Substitution and Elimination Reactions in Chloro Olefins. II.¹ Reactions of Methyl β -Chlorocinnamates with Methoxide and Ethoxide Ions

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The rates of the base-catalyzed eliminations of a series of trans para-substituted methyl β -chlorocinnamates have been determined in methanol and ethanol using methoxide and ethoxide ions as bases. Elimination products are obtained exclusively, and the rates of the reactions show a Hammett correlation with ρ values of 1.7 and 2.0 for methoxide and ethoxide ions, respectively, which suggests a certain carbanionic character of the transition state. An E2 mechanism, presumably with an E1cB-like transition state, has been suggested.

Simple vinyl halides are known for their inertness toward bimolecular nucleophilic substitution and base-catalyzed dehydrohalogenation compared to alkyl halides. The reactivity of vinyl halides toward nucleophiles can, however, be greatly enhanced by the presence of strongly electron-attracting groups attached directly to the alkene double bond. The activating groups not only enhance β eliminations but also substitutions. The competition between substitution and elimination is, indeed, one of the most intriguing features of the reactions of vinylic compounds with nucleophiles. This competition is generally controlled by the nature of the nucleophile, by the leaving group, and by the configuration of the substrate. In most cases vinylic substrates were found to react with a nucleophile either by direct substitution, which may merge in an addition-elimination mechanism, or by elimination which may or may not be followed by addition of solvent to the initially formed acetylene. The mechanisms of the reactions of vinyl halides with nucleophiles have attracted considerable interest in recent years and comprehensive reviews on this subject are available.^{2–6}

Whereas aromatic substitutions are satisfactorily correlated⁷ by the Hammett equation, the rates of vinylic substitutions do not always follow the sequence predicted by either σ or σ^- . On the other hand, when the effects of substituents not directly bonded to the β -ethylenic carbon are considered, good Hammett correlations are observed with positive values of ρ .⁸ A Hammett correlation has been also reported for elimination reactions of several saturated alkyl halides with phenyl substitution on the β carbon and in particular in the 2-phenylethyl system.⁹

To our knowledge no such Hammett correlation has been reported for the rates of vinylic eliminations. From our interest in the kinetics and mechanisms of alcoholysis of chloro olefins, the present work is designed to study the reactions of *trans*-methyl β -chlorocinnamates (Ia-d) with



methoxide and ethoxide ions, and the effect of substituents on the phenyl ring on a carbanion developed at the α carbon.

Results and Discussion

A convenient route for the synthesis of *trans*- β -chlorovinyl acids by the reaction of phosphorus pentachloride with the appropriate β -keto esters was recently reported by us.¹⁰ The isolation of only the trans isomer from this reac-

Table I	
$Ir,^{a} Uv,^{b}$ and NMR^{c} Spectra	for Ia-d

R	C=0, cm ⁻¹	C = C, cm^{-1}	λ _{max} , nm	E	Trans OCH ₃	Vinyl proton
Н	1725	1620	272	16, 240	3.92	6.73
p - CH ₃	1720	1615	282	17,990	3.70	6.45
$p - NO_2$	1730	1625	290	17,600	3.97	7.22
p -C1	1730	1620	277	19, 320	3.88	7.13

 a Nujol. b Absolute ethanol. c For solvent see Experimental Section; δ values are used for the chemical shifts.

tion can be visualized to take place by a mechanism similar to that suggested for the reactions of ketones with phosphorus pentachloride.¹¹ The assignment of the trans configuration to methyl β -chlorocinnamates (I) came from NMR and uv measurements for both the acids and esters. The data are compared with that reported for cis- and trans-methyl α -cyanocinnamates¹² and methyl α -chlorocinnamates.^{13a} The chemical shifts of the vinylic protons and the carbomethoxy groups appear constantly for the trans isomer at lower field than that of the cis, and are quite identical with those of the compounds (Ia-d). Furthermore, the calculated chemical shifts,^{13b} applying the NMR rules of additivity,^{14,15} of trans- β -chlorocinnamic acid and its methyl ester are found to be in excellent agreement with the observed values. A summary of the spectral properties of Ia-d is collected in Table I.

