Substituent Effects on the Carbonyl Stretching Frequency of Chalcones

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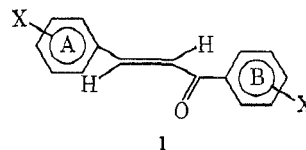
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The *s-cis* carbonyl stretching frequencies of three series of substituted chalcones (1) have been determined in chloroform. One series contains substituents in ring A, one series is substituted in ring B, and one series contains substituents in both rings. Substituents in ring A give a good correlation with σ^+ ($\nu = 6.24\sigma^+ + 1666.7$; $r = 0.977$); six *ortho*-substituted compounds included in this series fall on the same line as the *meta-* and *para*-substituted compounds. Previously reported pK_B data are correlated with the carbonyl stretching frequencies for substituents in ring A ($pK_B = 4.65\nu + 1642.5$; $r = 0.997$). Substituents in ring B, however, do not correlate as well as the first series ($\nu = 5.44\sigma^+ + 1665.6$; $r = 0.889$). Likewise, the correlation of frequencies with F and R parameters for the compounds substituted in ring A is better than that obtained from the series substituted in ring B. An expression relating substituents in both rings A and B to the independent series A and B suggests that substituents on the two different phenyl groups act reasonably independently of each other [$\Delta\nu_{A,B} = 1.53\Sigma(\Delta\nu_A + \Delta\nu_B) - 0.399$; $r = 0.963$].

The results of a number of investigations have been reported on the effect of substituents on the infrared carbonyl stretching frequencies of various systems.[2–6] The carbonyl group stretching frequency can be treated as an isolated vibration and has been demonstrated to be "mass insensitive." Furthermore, there are numerous examples of correlations of carbonyl stretching frequencies with Hammett substituent constants for series in which there is little change of carbonyl bond angles or presumedly of bond force constants with substituents.[4] Good correlations of carbonyl stretching frequencies with Hammett constants have been reported for acetophenones,[7] benzophenones,[8] and benzoyl chlorides.[9]

The effect of substituents on the ultraviolet spectra, on basicities, and on half-wave potentials of chalcones has been reported.[10–13] However, infrared studies on these systems are lacking. It is of interest to investigate the effect of substituents on the carbonyl stretching frequencies of these compounds to determine the effectiveness of the transmission of electronic effects through the double bond, to study conformational isomerism, and to examine the effects of multisubstitution. This report contains the results of a study of the carbonyl stretching frequencies of three series of substituted *trans*-chalcones, from which some information about the above points can be obtained. In one series, the substituents are placed on phenyl ring A, in the second on phenyl ring B, and the third series contains substituents on both rings A and B.

(1) This work represents a partial fulfillment of the requirements for the B.S. degree with Honors by N. L. S.

(2) L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, **19**, 1831 (1963).

(3) W. P. Hayes and C. J. Timmons, *ibid.*, **24A**, 323 (1968).

(4) M. Liler, *ibid.*, **23A**, 139 (1967).

(5) (a) R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, **82**, 4059 (1960); (b) R. Stewart and K. Yates, *ibid.*, **80**, 6355 (1958).

(6) C. N. R. Rao and R. Venkatargahenen, *Can. J. Chem.* **39**, 1759 (1961).

(7) (a) R. N. Jones, W. F. Forbes, and W. A. Mueller, *ibid.*, **35**, 504 (1957). The ir data by Jones for substituted acetophenones was analyzed by our statistical treatment. For *meta* and *para* substituents, $s = 0.911$; $r = 0.979$; $i = 1691.4$; $\rho = 12.33$; $n = 10$. For *ortho* substituents, $s = 1.11$; $r = 0.980$; $i = 1692.6$; $\rho = 11.42$; $n = 5$. For the *ortho* series, when two bands were reported, the higher frequency band was used in the statistical analysis. (b) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(8) N. Fuson, M. L. Josien and E. M. Shelton, *J. Amer. Chem. Soc.*, **76**, 2526 (1954).

(9) M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

(10) W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, **77**, 5134 (1955).

(11) H. H. Szmant and A. J. Basso, *ibid.*, **74**, 4397 (1952).

(12) D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962).

(13) (a) S. V. Tsukerman, L. A. Kutulya, V. F. Lavrushin, and M. T. Nguyen, *Zh. Fiz. Khim.*, **42**, 1930 (1968); (b) S. V. Tsukerman, Y. N. Surev, and V. F. Lavrushin, *Zh. Obshch. Khim.*, **37**, 364 (1967); (c) V. D. Bezuglyi, V. F. Lavrushin, and G. G. Belous, *ibid.*, **35**, 606 (1965).
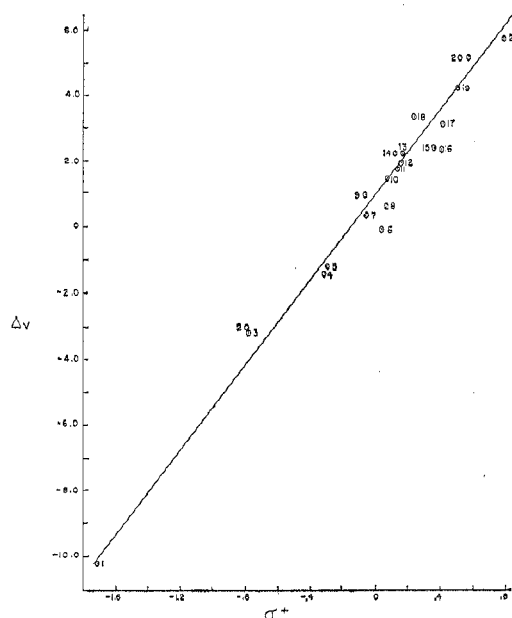

