being refluxed for 2 h, the solution was concentrated at reduced pressure and acidified with 6 N HCl. The precipitate was washed with water and dried to give the acid (mp 159–160 °C, 50%). The acid (0.5 mmol) was heated to 170 °C in a glass tube for 1 h and chromatographed on a silica-gel column (diethyl ether) to give **8** (oil, 85%).

7: IR (film) 1745, 1647, 1445; ^{1}H NMR 1.05 (t, J = 7 Hz, 3, β-H), 2.87 (m, 1, 4-H), 1.34 (s, 3, 3-CH_3), 2.33 (m, 1, 4-H), 3.08 (sextet, J = 7, 14 Hz, 1, α-H), 3.81 (sextet, J = 7, 14 Hz, 1, α-H), 3.62 (s, 3, OCH_3), 5.7–5.9 (m, 4, 5-H through 8-H); mass spectrum, m/e (relative intensity) 223 (30, M$^+$).

Anal. Calcd for $C_{12}H_{17}NO$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.19; H, 7.75; N, 6.07.

8: IR (film) 1660–1620, 1440, 1380; ^{1}H NMR 1.00 (d, J = 7 Hz, 3, 3-CH_3), 1.03 (t, J = 7 Hz, 3, β-H), 2.34 (br, 2, 4-H), 3.04 (sextet, J = 7, 14 Hz, α-H), 3.82 (sextet, J = 7, 14 Hz, α-H), 3.38 (m, 1, 3-H), 5.7–5.9 (m, 4, 5-H through 8-H); mass spectrum, m/e (relative intensity) 165 (80, M$^+$).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.34; H, 9.14; N, 8.32.

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Registry No. 1, 80753-91-9; **2**, 74142-27-1; **3**, 80753-92-0; **4**, 61856-34-6; **4** acid, 80753-93-1; **5**, 74142-22-6; **6**, 74142-24-8; **6** acid, 80753-94-2; **7**, 80753-95-3; **7** acid, 80753-96-4; **8**, 80753-97-5; 1-ethyl-2-pyridone, 13337-79-6; methyl methacrylate, 80-62-6.

Effects of α Substitution on the Carbonyl Stretching Frequencies of Phenyl Carboxylates

Maria Inês de Almeida,[1] Antonia T. do Amaral, and Luciano do Amaral*

Instituto de Química da Universidade de São Paulo, 01000 São Paulo, SP, Brazil

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The infrared carbonyl stretching frequencies for several esters of the general formula $R^1R^2R^3C$—COOPh were determined in carbon tetrachloride. The σ^* and E_s Taft parameters as well as the ν_{Charton} parameters for the same esters were determined. The carbonyl stretching frequencies are well correlated by a dual substituent parameter treatment: $\nu_{C=O} = \nu^0_{C=O} + \rho^*\sigma^* + \delta E_s$ or $\nu_{C=O} = \nu^0_{C=O} + \rho^*\sigma^* + \Psi\nu_{\mathrm{Charton}}$. In both cases the steric parameter is much larger than the polar parameter, suggesting that the effect of the substituents on the carbonyl stretching frequencies is of a steric nature, although a small contribution of the polar effect is observed.

An earlier investigation reported the effect of substitution at the α-position of phenyl carboxylates on the carbonyl stretching frequencies of the esters in carbon tetrachloride and chloroform solutions[2]. In continuation of this work, we have prepared several phenyl esters of allylacetic acid mono- and disubstituted at the α-position, with the general formula $CH_2{=}CHCH_2CR^1R^2COOPh$. These include phenyl allylacetate, phenyl allylethylacetate, phenyl allylphenylacetate, phenyl allylisopropylacetate, phenyl allylmethylacetate, phenyl allyldimethylacetate, phenyl allylethylphenylacetate, and phenyl allyldiphenylacetate. The Taft[3] and Charton[4] parameters of the groups $CH_2{=}CHCH_2{-}\dot{C}R^1R^2$ were determined, as were the carbonyl stretching frequencies of the esters in carbon tetrachloride. Our investigations were undertaken in order to obtain quantitative information pertinent to the steric and/or electronic effects on the carbonyl stretching frequencies of the esters caused by substituents at the α-position of the phenyl allylacetate.