The rates of the reactions of compounds Ia-d with methoxide and ethoxide ions in methanol and ethanol, respectively, were measured at various temperatures. They always follow a second-order kinetic equation. As expected, the rates with ethoxide ion are faster than with methoxide ion (ca. 13 times for Ia and 30 for Ic) because of its wellknown higher nucleophilic power and higher basicity.¹⁶ The rate coefficients together with the derived Arrhenius parameters are reported in Table II.

The reactions of compounds Ia-d with either methoxide or ethoxide ions are similar to those observed in other nucleophilic reactions of activated ethylenic halides.^{17,18} The configuration of the substrates determines the mechanism of the reactions. Consequently, all compounds react by elimination because of the favorable steric arrangement of the hydrogen trans to the halogen. The small positive entropy of activation is that expected for β anti elimination reactions. Under the kinetic conditions the formed acetylenic products do not undergo further addition as observed with p,p'-dinitrotolan obtained from the reactions of *cis*and *trans*-1-chloro-1,2-di(*p*-nitrophenyl)ethylene with methoxide and ethoxide ions.¹

Figure 1 shows a Hammett plot for the reactions of the compounds Ia-d with methoxide and ethoxide ions with ρ values of 1.7 and 2.0, respectively. The ρ value in a Ham-



Figure 1. A plot of log k_2 for base-catalyzed elimination reaction against Hammett σ constants.

mett correlation has been taken as a measure of the carbanion character developed in the transition state of an elimination reaction.¹⁹ The ρ values obtained in this study are comparable to those reported for the base-catalyzed eliminations of various saturated and vinylic systems where transition states of varying degrees of carbanionic character have been postulated.^{8,19,20} As shown in Figure 1, the ρ value is larger with the stronger base ethoxide ion, which indicates that the negative charge is greater in the transition state with stronger base.^{20a}

In conclusion, an E2 mechanism, presumably going through an E1cB-like transition state, is suggested for the elimination reactions studied as shown in the following scheme.



Experimental Section

Infrared and ultraviolet spectra were taken on Unicam SP 200 and SP 800 spectrometers, respectively. The NMR spectra²⁹ were measured at 60 MHz using tetramethylsilane as internal standard. Microanalyses were done at Cairo University microanalytical laboratory; melting points and boiling points are uncorrected.

Ethyl benzoylacetate was prepared in 70% yield as described earlier,²¹ colorless liquid, bp 130-140° (2.5-3.5 mm).

 β -Chlorocinnamic Acid. Ethyl benzoylacetate (14 g, 0.073 mol) was added dropwise (1 hr) to a cold suspension of phosphorus pen-

Table II	
Rate Coefficients and Activation Paramet	ters for
Reactions of trans-Ia-d $(1.0-0.25 \times 10^{-2} M)$	1) with
Methoxide and Ethoxide Ions $(5.0-0.25 \times 1)$	$(0^{-2}M)$
in Methanol and Ethanol	

$k_2 \times 10^3$, mol ⁻¹ l. sec ⁻¹							$E_{a},$ kcal Δ	∆s [‡] ,¢	
Comp	d Base	15 ^d	20	25	30	35	40	mol ^{-1b}	eu
Ia	MeO-				1.8	3.3	5.9	21.8	1
	EtO ⁻				23.8	42.2	81.2	21.7	+4
Ib	MeO ⁻				1.1	2.1	4.0	24.3	+6
	EtO ⁻	•			14.5	25.6	42.2	20.3	-2
Ic	MeO ⁻			23.4	41.0	69.2		19.9	-1
	EtO ⁻	215	356	661			3677°	20.8	+8
Id	MeO ⁻				5.6	9.7	17.6	21.5	+1
	EtO⁻			51.9	101	176	300ª	20.9	+4

