$CHXCH_3$ systems ($k_{Br}/k_{Cl} \cong 12/1$ in each instance at 25° in water).[23,24] In contrast, the leaving group effects for covalent participation to form three-membered rings appears to be unusually large.[25]

Hydrolysis of optically active $PhCHBrCO_2^-$ or $PhCHClCO_2^-$ leads to essentially racemic mandelic acid.[29] This result can be rationalized either by assuming the formation of a zwitterion intermediate of lifetime long enough to permit racemization or of an α-lactone intermediate which racemizes, presumably *via* the zwitterion, prior to capture by solvent.

In the following paper it will be shown that participation by the carboxylate ion is more effective in accelerating the overall rate for β-CO_2^- than for α-CO_2^-. Since for covalent participation formation of a three-membered ring is always much more effective than formation of a four-membered ring, this is further support for the electrostatic participation hypothesis. (This takes no account, of course, of internal return, which would be much greater for the α-CO_2^- system.)

Experimental Section

Aryl α-Bromoacetic Acids.—These compounds were prepared by methods described in the literature.[10,30]

Kinetics of Solvolysis of α-Bromophenylacetic Acid Anions.—Reaction was initiated by adding a weighed amount of the bromo acid to a base solution (0.03–0.07 *M* $NaHCO_3$ in water or 0.016 *M* NaOH in ethanol–water mixtures) that had attained the temperature of the thermostated bath. The mixture was agitated until dissolution was complete. The time taken for dissolution of the acid was disadvantageous in cases where the reaction half-life was short. This was overcome by dissolving the material in acetone (2 drops) prior to addition, whereupon dissolution was immediate. Insensitivity of reaction rate to the small concentration of acetone was verified.

Aliquot parts (containing 0–6 microequivalents of bromide ion) were withdrawn at intervals and quenched in a solution of acetone (3 ml) and 0.25 *M* nitric acid (5 ml). Bromide ion was titrated potentiometrically with 0.0015 *N* $AgNO_3$ using an automatic constant rate buret (Sargent Model C) linked with a chart recorder. The electrode assembly comprised a silver indicator and calomel half-cell reference electrode. The end point was determined from the inflection of a volume *vs.* mV trace in the usual way. It was confirmed that the presence of unreacted material and of reaction products was without effect on the titrations.

Product Analysis.—The bromo acid (0.005 mol) was kept with aqueous 0.06 *M* sodium bicarbonate (250 ml) at 50° for ten half-lives. The reaction mixture was acidified (HCl) to pH 5 and evaporated to a 50-ml volume. The solution was saturated with sodium chloride and continuously extracted with ether during a 100-hr period. The extract was dried ($MgSO_4$) and evaporated. In each case the corresponding mandelic acid was isolated in not less than 96% yield (based on the mass of crude material which in general melted 5° below the literature value). The purified products were identified by ir, nmr, and mixture melting point.

α-Bromo-*m*-methylphenylacetic Acids.—A mixture of *m*-methylmandelic acid (3.32 g, 0.02 mol) and 48% hydrobromic acid (10 ml) was refluxed during 3 hr. The mixture was poured onto crushed ice (30 g) and extraction was with ether. The ether extract was washed with water to remove unreacted mandelic acid, dried, and evaporated to give the product (1.5 g., 33% yield). The bromo acid had bp 134° (0.5 mm).

α-Bromo-*p*-methylphenylacetic Acid.—α-Bromo-*p*-methylphenylacetic acid was prepared from *p*-methylmandelic acid (0.02 mol) in 25% yield, in the same way as the *m*-methyl analog. It had bp 145° (0.1 mm) and mp 83°.

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(23) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957).

(24) W. R. Buloraig and H. M. Dawson, *J. Chem. Soc.*, 80 (1943).

(25) For the Ramberg–Bäcklund reaction of α-halo sulfones k_{Br}/k_{Cl} varies from 88 to 620 depending on the system, solvent, and temperature.[26] For ethylene oxide formation from $HOCH_2CH_2X$ initiated by base $k_{Br}/k_{Cl} \cong$ 88/1 in water, and *ca.* 153/1 in aqueous methanol, after correcting for the alcohol ionization constants.[27,28] For $ArCHXCH_2OH$ k_{Br}/k_{Cl} = 55 in water.[28]

(26) F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 435 (1968).

(27) C. L. McCabe and J. C. Warner, *ibid.*, **70**, 4031 (1948).

(28) A. C. Knipe, unpublished results.

(29) (a) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **93**, 811 (1908); **95**, 777 (1909). (b) A. McKenzie and N. Walker, *ibid.*, **107**, 1685 (1916); A. M. Ward, *ibid.*, **118**, 1184 (1926).

