The Nuclear Magnetic Resonance Spectra of Olefinic Protons and the Substituent Effects. III. Trans-forms of Methyl β-Substituted Acrylates, β-Substituted Vinyl Methyl Ketones and β-Substituted Acryloyl Chlorides[*]

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It was reported in Part I that a Hammett-type relationship was applicable to the chemical shifts of olefinic protons situated at the cis-position to terminal substituents in the trans-forms of ω-substituted styrenes and in those of 1-substituted propenes ($RCH_A=CH_BX$, invariable substituent; $R=C_6H_5$, CH_3).[1] In these systems, the invariable substituent was an electron-repulsive methyl group or an aromatic ring which might constitute a conjugated system with the olefinic part. The present authors are concerned with such systems in which the invariable substituent of a series of compounds is strongly electron-attractive and conjugates with the olefinic part.

As examples of such systems, a series of trans-forms of methyl β-substituted acrylates, β-substituted vinyl methyl ketones and β-substituted acryloyl chlorides were chosen. The authors have investigated the results of the NMR absorption of these compounds from the viewpoint of a Hammett-type relationship. Moreover, the trends of the proton shifts in these compounds have been compared with those of ω-substituted styrenes and 1-substituted propenes.

Experimental

Two Varian 4300-B type spectrometers operating at 56.4 Mc. and 60 Mc. were used in obtaining the spectra. The conditions of measurement were the same as described in Part I.[1]

All the compounds examined have a trans-configuration. The acrylate derivatives are as follows: Methyl β-methylcrotonate, methyl crotonate, methyl acrylate, methyl cinnamate, methyl β-bromoacrylate, methyl β-chloroacrylate, dimethyl fumarate, methyl β-acetylacrylate and β-methoxycarbonylacryloyl chloride. The spectra of the corresponding free acids were also measured in glacial acetic acid. The methyl vinyl ketone derivatives are as follows: Methyl vinyl ketone, methyl styryl ketone and methyl acetylacrylate. As for the acryloyl chloride derivatives, crotonyl chloride, cinnamoyl chloride and β-methoxycarbonylacryloyl chloride were used. The synthesized compounds had the following properties: β-Methyl crotonic acid, m. p. 66∼67°C; its ester, b. p. 132°C; β-chloroacrylic acid, m. p. 83.5∼84°C; its ester, b. p. 22°C under 12 mmHg; β-bromoacrylic acid, m. p. 115∼116°C; its ester, b. p. 20°C under 5 mmHg; β-methoxycarbonylacryloyl chloride, b. p. 65°C under 15 mmHg. Methyl

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[*] Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[1] H. Kasiwagi and J. Niwa, This Bulletin, 36, 405 (1963).

acrylate (b. p. 80.5°C), methyl crotonate (b. p. 118∼119°C), crotonic acid (m. p. 71∼72°C), fumaric acid (m. p. 286∼287°C), methyl β-acetyl acrylate (b. p. 196.8∼197.3°C) and methyl vinyl ketone (b. p. 33∼34°C under 130 mmHg) were commercially obtained and purified.* The physical properties of the other compounds were described in Part I.

Results and Discussion

The spectra of olefinic protons of methyl β-substituted acrylates, β-substituted vinyl methyl ketones and β-substituted acryloyl chlorides are of the simple AB-type, with the exception of those of methyl crotonates, methyl acrylate and methyl vinyl ketone. Methyl crotonate gives the spectra corresponding to the ABX_3-type, while the spectra of methyl acrylate and methyl vinyl ketone are attributed to the ABC-type. In the spectra of β-methoxycarbonylacryloyl chloride, a single signal was observed for the olefinic protons. The analyses of the spectra of methyl acrylate and methyl vinyl ketone have been compared with the results obtained by Castellano and Waugh[2] and by Brügel et al.[3] respectively. The chemical shifts obtained by the analysis of the spectra are summarized in Table I.