^a Extrapolated values. ^b Values from plots of log k_2 vs. 1/T. ^c $\Delta S^{\ddagger}/4.576 = \log k_2 - 10.753 - \log T + E_a/4.576T$ at 40°C. Rate constants are calculated by the standard deviation method and errors estimated to be within 1-6%. ^d Temp, °C.

tachloride (43.5 g, 0.21 mol) in dry benzene (50 ml) with stirring. The reaction mixture was refluxed for 0.5 hr and then thoroughly decomposed with ice-cold water. The benzene layer was separated and the aqueous layer was extracted twice with benzene. The combined benzene extract was washed with water and extracted with a saturated solution of sodium carbonate. Evaporation of benzene gave a sticky, oily product proved to be composed mainly of unreacted material, phosphorus pentachloride, besides other materials under investigation. Acidification of the cold carbonate extract gave a solid (5 g, 38%), mp 139-145°. This mixture of cis and trans acids was treated with a 30% ammonia solution and then a saturated solution of barium chloride. The barium salt of the trans isomer separated immediately and was collected and acidified to give a solid (4.2 g), crystallized from carbon tetrachloride as colorless needles, mp 145-146° (lit.²² mp 142°). Anal. Calcd for C₉H₇ClO₂: C, 59.17; H, 3.84; Cl, 19.45. Found: C, 59.16; H, 3.81; Cl, 19.46. Ir strong bands at 1700, 1610, 780, and 725 cm⁻¹; uv λ 218 nm (ϵ 9499), λ_{max} 262 nm (ϵ 13,170); NMR (CDCl₃) multiplet centered at δ 7.33 (aromatic protons, 5 H) and a singlet at δ 6.42 (=-CH).

trans-Methyl β -Chlorocinnamate (Ia). trans- β -chlorocinnamic acid was converted to Ia by reaction with thionyl chloride and addition of absolute methyl alcohol to the formed acid chloride. The ester was purified by repeated distillation in vacuo to give a colorless liquid, bp 128-130° (2.5 mm), which solidified on cooling, mp 29°. Anal. Calcd for C₁₀H₉ClO₂: Cl, 18.06. Found: Cl, 18.30. Ir strong bands at 2990, 1725, 1620, 770, and 690 cm⁻¹; uv λ 218 nm (ϵ 9761), λ_{max} 272 nm (ϵ 16,240); NMR (CDCl₃) multiplet centered at δ 7.72 (aromatic protons, 5 H), a singlet at δ 6.73 (=CH), and a singlet at δ 3.92 (-OCH₃).

Ethyl *p*-methylbenzoylacetate was prepared by the condensation of ethyl acetoacetate with *p*-methylbenzoyl chloride following the procedure of ethyl benzoylacetate, bp $160-170^{\circ}$ (2-4 mm), ir strong bands at 3075, 1750, 1690, 1620, and 815 cm⁻¹.

trans- β -Chloro-*p*-methylcinnamic Acid. Ethyl *p*-methylbenzoylacetate was converted to the acid by refluxing with phosphorus pentachloride in dry benzene for 7 hr. Work-up as before gave a solid separated from benzene in colorless plates (34% yield), mp 178°. Anal. Calcd for C₁₀H₉ClO₂: C, 61.07; H, 4.58; Cl, 18.06. Found: C, 61.30; H, 4.60; Cl, 18.00. Ir strong bands at 1695, 1600, 825, and 715 cm⁻¹; uv λ 216 nm (ϵ 13,514), λ_{max} 265 nm (ϵ 21,007); NMR (Me₂SO-d₆) quartet centered at δ 7.58 (aromatic protons, 4 H), singlet at δ 6.73 (==CH), and a singlet at δ 2.38 (*p*-CH₃).