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Results and Discussion

The Effect of Substituents on Ring A.—A recent report[3] contains the band assignments for the carbonyl stretching frequencies of chalcone in chloroform. The intense band at 1665 cm^{-1} was assigned to the *s-cis* conformer and the broad band of much weaker intensity at 1639 cm^{-1} was assigned to the *s-trans* conformer (or non-*s-cis* conformers). These band assignments were made on the basis of solvent dependency. It is difficult to identify the non-*s-cis* band for the various substituted chalcones by inspection, since the intensity and shapeo f it is similar to the aromatic hydrogen overtone bands in the 1600-cm^{-1} region. The 1600-cm^{-1} region of the spectra of all the substituted chalcones contained in the tables has been inspected and it is concluded that additional information is necessary to identify the non-*s-cis* band. In order to further define the non-*s-cis* band, a study of the temperature–intensity dependence of the *s-cis* and non-*s-cis* conformers is underway. This report describes the results of a study of the effect of substituents on the *s-cis* conformer. The assignment of the intense bands in the 1670-cm^{-1} region to the *s-cis* conformer is based on analogy to the assignment of Hayes and Timmons.[3] The values for the *s-cis* carbonyl stretching frequencies in chloroform are given in Table I.

The carbonyl stretching frequencies were measured in chloroform rather than in a nonhydrogen-bonding solvent such as carbon tetrachloride because of limited solubility of some of the chalcones in the latter solvent. The carbonyl stretching frequencies of a number of the chalcones were obtained in carbon tetrachloride and are listed in Table II. A shift of approximately 5 cm^{-1} was observed for this *s-cis* carbonyl band on changing the solvent from chloroform to carbon tetrachloride. Apparently, weak hydrogen bonding does not have a large influence on the transmission of substituent effects since the ρ values obtained from measurements in both solvents are not greatly different.

As expected, the lowest frequency is observed for the *p*-dimethylamino group and the highest for the *p*-nitro group. The values of $\nu_{C=O}$ have been correlated with

Figure 1.—Substituents in ring A.

TABLE I
SUBSTITUENTS IN RING A IN CHLOROFORM

Compound no.	Substituent	ν, cm^{-1}
1	4-$(CH_3)_2N$	1655.5
2	2-CH_3O	1662.5
3	4-CH_3O	1662.5
4	2-CH_3	1664.3
5	4-CH_3	1664.5
6	4-H	1665.7
7	3-CH_3	1666.1
8	3-CH_3O	1666.3
9	2-F	1666.7
10	4-F	1667.2
11	4-Cl	1667.5
12	4-Br	1667.7
13	2-Br	1667.9
14	2-Cl	1668.0
15	3-F	1668.1
16	3-Cl	1668.1
17	3-Br	1669.0
18	2,4-Di-Cl	1669.1
19	3,4-Di-Cl	1670.0
20	4-CN	1670.9
21	4-NO_2	1671.5

TABLE II
SUBSTITUENTS IN RING A IN CARBON TETRACHLORIDE

Compound no.	ν, cm^{-1}
5	1669.0
6	1670.3
8	1670.7
17	1672.9
21	1674.7

three σ constants, σ, σ^+, σ^0 as taken from Ritchie and Sager.[14] A computer program was written to carry out the least-squares and statistical treatment of the data with the σ constants according to the method of Jaffe.[15] The results of the computations are given in

(14) C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1964.

Table III. As can be seen from the correlation coefficients, the best relationship is obtained using σ^+, which is in agreement with the suggestion by Liler.[4]

A plot of σ^+ vs. $\Delta\nu$ for the chalcones substituted in ring A is shown in Figure 1; $\Delta\nu = \nu_X - \nu_H$. The correlation with σ^+ implies that there is significant resonance interaction between the substituent and the carbonyl group even though it is separated by an intervening group. The ρ value of 6.24 obtained for the chalcones should be compared with the value 12.3 obtained from a similar study on acetophenones.[7b] The ratio of ρ values gives a transmission coefficient of 0.51 for the ethylene group. This is in accord with results (0.50) reported from the ionization of substituted cinnamic and benzoic acids.[16-18]

In order to get a further estimate of the relative importance of resonance and field effects the treatment reported by Swain and Lupton[19] has been employed. The results of this two parameter correlation may be found in Table IV. These correlations were carried out using the IBM multiple linear regression program REGRE. Calculations of per cent R were made using the results from REGRE according to the reported approach.[19]

The correlation obtained with F and R is significantly poorer than the one obtained with σ^+. Swain and Lupton do not report the use of F and R with infrared frequency data. Included in Table IV are the results of correlations with REGRE using infrared data taken from earlier reports on acetophenones[7] and benzophenones.[3] It can be seen that these series also give poorer correlations with the two parameter approach. It is considered premature at this time to draw conclusions about the utility of the Swain–Lupton treatment for correlation of infrared carbonyl stretching frequency data; obviously the results from other investigations are required.

