

A CONTRIBUTION TO MECHANISM OF ADDITION
OF HYDROGEN BROMIDE TO THE α,β -UNSATURATED SYSTEM
OF 3-PHENYL-2-PROPENOIC ACID*

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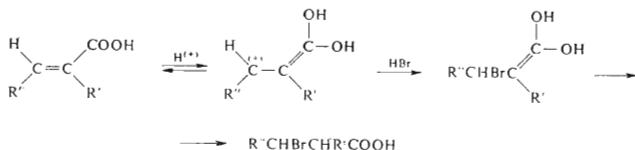
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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Rate of addition of hydrogen bromide to *meta*- and *para*-substituted 3-phenyl-2-propenoic acids I was followed by polarography and UV spectroscopy. Rate of protonation either is the overall rate determining step or is at least comparable with the rate of the subsequent nucleophile attack.

Addition reactions to unsaturated systems in which the carbon-carbon bond is conjugated with a carbonyl or other unsaturated group (α,β -unsaturated acids or ketones) can in principle take place in the 1,2 or 1,4 positions^{1,2}. For an addition of a hydrogen halide to (*E*)-2-ethyl-2-butenic acid a *trans*-addition mechanism is assumed³ and the observed stereospecificity speaks for the 1,2-addition to the carbon-carbon double bond. Other authors⁴ assume a 1,4-addition of hydrogen halides to α,β -unsaturated ketones on the basis of the non-stereospecific reaction course; however, they do not consider the possible isomerization of *trans*-products under the reaction conditions. Similarly, addition of hydrogen chloride to α,β -unsaturated cyclic carboxylic acids can give either *cis*- or *trans*-addition products⁵⁻⁷, depending on reaction conditions. From the kinetic studies and product analysis a multistep mechanism



SCHEME 1

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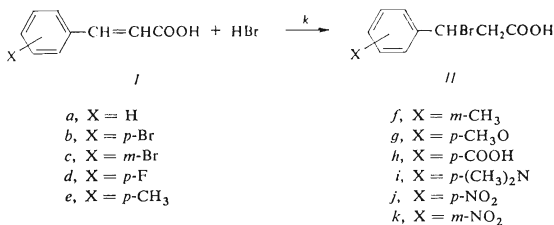
is assumed in which formation of the C—Br bond is the rate determining step. The bromide ion adds to the enol, formed by protonation of the acid (Scheme 1). Also the addition of hydrogen chloride to substituted acrylic acids has a nucleophilic character⁸.

For mechanistic studies of hydrogen halide additions to substituted 3-phenyl-2-propenoic acids hydrogen bromide solution in acetic acid seemed to be the reagent of choice. The unequivocal course of addition of hydrogen bromide to 3-phenyl-2-propenoic acid, leading to 3-bromo-3-phenylpropanoic acid, has been verified for a number of solvents⁹. Experimentally, the reaction is easier and hydrogen bromide is more stable than hydrogen iodide; on the other hand, reactions with hydrogen chloride would be too slow. The reaction of hydrogen bromide with α,β -unsaturated cyclic acids is first-order in the acid⁷ whereas for hydrogen bromide Vaughan and coworkers⁶ assume relationship of a higher order because the addition rate is significantly influenced by the hydrogen bromide concentration. Reaction of hydrogen bromide with diethyl butenedioate is first order both in the acid and hydrogen bromide¹⁰. In benzene, for which mechanism involving a π -complex of hydrogen bromide with benzene nucleus is suggested, the reaction is of nucleophilic character. In acetic acid the nucleophilic mechanism is not very probable, although acetic acid and hydrogen bromide form an oxonium complex, increasing thus the nucleophilic character of the bromine atom in hydrogen bromide¹¹. The assumed electrophilic course of hydrogen bromide addition in acetic acid¹⁰ seems to be confirmed by the substantial drop of reaction rate after addition of acetic anhydride to the reaction mixture.

