The Nuclear Magnetic Resonance Spectra of Olefinic Systems and the Substituent Effects. II. Methyl Esters of α- or β-Substituted Cinnamic Acids

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In the preceding paper**, a study of the possibility of Hammett's relationship being applicable to the chemical shifts of olefinic protons in ω-substituted *trans*-styrenes and in 1-substituted *trans*-propenes was reported on. A tentative plotting of the shifts against Hammett's substituent constants showed that such an application was reasonable. In fact, the correlation between the shifts and a certain combination of the potential inductive and resonance parameters for the substituent, that is, $0.40\ \sigma_I + 0.70\ \sigma_R$[1], has been found to fit the purpose even better.

This paper is concerned with the proton magnetic resonance spectra of a series of methyl cinnamates which carry substituents at the α- or β-position. Its main purpose is to examine whether the trends of olefinic proton shifts with regard to these compounds may be represented by the same relationship applied to substituted styrenes and 1-propenes.

Experimental

A Varian 4300-B spectrometer operating at 56.4 Mc. was used for obtaining the spectra. Glass tubes 5 mm. in outside diameter, containing the sample solution of a 10 mol. per cent concentration in carbon tetrachloride, were spun in the magnetic field. The other conditions of measurement were stated in the preceding paper.

Samples. — *Methyl Cinnamate.* — Dry hydrogen chloride gas was passed through a solution of pure cinnamic acid in anhydrous methanol. The product was rectified under reduced pressure. M. p., 33°C.

Methyl α-Chlorocinnamate and Methyl α-Bromocinnamate. — Prior to esterification, each isomer mixture of free acids, which are synthesized from cinnamic acid, is separated into cis- and trans-acids by means of the poorer solubility of the potasium salt of the latter in a buffered ethanol solution[2]. *trans-α*-Chloroester. M.p., 33～34°C; *trans-α*-bromoester: B. p., 150～152°C under 9 mmHg.

Methyl α-Methylcinnamate.—The free acid was prepared through the condensation of benzaldehyde with methylmalonic acid and esterified[3]. M. p., 37～38°C.

Methyl α-Cyanocinnamate.—The free acid, melting at 180.5°C, was obtained by the condensation of benzaldehyde with sodium cyanoacetate. As the ester, melting at 90～90.5°C, is sparingly soluble in carbon tetrachloride, a solution of about a 2 mol. per cent concentration was used for the measurement.

Methyl β-Chlorocinnamate and Methyl β-Bromocinnamate[4]. — From the isomer mixture of free acids, obtained by means of the addition of hydrogen chloride or hydrogen bromide to phenylpropiolic acid, the trans-isomer was separated by means of its poorer solubility[2] and esterified. Chloroester: M. p., 22～4°C; bromoester: 58°C.

Methyl β-Methylcinnamate. — The corresponding acid was converted into its methyl ester. M. p., 27°C; b. p., 109°C under 4.5 mmHg.

Results and Discussion

The signals of olefinic protons in methyl cinnamates, $C_6H_5CH_A{=}CH_BCO_2CH_3$, and the compounds in which H_A or H_B is substituted for by the other substituent, X, are simple and are easily characterized. The estimated values of each signal are summarized in the Table I.

If styrene is assumed to be the reference compound in considering the substituent effects, the resonance of the olefinic proton will take place under the effects of both substituents, i. e., an invariable methoxycarbonyl and a variable X. The correlation of cis-proton shieldings with substituent effects, discussed in Part I, will hold also in the case of the proton situated at the trans-position to the substituent X. The chemical shifts of the trans-proton may be computed from the same data as were applied to the cis-proton and so are governed by the identical combination of inductive and resonance parameters, namely, $0.40\ \sigma_I + 0.70\ \sigma_R$[5]. In Fig. 1, the individual proton shift with regard to the α-compounds is plotted against the combined substituent constants just mentioned. When the trends

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** H. Kasiwagi and J. Niwa, This Bulletin, 36, 405 (1963).

[1] R. W. Taft, Jr., *J. Am. Chem. Soc.*, 79, 1045 (1957).

[2] R. Störmer and P. Heymann, *Ber.*, 46, 1258 (1913).

[3] W. J. Gensler and E. Berman, *J. Am. Chem. Soc.*, 80, 4949 (1958).

[4] H. Kasiwagi, This Bulletin, 31, 985 (1958).

[5] About the used substituent parameters, cf. the preceding paper.

