series II and III, respectively. [b] Data taken from ref 2. [c] Data taken from ref 3.

The one exception in these ratios, for which there is no obvious explanation, is that of II obtained from the data arising from measurements in carbon tetrachloride solution.

Transmissive Factors for the Furan and Thiophene Rings.—As it was shown[7,10] the ν(C=O) *vs.* σ and ν(C=O) *vs.* σ^+ linear free-energy relationships with compounds containing a heterocyclic bridge between a substituted benzene ring and carbonyl group can be used in a quantitative study of the transmission of electronic effects by the given heterocyclic bridges. Similar to our earlier approach,[7] we have selected here the most significant free-energy relationships for calculation of transmissive factors. This selection was carried out on the basis of the highest value of the arithmetic means of the correlation coefficients $\bar{r} = (r_{\mathrm{I}} + r_{\mathrm{III}})/2$ and $\bar{r} = (r_{\mathrm{II}} + r_{\mathrm{III}})/2$ for the series of compounds I, II, and III, respectively. Following this procedure $\nu_{\text{s-cis}}$ *vs.* σ^+ and $\nu_{\text{s-trans}}$ *vs.* σ^+ correlations were chosen, since the $\bar{r}$ values in these cases are higher than those for $\nu_{\text{s-cis}}$ *vs.* σ and $\nu_{\text{s-trans}}$ *vs.* σ relationships (see Table IV).

Using data in Table IV we calculated the transmissive factors of the electronic effects for the 2,5-furylene and 2,5-thienylene bridges [π'(Fu)and π'(Thi)] from the equations

$$\pi'(\mathrm{Fu}) = \rho_{\mathrm{II}}/\rho_{\mathrm{III}} \qquad (1)$$

$$\pi'(\mathrm{Thi}) = \rho_{\mathrm{II}}/\rho_{\mathrm{III}} \qquad (2)$$

where ρ_{I}, ρ_{II}, and ρ_{III} are the slopes of the selected $\nu_{\text{s-cis}}$ *vs.* σ^+ or $\nu_{\text{s-trans}}$ *vs.* σ^+ linear free-energy relationships for the series of compounds I, II, and III, respectively. The transmissive factors π'(Fu) and π'(Thi) in both solvents, CCl_4 and $CHCl_3$, have been calculated using eq 1 and 2. The values obtained here are in agreement with those published earlier.[7-10] Since the transmissive factors determined from the linear free-energy relationships for the five various systems (this work and that previously reported[7,8]) are in good mutual agreement they are expressed as mean transmissive factors, $\bar{\pi}'$(Fu) and $\bar{\pi}'$(Thi).[16]

CCl_4 $\bar{\pi}'$(Fu) 0.64 ± 0.10 $\bar{\pi}'$(Thi) 0.44 ± 0.08

$CHCl_3$ $\bar{\pi}'$(Fu) 0.47 ± 0.06 $\bar{\pi}'$(Thi) 0.42 ± 0.06

It follows from the comparison of the $\bar{\pi}'$ values that the transmission by the furan ring is significantly sensitive to the solvent used. However, the transmission by the thiophene ring is practically independent of the CCl_4–$CHCl_3$ solvent change. The cause of this was suggested earlier[7-10] as hydrogen bonding interaction between the furan ring oxygen atom and the chloroform molecules. Comparing the $\bar{\pi}'$(Fu) and $\bar{\pi}'$(Thi) values in nonhydrogen-bonding CCl_4 solvent with the value of $\bar{\pi}'$(Ph) = 0.27 ± 0.03 (transmissive factor for 1,4-phenylene bridge),[17] we observe, as noted in our previous work,[10] that the transmission by the intervening groups decreases in the order furan, thiophene, benzene. Interestingly, this is the order in which the delocalization energies of the systems increase.

Experimental Section

Infrared Frequencies.—The ir stretching frequencies for all compounds of series I–III were determined on a Zeiss UR 20 three-prism spectrometer operated in the expanded scale mode at scan rates of 10 cm^{-1} min. The wavenumber scale of the instrument was calibrated using the spectra of a standard mixture of indene, camphor, and cyclohexanone.[18] The solvents CCl_4 and $CHCl_3$, both spectral grade, were purified and dried in the manner used before.[18] The concentrations of solutions were chosen to give absorption between 70 and 75%. NaCl cells with path lengths of 0.5, 1.0, and 2.5 mm were used. The carbonyl stretching bands of the s-trans conformers of compounds of series I and II, similar to the chalcones,[2,3] usually appeared as a shoulder on the lower frequency side of the intense $\nu_{\text{s-cis}}$ bands. Therefore, similar to the approach[2] previously reported, the frequency determination was done after graphic resolution of the overlapping bands. All frequencies reported were obtained from averaging three different scans, the maximum scattering of which was 0.5 cm^{-1}.

