Carbonyl-Stretching Frequencies in Substituted Phenyl Carboxylates[1]

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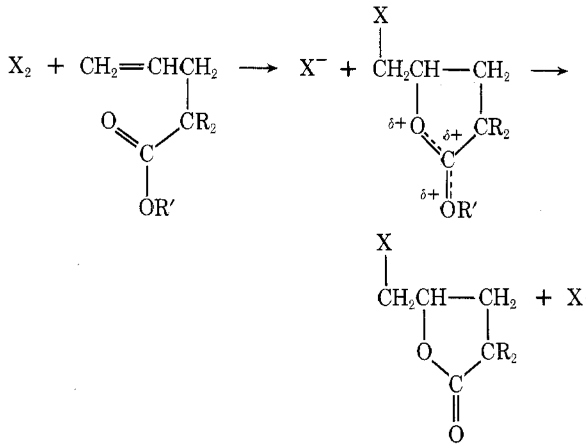
The infrared carbonyl-stretching frequencies for para-substituted phenyl allylacetates (set I), para-substituted phenyl diphenylacetates (set II), para-substituted phenyl allyldiphenylacetates (set III), phenyl acetate, phenyl allylphenylacetate, and phenyl propyldiphenylacetate were determined in carbon tetrachloride and chloroform. In the sets studied the values obtained are shown to correlate with Hammett substituent constants for the ring substituent. Using phenyl acetate as the basis for comparison, it was found that increasing the methyl substitution by alkyl or aryl substituents causes lowering of the infrared carbonyl-stretching frequency.

It is known that the γ,δ-unsaturated acids and their derivatives react with electrophilic reagents giving rise to δ-substituted γ-lactones.[3-5]



It was shown in a qualitative way that an increase of electron density on the carbonyl group[6] and/or the presence of substituents at the α position of the carboxylic acids[7,8] increases the rate of the lactonization.

Our infrared investigations were undertaken in order to obtain quantitative information pertinent to the electronic effects on the carbonyl-stretching frequencies of phenyl allylacetates caused by substituents on the para position of the benzene ring and by the substitution at the α position of the carboxylic acids.

Experimental Section

Materials. Allylacetic acid, diphenylacetic acid, and phenyl acetate were obtained commercially and were either redistilled or recrystallized before use. Allyldiphenylacetic acid and phenyl allylphenylacetate (XVII) were synthesized according to known procedures.[5]

Preparation of Para-Substituted Phenyl Allylacetates. *p*-Nitrophenyl allylacetate (I), *p*-bromophenyl allylacetate (II), phenyl allylacetate (III), *p*-methoxyphenyl allylacetate (IV), and *p*-tolyl allylacetate (V) were synthesized according to known procedures.[5] Compound II, yield 79%. Anal. Calcd: C, 52.21; H, 4.35. Found: C, 51.21; H, 4.58. Bp 94–95 °C (0.12 Torr); ir absorption (film) 3100, 1760, 1660, 1600, 1490, 1220, 1015, 840, and 520 cm^{-1}.

Preparation of Para-Substituted Phenyl Diphenylacetates. The diphenylacetic acid (0.10 mol) with 0.20 mol of thionyl chloride were heated until the evolution of gases ceased. After the excess of thionyl chloride was removed by distillation, 0.10 mol of the corresponding phenol was added and the mixture heated for 2–3 h. The product was washed with cold 10% sodium hydroxide solution and water, and extracted with ether; solvent was evaporated. The crude ester was recrystallized from methanol (Table I).

Preparation of Para-Substituted Phenyl Allyldiphenylacetates. *p*-Bromophenyl allyldiphenylacetate (XII), phenyl allyldiphenylacetate (XIII), *p*-methoxyphenyl allyldiphenylacetate (XIV), and *p*-tolyl allyldiphenylacetate (XV) were prepared by the following method. A solution of 11 mmol of n-butyllithium (solution 2 M in hexane) was added to a solution of 12 mmol of isopropylcyclohexylamine (ICA) in 30 ml of THF at −5 °C. The reaction mixture was cooled to −78 °C. A solution of 10 mmol of the ester (*p*-bromophenyl, phenyl, *p*-methoxyphenyl, and *p*-tolyl diphenylacetate) in 10 mmol of THF was added slowly. After 15 min, 10 ml of Me_2SO was added and the solution stirred for 15 min. Allyl bromide (15 mmol) was then added in one portion. After stirring at −78 °C for 2 h and then at room temperature for 2 h followed by distillation of the solvent, the residue was poured into water and extracted with petroleum ether. The ether solution was washed with 10% HCl cold and with water. After removal of the petroleum ether, the crude ester was obtained and distilled or recrystallized from methanol (Table II).