For determination of the overall order of hydrogen bromide addition to the unsaturated system in 3-phenyl-2-propenoic acid we have chosen ethyl 3-phenyl-2-propenoate which had suitable reaction rate and solubility. In acetic acid, this reaction obeys the second order kinetics up to 40% conversion. In spite of some doubts about the role of acetic anhydride only as a medium suppressing the electrophilic attack of hydrogen bromide¹², we verified the effect of its addition on the reaction rate. Under otherwise identical conditions, in a 1 : 1 or 1 : 2 mixture of acetic anhydride-acetic acid the addition of hydrogen bromide is at least 25 times slower than in acetic acid alone.

The problem whether the rate determining step is a nucleophilic or electrophilic attack of the unsaturated system by hydrogen bromide could be solved by comparing the reactivity of the used hydrogen bromide solution with styrene derivatives, substituted in the β -position with second class substituents. The reaction course was compared with the addition of molecular chlorine to the same compounds under conditions of electrophilic reaction (an addition of sodium acetate eliminates the electrophilic course) and nucleophilic reaction (upon addition of mineral acid the carbonyl oxygen is protonated)^{13,14}. Rates of hydrogen bromide addition, together with the published rates of addition of chlorine, are summarized in Table I.

Mechanism of addition to the α,β -unsaturated system of 3-phenyl-2-propenoic acid might be elucidated by a kinetic study of analogues, substituted in the aromatic nucleus¹⁴⁻¹⁸. We prepared therefore a series of 3-phenyl-2-propenoic acids, substituted in the *para*- and *meta*-positions with substituents of the I. and II. class. Their reaction with hydrogen bromide was followed polarographically and also, directly in the reaction mixture, UV-spectrophotometrically (Scheme 2).



SCHEME 2

Since neither in acidic nor in alkaline medium 3-phenyl-2-propenoic acid and their ring-substituted derivatives afford well-developed polarographic waves^{19,20} the method cannot be used in the presence of addition products in the reaction mixture. Therefore the unreacted 3-phenyl-2-propenoic acid was first isolated and then polarographed in lithium hydroxide solution in the presence of calcium ions. However, several extractions of the acid from one phase to another decreased substantially the accuracy of the determination and the direct UV-measurement was taken as more reliable for the kinetic studies. The polarographic results rather confirmed that the decrease of the ¹L_b band of the acid I corresponded to the amount of the irreversibly reacted acid.

TABLE I

Relative rates of addition of hydrogen bromide and chlorine in acetic acid under conditions of Ad_E and Ad_N reactions. (Taken as second-order reactions)

Unsaturated compound	HBr	Cl ₂ , Ad _E ^a	Cl ₂ , Ad _N ^b
C ₆ H ₅ —CH=CH—COOC ₂ H ₅	1	10	0.013
C ₆ H ₅ —CH=CH—CHO	45	1.8	27
C ₆ H ₅ —CH=CH—NO ₂	8 700	0.020	—

^a In the presence of CH₃COONa, ref.¹³; ^b in the presence of H₂SO₄, ref.¹⁴.

The hydrogen bromide addition was followed under conditions of reaction of the first order in 3-phenyl-2-propenoic acid (hydrogen bromide concentration being higher by six orders of magnitude). The rate constants for the addition according to Scheme 2, followed UV-spectrophotometrically and polarographically, are summarized in Tables II and III.

All the rate constants were calculated according to equation (1) from the linear region of the pseudomonomolecular reaction up to 30% conversion of 3-phenyl-2-propenoic acid

$$kt = \ln(a/x), \quad (1)$$

TABLE II

Rate constants, k (s^{-1}), for addition of hydrogen bromide to substituted 3-phenyl-2-propenoic acids *I* in acetic acid, followed by UV spectroscopy at various temperatures (4.26M-HBr, $7 \cdot 10^{-6}M$ -I)