(30) J. Krapcho, U. S. Patent 3,166,554 [*Chem. Abstr.*, **62**, 13157*e* (1965); B. Ekstrum, A. Gomes-Revilla, R. Mollberg, H. Thelin, and B. Stoberg, *Acta Chem. Scand.*, **19** (1), 281 (1965); K. Heyns and H. Schultze, *Justus Liebigs Ann. Chem.*, **611**, 55 (1958); B. Wladisclaw and A. Giora, *J. Chem. Soc.*, 5747 (1965)].

Electrostatic Participation by Carboxylate Groups in the Hydrolysis of β-Bromo- and α,β-Dibromo-β-arylpropionate Ions

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The rates of bromide ion release from β-bromo-β-phenylpropionate ion and five of its *meta*- and *para*-substituted derivatives, $ArCHBrCH_2CO_2^-$ (1), have been measured in aqueous sodium bicarbonate solution at three or more temperatures. The sizable negative ρ (−3.24 at 25°) and the insensitivity of the rate to salt and solvent effects has been interpreted as evidence for electrostatic participation in bromide ion release by the β-CO_2^- leading to a zwitterion intermediate which partitions itself between styrene and β-lactone products. The positive activation entropies are consistent with this interpretation, as are correlations of rate with structure. Salt, solvent, and substituent effects similar to those of **1** were observed also for the rate of bromide ion release from *erythro*-α,β-dibromo-β-phenylpropionate ion and five of its *meta*- and *para*-substituted derivatives (ρ = −3.19 at 37.8°). Here the zwitterion intermediate decomposes mainly to β-bromostyrenes.

Beginning with Einhorn's isolation of a β-lactone from the reaction of β-bromo-*o*-nitrohydrocinnamic acid with sodium carbonate,[1] there have been numerous examples wherein β-halo carboxylates have been shown to undergo hydrolysis to give β-lactones as intermediates or as final products.[2] The hydrolysis of chlorosuccinate ions was demonstrated by Holmberg to involve β-lactone intermediates,[3] and these were

(1) A. Einhorn, *Ber.*, **16**, 2208 (1883).

(2) For reviews, see (a) H. E. Zaugg, *Org. React.*, **8**, 315 (1954); (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 116–119; (c) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 75 (1964).

(3) B. Holmberg, *J. Prakt. Chem.*, **88**, 553 (1913).

later isolated by Johansson.[4] Recently the formation of β-lactones from the hydrolysis of α-bromo-α-methylsuccinates and related compounds have been followed by nmr.[5] β-Lactone formation is generally stereospecific and involves inversion at the C–X center.[2]

When a β-aryl group is present, as in $ArCHBrCH_2CO_2^-$ or $ArCHBrCHBrCO_2^-$, debromodecarboxylation to form a styrene competes favorably with the formation of the β-lactone.[6,7] Alkene formation occurs to a lesser extent in other systems, such as α-methyl-β-halobutyrates,[6d] α,α-diphenyl-β-halopropionates,[8] and α,β-dibromosuccinates.[5] β-Lactones will react to give alkenes, but this reaction is slow compared with that whereby alkenes are formed from β-halo carboxylates. Therefore, it is generally agreed that β-lactones are not intermediates in the formation of alkenes by the solvolysis of β-halo carboxylates.[6,7] It has been suggested, instead, that alkene formation and β-lactone formation occur by separate pathways; a duality of mechanisms is possible for each. SN1-like and SN2-like transition states are possbile for β-lactone formation. E2-like and E1-like elimination mechanisms have been suggested as occurring simultaneously for alkene formation, E2 predominating in nonpolar media (acetone, ethanol) and E1 predominating in water. Most authors regard the β-hydroxy acids formed on hydrolysis of β-halo carboxylates by arising by hydrolysis of β-lactone intermediates.

In the previous paper[9] evidence was presented to show that in the hydrolysis of $ArCHBrCO_2^-$ the C–Br bond was extensively ionized in the transition state ($\rho = -2.9$) and that the rate was accelerated *ca.* fourfold relative to $ArCH_2Br$. It was suggested that the α-CO_2^- group was exerting its anchimeric effect on ionization through an electrostatic participation rather than through a conventional direct nucleophilic covalent participation. In other words the transition state was considered to be zwitterion-like rather than α-lactone-like. In the present paper the study has been extended to include the $ArCHBrCH_2CO_2^-$ and $ArCHBrCHBrCO_2^-$ systems and a similar conclusion has been reached.

Results

Substituent, Temperature, and Medium Effects on the $ArCHBrCH_2CO_2^-$ System.—Rates of liberation of bromide ion from a series of *meta*- and *para*-substituted β-bromo-β-arylpropionate ions were measured in the presence of excess sodium bicarbonate at three or more temperatures (Table I).

The effect of solvent was determined by measuring the rates in aqueous ethanol in the presence of excess 0.0006–0.006 *M* sodium hydroxide. (The rates were found to be independent of base concentration.) Solutions containing 10, 20, 40, 60, 80, and 100 mol per cent water were used in each instance, and duplicate kinetic runs were made. The data are summarized in Table II.