Experimental Section

Materials. Allylacetic acid, butyric acid, isobutyric acid, isovaleric acid, phenylacetic acid, and phenyl acetate were obtained commercially and were either redistilled or recrystallized before use. Phenyl allylacetate, phenyl allylphenylacetate, and phenyl allyldiphenylacetate were prepared previously in our laboratories.[2]

Preparation of α-Substituted Allylacetic Acids. Allylethylacetic acid was prepared in accordance with the procedure of Pfeffer et al.[5] with some modifications: 108 mmol of n-butyllithium (2 M solution in hexane) was added to a solution of 96 mmol of diisopropylamine in 30 mL of THF. A solution of 48 mmol of butyric acid in 10 mL of THF was added slowly. After 15 min, 10 mL of HMPT was added and the solution stirred for 15 min. Allyl bromide (104 mmol) was then added. After stirring at room temperature for 2 h, followed by distillation of the solvent, the residue was poured into water and extracted with petroleum ether. The water layer was acidified and extracted with ethyl ether. The ether solution was washed with cold water and dried with $MgSO_4$. After removal of the ether, the crude acid was purified by the use of a silica gel column, employing ether/chloroform (4:1). The purified product was distilled to give the required acid. The same procedure was employed for the preparation of the acids shown in Table I.

Preparation of α-Substituted Phenyl Allylacetates. Phenyl allylethylacetate was prepared in accordance with the procedure of Kanaoka et al.[6] with some modifications: 112 mmol of P_2O_5 was added to 113 mmol of ethyl ether and 204 mmol of chloroform. Then, 15 mmol of allylethylacetic acid and 26 mmol of phenol were added. The reaction mixture was stirred during 24 h at room temperature. After removal of the solvents, the residue was poured into ice and almost neutralized with a 10% water solution of NaOH. The final neutralization was made with $NaHCO_3$. The water solution was extracted with chloroform. The chloroform solution was washed with a $NaHCO_3$ water solution and with water and then dried with $MgSO_4$. After removal of the chloroform, the crude ester was purified by the use of a silica

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[1] Fellow of the Fundação de Amparo à Pesquisa do Estado de São Paulo and of the Dow Chemical Co.

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Table I. Yield and Characterization of α-Substituted Allylacetic Acids

product	substrates	alkyl halide	yield, %	bp, °C (kPa)	IR[a] ν_{max}, cm^{-1}	^{1}H NMR,[b] ppm
allylethylacetic acid	butyric acid	allyl bromide	87	70-72 (0.27), 95-105 (1.6)[d]	2800-2500, 1680	0.90 (t, 3 H), 1.9 (m, 1 H), 2.1 (m, 2 H), 2.7 (d, 2 H), 4.7-5.2 (m, 2 H), 5.2-6.0 (m, 1 H), 12 (s, 1 H)
allylisopropylacetic acid	isovaleric acid	allyl bromide	73	78-80 (0.27), 78-80 (1.13)[d]	2800-2500, 1680	1.0 (d, 6 H), 1.9 (m, 1 H), 2.4 (m, 3 H), 5.2 (m, 2 H), 5.9 (m, 1 H), 12 (s, 1 H)
methylphenylacetic acid	phenylacetic acid	methyl iodide	84	110-112 (0.27), 144-147 (1.4)[e]	2800-2500, 1670	1.3 (d, 3 H), 3.7 (q, 1 H), 7.2 (s, 5 H), 12 (s, 1 H)
allylmethylphenylacetic acid[c]	methylphenylacetic acid	allyl bromide	67	165-168 (0.27)	2800-2500, 1680	1.5 (s, 3 H), 2.7 (m, 2 H), 4.7-5.2 (m, 2 H), 5.2-6.0 (m, 1 H), 7.2 (s, 5 H), 11 (s, 1 H)
allyldimethylacetic acid	isobutyric acid	allyl bromide	79	76-79 (0.27), 82-83 (0.53)[f]	2800-2500, 1675	1.2 (s, 6 H), 2.3 (d, 2 H), 4.7-5.2 (m, 2 H), 5.2-6.0 (m, 1 H), 12 (s, 1 H)

[a] Film. [b] Taken in carbon tetrachloride with an internal Me_4Si reference. [c] C = 75.72%, H = 7.35%, C_{calcd} = 75.76%, H_{calcd} = 7.42%. [d] Reference 14. [e] Reference 15. [f] Reference 16.

gel column, employing ether/chloroform (4:1). Boiling points were determined on a Kiegel-Rohr apparatus. The same procedure was employed for the preparation of the esters shown in Table II.