The value obtained for the resonance contribution to the correlation is 44%. It is interesting that the values for the resonance contribution for all the series in Table IV are approximately the same. The fact that per cent R values for the styryl-substituted series of 1 are similar to those of the acetophenones and benzophenones suggests that the double bond transmits resonance effects very efficiently.

Often, *ortho*-substituted compounds have not been included in Hammett-type correlations for it was believed that variable steric factors were a cause of nonlinear relationships. It has been shown recently that the Hammett equation is applicable to *ortho*-substituted series in which the reaction site and *ortho* substituent are well separated.[20,21] As a further test of this point, *ortho*-substituted chalcones in Table I were studied. Correlations of the stretching frequencies of *ortho*-substituted compounds were made using the σ^+ values for the *para* substituents and, as can be seen, the correlation obtained was good. The fact that the *ortho*-substituted

(15) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(16) A. B. Thigpen, Jr., and R. Fuchs, *J. Org. Chem.*, **34**, 505 (1969), and references cited therein.

(17) K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963).

(18) J. A. Caputo and R. Fuchs, *J. Org. Chem.*, **33**, 1959 (1968).

(19) (a) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968); (b) we acknowledge the suggestion of a reviewer to include this treatment.

(20) A. W. Baker and A. T. Shulgin, *J. Amer. Chem. Soc.*, **81**, 1523 (1958).

(21) I. J. Solomon and R. Filler, *ibid.*, **85**, 3492 (1963).

TABLE III

RESULTS OF STATISTICAL TREATMENT USING σ CONSTANTS[a]

Substituents in ring	Solvent	σ					σ^+					σ^0				
		s	ρ	r	i	n	s	ρ	r	i	n	s	ρ	r	i	n
A	CHCl₃	0.945	9.19	0.965	1665.3	21	0.770	6.24	0.977	1666.7	21	1.45	10.25	0.910	1664.6	21
A	CCl₄	0.445	6.06	0.986	1670.2	5	0.401	5.36	0.988	1670.5	5	5.24	5.89	0.980	1670.1	5
A *ortho*	CHCl₃	0.676	9.02	0.971	1665.6	6	0.643	6.54	0.974	1667.2	6	1.01	9.08	0.934	1664.9	6
B	CHCl₃	1.15	8.20	0.848	1664.9	9	0.994	5.44	0.889	1665.6	9	1.28	8.62	0.806	1664.5	9

[a] s = standard deviation; ρ = slope of the line; r = correlation coefficient; i = intercept; n = number of points.

TABLE IV

RESULTS OF STATISTICAL TREATMENT USING F AND R CONSTANTS[a]

Series	n[b]	f[c]	r[d]	i[e]	E[f]	C[g]	% R[h]
Substituents in ring A	18[i]	4.47 ± 0.73	7.04 ± 1.30	1666.0	1.04	0.917	44 ± 6
Substituents in ring B	9	3.56 ± 1.96	4.94 ± 3.97	1665.1	1.82	0.620	40 ± 23
Acetophenones	10[j]	8.52 ± 1.66	8.00 ± 3.70	1689.6	1.86	0.921	32 ± 11
Benzophenones	7[k]	6.46 ± 2.23	18.5 ± 5.67	1665.1	2.00	0.886	43 ± 11

[a] Swain field and resonance parameters; see ref 19. [b] Number of points. [c] Regression coefficient for field parameter. [d] Regression coefficient for resonance parameter. [e] Intercept. [f] Standard error of estimate. [g] Multiple correlation coefficient. [h] Per cent resonance contribution. These were calculated as indicated in ref 19; ϕ and ψ were calculated internally based upon the number of points used in the correlation. [i] Compounds 1, 18, and 19 were not used in this treatment. [j] The frequency values used were taken from ref 7a and the result of this statistical treatment using σ^+ is found in footnote 7a. The substituents were p-CH₃, p-H, p-F, p-Cl, p-NO₂, m-Cl, m-F, m-NO₂, p-Br, and p-I. [k] The frequency values used were taken from ref 8. The results of the statistical treatment using σ^+: $s = 1.08$; $r = 0.960$; $i = 1664.7$; $\rho = 8.77$; $n = 7$. The substituents were p-CH₃O, p-t-Bu, p-CH₃, p-H, p-Cl, p-Br, and m-Br.

compounds essentially fall on the same straight line (see Figure 1) as the other substituents indicates that there is no significant *ortho* effect in this system detectable from infrared data. This is in contrast to p*K* data (*vide infra*).