Phenyl *n*-propyldiphenylacetate (XVI) was prepared as above, employing phenyl diphenylacetate and *n*-propyl bromide. Compound XVI, yield 91%, mp 69–70 °C. Anal. Calcd: C, 83.58; H, 7.18. Found: C, 83.60; H, 6.71. Ir absorption (KBr) 3100–2860, 1746, 1595–1590, 1495–1485, 1210, 1100 cm^{-1}; ^{1}H NMR absorption (CCl_4) 0.67–1.43, 2.20–2.60, 6.67–7.50, and 7.35 ppm. *p*-Nitrophenyl allyldiphenylacetate (XI) was prepared by heating 12 mmol of allyldiphenylacetic acid with 71 mmol of thionyl chloride until the evolution of gases ceased. After the excess of thionyl chloride was removed by distillation, 14 ml of carbon tetrachloride and a solution of 42 mmol of *p*-nitrophenol in 28 ml of pyridine was added. The reaction mixture was kept at room temperature for 5 days. The product was washed with cold 10% cupric sulfate solution and extracted with ether. The ether solution was washed with 10% sodium hydroxide solution and water. The crude ester was obtained by distillation. This was recrystallized from methanol, yield 96%, mp 116–118 °C. Anal. Calcd: C, 73.98; H, 5.13. Found: C, 73.95; H, 5.05. Ir absorption (KBr) 3110–2860, 1759, 1640, 1590–1490, 1550, 1345, 1200, and 885 cm^{-1}; ^{1}H NMR absorption 3.22, 4.76–5.20, 5.23–6.00, 7.02, 7.32, 8–17 ppm.

Infrared Spectroscopy. Ir spectra (cm^{-1}) were measured in carbon tetrachloride and in chloroform (0.040, 0.060, and 0.080 M) on a Perkin-Elmer Model 457 grating spectrometer. The carbonyl region was scanned slowly, and spectra were recorded in triplicate, 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 1583.1-cm^{-1} polystyrene band on each spectrum. The transmittance minima given are the average of nine readings (on triplicate runs). The carbonyl absorption band had a symmetric shape that simplified the determination of its position in the spectrum. The standard deviation, *S*, was calculated for each compound. The carbonyl stretching frequency was not modified significantly dependent on the concentration (examples are shown in Table III). ^{1}H NMR spectra were recorded on carbon tetrachloride solutions on a Varian Model T-60 spectrometer with an internal Me_4Si reference. Melting points were determined on a Kofler hot stage apparatus and are uncorrected.

Results

Preparation of Esters. Esters from allylacetic acid and diphenylacetic acid were prepared by the usual method of converting the respective acids into their chlorides by reaction with thionyl chloride, followed by reaction with the appropriate phenol.[5] The reaction of the allyldiphenylacetic acid with thionyl chloride, followed by reaction with para-substituted phenol, has produced impure esters of difficult purification, except for the *p*-nitrophenyl allyldiphenylacetate. Esters from that acid have been prepared

Table I. Yield and Characterization of Para-Substituted Phenyl Diphenylacetates Prepared from Diphenylacetic Acid and Para-Substituted Phenols

Compd	Substituent	Yield, %	Mp, °C	Ir[d] ν_{max}, cm^{-1}	^{1}H NMR,[e] ppm
VI	*p*-Nitro	66	89–91[a]	1762, 1620	5.11, 7.11, 7.27, 8.12
VII[f]	*p*-Bromo	70	61–63	1750, 1590	5.08, 6.87, 7.27, 7.37
VIII	Unsubstituted	91	65–66[b]	1744, 1590	5.16, 6.83–7.40, 7.31
IX[f]	*p*-Methoxy	91	101–102	1751, 1600	3.73, 5.13, 6.67–7.00, 7.30
X	*p*-Methyl	91	76–78[c]	1751, 1600	2.30, 5.12, 6.83, 7.07, 7.30

[a] Lit.[9] 89–90 °C. [b] Lit.[9] 66–67 °C. [c] Lit.[9] 76–78 °C. [d] KBr. [e] Taken in carbon tetrachloride. [f] Satisfactory combustion analytical data for C and H (±0.4%) were reported for these compounds.