Kinetic measurements of the hydrolysis of the α-substituted phenyl allylacetates were carried out spectrophotometrically with the aid of a Zeiss PMQ-II spectrometer equipped with a cell holder through which water from a thermostated bath was continuously circulated. The measurements were carried out in 60% dioxane-water (v/v) at 25.0 °C. The acid-catalyzed hydrolysis of the esters was followed by observing the appearance of phenol at 270 nm, with an initial concentration of the ester of 4×10^{-3} M, at three values of H_0. The alkaline hydrolysis of the esters was followed by observing the appearance of the phenoxide ion at 287 nm, with an initial concentration of the ester of 5×10^{-4} M and an ionic strength 1.0×10^{-3}, at three values of pH. First-order rate constants were evaluated from slopes of plots of log ($OD_\infty - OD_t$) against time in the usual manner. Second-order rate constants ($k_{H_3O^+}$ or k_{OH^-}) were evaluated from the slopes of plots of first-order rate constants against the concentration of the hydronium ion or of the hydroxide ion.

Infrared Spectroscopy. IR spectra were measured in carbon tetrachloride (0.040 and 0.080 M solutions) on a Perkin-Elmer Model 547 grating spectrometer. The carbonyl region was scanned slowly, and spectra were recorded in quadruplicate at a chart speed of 50 cm^{-1}/min between 1900 and 1500 cm^{-1}. Calibration and paper alignment difficulties were minimized by recording the 1601-cm^{-1} polystyrene band on each spectrum. The transmitance minima given are the average of eight readings (on quadruplicate runs). The carbonyl absorption band had a symmetric shape that simplified the determination of its position in the spectrum. The carbonyl stretching frequency was not modified significantly with changes in concentration. ^{1}H NMR spectra were recorded on carbon tetrachloride solutions on a Varian Model T-60 spectrometer with an internal Me_4Si reference.

Results

We have prepared several α-substituted allylacetic acids, viz., allylethylacetic acid, allylisopropylacetic acid, allylmethylphenylacetic acid, and allyldimethylacetic acid, by direct alkylation of appropriate carboxylic acids, employing the bulky base lithium diisopropylamide.[7] Metal amides have been used as strong bases for metalation; however, only metal alkylamides can be used with carbonyl compounds to avoid the undesirable addition of the amide ion.[8] This base results in rapid formation of the dianion of the acid at room temperature, and its use seems more advantageous than the less bulky dimethyl- or diethylamide.[8] The alkylation reactions occur with excellent yields (Table I). No dialkylated compounds could be detected by GLC or NMR.

The reaction of α-substituted allylacetic acids with thionyl chloride, followed by reaction with the phenol, produced crude esters that were difficult to purify. We therefore prepared the phenyl esters employing the polyphosphoric ester (PPE) method[6] that gives pure esters in excellent yields (Table II).

The acid-catalyzed hydrolysis of phenyl esters of acetic acid, trimethylacetic acid, and α-substituted allylacetic acids in 60% dioxane at 25.0 °C were studied. The first-order rate constants were determined at three values of H_0 in the range between −1.1 and −0.50 (Table III). Solutions with the appropriate values of H_0 in 60% of dioxane at 25.0 °C were prepared in accordance with the procedure of Bunton et al.[9] The Taft E_s parameter was calculated by employing eq 1, where k_x is the $k_{H_3O^+}$ of the

$$E_s = (\log k_x/\log k_o)_A \qquad (1)$$

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Table II. Yield and Characterization of α-Substituted Phenyl Allylacetates

compound[a]	yield, %	bp, °C (kPa)	IR[b] ν_{max}, cm^{-1}	^1H NMR,[c] ppm
phenyl allylethylacetate	85	105 (0.27)	1750, 1185	0.90 (t, 3 H), 1.9 (m, 1 H), 2.1 (m, 2 H), 2.7 (d, 2 H), 4.7-5.2 (m, 2 H), 5.2-6.0 (m, 1 H), 7.0-7.2 (m, 5 H)
phenyl allylisopropylacetate	76	110 (0.27)	1750, 1185	1.0 (d, 6 H), 1.9 (m, 1 H), 2.4 (m, 3 H), 5.2 (m, 2 H), 5.9 (m, 1 H), 7.0-7.2 (m, 5 H)
phenyl allylmethylphenylacetate	92	138 (0.27)	1750, 1188	1.6 (s, 3 H), 2.8 (t, 2 H), 4.7-5.2 (m, 2 H), 5.2-6.0 (m, 1 H), 6.7-7.4 (m, 10 H)
phenyl allyldimethylacetate	93	102 (0.27)	1748, 1185	1.2 (s, 6 H), 2.3 (d, 2 H), 4.7-5.2 (m, 2 H), 5.2-6.0 (m, 1 H), 7.0-7.2 (m, 5 H)

[a] All compounds gave satisfactor C and H analyses. [b] Film. [c] Taken in carbon tetrachloride with an internal Me_4Si reference.