The reduction of the $\rho_{ortho}/\rho_{meta,para}$ ratio obtained for ionization of benzoic acids from about 2 to about 1 for the *trans*-cinnamic acids has been attributed to field effects.[22] A similar comparison between acetophenones and chalcones may be made using data from their carbonyl stretching frequencies. Data for the acetophenones were obtained from the report of Jones.[7a] The $\rho_{ortho}/\rho_{meta,para}$ ratio for both the acetophenones and chalcones is 1. These results suggest the absence of appreciable field effects on the ir stretching frequencies of acetophenones. This conclusion is in accord with the observation that field effects are operative only in conformations in which the polar group is near in space to the carbonyl oxygen.[23]

As might be expected, disubstitution in phenyl ring A, compounds **18** and **19** in Table I, gave carbonyl stretching frequencies which could be correlated using the sum of the σ constants. The disubstituted compound with one of the substituents in the *ortho* position also falls on the line.

The basicities of 4- and 4'-substituted chalcones have been reported to correlate with σ^+ constants.[12,13] The ρ value for the correlation with 4-substituted chalcones was found to be 1.26, which should be compared with 2.17 found for the basicity of acetophenones.[12] The value of the ratio of $\rho_{chalcone}/\rho_{acetophenone}$ from basicity studies is somewhat higher than that observed from the infrared work. This difference may simply reflect the sensitivity of ρ to solvent or it might suggest that transmission of electronic effects is more efficient on the demands of a fully charged cinnamoyl species.

(22) K. Bowden and D. C. Parkin, *Can. J. Chem.*, **46**, 3909 (1968).
(23) L. J. Bellamy in "Spectroscopy," M. J. Wells, Ed., the Institute of Petroleum, London, 1962.

Clearly, a plot of basicities (p*K*ᵦ)[12] *vs.* carbonyl stretching frequencies gives a good correlation. The expression for this line

$$p K_{BH^+} = 4.65\nu + 1642.5 \ (r = 0.997)$$

will have utility for calculation of p*K*ᵦ's for the other chalcones.

Noyce and Jorgenson also report p*K*ᵦ's for three *ortho*-substituted chalcones. The basicities of the 2-substituted chalcones were from 0.2 to 0.4 p*K* units lower than the corresponding 4-substituted chalcones. The variation of the p*K*₍BH⁺₎ values of 2-substituted chalcones compared with corresponding 4-substituted chalcones is in contrast to their carbonyl stretching frequencies. Clearly there is an *ortho* effect on the basicity of 2-substituted chalcones. This has been attributed to steric inhibition of resonance.

The appearance of an *ortho* effect for p*K*ᵦ suggests that the fully charged species involved in the determination of p*K*'s is more sensitive to substituent effects than the partially charged transition involved in the carbonyl stretching vibration. Obviously, since p*K*'s of 2-substituted chalcones do not fall on the same line as the corresponding 4-substituted chalcones, the above equation cannot be used to determine p*K*'s of *ortho*-substituted chalcones.

Effects of Substituents in Ring B.—The effect on the carbonyl stretching frequencies of substituents in ring B (3' and 4' substitution) was investigated. The compounds studied are shown in Table V. It was anticipated that a good correlation would be observed and that this system would be more sensitive to substituent effects since the carbonyl group is closer to the substituents. It is apparent from Figure 2 that only a poor correlation is obtained. It can be seen that there is some scatter in the plot of $\Delta\nu$ *vs.* σ^+ with some points deviating rather badly. The correlation coefficient is 0.89. This lack of a good fit may be due to variation in conformations of either the styryl or phenyl groups.
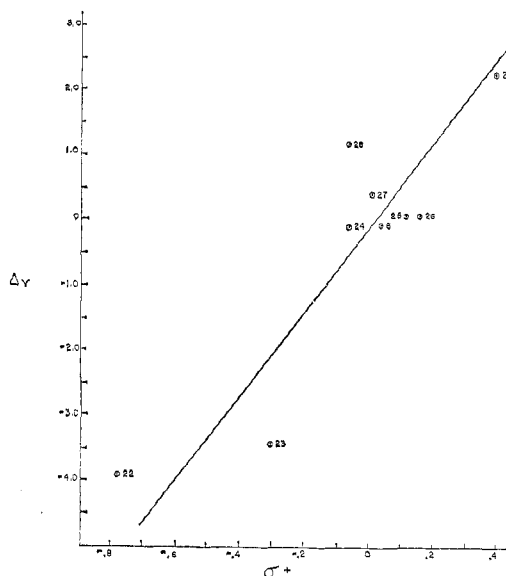
Figure 2.—Substituents in ring B.

