Notes

The Effect of Substituents on the Carbonyl and Acetylene Stretching Frequencies of Phenylbenzoylacetylenes

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The efficacy of the carbon–carbon triple bond as a unit which transmits substituent effects has been previously studied by measurement of the ionization constants of phenylpropiolic acids,[1] of rates of esterification of phenylpropiolic acids,[1] and of rates of hydrolysis of phenylpropiolic esters.[2] Comparison of ρ values obtained from ionization of *trans*-cinnamic and phenylpropiolic acids showed no difference between the two systems, *i.e.*, ρ = 0.43 and 0.42, respectively.[3,4] The ρ values obtained from esterification rates of *trans*-cinnamic and phenylpropiolic acids with diphenyldiazomethane were 0.42 and 0.33, respectively,[3] and the ρ values obtained from alkaline hydrolysis of the ethyl *trans*-cinnamates and phenylpropiolates were 1.31[5] and 1.10.[2] Thus it appears in aryl-substituted acetylenes, in spite of an earlier report to the contrary,[6] that the acetylene link transmits electronic effects somewhat less effectively than the ethylene unit. Results of studies on propiolic acids with the substituents directly attached to the triple bond led to the same conclusion.[7] Nevertheless, it seems desirable to test the effectiveness of the acetylene unit to transmit electronic effects by an independent probe, particularly one which in contrast to the previous studies on the arylacetylenes does not involve fully charged intermediates. In view of this and our continuing interest[8] in the effect of substituents on the carbonyl stretching frequency (C=O) of aryl ketones we have measured the C=O of a series of 4-substituted phenylbenzoylacetylenes.

The carbon–carbon triple bond stretching frequency ($\nu_{C\equiv C}$) is generally regarded to be relatively insensitive to substituent effects.[9] The $\nu_{C\equiv C}$ for substituted phenylacetylenes has been reported to show only a very qualitative correlation with the donating–withdrawing ability of the substituent.[10] Correlations between the intensity of the carbon–carbon triple bond stretch and σ^+ have been reported;[11] however, it seems that a correlation of $\nu_{C\equiv C}$ by the Hammett expression has not appeared. It is, therefore, of particular further interest to carefully measure the triple bond stretching frequency of the phenylbenzoylacetylenes under investigation and treat the results with the Hammett expression.

The phenylbenzoylacetylenes were prepared by the method of Bickel,[12] which involves addition of bromine to the chalcone, dehydrohalogenation by NaOAc–HOAc of the resulting chalcone dibromide to produce the corresponding α-bromochalcone, and finally KOH dehydrohalogenation of the latter to yield the desired acetylene. In our hands the final step gave erratic yields for most compounds and failed completely with certain compounds which were substituted with electron donors.

The 4-substituted phenylbenzoylacetylenes employed in this investigation and their stretching frequencies values, which were determined in carbon tetrachloride solution, are listed in Table I. The $\nu_{C=O}$ values were correlated employing σ^+ values obtained from the review of Ritchie and Sager.[13] Table II contains the results of a statistical analysis of the correlations carried out according to the approach of Jaffe.[14] The correlation between σ^+ and $\nu_{C=O}$ is only fair, r = 0.966. A comparison of the ρ value obtained from the

Table I

Phenylbenzoylacetylenes Stretching Frequencies

Compd	Substituent	$\nu_{C=O}$	$\nu_{C\equiv C}$
1	4-CH_3O	1645.0	2196.0
2	4-F	1649.7	2200.0
3	4-H	1649.2	2202.0
4	4-Cl	1650.5	2201.3
5	4-Br	1650.0	2202.0
6	3,4-DiCl	1650.7	2206.2
7	4-NO_2	1653.8	2207.0

Table II

Results of Statistical Treatment Using σ^+ Constants[a,b]

	n	ρ	s	i	c
$\nu_{C=O}$	7	5.10	0.74	1649.3	0.966
$\nu_{C\equiv C}$	7	7.39	0.83	2201.3	0.979

[a] See ref 8c. [b] n = number of points; ρ = slope as determined by the method of least squares; s = standard deviation; i = intercept; c = correlation coefficient.

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(4) This conclusion is questionable since the ionization of the cinnamic acids was measured in water and the propiolic acids ionization was measured in 50% ethanol.

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phenylbenzoylacetylene series (ρ 5.10) with those obtained from $\nu_{C=O,s\text{-}cis}$ (ρ 5.62) and $\nu_{C=O,s\text{-}trans}$ (ρ 7.20) of chalcone[8c,15] shows that transmission *via* the carbon–carbon triple bond to the carbonyl group is as effective as that through the double bond with the carbonyl group in the s-cis conformation and is somewhat less efficient than that through the double bond with the carbonyl group in the s-trans conformation. Thus it would appear that, in spite of the low polarizability[16] of the carbon–carbon triple bond, it functions well as a transmitting unit, albeit not quite so effectively as the carbon–carbon double bond.