Calculations.—The Hammett correlations were made with σ constants reported by McDaniel and Brown,[19] and σ^+ constants published by Brown and Okamoto[20] were used. The least-squares treatments were computed on a Regnezentralen Gier digital computer using standard statistical relations.[21] The two-

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(16) The microfilm edition of this journal contains the π'(Fu) and π'(Thi) values calculated from each data set together with π'(Fu) and π'(Thi) values reported in our previous papers[7-10] which were used to calculate $\bar{\pi}$ values recorded here. These will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-1807.

(17) J. A. Zhdanov and V. I. Minkin, "Korrelanionii Analiz v Organicheskoi Khimii," Izdatelstvo Rostovskovo Universiteta, Rostov, 1966, p 63.

(18) R. N. Jones, P. K. Fauer, and W. Zacharias, *Rev. Universelle Mines Met. Mec.*, **15**, 417 (1959).

(19) D. M. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(20) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(21) J. Eichler, *Chem. Listy*, **60**, 1203 (1966).

parameter relationships were computed using an IBM 7094 computer (*cf.* ref 6).

Compounds Studied.—The 1-phenyl-3-(5-aryl-2-furyl)propenones (I) and 1-phenyl-3-(5-aryl-2-thienyl)propenones (II) were prepared by condensation of acetophenone with 5-aryl-2-furfuraldehydes and 5-aryl-2-thiophenecarboxaldehydes, respectively, following the procedure described earlier.[22,23] All compounds were recrystallized from appropriate solvents[22,23] until constant melting point was obtained. The 1-phenyl-3-arylpropenones (III) were obtained by condensation of acetophenone with substituted benzaldehydes according to previous reports.[24,25] The chalcones were recrystallized from ethanol and the purity was checked by tlc on Al_2O_3 or SiO_2 (Silufol). The melting points of all compounds agreed well with those described.[22-25]

Registry No.—**1**, 38899-16-0; **2**, 38899-17-1; **3**, 38899-18-2; **4**, 38899-19-3; **5**, 38899-20-6; **6**, 38898-73-6; **7**, 38898-74-7; **8**, 38898-75-8; **9**, 38898-76-9; **10**, 38898-77-0; **11**, 38898-78-1; **12**, 38898-79-2; **13**, 38898-80-5; **14**, 38898-81-6; **15**, 38898-82-7; **16**, 38898-83-8; **17**, 38898-84-9; **18**, 22965-98-6; **19**, 22252-15-9; **20**, 22252-14-8; **21**, 614-47-1; **22**, 22966-07-0; **23**, 22252-16-0; **24**, 22966-13-8; **25**, 22966-17-2; **26**, 24721-24-2; **27**, 2960-55-6; furan, 110-00-9; thiophene, 110-02-1.

Acknowledgments.—We wish to thank Associate Professor Š. Toma for samples **18–27**.

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[22] J. Kováč, L. Fišera, and R. Frimm, *Chem. Zvesti*, in press.

[23] R. Frimm, A. Krutošíková, and J. Kováč, *ibid.*, in press.

[24] Š. Toma, *ibid.*, **19**, 703 (1965).

[25] Š. Toma, *Collect. Czech. Chem. Commun.*, **34**, 2771 (1969).

Synthesis and Spectral Properties of N-Sulfated and/or O-Sulfated Amino Alcohols

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Received November 7, 1972

N-Sulfated and/or O-sulfated amino alcohols and 2-deoxy-2-sulfoamino-D-glucose were synthesized and their nmr and ir spectra were measured for the analysis and structural elucidation of sulfated polysaccharides. N-Sulfation of alkylamines and amino alcohols results in a downfield shift of the signal of the proton attached to the carbon atom bearing the amino group by 0.21–0.48 ppm, while O-sulfation results in a downfield shift of the proton attached to the carbon atom bearing *O*-sulfate by 0.36–0.65 ppm. Some discussions are made on the effect of N-sulfation of 2-deoxy-2-amino-D-glucose on H-1 and H-2. Comparison of ir spectra of these sulfate esters revealed two characteristic absorptions (1420–1450 and 1200–1220 cm^{-1}) in *N*-sulfates.