In series of compounds here examined (RCH_A=CH_BX, R=CO_2CH_3, $COCH_3$, COCl), since the invariable substituent (R) conjugates with the olefinic part, it may be expected that the olefinic proton shifts would be governed by Hammett's substituent effect, at least qualitatively. Meanwhile, the authors have observed that a qualitative relationship exists between the shifts of protons (H_A) situated at the cis-position to substituents in mono-substituted ethylenes[4] (RCH_A=CH_BX, R=H) and Hammett's σ. The τ-values of the proton shifts are shown in the table. The authors examined Hammett's substituent effects for the proton shifts in these four systems, comparing the former systems with the latter. In this case, it must be taken into account that the magnetic anisotropy of the substituents and other magnetic effects act as disturbing factors in the investigation of polar substituent effects. As has been considered in Part I, however, such disturbing factors do not seem to be much for the shifts of H_A, with the exception of a few cases. This would imply that the chemical shifts of H_A in these compounds are governed mainly by the polar substituent effects.

Similarly, as in Part I, Fig. 1 shows the relationship between the τ-values of H_A in these compounds and Hammett's σ_p. Figure 2 also shows the relationship between the τ-values of H_A and Taft's parameter, 0.40 σ_I+ 0.70 σ_R.[5] In the figures, the plot for the H_A of styrene is corrected to 4.79 p. p. m.[1,4,6] and that of acrylonitrile, to 3.80 p. p. m.[7] In the series of β-substituted acrylates, the H_A of methyl cinnamate may also be lowered by the

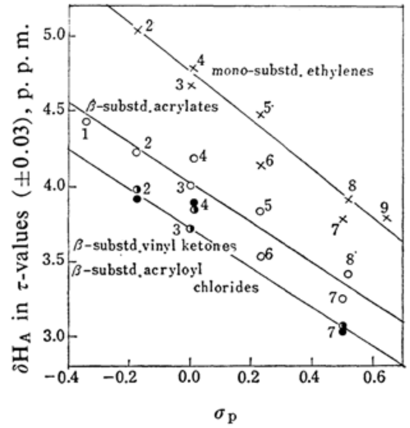

Fig. 1. The cis-proton chemical shifts of RCH_A=CH_BX, plotted vs. Hammett's σ_p. The substituents X are: 1, $(CH_3)_2$; 2, CH_3; 3, H; 4, C_6H_5; 5, Cl; 6, Br; 7, CO_2CH_3; 8, $COCH_3$; 9, CN.

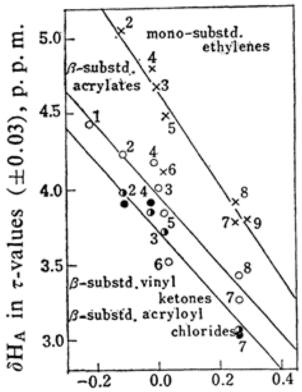

Fig. 2. The cis-proton chemical shifts of RCH_A=CH_BX, plotted vs. Taft's parameter, 0.40 σ_I+0.70 σ_R. The substituents X are: 1, $(CH_3)_2$; 2, CH_3; 3, H; 4, C_6H_5; 5, Cl; 6, Br; 7, CO_2CH_3, 8, $COCH_3$; 9, CN.

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* Products of the Tokyo Kasei Kogyo Co., Ltd., and of the Wako Pure Chemical Industries, Ltd.

[2] S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

[3] W. Brügel, Th. Ankel and F. Krückberg, *Z. Elektrochem.*, **64**, 1121 (1961).

[4] C. N. Banwell and N. Sheppard, *J. Mol. Phys.*, **3**, 351 (1960); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

[5] R. W. Taft, Jr., ibid., **79**, 1045 (1957); R. W. Taft, Jr., and I. C. Lewis, ibid., **80**, 2436 (1958).