TABLE V

SUBSTITUENTS IN RING B IN CHLOROFORM

Compound no.	Substituent	ν, cm^{-1}
22	4'-CH$_3$O	1661.8
23	4'-CH$_3$	1662.3
24	3'-CH$_3$	1665.6
25	4'-Cl	1665.6
26	4'-Br	1665.8
27	3'-CH$_3$O	1666.1
28	4'-F	1666.9
29	3'-Br	1668.0

The good correlation obtained with substituents in ring A suggests coplanarity of the styryl group (or at least a constant average conformation from substituent to substituent), at least without substituents in ring B, which might imply lack of coplanarity for the phenyl group for the case with substituents in ring B. The correlation obtained from treatment of the data with F and R parameters is very poor (C 0.62), much poorer than obtained in a similar treatment of the ring-A-substituted series. The differences in correlations obtained for series A and series B using the Swain-Lupton treatment draws further attention to the apparent conformational vagaries of this system. A relatively poor fit has been reported for pK's and ir stretching frequencies for substituted benzophenones.[24] This was explained in terms of competition for overlap of two potentially conjugating groups whose degree of conjugation may vary with substituent. Another poor fit was reported for the ir stretching frequencies of substituted phenylacetates.[25] This poor correlation was also explained in terms of variations in coplanarity of the phenyl groups with the carbonyl group. The good correlation obtained between pK's and σ^+ for 4'-substituted chalcones is in contrast to the poor ir correlation. This may be due to the stabilization achieved by conformational adjustment in the fully charged species involved in the pK_b determination.

(24) R. Stewart, M. R. Granger, R. B. Moodie, and L. J. Muenster, *Can. J. Chem.*, **41**, 1065 (1963).

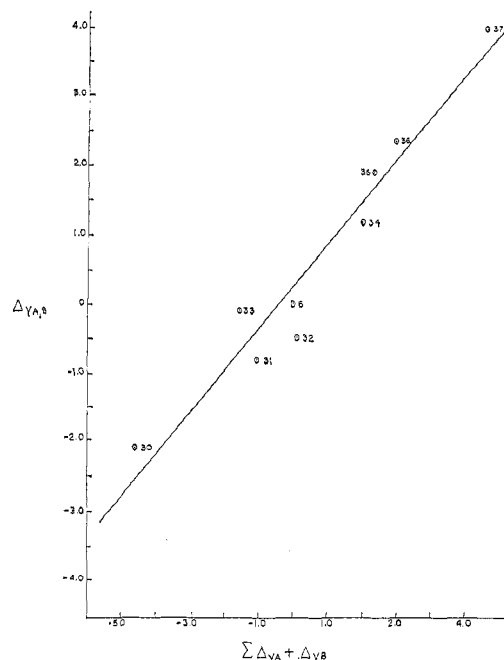(25) H. H. Freedman, *J. Amer. Chem. Soc.*, **82**, 2454 (1959).

Figure 3.—Substituents in rings A and B.

Substitution in Rings A and B.—In an attempt to gain further information as to the possible conformational changes in the chalcones and the influence of substituents on these conformers, the disubstituted chalcones in Table VI were studied. By maintaining

TABLE VI

SUBSTITUENTS IN RINGS A AND B IN CHLOROFORM

Compound no.	A substituents	B substituents	ν, cm^{-1}
30	4-CH$_3$	4'-CH$_3$	1663.6
31	4-CH$_3$	4'-Br	1664.9
32	4-CH$_3$O	3'-Br	1665.0
33	4-Cl	4'-CH$_3$	1665.6
34	4-Cl	4'-Cl	1666.9
35	3-Cl	3'-CH$_3$	1667.6
36	4-Cl	4'-F	1668.1
37	4-NO$_2$	3'-CH$_3$	1669.7

the substituent in ring A constant and varying the substituent in ring B and *vice versa*, information as to the influence of a styryl substituent on the phenyl ring or of a phenyl substituent on the styryl group may be obtained. If a substituent X has the same effect on the conformation of the group it is on, regardless of the substituent on the other group, then a plot of the sum of the $\Delta\nu$ values for the two monosubstituted compounds *vs.* the $\Delta\nu$ value for the corresponding disubstituted compounds should give a linear relationship. A plot of the data in Table VII is shown in Figure 3. The good correlation obtained suggests that substituents on the styryl group influence the carbonyl stretching frequency in a manner which is reasonably independent of substituents on the phenyl group and *vice versa*.

The poor correlation obtained for the monosubstituted compounds in ring B was attributed to either conformation changes of the styryl group and/or the phenyl group with change in substituents. Since a good correlation was obtained with substituents in the styryl position and since the effect of substituents in rings A and B appear to be essentially independent of one

TABLE VII

Δ VALUES FOR DISUBSTITUTED COMPOUNDS[a]

Compound no.	Δν_A	Δν_B	Σ Δν_A + Δν_B	Δ$\nu_{A.B}$
30	−1.2	−3.4	−4.6	−2.1
31	−1.2	0.1	−1.1	−0.8
32	−3.2	3.3	0.1	−0.7
33	1.8	−3.4	−1.6	−0.1
34	1.8	0.1	1.9	1.2
35	2.4	−0.1	2.3	1.9
36	1.8	1.2	3.0	2.4
37	5.8	−0.1	5.7	4.0

[a] s = 0.926; r = 0.963; i = 0.399; ρ = 1.53; n = 8.

another, it seems reasonable to attribute the poor correlation obtained for the series with substituents in ring B to conformational changes in the position of the phenyl group rather than the styryl group. Further support for the suggestion of conformational variation of ring B with substituents is found in a recent report on dipole moment measurements of pyrrole analogs of chalcones.[26] A better correlation of dipole moments with σ constants for 1-(2-pyrryl)-3-arylpropen-1-ones than with 1-(2-pyrryl)-3-arylpropen-3-ones was obtained. Speculations as to the factors which might cause these conformational differences seem unprofitable at this point.

