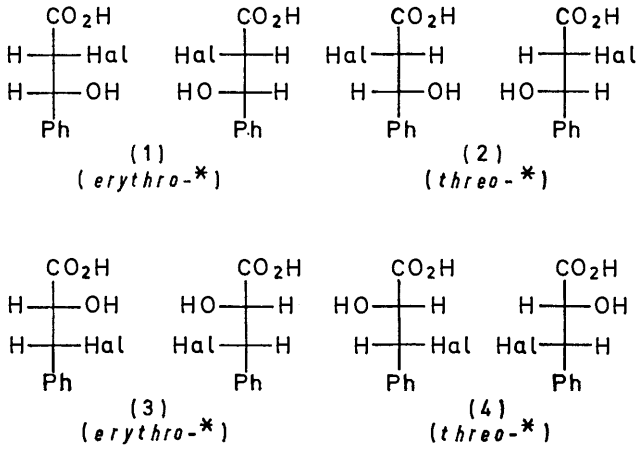
The Kinetics and Mechanisms of Additions to Olefinic Substances. Part X.[1] Stereochemistry of the Chloro- and Bromo-hydrins derived from Cinnamic Acid, and of Some Derivatives Thereof

By **Peter B. D. de la Mare** * and **Michael A. Wilson**, Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand

The racemic chlorohydrins and bromohydrins derived from cinnamic acid, together with their methyl esters, the acetates thereof, and the derived epoxides, have been prepared by routes which, when associated with their physical and chemical properties, establish their structures, including their stereochemistry. The results allow correction of some assignments of structure given in the literature.

THE addition of hypochlorous or hypobromous acid to *trans*-cinnamic acid could in principle give one, or any mixture, of four racemic chloro- or bromo-hydrins represented by the projection formulae (1)—(4).



* We follow here the convention used by others in this Journal [2] and elsewhere in describing such diastereoisomeric pairs as (1) and (2) or (3) and (4) as *erythro*- and *threo*-isomers respectively.

Derivatives of both (1) and (2) are obtained when methyl *trans*-cinnamate reacts with chlorine in acetic acid. Neither of the corresponding isomers derived from (3) or (4) has been detected in reaction mixtures from such chlorinations; this is understandable, since the polarisation, $Ph\text{–}CH{=}\overrightarrow{CH}\text{–}CO_2R$, will favour the observed orientation of addition.

Recently we have undertaken studies of the mechanisms of chlorination by other donors of electrophilic chlorine, including chlorine acetate, as has been described in a brief communication.[3] It seemed desirable to provide evidence for reactions involving these reagents that all the isomers were fully identified and could be distinguished in reaction mixtures. Not all the related chlorohydrins have previously been reported as far as we know; and, although all the related bromohydrins have been described, their stereochemistry seems not to have been revised on the basis of mechanistic considerations and therefore is not correctly described. Further, only one of the geometrically isomeric 2,3-epoxy-3-phenylglyceric acids seems to have been characterised. The results reported below allow us to put the stereochemistry of all these compounds on a firm basis.

EXPERIMENTAL

Methyl esters were prepared by heating the acid with excess of methanol and sulphuric acid at reflux temperature for up to 12 h; standard procedures for work-up followed. Acetyl derivatives were prepared by dissolving the methyl esters in acetic anhydride containing pyridine; the reaction mixture was usually allowed to stand overnight at room temperature, and was then poured into water, and extracted with ether. The ether extract was washed and dried ($MgSO_4$). Removal of the solvent was often followed by chromatography on silica gel (Riedel de Haen).