[6] C. E. Johnson, Jr., and E. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

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

TABLE I. PROTON CHEMICAL SHIFTS OF ACRYLIC ACID, METHYL ACRYLATE, METHYL VINYL KETONE, ACRYLOYL CHLORIDE, ETHYLENE AND THEIR DERIVATIVES, $RCH_A{=}CH_BX$ ($R: CO_2CH_3$, $COCH_3$, $COCl$, H)

Chemical shifts in τ-values in p. p. m., ± 0.03 p. p. m.

a) Trans-forms of β-substituted acrylic acid and their methyl esters

Substituent	$R: CO_2H$[a]			$R: CO_2CH_3$		
	δH_A	δH_B	δH_C	δH_A	δH_B	δCO_2CH_2-H
$(CH_3)_2$	4.31			4.44		6.40
CH_3	4.20	2.93		4.24	3.13	6.36
H	4.05	3.71	4.31	4.01	3.78	6.32
C_6H_5	3.54	2.21		3.69	2.43	6.31
Br	3.47	2.23		3.52	2.43	6.27
Cl	3.72	2.48		3.84	2.69	6.29
CO_2H	3.12	3.12				
CO_2CH_3				3.26[b]	3.26[b]	6.25[b]
$COCH_3$				3.43	3.06	6.22
COCl				3.04	3.04	6.15

b) Trans-forms of β-substituted vinyl methyl ketone and β-substituted acryloyl chloride

Substituent	$R: COCH_3$		$R: COCl$	
	δH_A	δH_B	δH_A	δH_B
CH_3	3.99	3.24	3.91	2.81
H	3.72	3.91		
C_6H_5	3.35	2.55	3.41	2.20
CO_2CH_3	3.06	3.43	3.04	3.04

c) Mono-substituted ethylenes

Substituent	$R: H$	
	δH_A	δH_B
CH_3[c]	5.04	4.27
H[d]	4.67	4.67
C_6H_5[d]	4.29	3.31
	4.36[e]	3.35[e]
Br[d]	4.12	3.51
Cl[d]	4.48	3.70
CO_2CH_3[e]	3.78	4.01
$COCH_3$[e]	3.91	3.72
CN[d]	4.09	4.47

a) The values were obtained from measurement with the glacial acetic solution owing to the low solubility of the compounds in carbon tetrachloride.
b) Measurement was performed with the saturated solution in carbon tetrachloride.
c) Adopted from tha data measured in the same concentration by Bothner-By et al. A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).
d) Cited from the data measured in the same concentration by Banwell et al. C. N. Banwell and N. Sheppard, *J. Mol. Phys.*, **3**, 351 (1960).
e) Measured by the authors.

long-range shielding effect of the benzene ring, which is situated at the cis-position to H_A. If the magnitude of the lowering effect is estimated as in styrene, the τ-value of H_A may be corrected to 4.19 p. p. m. This correction may, however, be overestimated, because the methoxycarbonyl group in this compound is strongly electron-attractive, which would diminish the effect of the benzene ring current. As for the Cl, Br, CO_2CH_3 and $COCH_3$ groups, the consideration made in Part I would hold in the present systems. In Figs. 1 and 2 a rough correlation may be observed, but it seems to be somewhat disintegrated compared with ω-substituted styrenes and 1-substituted propenes. Moreover, it is also observed that the plots for the corresponding substituents in the ethylene derivatives and in the β-substituted acrylates deviate similarly from the correlation line. Therefore, the same kind of correlation may be expected among the H_A-shifts themselves in both systems. In Fig. 3 a fairly clear

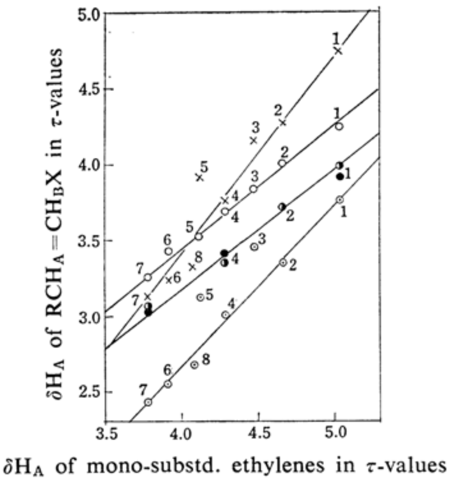

Fig. 3. The correlation among δH_A of methyl β-substd. acrylates (○), β-substd. vinyl methyl ketones (◑), β-substd. acryloyl chlorides (●), ω-substd. styrenes (⊙) and 1-substd. propenes (×). The substituents X are; 1, CH_3; 2, H; 3, Cl; 4, C_6H_5; 5, Br, 6, $COCH_3$, 7, CO_2CH_3, 8, CN.