The equation for the line in Figure 3

$$\Delta\nu_{A.B} = 1.53\Sigma(\Delta\nu_A + \Delta\nu_B) - 0.399$$

can be used also to predict the $\nu_{C=O}$ stretching frequencies of other disubstituted chalcones if the stretching frequencies of the corresponding monosubstituted chalcones are known.

Experimental Section

Infrared Frequencies.—The ir stretching frequencies for all the chalcones were determined using a Beckman IR-12 grating spectrometer operated in the expanded scale mode at scan rates of 8 cm^{-1} min, chart speed of 1 in./min, and period setting of 8. The spectra were recorded at 35 ± 3°. Band widths ranged from 10 to 20 cm^{-1}. Under the instrumental conditions employed the absolute tracking error in the frequencies computed as outlined in the Beckman IR-12 manual for a band width of 16 cm^{-1} may be as high as 0.9 cm^{-1}; *i.e.*, the reported values may be 0.9 cm^{-1} higher than they actually are. This possible absolute error in no way affects the purpose of this investigation or the conclusions drawn from the data. The resolution and accuracy of the instrument were checked using gas phase ammonia and H$_2$O bands. For determinations in CCl$_4$ spectral grade solvent dried over molecular sieves 5A was employed. The spectral grade CHCl$_3$ employed was passed through an alumina column immediately before use. The concentration of all solutions was *ca.* 5% and a matched set of KBr cells with 0.5-mm path lengths was used. All the chalcones exhibited a shoulder on the lower frequency side of the band. The height of each band was taken as the distance from the shoulder to the point of maximum absorption. The band frequencies were then taken at the half-width of the half-height; measurements were made using a K & E ruler with dimensions of 0.05 mm. All frequencies reported were obtained from averaging at least three different scans, all of which gave frequencies which were within 0.2 cm^{-1} of one another. The estimated relative error in frequencies is approximately 0.4 cm^{-1}.

Calculations.—The least-squares treatment, the multiple regression analysis, and other statistical computations[15] were performed using an IBM 7040 computer.

TABLE VIII

KNOWN CHALCONES

Compound no.	Mp, °C	Lit. mp, °C	Ref
1	110–111	110–112	*b*
2	58–59	58–59	*c*
3	73–74	76–77	*d*
4	165 (2.3 mm)[a]	218 (12 mm)[a]	*e*
5	92–94	96.5	*f*
6	55–56	55–57	*g*
7	64–65	68–69	*h*
8	59–61	64	*i*
9	47–48	53	*j*
10	83–84	84–85	*j*
11	112–113	114–115	*k*
12	125–127	127–128	*l*
14	49–51	52–53	*m*
16	73–74	74–76	*n*
17	83–85	84–85	*o*
18	74–75	75–76	*p*
19	109–110	114–116	*p*
21	160–161	163	*q*
22	106–107	106–107	*r*
23	96–97	96.5	*f*
24	56–57	59–60	*s*
25	98–100	101	*t*
26	100–102	104–105	*t*
28	76–78	77–79	*s*
29	89–90	92–94	*s*
30	94–95	97–98	*u*
34	152–154	155–157	*v*

[a] Boiling point. [b] E. B. Knott, *Chem. Abstr.*, **41**, 4730 (1947). [c] H. Stobbe and F. Wilson, *J. Chem. Soc.*, **97**, 1724 (1910). [d] N. Kochetkov and V. Belyaev, *Zh. Obshch. Khim.*, **30**, 1495 (1960). [e] C. Weygand and F. Schlacher, *Chem. Ber.*, **68**, 227 (1935). [f] V. Hazlik and A. Bianchi, *ibid.*, **32**, 2282 (1899). [g] See ref 27. [h] M. Giua, *Gazz. Chim. Ital.*, **46**, 293 (1916). [i] H. Bauer and P. Vogel, *J. Prakt. Chem.*, **88**, 329 (1913). [j] Z. Csuros and G. Deak, *Acta Chim. Acad. Sci. Hung.*, **17**, 1846 (1956). [k] V. Alexa, *Bull. Soc. Chim. Romania*, **18A**, 93 (1936). [l] See ref 10. [m] E. Weitz and A. Scheffer, *Chem. Ber.*, **54**, 2327 (1921). [n] G. McCasland, E. Blanz, and A. Furst, *J. Org. Chem.*, **24**, 999 (1959). [o] T. S. Stevens, *J. Chem. Soc.*, 2107 (1930). [p] See ref 11. [q] F. Iimura, *Nippon Kagaku Zasshi*, **77**, 1846 (1956). [r] F. Stockhausen and L. Galtermann, *Chem. Ber.*, **25**, 3536 (1892). [s] R. Lyle and L. Paradis, *J. Amer. Chem. Soc.*, **77**, 6667 (1955). [t] W. Dilthey, *J. Prakt. Chem.*, **101**, 202 (1921). [u] See ref 12. [v] H. O. House, *J. Amer. Chem. Soc.*, **83**, 979 (1961).