Table II. Yield of Allylation of Para-Substituted Phenyl Diphenylacetates, and Characterization of the Para-Substituted Phenyl Allyldiphenylacetates Formed

Compd	Substituent	Yield, %	Mp, °C	Ir[a] ν_{max}, cm^{-1}	^{1}H NMR,[b] ppm
XII[c]	*p*-Bromo	90	76–77	1759, 1630	3.20, 4.73–5.20, 5.27–6.00, 6.73, 7.27
XIII	Unsubstituted	91	40–42[d]	1753, 1630	3.21, 4.73–5.17, 5.33–6.00, 6.73–7.50
XIV[c]	*p*-Methoxy	97	71–73	1759, 1630	3.20, 3.73, 4.71–5.15, 5.28–6.00, 7.75
XV[c]	*p*-Methyl	93	54–55	1756, 1600	2.30, 3.22, 4.68–5.22, 5.25–6.00, 6.70

[a] KBr. [b] Taken in carbon tetrachloride. [c] Satisfactory combustion analytical data for C and H (0.04%) were reported for these compounds. [d] Lit.[5] 40–42 °C.

Table III. Carbonyl-Stretching Frequencies (cm^{-1}) of Phenyl Allylacetate (III), Phenyl Diphenylacetate (VIII), and Phenyl Allyldiphenylacetate (XIII) in Carbon Tetrachloride and Chloroform, as Function of the Concentration

	III		VIII		XIII	
Concn, M	CCl_4	$HCCl_3$	CCl_4	$HCCl_3$	CCl_4	$HCCl_4$
0.040	1765.3	1753.1	1773.4	1765.4	1754.8	1748.4
	1765.5	1753.7	1774.6	1765.0	1754.2	1748.0
	1765.5	1754.3	1773.8	1765.4	1755.2	1748.4
	1765.3				1755.1	1748.5
0.060	1765.3	1753.5	1773.9	1765.3		
	1765.3	1753.2	1773.9	1765.2		
	1765.4	1753.7	1774.5	1765.1		
	1765.2	1753.4				
0.080	1765.6	1752.8	1773.6	1765.6	1754.8	1748.6
	1765.0	1753.5	1773.9	1765.9	1755.3	1748.8
	1764.9	1753.4	1774.4	1765.3	1755.0	1748.9
	1765.3				1755.0	1748.4
	ν_m 1765.3	ν_m 1753.5	ν_m 1774.0	ν_m 1765.4	ν_m 1754.9	ν_m 1748.5
	$S = 0.2$	$S = 0.4$	$S = 0.4$	$S = 0.3$	$S = 0.3$	$S = 0.3$

by allylation of the para-substituted phenylic esters of the diphenylacetic acid, using as a base lithium isopropylcyclohexylamide.[11] The same method was used to introduce the *n*-propyl radical into the phenyl diphenylacetate. Alkylations were done with excellent yields, obtaining pure monoalkylated esters (Table II).

Infrared Spectroscopy. The position of the carbonyl group absorption band in carbon tetrachloride and in chloroform has been determined for each one of the esters synthesized, viz., set I, *p*-nitrophenyl (I), *p*-bromophenyl (II), phenyl (III), *p*-methoxyphenyl (IV), and *p*-tolyl allylacetates (V); set II, *p*-nitrophenyl (VI), *p*-bromophenyl (VII), phenyl (VIII), *p*-methoxyphenyl (IX), and *p*-tolyl diphenylacetates (X); set III, *p*-nitrophenyl (XI), *p*-bromophenyl (XII), phenyl (XIII), *p*-methoxyphenyl (XIV), and *p*-tolyl allyldiphenylacetates (XV), phenyl propyldiphenylacetate (XVI), phenyl allylphenylacetate (XVII), and phenyl acetate (XVIII).