Acid	3.8°C	16.5°C	18.2°C	25°C	33.4°C	35°C
<i>Ia</i>	$3.38 \cdot 10^{-6}$ $3.46 \cdot 10^{-6}$	$1.14 \cdot 10^{-5}$ $1.25 \cdot 10^{-5}$	$1.08 \cdot 10^{-5}$	$2.78 \cdot 10^{-5}$ $2.60 \cdot 10^{-5}$ $2.64 \cdot 10^{-5}$	$5.82 \cdot 10^{-5}$	$5.92 \cdot 10^{-5}$ $6.15 \cdot 10^{-5}$
<i>Ib</i>	$2.48 \cdot 10^{-6}$ $2.19 \cdot 10^{-6}$	$6.34 \cdot 10^{-6}$ $7.02 \cdot 10^{-6}$	—	$2.3 \cdot 10^{-5}$ $2.38 \cdot 10^{-5}$ $2.26 \cdot 10^{-5}$	$3.55 \cdot 10^{-5}$	$4.72 \cdot 10^{-3}$
<i>Ic</i>	$1.7 \cdot 10^{-6}$ $1.82 \cdot 10^{-6}$	$9.5 \cdot 10^{-6}$	$7.58 \cdot 10^{-6}$ $7.40 \cdot 10^{-6}$	$1.78 \cdot 10^{-5}$ $1.69 \cdot 10^{-5}$	$2.86 \cdot 10^{-5}$ $2.7 \cdot 10^{-5}$	$4.78 \cdot 10^{-5}$
<i>Id</i>	$2.45 \cdot 10^{-6}$	—	$1.28 \cdot 10^{-5}$ $1.02 \cdot 10^{-5}$	$2.76 \cdot 10^{-5}$ $2.74 \cdot 10^{-5}$	—	$6.06 \cdot 10^{-5}$
<i>Ie</i>	$7.5 \cdot 10^{-5}$	$1.59 \cdot 10^{-4}$ $1.69 \cdot 10^{-4}$	—	$4.23 \cdot 10^{-4}$ $3.89 \cdot 10^{-4}$	—	$9.02 \cdot 10^{-4}$
<i>If</i>	—	—	—	$3.82 \cdot 10^{-5}$ $3.51 \cdot 10^{-5}$	—	—
<i>Ig</i>	—	—	—	$2 \cdot 10^{-2}$	—	—
<i>Ih</i>	—	—	—	$2.69 \cdot 10^{-5}$ $2.56 \cdot 10^{-5}$	—	—
<i>Ii</i>	—	—	—	$3.06 \cdot 10^{-5}$ $3.02 \cdot 10^{-5}$	—	—
<i>Ij</i>	—	—	—	$1.99 \cdot 10^{-5}$ $1.88 \cdot 10^{-5}$	—	—
<i>Ik</i>	—	—	—	$2.01 \cdot 10^{-5}$ $1.94 \cdot 10^{-5}$	—	—

where a is the initial concentration of the substituted acid I and x its concentration at the time t .

From the plot of rate constant against $1/T$ for the acids $Ia-Ie$ (Fig. 1, 2) the slope was determined graphically and the activation energy E was obtained using the equation $\ln k = \ln A - E/RT$. Table IV shows the activation energies obtained from Fig. 1 and 2, together with the energy values obtained by the least squares method directly from the experimental data in Tables II and III.

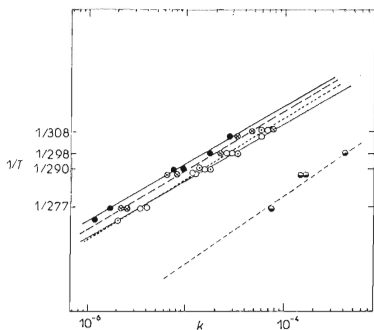


FIG. 1

Plot of $\log k$ against $1/T$ for addition of hydrogen bromide to substituted 3-phenyl-2-propenoic acids (followed by UV spectroscopy); ● —-Br, ⊙ p -Br, ⊙ p -F, ○ H, ⊙ p -CH₃

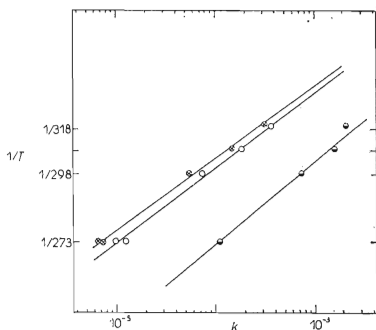


FIG. 2

Plot of $\log k$ against $1/T$ for addition of hydrogen bromide to substituted 3-phenyl-2-propenoic acids (followed polarographically); ⊙ p -Br, ○ H, ⊙ p -CH₃