Table III. First-Order Rate Constants (k_{obsd}, s^{-1}) and Second-Order Rate Constants ($k_{H_3O^+}$, $M^{-1}\ s^{-1}$) for the Acid-Catalyzed Hydrolysis of Some Phenyl Carboxylates at 25.0 °C in 60% Dioxane

ester	H_0	h_0	k_{obsd}	$k_{H_3O^+}$
phenyl acetate	−0.50	3.16	5.02×10^{-5}	2.36×10^{-6}
	−0.70	5.01	5.52×10^{-5}	
	−0.87	7.41	6.44×10^{-5}	
phenyl allylacetate	−0.50	3.16	8.67×10^{-5}	2.05×10^{-6}
	−0.70	6.01	9.02×10^{-5}	
	−0.87	7.41	9.54×10^{-5}	
phenyl allylethylacetate	−0.70	5.01	1.30×10^{-5}	1.79×10^{-6}
	−0.87	7.41	1.88×10^{-5}	
	−1.10	12.59	2.69×10^{-5}	
phenyl allylphenylacetate	−0.70	5.01	1.39×10^{-4}	6.87×10^{-6}
	−0.87	7.41	1.57×10^{-4}	
	−1.10	12.59	1.91×10^{-4}	
phenyl allylisopropylacetate	−0.70	5.01	1.24×10^{-4}	4.58×10^{-6}
	−0.87	7.41	1.42×10^{-4}	
	−1.10	12.59	1.59×10^{-4}	
phenyl allylmethylphenylacetate	−0.50	3.16	3.48×10^{-5}	2.42×10^{-6}
	−0.70	5.01	3.97×10^{-5}	
	−0.87	7.41	4.51×10^{-5}	
phenyl allyldimethylacetate	−0.50	3.16	0.90×10^{-5}	9.05×10^{-7}
	−0.70	5.01	1.05×10^{-5}	
	−0.87	7.41	1.28×10^{-5}	
phenyl allyldiphenylacetate	−0.50	3.16	0.90×10^{-5}	9.05×10^{-7}
	−0.70	5.01	1.05×10^{-5}	
	−0.87	7.41	1.28×10^{-5}	
phenyl trimethylacetate	−0.50	3.16	2.77×10^{-4}	2.75×10^{-5}
	−0.70	5.01	3.16×10^{-4}	
	−0.87	7.41	3.93×10^{-4}	

Table IV. First-Order Rate Constants (k_{obsd}, s^{-1}) and Second-Order Rate Constants (k_{OH^-}, $M^{-1}\ s^{-1}$) for the Alkaline Hydrolysis of Some Phenyl Carboxylates at 25.0 °C in 60% Dioxane

ester	pH	$[OH^-]$	k_{obsd}	k_{OH^-}
phenyl acetate	11.92	8.32×10^{-3}	0.937×10^{-2}	5.55×10^{-1}
	12.55	3.55×10^{-2}	2.22×10^{-2}	
	12.99	9.78×10^{-2}	5.69×10^{-2}	
phenyl allylacetate	11.92	8.32×10^{-3}	0.358×10^{-2}	1.94×10^{-1}
	12.55	3.55×10^{-2}	0.917×10^{-2}	
	12.99	9.78×10^{-2}	2.03×10^{-2}	
phenyl allylethylacetate	12.21	1.62×10^{-2}	0.768×10^{-2}	8.65×10^{-3}
	12.55	3.55×10^{-2}	2.06×10^{-2}	
	12.95	9.78×10^{-2}	4.61×10^{-2}	
phenyl allylphenylacetate	11.92	8.32×10^{-3}	0.274×10^{-2}	1.56×10^{-1}
	12.55	3.55×10^{-2}	0.738×10^{-2}	
	12.99	9.78×10^{-2}	1.71×10^{-2}	
phenyl allylisopropylacetate	12.21	1.62×10^{-2}	0.338×10^{-1}	2.57×10^{-2}
	12.55	3.55×10^{-2}	0.765×10^{-1}	
	12.95	8.91×10^{-2}	1.49×10^{-1}	
phenyl allylmethylphenylacetate	11.92	8.32×10^{-3}	0.292×10^{-2}	3.87×10^{-1}
	12.55	3.55×10^{-2}	1.40×10^{-2}	
	12.99	9.78×10^{-2}	3.82×10^{-2}	
phenyl allyldimethylacetate	12.21	1.62×10^{-2}	1.38×10^{-2}	9.04×10^{-4}
	12.55	3.55×10^{-2}	2.50×10^{-2}	
	12.95	8.91×10^{-2}	5.33×10^{-2}	
phenyl allyldiphenylacetate	11.92	8.32×10^{-3}	0.184×10^{-2}	1.19×10^{-1}
	12.55	3.55×10^{-2}	0.461×10^{-2}	
	12.99	9.78×10^{-2}	1.26×10^{-2}	