These determinations were obtained as described in the Experimental Section. Frequency values (cm^{-1}) determined for the three series of esters are shown in Table IV.

As can be seen in Table IV, the electron-attracting groups shift the absorption band to higher frequency values (cm^{-1}), as compared with the unsubstituted compound, in the three series studied. An opposite shift is observed in the compounds with substituent groups that supply electrons. In the three tables it can also be observed that the values of carbonyl absorption frequency determined in carbon tetrachloride are greater than the values determined in chloroform. As usually higher frequencies are found in nonpolar solvents (carbon tetrachloride) than in polar solvents (chloroform), this behavior was to be expected.[11,12]

Inspection of Table V shows that substitution of one hydrogen atom of the methyl group in phenyl acetate by the allyl radical shifts the carbonyl absorption to lower frequency. When two hydrogen atoms are substituted by radicals (phenyl diphenylacetates or phenyl allylphenylacetates), an even greater shift to lower frequency is observed. A still greater shift is observed when all three hydrogen atoms are substituted (phenyl propyldiphenylacetate and phenyl allyldiphenylacetate).

Discussion

Hammett's Equation Application. Freedman[13] determined the absorption frequencies of the carbonyl group in a series of meta- and para-substituted phenyl acetates, in both carbon tetrachloride and chloroform as solvent. He tried to correlate the results with the Hammett σ values, but the points indicated on the graph were scattered, indicating only a tendency of an increase of frequency with σ. To explain the behavior observed with the meta- and para-substituted phenyl acetates, Freedman concluded that the electronic effect was transmitted from the substituent group to the carbonyl by the inductive effect. The resonance effect would not be transmitted, or it would be transmitted with little intensity, owing to the lack of the needed coplanarity. Considering that in the para-substituted phe-

Table IV. Carbonyl Absorption (cm^{-1}) for Para-Substituted Phenyl Allylacetates (Set I), Para-Substituted Phenyl Diphenylacetates (Set II), and Para-Substituted Phenyl Allyldiphenylacetates (Set III)

	CCl_4		$HCCl_3$	
Substituent	ν_m	Δ_ν[a]	ν_m	Δ_ν[a]
		Para-Substituted Phenyl Allylacetates		
p-NO_2	1774.4 ± 0.2	9.1 ± 0.3	1762.4 ± 0.4	8.9 ± 0.4
p-Br	1766.9 ± 0.3	1.6 ± 0.4	1756.5 ± 0.3	3.0 ± 0.4
H	1765.3 ± 0.2	0.0	1753.5 ± 0.5	0.0
p-OCH_3	1761.3 ± 0.3	−4.0 ± 0.4	1749.6 ± 0.3	−3.9 ± 0.4
p-CH_3	1762.8 ± 0.2	−2.5 ± 0.3	1752.7 ± 0.2	−0.8 ± 0.3
		Para-Substituted Phenyl Diphenylacetates		
p-NO_2	1774.0 ± 0.4	10.3 ± 0.4	1765.4 ± 0.3	9.0 ± 0.4
p-Br	1764.7 ± 0.2	1.0 ± 0.2	1759.7 ± 0.1	3.3 ± 0.2
H	1763.7 ± 0.1	0.0	1756.4 ± 0.2	0.0
p-OCH_3	1762.0 ± 0.4	−1.7 ± 0.4	1754.2 ± 0.6	−2.2 ± 0.6
p-CH_3	1761.6 ± 0.2	−2.1 ± 0.2	1753.7 ± 0.1	−2.7 ± 0.2
		Para-Substituted Phenyl Allyldiphenylacetates		
p-NO_2	1760.5 ± 0.4	5.6 ± 0.5	1757.2 ± 0.2	8.7 ± 0.4
p-Br	1755.6 ± 0.1	0.7 ± 0.3	1750.0 ± 0.2	1.5 ± 0.4
H	1754.9 ± 0.3	0.0	1748.5 ± 0.3	0.0
p-OCH_3	1751.3 ± 0.2	−3.6 ± 0.4	1747.2 ± 0.5	−1.3 ± 0.6
p-CH_3	1750.8 ± 0.4	−4.1 ± 0.5	1747.4 ± 0.4	−2.1 ± 0.5

[a] $\Delta_\nu = \nu_m^R - \nu_m^H$.