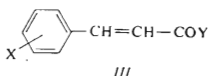
The rate constants for the addition to substituted 3-phenyl-2-propenoic acids or other compounds containing a double bond conjugated with phenyl have been correlated relatively successfully with the Hammett σ or Brown σ^+ constants. Thus, e.g. for the electrophilic addition of chlorine to 3-phenyl-2-propenoic acids¹⁵ $\rho = -3.9$, for methoxymercuration of 3-phenyl-2-propenoic acids²¹ $\rho = -1.57$, for reaction of 1,4-diphenyl-3-buten-1-one with HCl (rel.¹⁴) $\rho^+ = -3$ to -5 and for addition of bromine to 1-phenylethylene²² $\rho^+ = -4.2$, the correlation with the σ constants being good. In reactions of markedly nucleophilic character, such as addition of hydrazine to 3-phenyl-2-propenoates¹⁷ or hydration of α,β -unsaturated ketones¹⁸, the order of substituents is reversed than in electrophilic substitutions: $4\text{-NO}_2 < 3\text{-NO}_2 < 3\text{-Br} < 4\text{-Br} < \text{H} < 4\text{-OCH}_3$. As seen from the plot of $\log k$ against the σ or σ^+ constants for the acids 1 (Fig. 3, 4), it is very difficult to find a straight line which would at least symbolize a linear dependence. Since methyl and methoxy groups exhibit the greatest difference in reaction rates relative to other derivatives, it seems logical to include first of all these groups into the correlation straight line (line 1 in Fig. 3 and 4). On the other hand, the roughly estimated reaction rate for the 4-methoxy derivative *Ig* introduces a greater error into the value ρ^+ . Nevertheless, it is worth notice that the thus-obtained $\rho^+ = -4.7$ corresponds

TABLE III

Rate constants, k (s^{-1}), for addition of hydrogen bromide to substituted 3-phenyl-2-propenoic acids *I* in acetic acid, followed polarographically at various temperatures (4.8M-HBr, $1 \cdot 10^{-2}$ M-I)

Acid	0°C	25°C	35°C	45°C
<i>Ia</i>	$1.28 \cdot 10^{-5}$ $1.01 \cdot 10^{-5}$	$7.58 \cdot 10^{-5}$	$1.86 \cdot 10^{-4}$	$3.60 \cdot 10^{-4}$
<i>Ib</i>	$6.85 \cdot 10^{-6}$ $7.34 \cdot 10^{-6}$	$5.51 \cdot 10^{-5}$ $4.85 \cdot 10^{-5}$	$1.51 \cdot 10^{-4}$	$3.38 \cdot 10^{-4}$
<i>Ic</i>	$3.95 \cdot 10^{-6}$ $4.96 \cdot 10^{-6}$	—	—	—
<i>Id</i>	$1.37 \cdot 10^{-5}$ $1.22 \cdot 10^{-5}$	—	—	—
<i>Ie</i>	$1.16 \cdot 10^{-4}$	$7.75 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$2.14 \cdot 10^{-3}$
<i>If</i>	$2.5 \cdot 10^{-5}$	—	—	—
<i>Ij</i>	$4.95 \cdot 10^{-6}$ $7.05 \cdot 10^{-6}$	—	—	$4.86 \cdot 10^{-4}$ $4.37 \cdot 10^{-4}$

approximately to the value for the electrophilic addition of halogen or hydrogen halide to the system *III*.



A very good correlation is obtained with halogen-substituted 3-phenyl-2-propenoic acids and 3-phenyl-2-propenoic acid (*Ia*) itself using the Brown σ^+ constants (straight line 2 in Fig. 4, $\rho^+ = -0.45$); the position of the points corresponding to the halogeno acids in the graph is close enough to enable their including into the linear correlation of the methyl and methoxy derivatives. In both cases the points, corresponding to the nitro acids *Ij*, *Ik*, and also partly the carboxy acid *Ih*, do not fit the correlation. If they are included into the correlation, we get for points with positive σ or σ^+ constants the correlation straight line 3 with the slope $\rho = -0.21$ or $\rho^+ = -0.23$. The unexpectedly faster addition to the nitro acids could be explained