Lithium perchlorate was found to exert a small positive salt effect on the rate of liberation of bromide ion from *m*-$ClC_6H_4CHBrCH_2CO_2^-$: $k_{salt}/k_0 = 1.05$ (0.5 *M*), 1.06 (1.5 *M*), and 1.1 (2.5 *M*).

The distribution of products is shown in Table III.

Substituent, Temperature, and Medium Effects in the $ArCHBrCHBrCO_2^-$ System.—Rates of formation of β-bromostyrenes from a series of *meta*- and *para*-substituted α,β-dibromo-β-arylpropionate ions were measured in the presence of excess 0.033 or 0.066 *M* sodium bicarbonate at two or more temperatures by following the increase in absorbance at or near 257 nm (Table IV).

Trumbull and coworkers[7] report the following kinetic data obtained by a titration method in 89% (v/v) aqueous ethylene glycol in a phosphate buffer for the parent compound: $k^{35°}$ 8.6×10^{-5}; E_a, 32.0 kcal/mol; $\Delta S^{\pm}$ +23.1 eu. The presence of *ca.* 11% (v/v) ethylene glycol in their solution accounts for most of the discrepancy in the rate constant. There is, however, a serious discrepancy in the activation parameters. It should be noted in this connection that our rate mea-

TABLE I

KINETIC DATA FOR THE HYDROLYSIS OF β-BROMO-β-ARYLPROPIONATES, $YC_6H_4CHBrCH_2CO_2^-$

Y	Registry no.	T, °C	$10^5 k$,[a] sec^{-1}	$\Delta H^{\pm}$ kcal/mol[b]	$\Delta S^{\pm}$ eu[c]
H	25297-23-8	0.0	278	25.0	21.6
		4.70	665		
		9.55	1,480		
		25.0	14,000		
p-Cl	25356-16-5	4.70	365	22.6	12.2
		9.70	986		
		25.0	7,000		
m-Cl	25356-17-6	0.0	10.3	24.1	11.8
		4.75	23.8		
		9.8	58.1		
		25.0	594		
		32.7	1,380		
		38.4	2,650		
m-Br	25297-24-9	0.0	9.91	24.6	13.3
		25.0	500		
		32.7	1,360		
		38.4	2,630		
m-NO_2	25297-25-0	0.0	1.07	26.3	10.9
		25.0	72.8		
		41.5	714		
p-NO_2	25297-26-1	0.0	0.74	25.6	12.0
		25.0	46.2		
		41.4	416		

[a] Average of three or more runs carried to at least three half-lives. Standard deviations did not exceed ±2%. [b] E_a values were calculated from an Arrhenius plot by the method of least squares; correlation coefficients were 0.996 or better. [c] Calculated at 25°.

TABLE II

SOLVOLYSIS OF β-BROMOARYLPROPIONATE IONS IN AQUEOUS ETHANOL AT 25°

Substituent	Log k_0,[a] sec^{-1}	*m*[b]	*r*[c]
p-Cl	−2.4762	0.305	0.9985
m-Cl	−3.0041	0.23	0.9855
m-Br	−3.0021	0.224	0.9630
p-NO_2	−3.5141	0.080	0.9911

[a] Intercept on the ordinate. [b] Slope of a plot of log *k* *vs.* Grunwald–Winstein *Y* values. [c] Correlation coefficient.

(4) H. Johansson and S. M. Hagman, *Ber.*, **55**, 647 (1922).
(5) C. A. Kingsbury, *J. Org. Chem.*, **33**, 3247 (1968).
(6) (a) E. Erlenmeyer, *Ber.*, **13**, 303 (1880); (b) H. Johansson and S. M. Hagman, *ibid.*, **55**, 647 (1922); (c) S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, **75**, 632, 2645 (1953); (d) E. Grovenstein, Jr., and D. E. Lee, *ibid.*, **75**, 2639 (1953).
(7) E. R. Trumbull, R. T. Finn, K. M. Ibne-Rasa, and C. K. Saunders, *J. Org. Chem.*, **27**, 2339 (1962).
(8) H. E. Zaugg, *J. Amer. Chem. Soc.*, **72**, 2998 (1950).
(9) F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 2956 (1970).

TABLE III

PRODUCTS FROM THE HYDROLYSIS OF β-BROMO-β-ARYLPROPIONATES IN THE PRESENCE OF EXCESS SODIUM BICARBONATE

Substituent	T, °C	% β-lactone[a]	% styrene[a]	% recovery[b]
H	0	29	71	90
m-Br	25	43	57	94
		45	55	88
m-Cl	0	52	48	89
	25	49	51	95
	25	50	50	95
	25	46	54	95
	25	46[c]	54[c]	81[c]
	25	14[d]	86[d]	73[d]
	50	40	60	100
m-NO_2	25	73	27	84
		73	27	95
		74	26	95
p-NO_2	25	83	17	92
		87	13	98
		89	11	98

[a] Analysis by nmr (see Experimental Section). [b] Analysis by nmr using DMSO as a standard. [c] In 2 *N* $NaBH_4$. [d] Reaction mixture allowed to stand for 30 min before chloroform extraction. Hydrolysis of the β-lactone probably accounts for the low recovery and high styrene/lactone ratio.