In recent years, some reports have appeared on the structural elucidation of natural mucopolysaccharides[1-3] and synthetic sulfated polysaccharides[4] by using nmr spectra. In general, nmr spectra of these compounds are fairly complicated even by using a high-resolution nmr spectrograph, but the chemical shift of the proton attached to the carbon atom bearing the *O*-sulfate and *N*-sulfate group, and that on the adjacent carbon atom, give important clues for spectral analyses of these compounds. As a model compound for sulfated sugars, we synthesized N-sulfated and/or O-sulfated cyclic and acyclic amino alcohols, and their nmr spectra were measured to examine the effect of N- or O-sulfation on the chemical shift of the proton attached to the carbon atom bearing the sulfate group and that on the adjacent carbon.

Although ir spectra of *O*-sulfates have been reported,[5] those due to *N*-sulfate have hardly been documented.[6,7] Therefore, ir spectra of the synthesized compounds were also measured to examine the absorptions characteristic of the *N*-sulfate group.

Results and Discussion

Cyclic and acyclic alkylamine and amino alcohol sulfates were synthesized systematically. Analytical data for amino alcohol sulfates are given in Table I.

Since it is difficult to avoid contamination of *O*-monosulfate in acyclic *N*,*O*-disulfates by the method of Reitz and others,[8] we modified the method of Wolfrom and Juliano[9] to synthesize *N*,*N*,*O*-trisulfates, and their mild acid hydrolysis afforded *N*,*O*-disulfates in a comparatively good yield. On the other hand, cyclic *N*,*O*-disulfates are invariably accompanied with *O*-monosulfates, and trisulfate is not formed even on modification of the reaction conditions. Trans and cis cyclic *N*,*O*-disulfates were isolated by repeated recrystallization in 19.5 and 22.1% yield, respectively.

The starting 2-aminocyclohexanol was obtained by low-pressure hydrogenation of 2-acetaminophenol over rhodium catalyst, which was used in hydrogenation of alkoxyaniline,[10] separation of trans and cis compounds from the resultant product by chromatography over silica gel, and acid hydrolysis. These trans and cis compounds were identified by nmr spectra. This is simpler and gives a better yield than by the known definitive synthesis of trans[11] and cis[12] compounds.

Dodgson[6] obtained the potassium salt of 2-deoxy-2-sulfoamino-D-glucose by sulfation of 2-deoxy-2-amino-D-glucose with pyridine–sulfur trioxide. We used the same reagents and obtained 2-deoxy-2-sulfoamino-D-glucose as its sodium salt as needle crystals by recrystallization from methanol–water.

Nmr spectra of acyclic alkylamine and amino alcohol sulfates are summarized in Table II. As will

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[1] (a) L. B. Jaques, L. W. Kavanagh, M. Mazurek, and A. S. Perlin, *Biochem. Biophys. Res. Commun.*, **24**, 447 (1966); (b) A. S. Perlin, M. Mazurek, L. B. Jaques, and L. W. Kavanagh, *Carbohyd. Res.*, **7**, 369 (1968).

[2] S. Inoue and Y. Inoue, *Biochem. Biophys. Res. Commun.*, **23**, 513 (1966).

[3] A. S. Perlin, B. Casu, G. R. Sanderson, and L. F. Johnson, *Can. J. Chem.*, **48**, 2260 (1970).

[4] W. M. Pasika and L. H. Cragg, *Can. J. Chem.*, **41**, 777 (1963).

[5] A. G. Lloyd, N. Tudball, and K. S. Dodgson, *Biochem. Biophys. Acta*, **52**, 413 (1961).

[6] K. S. Dodgson, *Biochem. J.*, **92**, 68 (1964).

[7] A. B. Foster, E. F. Martlew, M. Stacey, P. J. M. Taylor, and J. M. Weber, *J. Chem. Soc.*, 1204 (1961).

[8] H. C. Reitz, R. E. Ferrel, H. S. Olcott, and H. Fraenkel-Conrat, *J. Amer. Chem. Soc.*, **68**, 1031 (1946).

[9] M. L. Wolfrom and B. O. Juliano, *J. Amer. Chem. Soc.*, **82**, 2588 (1960).

[10] M. Freifelder, Y. H. Ng, and P. F. Helgren, *J. Org. Chem.*, **30**, 2485 (1965).

[11] N. A. B. Wilson and J. Read, *J. Chem. Soc.*, 1269 (1935).

[12] G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, *J. Amer. Chem. Soc.*, **71**, 637 (1949).