TABLE IV

Activation energy of the reaction according to Scheme 2 for substituted acids *I*

Acid	<i>E</i> from graph	<i>E</i> calculated	Number of discarded values	Standard deviation	Maximum deviation, %
Determined UV spectroscopically ^a					
<i>Ia</i>	16.23	15.89	2	0.03398	0.96
<i>Ib</i>	16.68	16.52	1	0.05701	1.62
<i>Ic</i>	17.13	16.61	—	0.07811	2.75
<i>Id</i>	17.69	17.79	1	0.05649	1.08
<i>Ie</i>	14.40	13.47	—	0.06193	2.71
Determined polarographically ^b					
<i>Ia</i>	13.60	13.23	1	0.05151	1.05
<i>Ib</i>	14.03	14.53	1	0.04900	1.69
<i>Ic</i>	12.37	11.18	—	0.11916	3.12

^a 4.26M-HBr, $7 \cdot 10^{-6}$ M-I in acetic acid; ^b 4.8M-HBr, 0.01M-I in acetic acid.

by a combination of the mesomeric and inductive effects, lowering the electron density at the β -carbon atom. The initial nucleophilic attack by the Br^- ion can compete with the assumed protonation of the carboxyl oxygen. Since the same deviation was observed also with 3-(4-carboxyphenyl)-2-propenoic acid (*Ih*), it is worth consideration whether this is not a general property of second class substituents. It is known^{20,22} that polarographic half-wave potentials of ring-substituted 3-phenyl-2-propenoic acids *I* depend linearly on the Hammett σ constants; it is interesting that the only studied second class substituent, the $\text{C}\equiv\text{N}$ group, does not fit this correlation. In the transfer of substituent effect across the furan ring, „inserted” between the aromatic nucleus and the $\text{C}=\text{C}$ bond in the acids *I*, there is practically no anomalous behaviour of the nitro group with respect to the linear dependence of $v(\text{CO})$ or polarographic half-wave potential on the σ constants²³. For comparison, Table V gives relative reaction rates of nucleophilic or electrophilic additions to the noble *V* unsaturated system *III*.

For the hydrogen halide addition to non-aromatic α,β -unsaturated carboxylic acids Vaughan⁷ assumes a very fast equilibrium leading to an oxygen-protonated form of the acid (Scheme 1). The addition itself is then controlled by a nucleophilic attack at the β -carbon atom. In our case the invariably negative ρ value indicates that in the addition to the conjugated system of 3-phenyl-2-propenoic acids *I* the

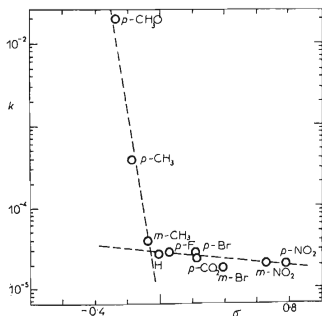


FIG. 3

Plot of $\log k$ against σ constants for addition of hydrogen bromide to substituted 3-phenyl-2-propenoic acids (followed by UV spectroscopy at $t = 25^\circ\text{C}$)

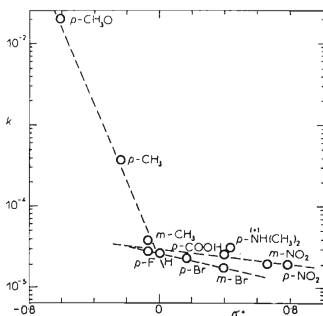
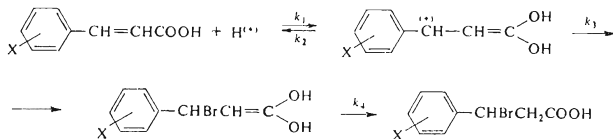


FIG. 4

Plot of $\log k$ against σ^+ constants for addition of hydrogen bromide to substituted 3-phenyl-2-propenoic acids (followed by UV spectroscopy at $t = 25^\circ\text{C}$)

protonation influences the overall reaction rate. If we consider the Vaughan's mechanism to be valid also for the studied addition (Scheme 3), it is necessary to as-



SCHEME 3

sume that for the methyl- and methoxy-substituted acids the protonation rate is the slowest, and thus the overall rate-determining, step ($k_1 < k_3, k_4$). For the other acids we assume that the protonated form is reactive; however, also the constant k_3 of the subsequent nucleophilic attack contributes to the overall reaction rate.