TABLE IX

NEW CHALCONES[a]

Compound no.	Mp, °C	λ_1, mμ (ϵ)	λ_2, mμ (ϵ)	λ_3, mμ (ϵ)
13[c]	46–47	210 (17,600)	238 (10,100)	305 (19,700)
15	51–52	208 (13,100)	227 (9,450)	302 (31,900)
20	151–152	208 (11,700)	225 (10,400)	305 (24,600)
27	43–45	208 (10,800)	225 (12,600)	315 (16,600)
31	159–160	207 (14,500)	231 (9,600)	328 (19,900)
32	73–75	210 (18,700)	251 (15,200)	352 (18,700)
33	147–149	207 (12,700)	229 (12,700)	319 (26,600)
35	79–80	212 (20,700)	234 (11,500)	304 (23,300)
36	135–137	208 (11,800)	230 (12,300)	317 (24,400)
37	139–140	209 (20,100)		320 (28,700)

[a] Satisfactory combustion data (±0.35 %) have been obtained on these compounds. [b] Ultraviolet absorptions were determined on a Perkin-Elmer 202 spectrophotometer in *ca.* 10^{-5} *M* solutions of absolute ethanol. [c] 2-Bromochalcone has been reported: W. Davey and J. R. Gilt, *J. Chem. Soc.*, 1008 (1967), mp 72°.

Chalcones.—All chalcones were made following the procedure of Kohler.[27] All compounds were recrystallized from ethanol

(26) S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, *Zh. Fiz. Khim.*, **42**, 2159 (1968).

(27) E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p 78.

until constant melting point was obtained and were then dried *in vacuo*. Table VIII lists the uncorrected melting points obtained with a Thomas-Hoover Uni-Melt, and literature references for compounds which had been previously reported. Table IX contains data on the new chalcones which were prepared.

β-Keto Sulfoxides. VIII. Acid-Catalyzed Reactions of β-Hydroxy Sulfides and the Hydration of Vinyl Sulfides. Synthesis of Ketene Mercaptals, α-Substituted Phenylthioacetic Acids, and α-Substituted Phenylacetaldehydes[1]
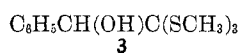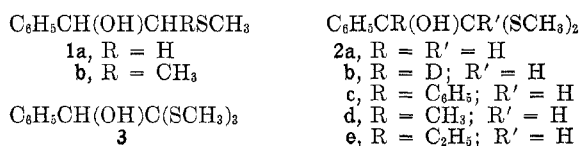
Glen A. Russell and Leo A. Ochrymowycz

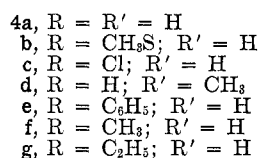*Department of Chemistry, Iowa State University, Ames, Iowa 50010*
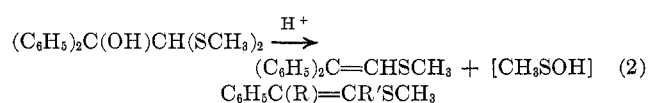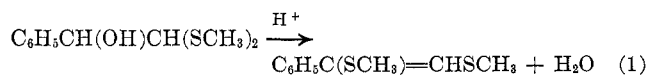
Secondary benzylic alcoholates adjacent to the thioacetal function $[C_6H_5CH(O^-)CH(SCH_3)_2]$ react with thionyl chloride or tosyl chloride to yield a 1,2-di(methylmercapto)ethylene $[C_6H_5C(SCH_3)=CHSCH_3]$. Tertiary benzylic alcohols adjacent to the thioacetal function $[C_6H_5CR(O^-)CH(SCH_3)_2]$ react with benzoyl chloride, thionyl chloride, or tosyl chloride to yield the β-styrenyl sulfides $(C_6H_5CR=CHSCH_3)$. Hydroboration of β-styrenyl sulfides followed by chromic trioxide oxidation is a convenient synthesis of phenylacetaldehyde and various α-substituted derivatives. Treatment of the anion of the thioacetal of benzilaldehyde with acetyl chloride followed by hydrolysis leads to the formation of α-phenyl-α-(methylmercapto)phenylacetaldehyde. Base-catalyzed eliminations of methanol from α-methoxy thioacetals $[C_6H_5CR(OCH_3)CH(SCH_3)_2]$ yields the ketene thioacetals $[C_6H_5CR=C(SCH_3)_2]$. Treatment of the methyl thioacetal of diphenylketene with aqueous acid leads to the formation of α-phenyl-β-(methylmercapto)styrene. Hydration of ketene thioacetals is a convenient route to S-methyl phenylthioacetate and its α-substituted derivatives.