Spectra were recorded by using a Varian T60 spectrometer (^1H n.m.r.) or a Perkin-Elmer 237 spectrometer (i.r.). Mass spectra were recorded by Dr. R. Hodges (Massey University, Palmerston North) and microanalyses are by Dr. A. D. Campbell and his staff (University of Otago, Dunedin). All the compounds described herein are racemic mixtures of enantiomorphs.

erythro-2-*Chloro*-3-*hydroxy*-3-*phenylpropanoic Acid* (1; Hal = Cl), *and its Derivatives*.—The acid was prepared by Forster and Saville's method [4] from sodium *trans*-cinnamate and hypochlorous acid. The resulting solution was then extracted with ether, and the extract was dried ($MgSO_4$). Removal of solvent then gave an oil which slowly crystallised and was recrystallised from chloroform–n-hexane. The resulting acid had m.p. 96 °C; on being allowed to stand in a desiccator (H_2SO_4), the m.p. rose to 102—104 °C (lit.,[4] two forms, m.p. 96 °C and 104 °C; a hydrate has been reported also [4]) (Found: C, 54·1; H, 4·4; Cl, 17·9. Calc. for $C_9H_9ClO_3$; C, 53·9; H, 4·5; Cl, 17·7%), τ ($CDCl_3$) 5·65 (1H, d, *J* 8·0 Hz), 5·00 (1H, d, *J* 8·0 Hz), 3·25 (s, exch. D_2O, CO_2H) and 2·65 (5H, s, ArH), *m/e* 202, 200, 107, 79, and 77. Esterification of the above acid gave a colourless oil which slowly crystallised to give *methyl* erythro-2-*chloro*-3-*hydroxy*-3-*phenylpropanoate*, m.p. 55—56 °C (Found: C, 56·0; H, 5·2. $C_{10}H_{11}ClO_3$ requires C, 56·0; H, 5·2%), τ ($CDCl_3$) 6·25 (3H, s, Me), 5·8 (1H, s, exch. D_2O, OH), 5·6 (1H, d, *J* 8·0 Hz) 5·0 (1H, d, *J* 8·0 Hz) and 2·65

[1] Part IX, P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 1963, 3429.
[2] M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 565.
[3] P. B. D. de la Mare, C. J. O'Connor, M. J. Rosser, and M. A. Wilson, *Chem. Comm.*, 1970, 731.
[4] M. D. Forster and W. B. Saville, *J. Chem. Soc.*, 1922, **121**, 2595; L. Smith, *Z. phys. Chem.*, 1913, **81**, 371.

(5H, s, ArH), $\nu_{max.}$ 1170, 1290, 1440, 1750 (C=O), 3480 (OH), and 3570 cm^{-1}.

Acetylation of the above ester, followed by chromatography on silica gel, diethyl ether (10%)–n-hexane being used as eluant, gave pure *methyl* erythro-3-*acetoxy*-2-*chloro*-3-*phenylpropanoate* as an oil, τ ($CDCl_3$) 7·95 (3H, s, OAc), 6·2 (3H, s, OMe), 5·4 (1H, d, *J* 8·05 Hz), 3·9 (1H, d, *J* 8·05 Hz), and 2·6 (5H, s, ArH), *m/e* 258, 256, 227, 225, 220, 178, 165, 149·0599 ($C_9H_9O_2^+$ requires 149·0603), and 107 (Found: C, 56·3; H, 5·0; Cl, 13·5. $C_{12}H_{13}ClO_4$ requires C, 56·2; H, 5·1; Cl, 13·8%).

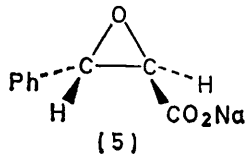
erythro-2-*Bromo*-3-*hydroxy*-3-*phenylpropanoic Acid* (1; Hal = Br).—This acid was prepared from *trans*-cinnamic acid *via* the corresponding dibromide.[5,6] It had m.p. 125 °C (lit.,[6] 125 °C), τ (CD_3·CO·CD_3) 5·65 (1H, d, *J* 9·2 Hz), 5·0 (1H, d, *J* 9·2 Hz), and 2·8—2·5 (5H, m, ArH) *m/e* 246, 244, and 107.