Table VI lists the rate constants for electrophilic addition of Cl_2 (ref.²⁴) which are compared with the rates of addition of hydrogen bromide to acids with substituents in the olefinic chain: 2-bromo-3-phenyl-2-propenoic and 3-bromo-3-phenyl-2-propenoic acids. The markedly slower reaction of hydrogen bromide than the electrophilic addition of chlorine indicates that the rate-determining attack very probably does not occur at the α - or β -carbon atom of the chain. In principle, this fact confirms that the reaction scheme suggested by Vaughan⁷ holds also for conjugated aromatic α,β -unsaturated acids, save the above-mentioned exceptions: the protonation rate either determines the overall reaction rate or the rate of the subsequent nucleophilic attack is at least comparable with the carboxyl protonation rate.

TABLE V

Relative rate constants for addition of hydrogen halides and halogens (Z) to the unsaturated system III

Substituent X	Y = OH, Z = HBr	Y = OH, Z = Cl_2 Ad _E (ref. ¹⁶)	Y = C_6H_5 , Z = HCl Ad _E (ref. ¹⁴)	Y = C_6H_5 , Z = Br_2 Ad _N (ref. ¹⁴)
<i>p</i> - CH_3	14.5	21	13	2
H	1	1	1	1
<i>p</i> -Br	0.8	—	—	—
<i>p</i> -Cl	—	0.55	0.38	—
<i>m</i> - NO_2	0.62	0.0002	0.0008	1.15

EXPERIMENTAL

Hydrogen bromide was prepared by decomposition of phosphorus tribromide with azeotropic hydrobromic acid. Only this procedure afforded colourless solutions in acetic acid even at concentrations up to 6 mol l^{-1} which did not absorb at about 300 nm.

Substituted 3-phenyl-2-propenoic acids *I* were synthesized by heating the substituted benzaldehyde with malonic acid in pyridine in the presence of a small amount of piperidine²⁵. The yields and melting points of the obtained acids are summarized in Table VII. Substituted benzaldehydes were prepared by oxidation of toluene derivatives with chromium trioxide in acetic anhydride and acetic acid^{26,27}. *m*-Tolualdehyde was obtained by Stephen reduction of *m*-toluonitrile²⁸. Substituted 3-phenylpropanoic acids were prepared by reduction of the corresponding 3-phenyl-2-propenoic acids *I* with 2% sodium amalgam in 3% sodium hydroxide²⁹ and purified by two crystallizations from water.

3-Bromo-3-phenyl-2-propenoic Acid³⁰

3-Phenylpropanoic acid (12 g; 0.08 mol) was dissolved under shaking in nitromethane (90 g) which had been saturated with hydrogen bromide under cooling. After standing overnight, the separated crystals were filtered (7.8 g), dissolved in aqueous ammonia and precipitated with barium chloride. After washing with water and ethanol, the acid was liberated and taken up in benzene. Crystallization from benzene yielded 4.1 g (22%) of the product, melting at 135°C (reported³⁰ m.p. 134–135°C).

2-Bromo-3-phenyl-2-propenoic Acid

A solution of 3-phenylpropanoic acid (12 g; 0.08 mol) in benzene (70 ml) was saturated at 0°C with gaseous hydrogen bromide and set aside at room temperature for 24 h. The crystals (9.2 g) were filtered, purified *via* the barium salt as described in the preceding experiment and crystallized twice from benzene, affording 2.6 g (14%) of the pure product, m.p. 131–132°C (reported³¹ m.p. 131°C).