Previous studies have made available a number of β-hydroxy sulfides, including compounds **1–3**.[2,3] It

$$C_6H_5CH(OH)CHRSCH_3$$
1a, R = H
b, R = CH₃

$$C_6H_5CH(OH)C(SCH_3)_3$$
3

$$C_6H_5CR(OH)CR'(SCH_3)_2$$
2a, R = R' = H
b, R = D; R' = H
**c**, R = C₆H₅; R' = H
d, R = CH₃; R' = H
e, R = C₂H₅; R' = H

had been previously established that **1a** is dehydrated under acidic conditions to yield β-(methylmercapto)-styrene, **4a**.[2] The reaction of the α-hydroxy thioacetals **2** under acidic conditions has now been examined in expectation of preparing ketene thioacetals. However, the reaction led instead to either rearrangement products (reaction 1) or to the elimination of the elements CH₃S–OH (reaction 2) to yield the substituted β-styrenyl

$$C_6H_5CH(OH)CH(SCH_3)_2 \xrightarrow{H^+}$$
$$C_6H_5C(SCH_3)=CHSCH_3 + H_2O \quad (1)$$

$$(C_6H_5)_2C(OH)CH(SCH_3)_2 \xrightarrow{H^+}$$
$$(C_6H_5)_2C=CHSCH_3 + [CH_3SOH] \quad (2)$$
$$C_6H_5C(R)=CR'SCH_3$$

4a, R = R' = H
b, R = CH₃S; R' = H
c, R = Cl; R' = H
d, R = H; R' = CH₃
e, R = C₆H₅; R' = H
f, R = CH₃; R' = H
g, R = C₂H₅; R' = H

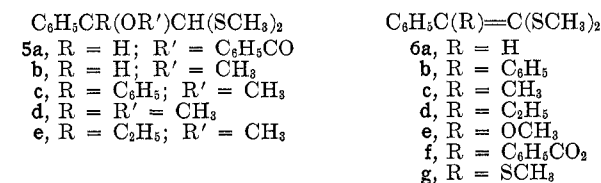sulfides **4b–4g**. Rearrangements similar to reaction 1 have been previously observed for some α-halo thioacetals (reaction 3)[4,5] and interpreted in terms of an

$$CH_3CH(Br)CH(SC_2H_5)_2 \longrightarrow$$
$$CH_3CH(SC_2H_5)=CHSC_2H_5 + HBr \quad (3)$$
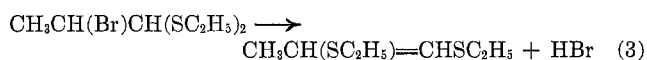
episulfonium ion intermediate.[6] When the thioalkyl group of an α-hydroxy thioacetal cannot migrate or be eliminated, the normal catalyzed dehydration is observed, for example, in the β-hydroxy-*m*-dithianes (reaction 4).[7] The methyl ethers or benzoate esters
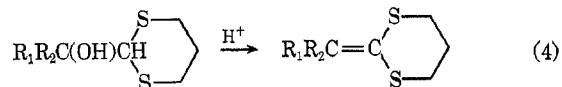
(5) of α-hydroxy thioacetals will undergo a base-catalyzed elimination to yield the ketene thioacetals **6a–6d**.

$$C_6H_5CR(OR')CH(SCH_3)_2 \qquad C_6H_5C(R)=C(SCH_3)_2$$
5a, R = H; R' = C₆H₅CO   **6a**, R = H
b, R = H; R' = CH₃   **b**, R = C₆H₅
c, R = C₆H₅; R' = CH₃   **c**, R = CH₃
d, R = R' = CH₃   **d**, R = C₂H₅
e, R = C₂H₅; R' = CH₃   **e**, R = OCH₃
                                 f, R = C₆H₅CO₂
                                 g, R = SCH₃

(2) G. A. Russell, E. Sabourin, and G. J. Mikol, *ibid.*, **31**, 2854 (1966).
(3) G. A. Russell and L. A. Ochrymowycz, *ibid.*, **34**, 3618 (1969).
(4) E. Rothstein, *J. Chem. Soc.*, 1553 (1940); E. Rothstein and R. Whitely, *ibid.*, 4012 (1953).
(5) W. E. Parham, J. Heberling and H. Wynberg, *J. Amer. Chem. Soc.*, **77**, 1169 (1955).
(6) K. D. Grundermann, *Angew. Chem. Intern. Ed.*, **2**, 674 (1963).
(7) E. J. Corey and D. Seebach, *Angew. Chem.*, **77**, 1134 (1965).

(1) This work was supported by a grant from the Army Research Office (Durham). For part VII, see G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3624 (1969).