threo-2-*Chloro*-3-*hydroxy*-3-*phenylpropanoic Acid* (2; Hal = Cl) *and its Derivatives*.—To an ice-cold solution (100 ml) of *cis*-cinnamic acid (4·3 g), prepared by Stoermer's method,[7] in aqueous sodium hydroxide (1·15 g in 35 ml) and anhydrous sodium carbonate (3·1 g) was added a saturated cold solution of chlorine in aqueous sodium carbonate (57 ml, 0·5M). The mixture was allowed to stand for 30 min at 0 °C; it was then neutralised and extracted with n-hexane. The aqueous mixture was then extracted repeatedly with diethyl ether; the ether extract was dried, and the solvent was removed to give a yellow oil which solidified on cooling. Its ^1H n.m.r. spectrum showed that it contained approximately equal amounts of each of the diastereoisomeric 2-chloro-3-hydroxy-3-phenylpropanoic acids. Repeated chromatography gave threo-2-*chloro*-3-*hydroxy*-3-*phenylpropanoic acid monohydrate*, m.p. 72—75 °C (Found: C, 49·8; H, 5·2. $C_9H_{11}ClO_4$ requires C, 49·5; H, 5·1%). On being dried at 100 °C to constant weight, or by heating at 75 °C, or by crystallisation from n-hexane–chloroform, the *acid*, m.p. 103 °C, was obtained (Found: C, 54·0; H, 4·7%), τ (CD_3·CO·CD_3) 5·45 (1H, d, *J* 6·0 Hz), 4·75 (1H, d, *J* 6·0 Hz), 4·6 (s, exch. D_2O, OH), and 2·4—2·7 (5H, m, ArH); its mass spectrum had peaks as found for its *erythro*-isomer.

Its crude methyl ester had τ ($CDCl_3$) 7·3 (s, exch. D_2O, OH), 6·3 (3H, s, OMe), 5·55 (1H, d, *J* 6·2 Hz), 4·9 (1H, d, *J* 6·2 Hz), and 2·65 (5H, s, ArH); this was acetylated to give *methyl* threo-3-*acetoxy*-2-*chloro*-3-*phenylpropanoate* as an oil, τ ($CDCl_3$) 7·9 (3H, s, OAc), 6·4 (3H, s, OMe), 5·4 (1H, d, *J* 7·6 Hz), 3·75 (1H, d, *J* 7·6 Hz), and 2·65 (5H, s, ArH); its mass spectrum had peaks as found for its *erythro*-isomer (Found: C, 56·4; H, 5·3; Cl, 13·5%).

threo-2-*Bromo*-3-*hydroxy*-3-*phenylpropanoic Acid* (2; Hal = Br).—This acid was prepared from *cis*-cinnamic acid by reaction with bromine in aqueous sodium carbonate. Chromatography of the crude product (which contained also *ca.* 25% of the *erythro*-diastereoisomer) on silica gel, eluting first with n-hexane and then with n-hexane containing 10% diethyl ether, gave the acid as plates, m.p. 65 °C (lit.,[6] 69 °C), τ 5·6 (1H, d, *J* 6·2 Hz), 4·95 (1H, d, *J* 6·2 Hz), 3·9 (s, exch. D_2O, OH), and 2·7 (5H, s, ArH); its mass spectrum had peaks as found for its *erythro*-isomer.

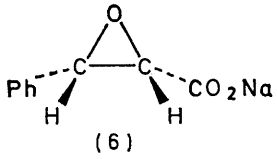
erythro-3-*Chloro*-2-*hydroxy*-3-*phenylpropanoic Acid* (3; Hal = Cl), *and its Derivatives*.—Sodium *trans*-2,3-epoxy-3-phenylpropanoate (5, and its enantiomorph) was prepared from the bromohydrin (1; Hal = Br),[8] or from the



(5)