TABLE IV

KINETIC DATA FOR THE HYDROLYSIS OF *erythro*-α,β-DIBROMO-β-ARYLPROPIONATES, $YC_6H_4CHBrCHBrCO_2^-$ (0.006 *M*), IN AQUEOUS SODIUM BICARBONATE (0.006 *M*)

Y	Registry no.	T, °C	$10^5 k_1$,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol[b]	$\Delta S^{\ddagger}$, eu[c]
p-Me	25297-27-2	25.0	564[d]	24.6	13.9
		37.0	3,300		
H	25297-28-3	25.0	3.22	26.8	11.0
		37.8	22.6		
		56.5	336[d]		
		63.1	692		
		70.5	1,560[d]		
		79.9	4,060		
m-MeO	25297-29-4	37.8	12.8	26.4	8.5
		56.5	176		
		63.1	382		
		70.5	845		
		79.9	2,380		
m-Cl	25297-30-7	56.5	17.9	27.0	5.7
		63.1	35.6		
		70.5	89.0[d]		
		79.9	287		
p-Cl	25297-31-8	56.5	244	24.2	2.8
		63.1	479		
		70.5	1,080[d]		
		79.9	2,990		
m-NO_2	25356-18-7	70.5	28.4		
		80.1	94.2		

[a] Single runs except where noted. [b] Calculated from E_a determined from the least-squares slope of an Arrhenius plot; correlation coefficients were 0.997 or better. [c] Calculated at 25°. [d] Average of two or more runs (standard deviation ±2%).

surements were made by a much simpler method, that the rates were determined over a range of 55° compared with 15°, and that the correlation coefficients for all of the compounds studied were high. (Analysis of the data of Trumbull and coworkers gave a correlation coefficient of 0.996.) Lithium perchlorate was found to exert a small positive salt effect on the rate of formation of β-bromostyrene from *erythro*-α,β-dibromo-β-phenylpropionate ion: k_{salt}/k_0 = 1.05 (0.5 *M*); 1.4 (1.5 *M*); 1.6 (2.5 *M*).

Attempts to determine solvent effects by measuring rates of reactions for $ArCHBrCHBrCO_2^-$ in aqueous ethanol in the presence of excess sodium acetate were not altogether successful. For p-Me the plot was linear from 0 to 60 mol % water (m = 0.5), but then curved upward; for $C_6H_5CHBrCHBrCO_2^-$ the plot curved steadily from 10 to 80 mol % water (mean m = 0.2); for m-Cl there was essentially no change in rate from 10 to 40 mol % water, and only a twofold increase in rate from 60 to 100 mol % water.

The Hammett ρ values for the $ArCHBrCH_2CO_2^-$ and $ArCHBrCHBrCO_2^-$ systems for a range of temperatures were evaluated from results for six substituents and are listed in Table V.

TABLE V

HAMMETT ρ VALUES FOR THE HYDROLYSIS OF $ArCHBrCH_2CO_2^-$ AND $ArCHBrCHBrCO_2^-$ AT VARIOUS TEMPERATURES

System	T, °C	ρ[a]	r
$ArCHBrCH_2CO_2^-$	0.0	−3.38	0.994
	25.0	−3.24	0.994
$(ArCHBrCHBrCO_2^-)$[b]	37.8	−3.19	0.979
		(−3.80)	(0.973)
	56.5	−2.95	0.989
		(−3.58)	(0.974)
	63.1	−3.85	0.986
		(−3.51)	(0.970)
	70.5	−2.69	0.987
		(−3.40)	(0.965)
	79.9	−2.54	0.987
		(−3.29)	(0.960)

[a] σ^+ values were used for p-Me and p-Cl since better correlation was obtained thereby; figures in parentheses were obtained by inclusion of p-Me points.[11] [b] Rates of reaction of the p-nitro derivative were extrapolated from results of Trumbull, *et al.*[7]

The Hammett ρ values were observed to be strongly solvent dependent (Table VI).