trans-Methyl β -Chloro-*p*-methylcinnamate (Ib). The above acid was converted to Ib following the usual procedure, separated from methanol in colorless plates, mp 71-72°. Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.23; Cl, 16.86. Found: C, 63.10; H, 5.4; Cl, 17.10. Ir strong bands at 1720, 1615, 820, and 710 cm⁻¹; uv λ 227 nm (ϵ 8322), λ_{max} 282 nm (ϵ 17,990); NMR (CDCl₃) quartet centered at δ 7.28 (aromatic protons, 4 H), singlet at δ 6.45 (==CH), singlet at δ 3.70 (-OCH₃), and singlet at δ 2.35 (*p*-CH₃).

Ethyl p-Nitrobenzoylacetate. The procedure of Bülow and Hailer²³ for the synthesis of ethyl p-nitrobenzoylacetoacetate was modified as follows. Ethyl acetoacetate was treated successively with small equal amounts of sodium ethoxide in absolute ethanol and p-nitrobenzoyl chloride in ether while cooling and stirring.

When addition was completed, the separated solid was filtered, dried, and acidified to give ethyl p-nitrobenzoylacetoacetate (84% yield), mp 54°. This ester (30 g) was hydrolyzed by treatment with an alcoholic ammonia solution (450 ml of 10%) while shaking gently from time to time at 45° for 30 min. The solution was cooled and the separated solid filtered and dried. This solid was suspended in water and acidified and the separated solid filtered and crystallized in yellow prisms from alcohol (15 g, 59%), mp 73° (lit.²³ mp 71°).

trans-\$-Chloro-p-nitrocinnamic Acid. Ethyl p-nitrobenzoylacetate (3 g, 0.013 mol) was refluxed with phosphorus pentachloride (9 g) in dry benzene for 40 hr. Decomposition and work-up gave a solid (1.4 g, 47%), crystallized from benzene, mp 196-198°. Experiments carried out with larger amounts gave a low yield. Anal. Calcd for C9H6NClO4: C, 47.46; H, 2.64; N, 6.15; Cl, 15.60. Found: C, 47.22; H, 2.78; N, 6.29; Cl, 15.50. Ir strong bands at 1705, 1615, 1355, 760, and 720 cm $^{-1}$; uv λ 217 nm (ϵ 10, 764), λ_{max} 304 nm (ϵ 12,384); NMR (Me₂SO-d₆) quartet centered at δ 8.33 (aromatic protons, 4 H) and singlet at δ 7.23 (=CH).

trans-Methyl β -Chloro-p-nitrocinnamate (Ic). The above acid was converted to Ic in the usual manner, crystallized from methanol-benzene mixture in pale yellow needles, mp 157-158°. Anal. Calcd for C10H8ClO4: C, 49.69; H, 3.31; N, 5.79; Cl, 14.69. Found: C, 49.30; H, 3.50; N, 6.00; Cl, 14.37. Ir strong bands at 1730, 1625, 1520, 1355, 850, and 700 cm⁻¹; uv λ 215 nm (ϵ 15,600), λ_{max} 290 nm (ϵ 17,600); NMR (Me₂SO-d₈) quartet centered at δ 8.37 (aromatic protons, 4 H), singlet at δ 7.22 (=CH), and singlet at δ 3.97 (-OCH₃).

Ethyl p-chlorobenzoylacetate was prepared (88% yield) by the condensation of ethyl acetoacetate with p-chlorobenzoyl chloride following the method of ethyl benzoylacetate, as a pale yellow liquid: bp 170-180° (4.5-5.5 mm); ir strong bands at 3025, 1745, 1720, 1600, 860, 780, and 745 cm⁻¹