chlorohydrin (1; Hal = Cl). It was freed from sodium halide by crystallisation from aqueous acetone and had τ (D_2O) 6·45 (1H, d, *J* 2·3 Hz), 6·0 (1H, d, *J* 2·3 Hz), and 2·6 (5H, s, ArH). This salt, or its mixture with sodium chloride as obtained directly from the reaction, was covered with dry diethyl ether, and dry hydrogen chloride was passed through the solution for 30 min. The mixture was allowed to stand overnight; evaporation of the solvent left a pale yellow oil which crystallised slowly, and was then recrystallised from chloroform to give (3; Hal = Cl) as needles, m.p. 144 °C (lit.,[9] 141—142 °C), τ (CD_3·CO·CD_3) 5·4 (1H, d, *J* 6·2 Hz), 4·7 (1H, d, *J* 6·2 Hz), 4·2 (s, exch. D_2O, OH), and 2·8—2·3 (5H, m, ArH), *m/e* 202, 200·0238 ($C_6H_9{}^{35}ClO_3^+$ requires 200·0240), 184, 182, 127, and 125·0158 ($C_7H_6{}^{35}Cl^+$, *i.e.* $C_9H_9{}^{35}ClO_3 - C_2H_3O_3$, metastable by defocusing technique) (Found: C, 54·1; H, 4·6; Cl, 18·3%). The acid was esterified to give the crude methyl ester, τ ($CDCl_3$) 7·1 (1H, s, exch. D_2O, OH), 6·35 (3H, s, OMe), 5·40 (1H, d, *J* 4·6 Hz), 4·9 (1H, d, *J* 4·6 Hz), and 2·75 (5H, s, ArH), *m/e* 216, 214, 198, 196, 127, and 125. Acetylation of the methyl ester gave *methyl* erythro-2-*acetoxy*-3-*chloro*-3-*phenylpropanoate* which crystallised from n-hexane as needles. As first prepared, it had m.p. 69 °C; after being allowed to stand, it appeared to melt over a range 69—83 °C. The ^1H n.m.r. spectrum was unchanged and showed no sign of any impurity; t.l.c. confirmed this. Rapid cooling of the melt by rubbing it between two plates gave materials melting at 69 °C (Found: C, 56·3; H, 5·3; Cl, 13·8), τ ($CDCl_3$) 7·95 (3H, s, OAc), 6·3 (3H, s, OMe), 4·75 (1H, d, *J* 6·0 Hz), 4·5 (1H, d, *J* 6·0 Hz), and 2·7 (5H, m, ArH), *m/e* 258 (very weak), 256 (very weak), 227, 225, 198, 196, 167, 165, 162, 131, 127, and 125.

erythro-3-*Bromo*-2-*hydroxy*-3-*phenylpropanoic Acid* (3; Hal = Br).—This was prepared in a manner similar to that used for its chloro-analogue by allowing sodium *trans*-2,3-epoxy-3-phenylpropanoate (5) to react with hydrogen bromide. It had m.p. 143 °C (lit.,[6] 165 °C; this discrepancy is discussed later), τ (CD_3·CO·CD_3) 5·3 (1H, d, *J* 6·0 Hz), 4·65 (1H, d, *J* 6·0 Hz), and 2·8—2·3 (5H, m, ArH), *m/e* 246, 244, 171, 169, 165, 120, and 91 (Found: C, 43·8; H, 3·8. Calc. for $C_9H_9BrO_3$: C, 44·1; H, 3·7%).



(6)

threo-3-*Chloro*-2-*hydroxy*-3-*phenylpropanoic Acid* (4; Hal = Cl) *and its Derivatives*.—Sodium *cis*-2,3-epoxy-3-phenylpropanoate (6, and its enantiomorph) was pre-

[5] J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, 1903, **83**, 666.
[6] E. Berner and C. N. Riiber, *Ber.*, 1921, **54**, 1945.
[7] R. Stoermer, *Ber.*, 1909, **42**, 4865.
[8] W. Dieckmann, *Ber.*, 1910, **43**, 1035.
[9] E. Erlenmeyer, jun., *Annalen*, 1892, **271**, 150.