TABLE VI

VARIATION OF ρ WITH SOLVENT COMPOSITION IN THE SOLVOLYSIS OF β-BROMO-β-ARYLPROPIONATES AND α,β-DIBROMO-β-ARYLPROPIONATES IN AQUEOUS ETHANOL AT 25°

Mol % H_2O	ρ[a]	ρ[b]
100	−3.3	−3.3
80	−2.2	−2.6
60	−1.8	−1.9
40		−1.8
20	−1.2	−1.4
10	−1.1	−1.0

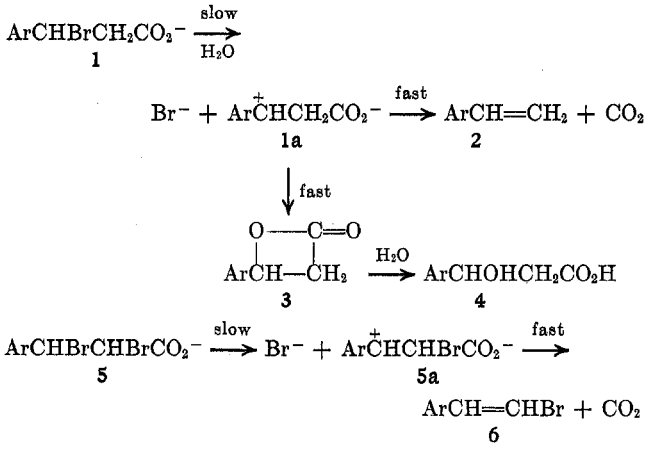
[a] Estimated from the relative rates of reaction of the p-Cl- and p-$NO_2C_6H_4CHBrCH_2CO_2^-$. [b] Estimated from the relative rates of $C_6H_5CHBrCHBrCO_2^-$ and its m-Cl derivative.

Discussion

Substituent, Salt, and Solvent Effects.—Comparison of the data in the previous section with that given in the preceding paper[9] shows that the substituent, salt, and solvent effects for hydrolysis of bromide ion from the $ArCHBrCO_2^-$, $ArCHBrCH_2CO_2^-$, and $ArCHBrCHBrCO_2^-$ systems are remarkably similar. In all

three systems, ρ is about -3, and, in all three systems the hydrolyses are relatively insensitive to salt effects and to changes in the ionizing power of the solvent. The sizable negative ρ shows that the C–Br bond is developing a high degree of ionic character in the transition state. It was concluded in the previous paper that these effects in the $ArCHBrCO_2^-$ system could be best interpreted as electrostatic participation by the carboxylate ion, which serves to facilitate the ionization and to produce a leveling influence on salt and solvent effects. We believe that this mechanism also offers the simplest explanation for the $ArCHBrCH_2CO_2^-$ and $ArCHBrCHBrCO_2^-$ systems, *i.e.* Scheme I.

SCHEME I



According to this interpretation the intermediate zwitterion **1a** partitions itself the styrene (**2**) and the β-lactone (**3**). The presence of electron-withdrawing groups promotes collapse to the β-lactone. Similar possibilities are available to zwitterion **5a**, but here the bromostyrene is essentially the only product, regardless of the substituent.

The change in ρ values with changes in solvent composition appears to be rather large, but there are relatively few data available for comparison.[10] Kochi and Hammond observed a similar but somewhat smaller change in the solvolysis of benzyl tosylates on increasing the water content of aqueous acetone, judging from the effect of one substituent (*p*-Me). Assuming their experimental value of -0.63 for $\sigma_{p\text{-Me}}$, the mole per cent water and respective ρ values were 29.0, -1.9; 44.8, -2.1; 55.0, -2.2; 62.0, -2.3; 67.0, -2.4; 74.1, -2.4; 76.6, -2.4.[11] Jaffé suggests a possible dependence of ρ on solvent ionizing power, Y, and this is borne out qualitatively by the Kochi and Hammond data. In the present instant ρ also increases (nonlinearly) with increasing values of Y. The lower sensitivity to substituent effects in less polar solvents for **1** and **5** could mean that the influence of electrostatic field of the carboxylate ion on the developing carbonium ion is greater in these solvents. It could, of course, also be explained by assuming a duality of mechanism.

A comparison of the rate of bromide ion release from $PhCHBrCH_2CO_2^-$ on hydrolysis (Table VII) shows it to be *ca.* 480 times as fast as that for $PhCHBrCO_2^-$. Similarly, $CH_3CHBrCH_2CO_2^-$ hydrolyzes 43 times as rapidly as does $CH_3CHBrCO_2^-$.[12] This order of reactivity is just opposite to that observed in covalent participations where the rates of formation of three-membered rings is much greater than that to form four-membered rings.[13] These results can be accounted for by electrostatic participation in which a β-CO_2^- is more effective than an α-CO_2^- because of less attenuation by the electron-withdrawing effect[9] of the CO_2^- group. It will be observed that substitution of either an α-CO_2^- or β-CO_2^- for hydrogen in the parent $PhCHBrCH_3$ is actually rate retarding. However, the relative insensitivity of the solvolyses of the β-bromoalkanecarboxylates to solvent ionizing power makes $k_{CO_2^-}/k_H$ = 95:1.0 when comparison is made in 80% ethanol (Table VII).