correlation among them may be observed. This suggests that, in these systems, the modes of the transmission of substituent effects are essentially similar. Figure 3 also shows the relation between the H_A-shifts of ω-substituted styrenes (and 1-substituted propenes) and those of the ethylene derivatives. In this case, however, the correlation is considerably disintegrated. Especially, the plots for halogen substituents deviate largely from the correlation line. (With regard to the origin of the anomalous behavior of the H_A-shifts caused by halogen atoms, further invetigation is necessary.) On the other hand, it was reported in Part I that a fairly clear correlation existed between the H_A-shifts of ω-substituted styrenes (and 1-substituted propenes) and the ortho-proton shifts of mono-substituted benzenes. From what has been stated above with regard to the modes of the transmission of substituent effects, these six olefinic systems may be classified into two types — one is the system rather resembling the benzene derivatives, and the other, the ethylene derivatives. This may correspond to the difference between the natures of the conjugated systems, of which the former has the electron-repulsive invariable substituents and the latter, the electron-attractive. Also, the slope of each correlation line decreases, on the whole, in the order of the σ-value of the invariable substituent, namely, $CH_3>H\simeq C_6H_5>CO_2CH_3\simeq COCH_3\simeq COCl$. This probably illustrates how the overall trends of the H_A-shifts in each system are uniformly governed by the polar nature of the invariable substituent.

As for the shielding of the H_B protons at the β-position, their behavior can not be discussed concurrently with those of the H_A-shifts from the viewpoint of Hammett's substituent effect. Moreover, there is no clear correlation between the H_B-shifts of β-substituted acrylates and those of the ethylene derivatives. Similarly to what has been reported in Part I, however, the order of the H_B-shifts of these compounds may be qualitatively determined by both the electronegativity of the first atom and the magnetic anisotropy of the substituent group.

As is shown in Fig. 4, in trans-forms of methyl β-substituted acrylates the chemical shifts of the methyl proton of the methoxycarbonyl group are determined by Hammett's σ_p, although their spread does not exceed about 0.2 p. p. m. in any of the derivatives. This relation corresponds with the fact that the pK_a-values of the trans-forms of β-substituted acrylic acids are represented by the usual Hammett equation.[8]

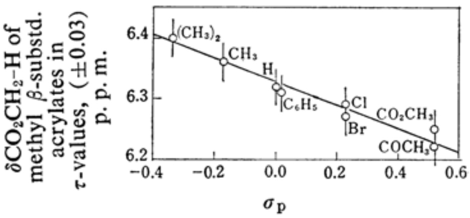

Fig. 5. The methyl proton shifts of methoxycarbonyl groups of methyl β-substituted acrylates, plotted vs. Hammett's substituent constants, σ_p.

Summary

In the NMR absorption of the trans-forms of β-substituted acrylates, β-substituted vinyl methyl ketones and β-substituted acryloyl chlorides, the chemical shifts of protons situated at the cis-position to the substituents have been roughly determined by Hammett's σ_p and Taft's parameter, 0.40 σ_I+0.70 σ_R. From a comparison of the H_A-shifts of the six olefinic systems ($RCH_A=CH_BX$, R=CH_3, C_6H_5, H, CO_2CH_3, $COCH_3$, COCl), these systems have been classified into two types—one, systems resembling the benzene derivatives, and the other, resembling the ethylene derivatives. Nevertheless, it has also been observed that the slope of each correlation line, on the whole, decreased in the order of the σ-value of the invariable substituent. The methyl proton shifts of β-substituted *trans*-acrylates, too,

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[8] M. Charton and H. Meislich, ibid., **80**, 5941 (1958).

depend upon Hammett's σ_p. The shifts of the proton (H_B) at the β-positon can not be discussed from the viewpoint of Hammett's substituent effect. However, they relate qualitatively with the electronegativity of the first atom of the substituent group.

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