pared from (2; Hal = Br or Cl) by dissolving it in water and treating it with two molecular proportions of alkali. It had τ (D_2O) 6·1 (1H, d, *J* 5·1 Hz), 5·7 (1H, d, *J* 5·1 Hz), and 2·55 (5H, s, ArH). A sample free from sodium halide was obtained by crystallisation from methanol–acetone. This was converted into the required threo-3-*chloro*-2-*hydroxy*-3-*phenylpropanoic acid*, m.p. 153 °C, by treatment with dry hydrogen chloride in ether, as described above for the *erythro*-isomer (Found: C, 53·4; H, 4·5%), τ (CD_3·CO·CD_3) 5·45 (1H, d, *J* 2·6 Hz), 4·6 (1H, d, *J* 2·6 Hz), 3·5 (s, OH), and 2·75—2·3 (5H, m, ArH), *m/e* 202, 200, 184, 182, 127, 125, 120, and 91. This acid was methylated and acetylated to give *methyl* threo-2-*acetoxy*-3-*chloro*-3-*phenylpropanoate* as an oil (Found: C, 56·1; H, 5·4; Cl, 13·6%), τ ($CDCl_3$) 7·85 (3H, s, OAc), 6·3 (3H, s, OMe), 4·6 (1H, d, *J* 4·0 Hz), 4·55 (1H, d, *J* 4·0 Hz), and 2·65 (5H, m, ArH); its mass spectrum had peaks as found for its *erythro*-isomer.

threo-3-*Bromo*-2-*hydroxy*-3-*phenylpropanoic Acid*.—This acid, which Berner and Riiber [6] obtained from 3-phenylglyceric acid of m.p. 122 °C, was prepared from sodium *cis*-2,3-epoxy-3-phenylpropanoate (6, and its enantiomorph) by treatment with hydrogen bromide in dry ether. It had m.p. 155 °C (lit.,[6] 157 °C), τ (CD_3·CO·CD_3) 5·5 (1H, d, *J* 3·2 Hz), 4·65 (s, OH), 4·5 (1H, d, *J* 3·2 Hz), and 2·75—2·2 (5H, m, ArH); its mass spectrum had peaks as for its *erythro*-isomer.

erythro-2,3-*Dichloro*-3-*phenylpropanoic Acid*. Chlorination of cinnamic acid in chloroform gave a crude product whose ^1H n.m.r. spectrum was consistent with the presence of the *threo*- and *erythro*-dichlorides in the ratio *ca.* 4 : 3. The *erythro*-isomer crystallised slowly from the dark brown oily product, and on recrystallisation from chloroform–n-hexane had m.p. 168 °C (lit.,[10,11] 167—168°), τ ($CDCl_3$) 5·35 (1H, d, *J* 10·8 Hz,), 4·8 (1H, d, *J* 10·8 Hz), and 2·6 (5H, ArH). This acid (0·5 g) was heated with water (50 ml) at reflux temperatures for 2 h. The ^1H n.m.r. spectrum of the product showed that it contained a mixture of *erythro*- and *threo*-2-chloro-3-hydroxy-3-phenylpropanoic acids in the ratio 65 : 35.

The corresponding *threo*-dichloride, obtained by chlorinating cinnamic acid in carbon tetrachloride, had τ ($CDCl_3$) 5·3 (1H, d, *J* 8·0 Hz), 4·65 (1H, d, *J* 8·0 Hz), and 2·65 (5H, s, ArH). On hydrolysis with water, the initial products decomposed under the conditions of reaction to give products of elimination and decarboxylation.

DISCUSSION

The courses taken in the reactions described above are those which would be expected from what is known or expected concerning the chemical and stereochemical selectivity of the reactions. Thus *trans*-cinnamic acid gives the *erythro*-, and *cis*-cinnamic acid mainly the *threo*-2-bromo-3-hydroxy-adduct by *trans*-addition of hypobromous acid.[6] The same *erythro*-bromohydrin can be obtained by hydrolysis of the corresponding *erythro*-dibromide with water;[5,6] retention of configuration would be expected in an S_N1 solvolysis of this compound by virtue of the presence of the adjacent bromine substituent.[12] Treatment of the *erythro*-bromohydrin with alkali gives the sodium salt of the well known [8] *trans*-2,3-epoxy-3-phenylpropanoic acid [*trans*-3-phenylglycidic acid; (5), and its enantiomorph] by the expected stereospecific intramolecular S_N2 displacement of Br^- by O^-. The *threo*-bromohydrin similarly gives the sodium salt of the hitherto unreported *cis*-2,3-epoxy-3-phenylpropanoic acid (6, and its enantiomorph). The isomeric glycidic acids are converted by HCl or HBr into the expected 3-halogeno-2-hydroxy-3-phenylpropanoic acids. Ring-opening was in the direction of that expected by virtue of the influence of the activating phenyl substituent, and stereochemically occurred predominantly in the *trans*-sense, but with both epoxides a small proportion of the product of ring-opening in the *cis*-sense was detected also; from the *trans*-epoxide, the crude product of reaction with HCl contained *ca.* 75%, and with HBr *ca.* 85% of the stereochemically preferred halogenohydrin.