Kinetic Studies of the Reaction with Hydrogen Bromide Using UV Spectroscopy

A solution of 3-phenyl-2-propenoic acid (*Ia*) in acetic acid ($3.5 \cdot 10^{-5} \text{ mol l}^{-1}$, 2 ml) was made up to 10 ml with a solution of hydrogen bromide in acetic acid (5.2 mol l^{-1}) at the given tempe-

TABLE VI

Relative rate constants for addition of chlorine and hydrogen bromide to unsaturated acids in acetic acid

Acid	HBr	Cl ₂ , Ad _E (ref. ²²)
3-Phenyl-2-propenoic	10	10
2-Bromo-3-phenyl-2-propenoic	3.5	0.42
3-Bromo-3-phenyl-2-propenoic	0.38	0.015

perature in a thermostated flask. The concentration of 3-phenyl-2-propenoic acid in the reaction mixture was followed in a thermostated cell of an Optica Milano UV spectrometer and was calculated from the extinction of the aromatic band of *Ia* using a calibration graph.

Analogously we followed the addition of hydrogen bromide to acids *I*, substituted in the aromatic nucleus, and to 2-bromo- and 3-bromo-3-phenyl-2-propenoic acids, using the aromatic band at 270–305 nm.

Polarographic Study of Reaction with Hydrogen Bromide

The unreacted substituted acids *I* were determined with an LP 55 polarograph equipped with an EZ-2 recorder. A solution of 3-phenyl-2-propenoic acid in acetic acid (0.1 mol l^{-1} ; 10 ml) was made up to 50 ml with a solution of hydrogen bromide in acetic acid (6 mol l^{-1}) in a closed thermostated flask. At appropriate time intervals exactly 2 ml of the reaction mixture was withdrawn and the reaction was quenched by pouring into water (15 ml). The solution was extracted with ether ($3 \times 8 \text{ ml}$), the extracts were combined and the organic acids were taken up into 0.2 M-LiOH ($2 \times 10 \text{ ml}$). After standing for 1 h, the alkaline solution was washed with ether and a saturated solution of calcium chloride (0.2 ml) was added. The sample was made up to 25 ml with 0.2 M-LiOH , placed into a polarographic cell, a stream of nitrogen was introduced to remove oxygen and the solution was immediately polarographed. The substituted acids were treated analogously. The linear dependence of wave height on concentration of the acids was verified by calibration of their solutions in 0.2 M-LiOH in the presence of calcium ions.

TABLE VII

Yields and melting points of substituted acids $\text{X-C}_6\text{H}_5\text{CH=CH-COOH}$

Acid	X	Yield, %	M.p., °C	M.p., °C (ref.)
<i>Ia</i>	H	—	136	136 (25)
<i>Ib</i>	<i>p</i> -Br	86	263	264–265 (35)
<i>Ic</i>	<i>m</i> -Br	76	177	178 (25)
<i>Id</i>	<i>p</i> -F	83	208–209	208 (33)
<i>Ie</i>	<i>p</i> -CH ₃	85	199–200	198 (25)
<i>If</i>	<i>m</i> -CH ₃	72	112–113	114–115 (32)
<i>Ig</i>	<i>p</i> -CH ₃ O	77	175–175.5	172 (25)
<i>Ih</i>	<i>p</i> -COOH	89	352 ^a	358 ^a (36)
<i>Ii</i>	<i>p</i> -(CH ₃) ₂ N	52	219 ^a	216 ^a (25)
<i>Ij</i>	<i>p</i> -NO ₂	88	288 ^a	285 ^a (25)
<i>Ik</i>	<i>m</i> -NO ₂	86	196	196 (25)
<i>Il</i>	<i>p</i> -Cl	80	245	245 (34)

^a Decomposition.

Study of Reaction of Ethyl 3-Phenyl-2-propenoate with Hydrogen Bromide

A mixture of the ester (15 g) and hydrogen bromide in acetic acid ($6 \cdot 005 \text{ mol l}^{-1}$; 50 ml) was kept in a thermostated vessel at $14\text{--}8^\circ\text{C}$. Samples (2 ml) were withdrawn in the interval 10–120 min. After pouring into a solution of potassium acetate in acetic acid (1 mol l^{-1} ; 10 ml), the unreacted hydrogen bromide was titrated with $0.25\text{M-H}_2\text{SO}_4$ in acetic acid to Methyl Violet.

The addition of hydrogen bromide to 3-phenyl-2-propenal and 2-phenyl-1-nitroethylene was followed analogously.

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