The stretching frequencies for the carbon–carbon triple bond are correlated reasonably well with σ^+ values; $r = 0.979$ (Table II). This apparently constitutes the first reported case of a quantitative correlation of carbon–carbon triple bond stretching frequencies by the Hammett expression. It is of interest to note that the correlations between $\nu_{C\equiv C}$ and σ or σ^0 are significantly poorer than with σ^+. This is in contrast to the correlation of the carbon–nitrogen bond stretch for benzonitriles, which has been found to be better correlated by σ.[17] This result suggests that during the carbon–carbon triple-bond stretch a partial positive change is generated on the benzyl type carbon analogous to that for the carbonyl stretch. In this case this result may be a consequence of the fact that the triple bond is part of an α,β-unsaturated ketone system. Comparison of the magnitude of the ρ value (7.39) obtained from the carbon–carbon triple-bond data with that obtained from benzonitriles[17] for the carbon–nitrogen triple bond (ρ 5.4) indicates, in contrast to previous suggestions, that $\nu_{C\equiv C}$ is relatively sensitive to substituent effects. Additional sets of $\nu_{C\equiv C}$ and $\nu_{C\equiv N}$ data must be collected before the questions of the relative sensitivity of these stretches to substituents and of the best choice of σ constants to assess this sensitivity can be answered with a reasonable degree of confidence.

Experimental Section

Infrared Frequencies.—The ir stretching frequencies were determined using a Beckman IR-12 spectrometer operated in the expanded scale mode at scan rates of 8 cm^{-1}/min, chart speeds of 1 in./min, and period setting of 8 (see ref 8c for comments on error). The instrument was calibrated as previously described;[8c] see also ref 8c for comments about errors. The spectra were taken on *ca.* 5% solutions in spectral grade carbon tetrachloride at 35 ± 4° in a matched set of KBr cells of path length of 0.05 mm. The frequencies were taken as the point of half-band height at half-band width. The values shown in Table I are the average of six different scans taken on two different days, all of which gave frequencies which were within 0.3 cm^{-1} of one another.

Phenylbenzoylacetylenes.—The method used to prepare the phenylbenzoylacetylenes is essentially as described by Bickel[12] and modified by Lutz and Black.[18] In a typical reaction sequence 6.0 g of Br_2 was added dropwise to 10.0 g of 4-bromochalcone in 200 ml of HOAc at 50–60°. After addition was complete the solution was heated to reflux, 4.0 g of Na_2CO_3 was cautiously added, and refluxing was continued for 3 hr. The solution was poured into H_2O and extracted with Et_2O. The organic layer was washed (H_2O), dried ($CaSO_4$), and evaporated. The oily α-bromochalcone was used directly in the next reaction by dissolving it in 50 ml of acetone, adding to it 30 ml of H_2O, and heating to reflux. To the refluxing solution was added dropwise during *ca.* 20 min a solution of 4.0 g of KOH in 20 ml of H_2O. The reaction mixture was allowed to reflux for an additional 20 min, then it was poured into H_2O, extracted (Et_2O), dried ($CaSO_4$), and evaporated. The black residue obtained was purified by column chromatography over alumina employing benzene–low-boiling petroleum ether mixtures as the eluent. The final dehydrohalogenation step failed for 4-methyl- and 4-dimethylamino-α-bromochalcone.

Table III contains melting points obtained with a Thomas-Hoover Uni-Melt and they are uncorrected. Also included in Table III are the uv data obtained on the phenylbenzoylacetylenes in *ca.* 10^{-5} *M* absolute ethanol solutions using a Beckman Acta-V spectrometer. Analyses were obtained by Atlantic Microlab, Atlanta, Ga.

TABLE III

PHENYLBENZOYLACETYLENES[a]

Compd	Mp, °C	$\lambda \times 10^{-3}$, cm^{-1}	($\epsilon \times 10^{-3}$)
1	81–82 (82.5–83.5)[b]	30.6	(23.7)
		38.0	(17.6)
		40.8	(16.5)
2	79–79.5	33.1	(15.4)
		34.7	(15.5)
		37.1	(18.7)
		45.2	(18.8)
3	48–49.5 (49–50)[c]	33.3	(17.7)
		34.8	(17.8)
		36.9	(15.7)
		45.2	(14.0)
4	101–102	32.5	(23.0)
		34.2	(21.3)
		36.6	(16.0)
		43.8	(14.5)
5	117–118	32.4	(36.1)
		34.1	(34.0)
		37.4	(28.4)
		44.2	(21.6)
6	113–114	32.6	(19.4)
		34.8	(22.5)
		43.0	(14.9)
7	148–148.5	33.8	(26.6)

[a] All compounds except **1** and **3** were analyzed for C, H, and all results were within ±0.3 of theory. [b] Literature melting point in parenthesis; see ref 18. [c] C. Dufraisse, *Ann. Chim. (Paris)*, **17**, 133 (1922).

Registry No.—**1**, 20442-66-4; **2**, 39833-45-9; **3**, 7338-94-5; **4**, 29776-35-0; **5**, 39833-48-2; **6**, 39900-69-1; **7**, 39833-49-3.

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(15) These values for ρ were obtained by taking $\nu_{C=O}$ data for 4-$(CH_3)_2N$-, 4-NH_2-, 4-CH_3O-, 4-CH_3-, 4-H-, 4-F-, 4-Cl-, 3-Cl, 4-CN, and 3-NO_2 chalcones from A. Perjessy, *Chem. Zvesti*, **23**, 343 (1969), and treating the data with σ^+ by our statistical method.

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