Table V. Carbonyl Absorptions (cm^{-1}) of α-Substituted Phenyl Acetates, $R_1R_2R_3C-CO_2C_6H_5$

			CCl_4		$HCCl_3$	
R_1	R_2	R_3	ν_m, cm^{-1}	$\Delta\nu$	ν_m, cm^{-1}	$\Delta\nu$
H	H	H	1767.4 ± 0.3	0.0	1765.1 ± 0.3	0.0
H	H	$H_2C{=}CHCH_2$	1765.3 ± 0.2	−2.1 ± 0.4	1753.5 ± 0.5	−11.6 ± 0.6
H	C_6H_5	C_6H_5	1763.7 ± 0.1	−3.7 ± 0.3	1756.4 ± 0.2	−8.7 ± 0.4
H	C_6H_5	$H_2C{=}CHCH_2$	1760.7 ± 0.2	−6.7 ± 0.4	1753.9 ± 0.2	−11.2 ± 0.4
C_6H_5	C_6H_5	$H_3C-CH_2CH_2$	1755.8 ± 0.4	−11.6 ± 0.5	1749.2 ± 0.2	−15.9 ± 0.4
C_6H_5	C_6H_5	$H_2C{=}CHCH_2$	1754.9 ± 0.3	−12.5 ± 0.4	1748.5 ± 0.3	−16.6 ± 0.4

nyl acetates there has been a great predominance of the inductive effect, it seemed to us that Hammett's equation might be applied using σ^n values. We calculated the correlation coefficient (r) between the values determined by Freedman for the meta- and para-substituted phenyl acetates in carbon tetrachloride and in chloroform and the values σ^n. We found the value 0.81, which is not satisfactory according to the criterion proposed by Jaffé.[14]

More recently, Cohen and Takahashi[15] determined the carbonyl absorption frequencies of polysubstituted phenyl hydrocinnamates. These authors proposed that the carbonyl electronic density would depend on the electronic effects (inductive and resonance) that the substituting group would exercise on the carbon C-1. So the carbonyl stretching frequency values would be better correlated to the values of σ^o. With the values determined by Cohen and Takahashi, we calculated the correlation coefficients achieved by applying Hammett's equation to the esters p-nitrophenyl, p-bromophenyl, phenyl, tolyl, and p-methoxyphenyl hydrocinnamates, that is, for the esters corresponding to the ones synthesized by us in accordance with the values of σ, σ^n, and σ^o obtaining the values 0.992, 0.997, and 0.998, respectively. We have therefore verified that Hammett's equation fits in perfectly with the values determined by the two authors for the esters mentioned above, using any of the above mentioned σ values.

We could satisfactorily apply Hammett's equation for the carbonyl group absorption frequencies on our three series of esters for σ, as well as for σ^n and σ^o. (See Table VI and Figure 1). Values of σ, σ^n, and σ^o were taken from the compilation of Ritchie and Sager.[16] It can be observed in Table VI that correlation coefficients do not permit a judgment as to which one of the σ value series our results fit best. It can be observed that values of ρ, ρ^n and ρ^o are slightly greater in carbon tetrachloride than in chloroform; this signifies that the sensitivity of the carbonyl absorption frequency to the para groups is a little higher in carbon tetrachloride than in chloroform. This slight difference observed could be attributed to a greater sensitivity of the carbonyl frequency to the substituents in nonpolar solvents.

Effects of the Introduction of Substituting Groups in the α Position of the Acetic Acid Phenylic Esters on the Carbonyl Stretching Frequency. The shift to lower frequency caused by the substitution of the methyl radical hydrogens of the phenyl acetate by alkyl or aryl radicals can have various explanations. (1) An inductive effect due to the radicals. The phenyl group exerts only a small inductive effect (−I). If this effect is significant, the phenyl group's presence in the α position would shift the carbonyl absorption band to higher frequency. The shift in the same direction, but of smaller magnitude, would be observed in the presence of the allyl radical. The propyl radical, on the other hand, exerts a small +I inductive effect causing a shift to the lower frequency values. The observations made do not agree with these considerations. (2) Interaction between the carboxyl group and the double bond of the allyl radical. Conformational analysis of these esters shows that successive introduction of substituents in the α position causes greater stability to the conformation that has the carbonyl group and the double bond closer; this would facilitate a possible interaction between these two groups which would be reflected in the carbonyl absorption position. The more stable conformation in the phenyl n-propyl-