Introduction of a β-Br into $PhCHBrCH_3$ retards the solvolysis rate (in 80% EtOH) by *ca.* 1.5×10^4 (Table VII). A similar but somewhat smaller difference (*ca.* 4.3×10^3) is observed for the hydrolysis rates of *erythro*-$PhCHBrCHBrCO_2^-$ *vs.* $PhCHBrCH_2CO_2^-$. These differences can be ascribed to the retarding electron-withdrawing inductive effect of the β-Br on the ionization of the benzylic C–Br bond.[14]

Vaughan, Caple, Csapilla, and Scheiner have clearly demonstrated the existence of a rate accelerating electrostatic participation by β-CO_2^- through measurements made on systems where covalent participation is made impossible due to steric effects.[15] Some of their data are included in Table VII. Note that the *cis*-β-bromocyclopentanecarboxylate ion reacts 5.8 times as fast as the parent bromide.

Examination of Tables I and III shows that the hydrolyses of $ArCHBrCH_2CO_2^-$ and of $ArCHBrCHBrCO_2^-$ exhibit positive activation entropies. They are not as strongly positive as for $ArCHBrCO_2^-$, but are nevertheless more positive than the usual range for unimolecular (A-1, SN1) solvolyses (0 to 10),[16] and much more positive than those of the parent bromides (Table VII).

The commonly accepted view is that β-halo carboxylates react by three separate pathways: (a) intramolecular nucleophilic diplacement to form a β-lactone,[2] (b) a concerted E2-like debromodecarboxylation,[6] and (c) and E1-like debromodecarboxylation. The principal basis for these mechanisms is that they account for the stereochemistry.

For β-lactone formation covalent participation has been assumed on the basis of the modest rate enhancements observed and the overall retention of configuration in forming the β-hydroxy acid. We have seen, however, that electrostatic participation also can lead

(10) H. H. Jaffé, *Chem. Rev.*, **53**, 119 (1953).

(11) J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3445 (1953).

(12) There are a number of instances wherein β-lactone formation is known to be preferred to α-lactone formation where the two processes are in direct competition. An early example is Holmberg's hydrolysis of $^-O_2CCH_2CHClCO_2^-$ from which a β-lactone was isolated.[2b,3,4]

(13) See A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc. B*, 67 (1968).

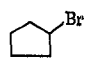
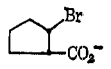
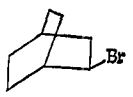
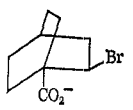
(14) The rate of bromide ion liberation from *threo*-α,β-dibromo-β-phenylpropionate ion is much faster than that for the *erythro* isomer, but exact kinetic data are lacking. It has been suggested that the *erythro* isomer reacts by a carbonium ion mechanism to the extent that it forms *trans*-β-bromostyrene (78%) and that the rate acceleration is due to a concerted elimination for the *threo* isomer.[6,7] For reasons stated below we prefer to assume that electrostatic participation leading to the formation of zwitterion occurs in each instance. One possible interpretation of the rate difference would be to assume a higher ground state energy for the *threo* isomer and zwitterion-like transition states of about equal energy.

(15) W. R. Vaughan, R. Caple, J. Csapilla, and P. Scheiner, *J. Amer. Cehm. Soc.*, **87**, 2204 (1965).

(16) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

TABLE VII

KINETIC DATA FOR THE SOLVOLYSES OF β-BROMOALKANECARBOXYLATES AND RELATED COMPOUNDS

Bromide	T, °C	k,[a] sec⁻¹	$k_{CO_2^-}/k_H$	ΔS‡, eu	Ref
$PhCHBrCO_2^-$	25	2.93×10^{-4}		18	9
$PhCHBrCH_3$	25	5.6×10^{-1}		5	*e*
	25	$(1.91 \times 10^{-4})^b$		−7.7	*e*
	50	$(2.89 \times 10^{-3})^b$			*e*
$PhCHBrCH_2CO_2^-$	25	1.4×10^{-3}	0.25	22	*f*
	25	$(1.8 \times 10^{-2})^b$	95		
$PhCHBrCH_2Br$	55	$(1.90 \times 10^{-7})^c$			*g*
$PhCHBrCHBrCO_2^-$	25	3.22×10^{-5}			*h*
	55	$(5.4 \times 10^{-5})^d$	280		
$CH_3CHBrCO_2^-$	25	4.17×10^{-7}			*i*
$CH_3CHBrCH_2CO_2^-$	25	1.8×10^{-5}			*j*
	62	$(1.70 \times 10^{-5})^b$		−28	*k*
	62	$(9.73 \times 10^{-5})^b$	5.7	−8	*k*
		1.64×10^{-3}		10	
	62	$(6.65 \times 10^{-6})^b$		−25	*k*
	62	2.12×10^{-1}		20	*k*

[a] In water unless otherwise stated. [b] In 80% (v/v) EtOH–H_2O. [c] In 100% EtOH. [d] Estimated assuming $m = 0.5$. [e] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 79, 1602 (1957). [f] Table I. [g] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 828 (1948). [h] Table IV. [i] J. F. Lane and H. W. Heine, *J. Amer. Chem. Soc.*, 73, 1348 (1951). [j] A. R. Olson and R. J. Miller, *ibid.*, 60, 2687 (1938). [k] Reference 15.