Chlorinations of *trans*- and of *cis*-cinnamic acid, whether with hypochlorous acid or with chlorine, give mixtures of the diastereoisomeric adducts, and the hydrolysis of the dichloride also gives a mixture of chlorohydrins, the neighbouring chlorine substituent providing (as expected [12]) less stereochemical control than is exerted by bromine over the course of replacement. The assignments of configuration to the individual products are made certain by the inter-relation of both the *erythro*-halogenohydrins with *trans*-2,3-epoxy-3-phenylpropanoic acid, and of both the *threo*-halogenohydrins with *cis*-2,3-epoxy-3-phenylpropanoic acid. The structures of these central reference compounds, isolated only as the sodium salts, are, in our view, firmly established by the fact that they have characteristic different ^1H n.m.r. spectra with coupling constants between the 2- and 3-protons of 2·3 (*trans*-isomer) and 5·1 Hz (*cis*-isomer). The corresponding coupling constants in styrene oxide [13] are respectively 2·4 and 4·1 Hz, and establish the expectation that the coupling constant for the *cis*- be higher than that for the *trans*-isomer, as appears to be general for ethylene oxide and its derivatives.[14]

That the solvolysis of the dichlorides of cinnamic acid gives mixtures of chlorohydrins establishes also that the carboxylic acid group is not able very effectively to hold the configuration at the adjacent carbon atom, as has been deduced also by Streitwieser [15] from consideration of rates of solvolysis.

Proof (if this were needed) that we have correctly assigned compounds to the 2-halogeno- and 3-halogeno-series respectively comes from the patterns of decomposition in the mass spectrometer. All the 3-halogeno-2-hydroxy-3-phenylpropanoic acids and their derivatives give $C_7H_6Cl^+$ or $C_7H_6Br^+$ fragments characteristic of

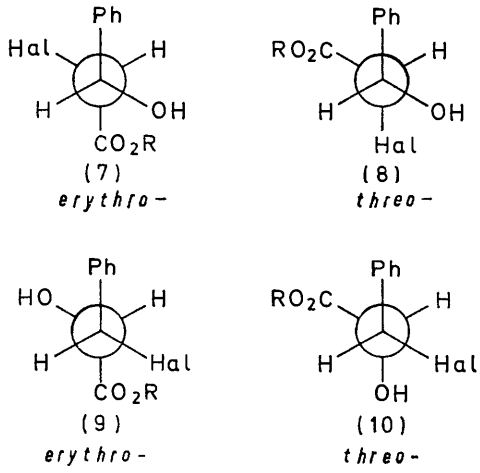
[10] C. Leibermann and H. Finkenbeiner, *Ber.*, 1895, **28**, 2235.
[11] M. D. Johnson, M. C. Cabaleiro, B. E. Swedlund, and J. G. Williams, *J. Chem. Soc.* (*B*), 1968, 1022.
[12] S. Winstein, *Bull. Soc. chim. France*, 1951, c55.
[13] D. D. Elleman and S. L. Manatt, *J. Mol. Spectroscopy*, 1962, **9**, 477; C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, 1960, **32**, 1378.
[14] D. D. Elleman, S. L. Manatt, and C. D. Pearce, *J. Chem. Phys.*, 1965, **42**, 650.
[15] A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 571.

the halogenotropylium ion, as is expected;[16] whereas all the 2-halogeno-3-hydroxy-3-phenylpropanoic acids and their derivatives give $C_7H_7O^+$ fragments characteristic of the hydroxytropylium ion. This provides a sensitive method of detecting small proportions of orientational isomers in reaction mixtures.