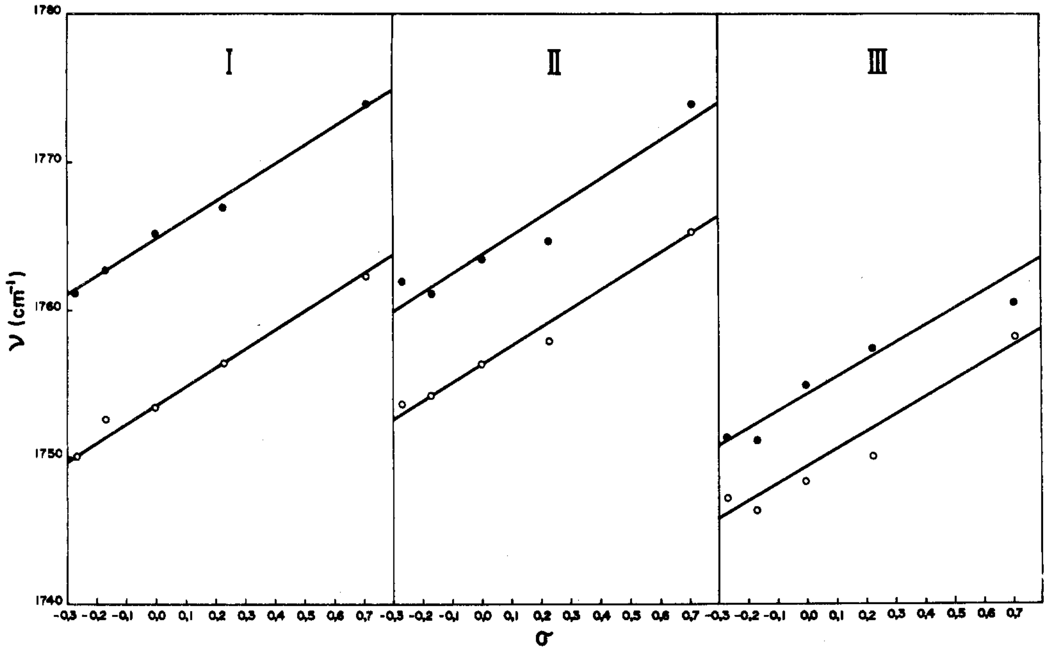


Figure 1. Correlation of carbonyl-stretching frequencies (cm^{-1}) for para-substituted phenyl allylacetates (set I), para-substituted phenyl diphenylacetates (set II), and para-substituted phenyl allyldiphenylacetates (set III) with σ in carbon tetrachloride (●) and in chloroform (○).

Table VI. Correlations between the Carbonyl Absorptions (cm^{-1}) of Para-Substituted Phenyl Allylacetates (Set I), Para-Substituted Diphenylacetates (Set II), and Para-Substituted Allyldiphenylacetates (Set III), and the Hammett Substituent Constants