to rate acceleration,[15] and that, although overall retention of configuration is most readily explained by assuming a lactone intermediate, this does not preclude the formation of a zwitterion intermediate by loss of bromide ion followed by collapse to a β-lactone in a rapid step.[9]

The data in Tables I–III show that substitution of electron-withdrawing groups causes a sharp drop in overall rate which is accompanied by a gradual progressive shift in products from mainly olefin to mainly β-lactone. There also appears to be a decrease in sensitivity to solvent ionizing power with the substitution of electron-withdrawing groups, but there is no obvious trend in activation parameters. If the olefins and β-lactones are being formed by separate paths, *e.g.*, intramolecular displacement and E2 elimination, one might expect to see a curved Hammett plot and/or marked changes in activation parameters as the change from one reaction path to the other occurs. The constancy of the ρ value and of the activation parameters and their similarity to those in the $ArCHBrCO_2^-$ and $ArCHBrCHBrCO_2^-$ systems strongly suggests that all are forming similar (zwitterion) intermediates in the rate-determining step, and that these intermediates behave differently in the product-forming step. Ionization of the C–Br bond requires more assistance from carboxylate participation as the developing benzylic carbonium ions are made less stable through substitution of electron withdrawing groups. The resulting zwitterions collapse more rapidly to β-lactones in the latter instances (Table III).

The duality of mechanisms for $ArCHBrCHBrCO_2^-$ systems is based on the fact that, whereas the *erythro* and *threo* isomers undergo stereoselective *trans* elimination (E2-like) in nonpolar solvents,[6,7] in water the reactions become stereoconvergent. The change in stereochemistry has been attributed to a crossover to a carbonium ion (E1-like) mechanism. An alternative view would be that the β-CO_2^- facilitates the ionization of the C–Br by *trans* electrostatic participation to form a zwitterion, which in nonpolar (non stabilizing) solvents undergoes stereoselective loss of CO_2, but in stabilizing solvents (water) racemizes prior to loss of CO_2. Once again this interpretation is supported by the linearity of the Hammett plots and the relative constancy of the activation parameters. The salt and solvent responses also appear to be similar to those in the $ArCHBrCO_2^-$ and $ArCHBrCH_2CO_2^-$ systems.

Recently, Noyce and Banitt have studied the hydrolysis of *cis*- and *trans*-β-hydroxy-α-methyl-β-*m*-chlorophenylpropionic acid lactones in water at pH 6 and have obtained evidence that loss of carbon dioxide from the diastereomeric $m\text{-}ClC_6H_4C^+HCH(Me)CO_2^-$ zwitterions can be stereospecific.[17] The principal argument for a duality of mechanism in the debromodecarboxylation of $ArCHBrCHBrCO_2^-$ is negated if this conclusion is accepted for this system as well. At least until more definitive information becomes available it seems best to consider the ionizations of bromide ion from $ArCHBrCO_2^-$, $ArCHBrCH_2CO_2^-$, and $ArCHBrCHBrCO_2^-$ as all proceeding by similar reaction paths involving zwitterion-like transition states and zwitterion intermediates.

Experimental Section

Materials.—The β-bromo-β-phenylpropionic and *erythro*-β-phenyl-α,β-dibromopropionic acids were prepared by methods

(17) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966).

described in the literature.[18-23] Identification was by melting point, ir, and nmr.

The Kinetics of Reaction of β-Bromo-β-phenylpropionic Acid Anions.—Two analytical procedures were used to follow reactions of the β-bromo acid anions. (a) Reaction was initiated by adding a weighed amount of the bromo acid to a base solution (sodium bicarbonate in water or sodium hydroxide in ethanol–water mixtures) that had attained the temperature of the thermostated bath. The reaction was followed by potentiometric estimation of bromide ion released. Aliquot parts of the reaction mixture were titrated with silver nitrate at appropriate time intervals. The electrode assembly and titration procedure have been described previously.[9] It was confirmed that neither starting material or products interfered with the analytical method. (b) For those reactions leading to formation of the appropriate styrene in high yield it was convenient to follow the course of the reaction by observation of the increase in absorbance at 258 mμ. The substrates also had absorbance maxima at this wavelength, but with lesser extinction coefficients.

Reaction was initiated by addition of 5 μl of a solution (0.03 *M*) of the bromo acid in acetone to the solvent (3 ml) contained in a cuvette of 1-cm path length. The reaction vessel and contents had previously been allowed to attain the temperature of the thermostated cell compartment. In ethanol–water solution the wavelength at which the absorbance change was a maximum during the course of reaction was chosen by inspection and found always to be in the range of 245–255 mμ. All rate constants were evaluated by least-squares analysis of data recorded during a minimum time span of three reaction half-lives. The data were processed with the aid of a CDC 6400 computer at the Northwestern University Vogelback Computing Center.