trans-\$-Chloro-p-chlorocinnamic Acid. Ethyl p-chlorobenzoylacetate was refluxed with phosphrous pentachloride for 20 hr in dry benzene. Work-up gave a solid (30% yield), separated from benzene in colorless needles, mp 178-180°. Anal. Calcd for C₉H₆Cl₂O₂: C, 49.76; H, 2.77; Cl, 32.72. Found: C, 49.50; H, 2.89; Cl, 32.80. Ir strong bands at 1680, 1605, 840, and 715 cm⁻¹; uv λ 225 nm (ϵ 6595), λ_{max} 275 nm (ϵ 16,390); NMR (Me₂SO- d_6) quartet centered at δ 7.93 (aromatic protons, 4 H) and singlet at δ 7.07 =CH)

trans-Methyl β -chloro-p-chlorocinnamate (Id) was prepared by the esterification of β -chloro-p-chlorocinnamic acid in the usual manner, separated from methanol as colorless prisms, mp 43-44°. Anal. Calcd for C10H8Cl2O2: C, 51.95; H, 3.46; Cl, 30.74. Found: C, 52.30; H, 3.50; Cl, 30.40. Ir strong bands at 1730, 1620, 835, and 740 cm⁻¹; uv λ 226 nm (ϵ 7663), λ_{max} 277 nm (ϵ 19,320); NMR (Me₂SO- d_6) quartet centered at δ 7.93 (aromatic protons, 4 H), singlet at δ 7.13 (=CH), and singlet at δ 3.88 (-OCH₃).

Reaction Products. The following procedure was adopted for all compounds (Ia-d). The compound (0.5 g) was dissolved in absolute methanol or ethanol (50 ml) and the equivalent amount of metallic sodium (ten times the molarity of the compound) was added. The solution was thermostated at 40° for 10 half-lives in each case. The reaction mixture was diluted with a large volume of water, acidified with dilute sulfuric acid, and extracted with ether. The ethereal layer was extracted twice with a saturated solution of sodium carbonate. The ether extract was washed, dried, and evaporated to give no materials in all cases. Acidification of the sodium carbonate extract gave the product (yields more than 80%). All the products were proved to be the corresponding acetylenic compounds (IIa-d), characterized by the presence of the sharp acetylenic band at 2225 cm⁻¹ in the infrared spectra,²⁴ and by melting points and mixture melting points with authentic samples in some cases. The products obtained from the reactions of compounds

Ia-d with base are respectively phenylpropiolic acid (IIa, needles from carbon tetrachloride), mp and mmp 139° (lit.25 mp 137°); pmethylphenylpropiolic acid (IIb, needles from water), mp 151-152° (lit.²⁶ mp 151°); p-nitrophenylpropiolic acid (IIc, yellow needles from water), mp and mmp 180-181° (lit.27 mp 180°); p-chlorophenylpropiolic acid (IId, needles from water), mp 186° (sealed tube) (lit.²⁸ mp 185°).

Kinetic Measurements. The rates of reaction were determined by following the rates of liberation of chloride ions by the electrometric method as previously reported.¹ Most reactions were followed to 70-80% completion, and in all cases the infinity titer was found to agree with the calculated. The results are quite reproducible and the reactions showed simple second-order kinetics. Rate coefficients and activation parameters were calculated in the usual way and are collected in Table II.

Registry No.-Ia, 56377-29-8; Ib, 56377-28-7; Ic, 56377-30-1; Id. 56377-31-2; B-chlorocinnamic acid, 18819-66-4; ethyl benzoylacetate, 94-02-0; phosphorus pentachloride, 7647-19-0; ethyl pmethylbenzoylacetate, 27835-00-3; trans-β-chloro-p-methylcinnamic acid, 56377-32-3; ethyl p-nitrobenzoylacetate, 838-57-3; ethyl acetoacetate, 141-97-9; p-nitrobenzoyl chloride, 122-04-3; trans- β -chloro-p-nitrocinnamic acid, 56377-33-4; ethyl p-chlorobenzoylacetate, 2881-63-2; p-chlorobenzoyl chloride, 122-01-0; trans-βchloro-p-chlorocinnamic acid, 56377-34-5.

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