Best fit linear equation	Solvent	r	ρ[a]
Para-Substituted Phenyl Allylacetates			
$\nu = 1764.8 + 12.2\ \sigma$	CCl_4	0.996	12.2
$\nu = 1764.0 + 13.2\ \sigma^n$	CCl_4	0.981	13.2
$\nu = 1764.2 + 13.5\ \sigma^o$	CCl_4	0.986	13.5
$\nu = 1753.6 + 11.5\ \sigma$	$HCCl_3$	0.989	11.5
$\nu = 1753.0 + 12.3\ \sigma^n$	$HCCl_3$	0.967	12.3
$\nu = 1753.2 + 12.7\ \sigma^o$	$HCCl_3$	0.976	12.7
Para-Substituted Phenyl Diphenylacetates			
$\nu = 1763.8 + 11.8\ \sigma$	CCl_4	0.969	11.8
$\nu = 1763.1 + 13.1\ \sigma^n$	CCl_4	0.978	13.1
$\nu = 1763.4 + 13.2\ \sigma^o$	CCl_4	0.970	13.2
$\nu = 1756.6 + 11.4\ \sigma$	$HCCl_3$	0.991	11.4
$\nu = 1755.8 + 12.6\ \sigma^n$	$HCCl_3$	0.995	12.6
$\nu = 1756.1 + 12.9\ \sigma^o$	$HCCl_3$	0.998	12.9
Para-Substituted Phenyl Allyldiphenylacetates			
$\nu = 1753.6 + 9.1\ \sigma$	CCl_4	0.972	9.1
$\nu = 1753.0 + 9.9\ \sigma^n$	CCl_4	0.959	9.9
$\nu = 1753.2 + 10.2\ \sigma^o$	CCl_4	0.968	10.2
$\nu = 1748.7 + 10.1\ \sigma$	$HCCl_3$	0.998	10.1
$\nu = 1748.0 + 11.3\ \sigma^n$	$HCCl_3$	0.989	11.3
$\nu = 1748.3 + 11.4\ \sigma^o$	$HCCl_3$	0.983	11.4

[a] Hammett's ρ value is dimensionless. In this work it has the dimension of cm^{-1} as is common in the literature in spectroscopic comparison (See ref 11 and 15).

diphenylacetate is the one that has the carbonyl and the ethyl radical closer. This *n*-propyldiphenylacetate is saturated and serves as a saturated model to compare with the allyl-substituted esters. However, the position of the carbonyl absorption band of the saturated model is very close to the phenyl allyldiphenylacetate's. These results seem to indicate that there is no interaction between the carboxyl and the vinyl groups, or, if there is some interaction, it has no influence on the carbonyl frequency. These observations agree with those which were established by Leonard and Owens,[17] who observed that transannular interaction between C=C and C=O groups in cyclic ketones is not detected by infrared spectroscopy. (3) The effect of changing angles on adjacent bonds. It has been shown[18] with aliphatic esters that it is not necessary to distort the carbonyl group valency angles in order to accommodate groups linked to it. Bowden et al.[19] suggest that interactions involving the methoxyl group are small even in the methyl propyldiphenylacetate. (4) Mass effect result of the carbonyl substituent in α, as successive substituting groups are introduced into α carbon. The importance of this effect has been suggested by various authors.[18-20] Thus, it has been observed that the carbonyl band position shifts to lower frequency upon deuteration of the methyl acetate.[20] We suggest, then, that shifts of ir band to lower frequency observed in carbonyl groups when hydrogen atoms of the α carbon of the phenyl acetate are substituted can be due a mass effect.

Registry No.—I, 51231-11-9; II, 51231-10-8; III, 51231-09-5; IV, 51231-07-3; V, 51231-08-4; VI, 58241-10-4; VII, 58241-11-5; VIII, 58241-12-6; IX, 58241-13-7; X, 58241-14-8; XI, 58241-15-9; XII, 58241-16-0; XIII, 51231-12-0; XIV, 58241-17-1; XV, 58267-79-1; XVI, 58241-18-2; XVII, 51231-03-9; XVIII, 122-79-2; diphenylacetic acid, 117-34-0; *p*-nitrophenol, 100-02-7; *p*-bromophenol, 106-41-2; phenol, 108-95-2; *p*-methoxyphenol, 150-76-5; *p*-methylphenol, 106-44-5; allyl bromide, 106-95-6; *n*-propyl bromide, 106-94-5; allyldiphenylacetic acid, 6966-03-6.

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Aromatic Substitution. XXXVIII.[1a] Chloromethylation of Benzene and Alkylbenzenes with Bis(chloromethyl) Ether, 1,4-Bis(chloromethoxy)butane, 1-Chloro-4-chloromethoxybutane, and Formaldehyde Derivatives

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The chloromethylation of benzene and alkylbenzenes was studied with bis(chloromethyl) ether, 1,4-bis(chloromethoxy)butane, 1-chloro-4-chloromethoxybutane, and formaldehyde derivatives. Relative rate data of chloromethylations compared to benzene as well as isomer distributions were determined. The mechanisms of the reactions are considered in view of the experimental data. Preparative aspects of the novel chloromethylations with 1,4-bis(chloromethoxy)butane and 1-chloro-4-chloromethoxybutane are also discussed.