Product Analysis.—The bromo acid (1 g) was stirred in a heterogeneous mixture of aqueous sodium bicarbonate (50 ml, 0.15 *M*) and chloroform (50 ml) at the appropriate temperature for 10 half-lives. The aqueous layer was saturated with sodium chloride and extracted with four 100-ml portions of chloroform. The combined chloroform extract was washed with water (50 ml), dried ($MgSO_4$), and evaporated to a volume of 1.5 ml by rotary evaporation at 25° (20 mm). DMSO (150 μl) was added and the nmr spectrum of the solution was recorded immediately. In every case the spectrum was that of a mixture of the appropriate lactone and styrene. The percentage composition of each product was evaluated from the integral and the overall recovery of products was evaluated with reference to the integral of the DMSO protons. The analyses were repeated in triplicate with good reproducibility as revealed in Table III.

Acknowledgment.—We are grateful to the National Science Foundation (GP 7065) for support of this investigation.

(18) E. Fourneau and J. R. Billeter, *Bull. Soc. Chim. Fr.*, **7**, 593 (1940).
(19) A. Basler, *Ber.*, **16**, 3002 (1883).
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(21) J. I. Jones and T. C. James, *J. Chem. Soc.*, 1600 (1935).
(22) H. Willstaedt, *Ber.*, **64B**, 2688 (1931).
(23) S. J. Cristol and H. P. Norris, *J. Amer. Chem. Soc.*, **75**, 632 (1953).

Silicon-Functional 1,2,5-Oxadisilacyclopentane Heterocyclics

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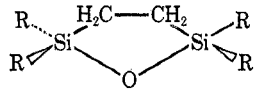
Ligand redistribution of appropriate alkoxy- or chlorosiloxane substrates at elevated temperatures afforded examples of the title heterocyclic system bearing easily solvolyzable substituents at one or both silicon sites. Also described are novel spirocyclic derivatives of the bidentate alkoxy ligand, $-OCMe_2CH_2CH_2CMe_2O-$.

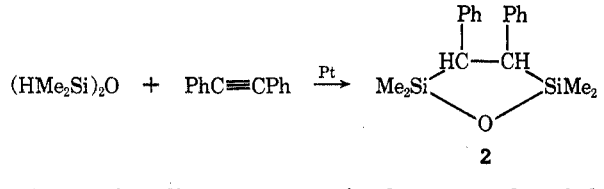
The first examples of the strained 1,2,5-oxadisilacyclopentane heterocyclic system, **1** (R = all combinations of Ph and CH_3), were reported by Merker[1] and



1

his coworkers who employed alkaline thermal siloxane rearrangement of appropriate polymeric substrates.

Other members of this interesting system (*e.g.*, **2**) have been reported[2] to form directly from certain hydrosilation reactions.



2

The previous literature contained no examples of this heterocyclic system containing easily hydrolyzable silicon substituents. We describe herein the first examples of chloro- and alkoxy-substituted 1,2,5-dioxasilacyclopentanes.[3]

Results and Discussion

During an attempt to prepare a linear polymer (**4**) by the combined base-catalyzed partial hydrolysis and alkoxy exchange reaction of **3**, overheating occurred and the novel spirocyclic **5** distilled from the reaction mixture. By a very similar approach, using $(MeO)_3SiCH_2CH_2Si(OMe)_3$ rather than **3**, we were able to prepare very readily the related structure **6** containing *two* spiro sites. Although compounds **5** and **6** did indeed constitute representatives of the previously unknown alkoxy-functional 1,2,5-oxadisilacyclopentanes, it was of interest to attempt the synthesis of simpler examples bearing monodentate silicon ligands. With this objective, **3** was subjected to alkaline pyrolysis which did indeed afford good yields of **7** *via* alkoxy–siloxy redistribution as well as the expected by-product **8**. This type of synthesis is fairly general if the alkoxy ligand is selected with due regard for favorable volatility relationships among the species to be expected at equilibrium. Thus, **9** can be prepared in good yield *via* the reaction shown since it is the most volatile species

(1) (a) W. A. Piccoli, G. C. Haberland, and R. L. Merker, *J. Amer. Chem. Soc.*, **82**, 1883 (1960); (b) R. L. Merker and M. J. Scott, *J. Polym. Sci.*, **43**, 297 (1960).
(2) A. M. Polyakova, M. D. Suchkova, V. V. Korshak, and V. M. Vdovin, *Izv. Akad. Nauk. SSSR, Ser. Khim*, **7**, 1267 (1965).
(3) Information concerning the utility of such species may be found in U. S. Patent 3,427,338 (Feb 11, 1969) (C. L. Frye). Subsequent to the completion of our work, related acetoxy-substituted examples were disclosed in U. S. Patent 3,338,951 (Aug 29, 1967) (E. W. Khaub).