TABLE I. CHEMICAL SHIFTS OF METHYL ESTERS OF α- OR β-SUBSTITUTED CINNAMIC ACIDS
$C_6H_5C(H_A, X)=C(H_B, X)CO_2CH_3$

Substituent X	Chemical shifts in τ-values, ± 0.03 p. p. m.				
	δ_{H_A}	δ_{H_B}	δ_{Ph-H}*	δ_{OCH_3-H}	δ_{CH_3-H}
H	2.43	3.69	2.63	6.25	
α-Cl	2.04		2.20 ; 2.60	6.12	
α-Br	1.81		2.16 ; 2.59	6.12	
α-CH_3	2.38		2.67	6.22	7.90
α-CN	1.87		2.10 ; 2.47	6.15	
β-Cl		3.54	2.34 ; 2.62	6.23	
β-Br		3.29	2.34 ; 2.61	6.21	
		(3.41**)		(6.43**)	
β-CH_3		3.92	2.65	6.31	7.44
				(6.48***)	(7.83***)

* The double values are estimated from the principal two peaks of the phenyl proton resonance.

** Presumably attributable to the cis-isomer.

*** It cannot be determined whether these values belong to the cis-isomer or to methanol.

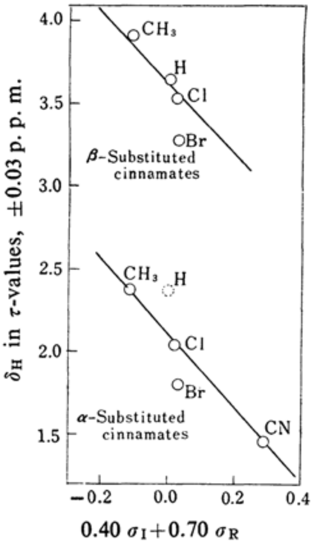

Fig. 1. The plots of the olefinic proton shifts of methyl esters of α- or β-substituted cinnamic acids vs. the substituent parameters, $0.40\,\sigma_I+0.70\,\sigma_R$.

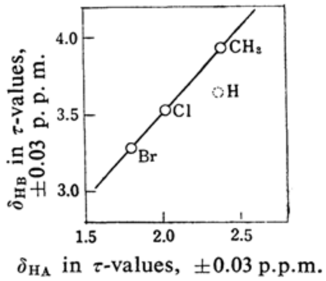

Fig. 2. The correlation of olefinic proton shifts between methyl esters of α- and β-substituted cinnamic acids.

are compared with the correlation line obtained with respect to ω-substituted styrenes, thier regularity, otherwise obscure, may become fairly clear. The introduction of a cyano group causes the proton shifts, here also, to move into a higher region of the field owing to the diamagnetic anisotropy of that group around its triple-bond axis. Reddy et al. have reported that the value of the exaggeration of the trans-proton chemical shift should amount to as much as 0.38 p. p. m. in acrylonitrile[6]. For plotting the proton shift for the cyano substituent, before being used the value is corrected by subtracting this magnitude. From an inspection of Fig. 1, it can be noticed that the plot for H_A in methyl cinnamate keeps a distance from the correlation line. The reason for this can easily be explained. In the case of methyl cinnamates with a substituent at the α-position, the substituent X, interfering with the benzene ring, gives rise to the rotation of the ring. Such a conformation would effectively alter the trends of correlation with substituent parameters originally obtained with the styrene system. Hence, the shift of H_A in methyl cinnamate itself should not be compared directly with proton shifts in other α-derivatives. The δ_{H_A} value for this compound would, then, deviate from the correlation line. This deviation is presumably reflected in Fig. 2, in which the proton chemical shifts for α- and β-substituted cinnamates are shown to correlate with each other, while for the value of hydrogen as the substituent X, the linear correlation does not hold. In β-substituted cinnamates the invariable substituent should be the phenyl group, as

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[6] G. S. Reddy, J. H. Goldstein and L. Mandell, *J. Am. Chem. Soc.*, **83**, 1300 (1961).

the proton H_B is under the influence of both the phenyl group and the variable substituent X, which are placed in the cis- and the trans-position respectively to the proton under consideration. Here the correlation occurs at a higher part of the figure than that for α-substituted cinnamates, largely because of the diminution of the long-range shielding contribution effected by the benzene ring in β-substituted cinnamates.

Summary

The proton magnetic resonance spectra with regard to methyl esters of α- or β-substituted cinnamic acids have been investigated from the viewpoint of the substituent effect. When the results are compared with the correlation obtained with ω-substituted styrenes, the trends are also explicable as being controlled by the polar nature of the substituents.

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