Table V. Values of Taft's Parameters E_s and σ^* and ν_{Charton} Parameters for Some Substituent Groups of the General Formula $R^1R^2R^3C$

substituents					
R^1	R^2	R^3	E_s	σ^*	ν_{Charton}
H	H	H	0.00	0.00	0.52[a]
allyl	Et	H	−0.60	+0.58	0.74[a]
allyl	Ph	H	−0.78	−0.415	0.81
allyl	*i*-Pr	H	−0.91	+0.145	0.86
allyl	Me	H	−0.91	−0.169	0.86
allyl	Me	Ph	−1.05	+0.360	0.92
allyl	Ph	Me	−1.13	−0.669	0.94
allyl	Ph	Ph	−1.48	+0.327	1.07
Me	Me	Me			1.24[a]

[a] Values from ref 11.

acid-catalyzed hydrolysis of the phenyl α-substituted allylacetates and k_0 is $k_{H_3O^+}$ of the acid-catalyzed hydrolysis of phenyl acetate. The values of E_s are shown in Table IV.

The alkaline hydrolysis of phenyl esters of acetic acid and of the α-substituted allylacetic acids at 25.0 °C in 60% dioxane were studied. The first-order rate constants were determined at three values of pH in the range between 11.92 and 12.99 (Table VI). Solutions with the appropriate values of pH were prepared in accordance with the procedure of Bates et al.[10] The Taft σ^* parameters were calculated by employing eq 2. The σ^* values are shown in Table V.

$$\sigma^* = 1/2.48[\log (k_x/k_0)_B - \log (k_x/k_0)_A] \qquad (2)$$

Charton proposed a steric parameter[11] that is a function of the van der Waals radius of the substituent as in eq 3,

$$\nu_x = r_{v,x} - r_{v,H} = r_{v,x} - 1.20 \qquad (3)$$

where $r_{v,x}$ is the van der Waals radius of substituent group and $r_{v,H}$ is the van der Waals radius of the hydrogen atom. Charton also proposed that the rates of the esterification of substituted carboxylic acids, in methanol, were a function of the ν value (eq 4). Values of ν that cannot be

$$\log k = \Psi\nu_{\text{Charton}} + h \qquad (4)$$

determined by eq 3 were determined by eq 4. The values of $k_{H_3O^+}$ that we determined for the hydrolysis of phenyl acetate, allylacetate, and trimethylacetate (Table III) were well correlated with ν values from the literature[11] by employing eq 5. Employing eq 5 and values of $k_{H_3O^+}$ from

$$\log k_{H_3O^+} = 2.66\nu_{\text{Charton}} - 3.18 \ (r = 0.99997) \qquad (5)$$

Table III, we calculated the ν values that are in Table V.

The position of the carbonyl group absorption band in carbon tetrachloride has been determined for each of the esters prepared. Frequency values (cm^{-1}) of esters are shown in Table VI. As can be seen in Table VI, the introduction of one substituent at the α-position of the phenyl allylacetate shifts the absorption band to a lower frequency compared to that for the unsubstituted compound. When two substituents are introduced at the α-position, an even greater shift to lower frequency is observed.