Within each series, we regard our assignments of configuration to be based on the inter-relations between the 2,3-epoxy-3-phenylpropanoic acids, formed from the halogenohydrins of either series by stereospecific antiperiplanar intramolecular displacement of halogen by O^-, and converted by hydrogen halides with incomplete stereospecificity into the 3-halogeno-2-hydroxy-3-phenylpropanoic acids. The stereochemistry of the well known *trans*-epoxide and of the hitherto unreported *cis*-epoxide is established clearly by the ^1H n.m.r. spectra, as we have noted above.

The ^1H n.m.r. spectra of the halogenohydrins are consistent with these assignments; uniformly the coupling constant $J_{2.3}$ is higher for the *erythro*- than for the corresponding *threo*-isomer. Such coupling constants have been discussed extensively; for the generalised case, with groups identifiable respectively as large and small on each carbon atom, Jackman and Sternhell[17] have argued that in the absence of factors other than those attributable directly to steric hindrance, the *erythro*- will have a larger coupling than the *threo*-isomer. Some exceptions have been noted;[18,19] and extension of the above generalisation to the methyl 3-acetoxy-2-chloropropionates (this paper and ref. 20) would probably be uncertain in the absence of other proof, since among the 2,3-disubstituted butanes[21] the *meso*- has a larger $J_{2.3}$ coupling constant than the (±)-isomer in the dibromo-, dichloro-, and diphenyl derivatives, but not in the case of the diacetoxy-derivative.

The force of any definite structural assignment by way of this difference in coupling constants is made weaker in our series also by the fact that if the halogen is changed from chlorine to the considerably larger bromine, the difference between the coupling constants characteristic of the *erythro*- and *threo*-isomers respectively is maintained. The results, however, indicate that of the conformations (7)—(10) expected to have high 2,3-coupling constants, (7) must be important for the *erythro*-2-halogeno-3-hydroxy-3-phenylpropanoic acids and their esters and acetates; (8) and (9) are of some, but not dominant, importance for the corresponding *threo*-isomers and for the *erythro*-3-halogeno-2-hydroxy-3-phenylpropanoic acids and their esters and acetates; and (10) is unimportant for the *threo*-3-halogeno-2-hydroxy-3-phenylpropanoic acids and their esters. It seems possible that the dominance of (7) in the appropriate conformational equilibrium may result, as in other cases cited,[19] from the help given by intramolecular attractions between CO_2R and OH or O·COR groups, favouring situations in which these groups are adjacent.



The m.p.s which we have recorded for the bromohydroxy-3-phenylpropanoic acids agree with Berner and Riiber's[6] description, except for the m.p. of the *erythro*-3-bromo-isomer; our sample melted at the lower temperature recorded by Berner and Riiber for the resolved compound rather than that recorded for the racemic mixture. It seems quite possible that the latter compound can be obtained in two crystalline forms of different m.p. Our assignments of stereochemistry are, of course, the reverse of those made by the earlier workers, essentially because they were considering that additions of bromine or of hypobromous acid occur in the *cis*-sense.

Our descriptions of the two known chlorohydroxy-3-phenylpropanoic acids also agree with those in the literature.[4,9] Johnson and his co-workers[2,11] had correctly assigned the stereochemistry of one of these by use of conformational analysis of the corresponding methyl-3-acetoxy-2-chloropropanoates known to be obtainable from the corresponding acid. All of these chlorohydrins tend to be hygroscopic and to crystallise as more or less definite hydrated forms.

[2/2110 *Received*, 7*th September*, 1972]

[16] F. W. McLafferty, 'Interpretation of Mass Spectra,' W. A. Benjamin, New York, 1967, p. 92.
[17] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon, London, 1969, p. 291 *et seq.*
[18] C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, 1966, **31**, 1000.
[19] J. C. Randall, R. L. Vaulx, M. E. Hobbs, and C. R. Hauser, *J. Org. Chem.*, 1965, **30**, 2035.
[20] M. D. Johnson and E. N. Trachtenberg, *J. Chem. Soc.* (*B*), 1968, 1018.
[21] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1962, **84**, 743.