Since the discovery of the chloromethylation reaction by Grassi-Cristaldi and Maselli,[2] mechanistic studies have centered on establishing the role of formaldehyde in the reaction.[3] It is now generally accepted that the electrophilic reagent in chloromethylations in aqueous or polar solvents (such as glacial HOAc) is the hydroxycarbenium ion (protonated formaldehyde, $CH_2{}^+{=}OH$).[3,4] Interestingly, however, in our recent work[5] protonated chloromethyl alcohol, $ClCH_2O^+H_2$, was obtained as a stable species, thus indicating its possible significance in chloromethylations.

It was reported by Brown and Nelson[6] that chloromethylation shows high substrate and positional selectivity. The competitive rate between toluene and benzene in chloromethylation with paraformaldehyde, HCl gas, and $ZnCl_2$ in glacial acetic acid solution at 65 °C was found to be 112, with an ortho/para ratio of 0.54. At the same time they claimed that previously reported investigations of chloromethylation reactions,[7] showing low substrate selectivity, while maintaining high positional selectivity, were found to be unreproducible.

We have previously reported[8] that electrophilic aromatic substitution reactions generally can display variable substrate selectivity, not necessarily showing substantial loss of positional selectivity, as evidenced by generally low meta isomer contents observed in substitution of toluene.

We wish to report now related observations of the chloromethylation of benzene and alkylbenzenes with bis(chloromethyl) ether, 1,4-bis(chloromethoxy)butane, 1-chloro-4-chloromethoxybutane, and formaldehyde derivatives. The varied chloromethylations cannot be characterized by a single selected value of substrate and positional selectivity, which can vary widely depending on specific reaction systems and conditions used.

Results and Discussion

Chloromethylation with Bis(chloromethyl) Ether. Since reproducible kinetic data cannot be obtained in heterogeneous systems, it was decided to confine our studies to those chloromethylating agents which displayed good solubility in aromatic hydrocarbons or in a common solvent, thus allowing homogeneous reaction conditions. After preliminary experiments with paraformaldehyde in a number of solvent systems, it was discarded in favor of bis(chloromethyl) ether, which displays good solubility in aromatic hydrocarbons. Bis(chloromethyl) ether has found extensive use in the chloromethylation of aromatic compounds and was generally assumed to generate monomeric formaldehyde in situ, which then reacts analogously to paraformaldehyde or aqueous formaldehyde.[3] Our work shows, however (vide infra), that this is not the real reaction mechanism of chloromethylation with bis(chloromethyl) ether or other halomethyl ethers.

Early in our study it was realized that improved analytical methods were necessary for quantitative analysis of chloromethylated products formed in the reaction mixtures. Previous studies have relied on titrimetric methods, ir spectroscopy, or on analysis after isolating and subsequently converting the chloromethylated products by reduction with $LiAlH_4$ and uv analysis of the resultant methylarenes (utilized for example by Brown and Nelson[6]). We have developed a suitable GLC method to obtain unequivocal data of product compositions, which permits the reaction mixture to be analyzed directly for chloromethylated products (i.e., benzyl chloride and methylbenzyl chlorides). Product compositions could thus be directly determined with an accuracy of better than 1%.

With the choice of chloromethylating agent decided upon and using as solvent excess of neat aromatics, it was then necessary to select a suitable catalyst for the chloromethylation reactions to be studied. In our initial studies, zinc chloride was used because of the general utility it has enjoyed in chloromethylations. Its solubility in aromatic hydrocarbons, however, is poor, and we found that only after the chloromethyl ether was added to a slurry of aromatic hydrocarbon and zinc chloride did the zinc chloride go into solution. Consequently stannic chloride was chosen as a catalyst for the chloromethylation studies. It is a highly soluble catalyst, and generally not so active as to cause secondary reactions (i.e., condensation of chloromethylated products and excess aromatics to give diarylmethanes). Finally, our studies were carried out at 65 °C to allow comparison with the work of Brown and Nelson,[6] which was carried out at this temperature.