Discussion

Table VI. Carbonyl Absorption (cm^{-1}) for Some α-Substituted Phenyl Allylacetates in Carbon Tetrachloride

ester	$\nu_{C=O}$	$\nu_{C=O}$[a]	$\nu_{C=O}$[b]
phenyl allylacetate	1765.3 ± 0.2	1765.3	1765.4
phenyl allylethylacetate	1761.4 ± 0.7	1761.9	1761.9
phenyl allylphenylacetate	1760.7 ± 0.2	1761.2	1761.1
phenyl allylisopropylacetate	1760.4 ± 0.2	1760.8	1760.7
phenyl allylmethylphenylacetate	1759.9 ± 0.2	1759.9	1759.7
phenyl allyldimethylacetate	1758.1 ± 0.5	1751.6	1757.6
phenyl allyldiphenylacetate	1754.9 ± 0.3	1754.9	1755.0

[a] Calculated from eq 14 and values from Table V.
[b] Calculated from eq 15 and values from Table V.

The shift to lower frequency caused by the substitution of α-hydrogen atoms of the phenyl allylacetate by alkyl or aryl groups can arise from polar (inductive) effects, from steric effects, or from a combination of the two effects. The phenyl group exerts only a small inductive effect (−*I*). If this effect is significant, the presence of the phenyl group in the α-position would shift the carbonyl absorption band to higher frequency. The alkyl groups, on the other hand, would exert a small positive (+*I*) inductive effect, causing a shift to the lower frequency values. The observations made do not agree with these considerations. The alkyl or aryl groups may exert a steric effect. In order to gain quantitative information about the nature of the effect exerted by the substituent groups, we correlated the values of the carbonyl stretching frequencies (Table VI) of the esters studied with polar (eq 6) and steric parameters (eq 7 and 8).

$$\nu_{C=O} = \nu^0_{C=O} + \rho^*\sigma^* \qquad (6)$$

$$\nu_{C=O} = \nu^0_{C=O} + \delta E_s \qquad (7)$$

$$\nu_{C=O} = \nu^0_{C=O} + \Psi\nu_{\text{Charton}} \qquad (8)$$

The least-squares fits are shown, respectively, in eq 9–11.

$$\nu_{C=O} = 1760.1 - 0.71\sigma^* \ (r = 0.088) \qquad (9)$$

$$\nu_{C=O} = 1770.9 + 11.0E_s \ (r = 0.976,\ s = 0.744) \qquad (10)$$

$$\nu_{C=O} = 1786.2 - 29.4\nu_{\text{Charton}} \ (r = 0.976,\ s = 0.747) \qquad (11)$$

It is apparent from eq 9 that there is no correlation between the carbonyl stretching frequencies and the σ^* polar parameter. On the other hand, there are reasonable correlations between the carbonyl stretching frequencies and the E_s and ν_{Charton} steric parameters.

We also correlated the carbonyl stretching frequencies of the esters with a dual-parameter treatment, including polar and steric effects (eq 12 and 13). The least-squares

$$\nu_{C=O} = \nu^0_{C=O} + \delta E_s + \rho^*\sigma^* \qquad (12)$$

$$\nu_{C=O} = \nu^0_{C=O} + \Psi\nu_{\text{Charton}} + \rho^*\sigma^* \qquad (13)$$

fits are shown, respectively, in eq 14 and 15.

$$\nu_{C=O} = 1771.4 + 11.4E_s + 1.3\sigma^* \ (R = 0.988,\ s = 0.520) \qquad (14)$$

$$\nu_{C=O} = 1787.3 - 30.6\nu_{\text{Charton}} + 1.4\sigma^* \ (R = 0.989,\ s = 0.565) \qquad (15)$$

The correlation coefficient (*R*) and standard deviation (*s*) values of eq 14 and 15 indicate that there is a good correlation between the carbonyl stretching frequencies and both the polar and steric effects. The results show that both effects are present, but the steric effect is much larger than the polar one (Table VI).

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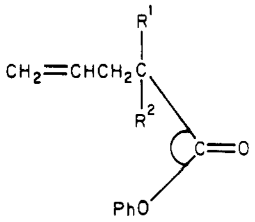
(11) M. Charton, *J. Am. Chem. Soc.*, **97**, 1552 (1975); M. Charton, *J. Org. Chem.*, **41**, 2217 (1976).

During the vibration of the carbonyl bond both atoms move with almost equal amplitudes. For accommodation of the movement of the carbon atom some compression or deformation of the adjacent C–C or C–O bonds must take place. A coupling effect then comes into play, which can lead to a change of the carbonyl frequencies without any corresponding change in the carbonyl force constant. Bellamy[12] suggests that the greater part of the observed changes of the carbonyl frequencies with ring size originate in coupling effects of the type discussed above. Similarly, the low carbonyl frequencies shown by di-*tert*-butyl ketone and by α-substituted methyl aryl ketones are due primarily to increases in the C–C–C bond angles.[13]

We suggest, then, that the shifts of IR bands to lower frequency observed for the carbonyl group when hydrogen atoms of the α-carbon in allylacetate are substituted by alkyl or phenyl groups are due to a change in the carbonyl group valency angle as shown below.



Registry No. Allylethylacetic acid, 1575-73-1; allylisopropylacetic acid, 1575-71-9; methylphenylacetic acid, 492-37-5; allylmethylphenylacetic acid, 76403-17-3; allyldimethylacetic acid, 16386-93-9; phenyl allylethylacetate, 80765-41-9; phenyl allylisopropylacetate, 80765-42-0; phenyl allylmethylphenylacetate, 80765-43-1; phenyl allyldimethylacetate, 80765-44-2; phenyl acetate, 122-79-2; phenyl allylacetate, 51231-09-5; phenyl allylphenylacetate, 51231-03-9; phenyl allyldiphenylacetate, 51231-12-0; phenyl trimethylacetate, 4920-92-7.

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Notes

2-(2-Methyl-3-indolyl)-1,4-benzoquinone, a Reversible Redox Substrate at the Carbon-Paste Electrode in Acidic Aqueous–Ethanolic Media

Thomas E. Young* and Brion W. Babbitt

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

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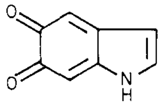
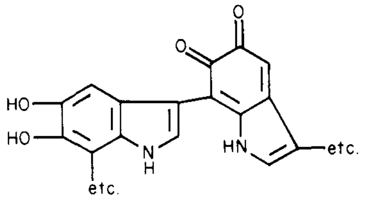
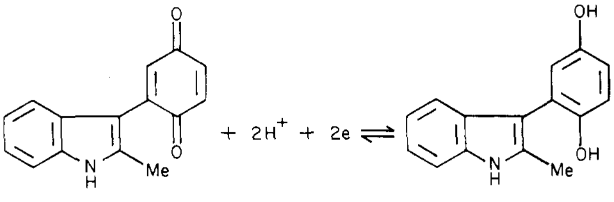
The oxidative polymerization of dopa (3,4-dihydroxyphenylalanine) to the mammalian pigment melanin has long been considered to proceed via a pathway involving a series of fugitive quinonoid intermediates,[1] of which indole-5,6-dione (**1**) was first postulated as the principal building block of the polymeric pigment.[2] Since model studies[3] had demonstrated that indoles readily react with simple *o*- and *p*-quinones to yield indolyl quinones (such as **3** from 2-methylindole and *p*-benzoquinone), it was considered likely that **1** would condense with its reduced form, 5,6-dihydroxyindole (DHI), to yield a dimeric species, which on further repetitive oxidation and addition would yield a polymer having a structure of type **2** (or variant involving other modes of ring–ring coupling) as a primary repeating unit. Although melanin is now considered to be a variegated polymer, comprising structural contributions from each of several precursors,[4] the dominant redox structure of the pigment is still believed to be an indolyl quinone moiety. For these reasons, and as part of our ongoing electrochemical studies of the melanization reactions of dopa[5] and its analogues,[6] it became of interest to examine the redox behavior of 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3**) as an easily accessible, prototypical indolyl quinone system.



1



2



3 **4**

Cyclic voltammetry of 0.211 mM 2-(2-methyl-3-indolyl)-1,4-benzoquinone (**3**) in the mixed solvent 1 M perchloric acid/95% ethanol (4:1, v/v) of apparent pH 0.60 at 25 °C showed that the system ($\mathbf{3} \rightleftharpoons \mathbf{4}$) is essentially reversible at the carbon-paste electrode. Within the potential window from +0.7 to 0.0 V (SCE) and at a scan rate of 0.050 V/s the cyclic voltammogram, initiated from +0.07 V toward more negative potentials, exhibited a cathodic peak at $E_{pc} = +0.460$ V for the reduction (**3** → **4**) and an anodic peak $E_{pa} = +0.490$ V for the oxidation (**4** → **3**). The peak separation, $E_{pa} - E_{pc} = 0.030$ V, is comparable with that expected (0.029 V) for a reversible two-electron transfer,[7] and, in corroboration, the cathodic half-peak

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