from lack of time) of a number of bivalent metal acetates in aqueous solution.

Experimental

Barium acetate of analytical reagent quality was made into a stock solution which was analyzed by evaporating suitable portions with excess sulfuric acid and weighing the dry barium sulfate. Magnesium acetate was prepared by dissolving the calculated amount of pure MgO (calcined at 900°) in an acetic acid solution of known concentration. These solutions were equilibrated against sodium chloride solutions in an isopiestic vapor pressure apparatus of the usual pattern.[1] The molalities of the pairs of isopiestic solutions are given in Table I. Table II gives the molal-scale osmotic coefficients $\phi = -55.51/3m \ln (p/p_0)$ and activity coefficients γ. There is some difficulty in estimating the value to be assigned to γ at 0.1 m owing to the form of the osmotic coefficient curves; ϕ evidently has a minimum somewhere below the experimental range and then turns sharply upward to reach the value unity at zero concentration. The value $\gamma_{0.1m} = 0.450$ has been rather arbitrarily assigned to both salts from a comparison with some other 2:1 electrolytes; the remaining values are correct relative to these, but the absolute values could well be as much as 5% different.

TABLE I

MOLALITIES OF ISOPIESTIC SOLUTIONS AT 25°

m_1 = molality of acetate solution, m_2 = molality of sodium chloride solution

m_1	m_2	m_1	m_2	m_1	m_2
		Barium acetate			
0.1073	0.1384	0.6496	0.8926	1.870	2.454
.1510	.1964	1.087	1.493	2.062	2.649
.1902	.2500	1.283	1.755	2.822	3.332
.2593	.3434	1.464	1.973	3.474	3.812
.5045	.6880	1.667	2.220		
		Magnesium acetate			
0.1431	0.1847	0.8053	1.337	2.205	3.173
.2013	.2597	.9605	1.355	2.748	3.994
.2503	.3245	1.053	1.443	3.300	4.794
.3799	.4930	1.259	1.740	4.149	5.984
.4286	.5588	1.728	2.439		

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF BARIUM AND MAGNESIUM ACETATES AT 25°

	$\mathrm{Ba\overline{Ac}_2}$		$\mathrm{Mg\overline{Ac}_2}$	
m	ϕ	γ	ϕ	γ
0.1	0.800	(0.450)	(0.797)	(0.450)
.2	.807	.395	.793	.389
.3	.817	.370	.795	.359
.5	.841	.347	.807	.328
.7	.857	.335	.826	.314
1.0	.873	.325	.861	.307
1.2	.881	.320	.886	.308
1.4	.884	.315	.910	.310
1.6	.885	.311	.935	.315
1.8	.884	.306	.961	.321
2.0	.878	.301	.987	.329
2.5	.856	.286	1.049	.351
3.0	.832	.271	1.109	.378
3.5	.804	.256	1.159	.406
4.0			1.207	.436

The relative positions of the osmotic coefficient curves are noteworthy. At low concentrations that for barium acetate is slightly the higher, in contrast to the nitrates and halides where the magnesium salts have the higher osmotic coefficients. A similar reversal has been remarked with the alkali metal acetates.[2] Potassium acetate for example, has a higher osmotic coefficient than lithium acetate, though that of potassium chloride is lower than that of lithium chloride. This effect has been tentatively explained by Robinson and Harned[2] in terms of a "localized hydrolysis" resulting from interaction of a proton from the hydration sheath of the Li^+ ion with the acetate ion, the effect being most marked with the most strongly hydrated cation. A similar effect would appear to be operating in the present case. Above 1 M however the position is different; the osmotic coefficient of magnesium acetate continues to rise, while that of barium acetate passes through a maximum. It seems likely that here we have the effect of Bjerrum ion association dominating the osmotic coefficients; the heavily hydrated magnesium ion is larger than the less hydrated barium ion, and hence shows less tendency to form ion pairs. The behavior of these two salts thus provides a striking example of the complexities which may be encountered in moderately concentrated electrolytes, and which can be qualitatively explained by considerations of ion–ion and ion–solvent interactions.

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[1] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[2] R. A. Robinson and H. S. Harned, *Chem. Revs.*, **28**, 454 (1941).

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The Configurations of the 3-Bromocyclohexanecarboxylic Acids[1]

BY SAMUEL SIEGEL[2] AND JEROME G. MORSE

RECEIVED DECEMBER 3, 1952

The configurations of the 3-bromocyclohexanecarboxylic acids were originally assigned by Perkin[3] on the basis of their mode of formation. The reaction of the lactone I with aqueous hydrobromic acid at room temperature yields a bromo acid, m.p. 65°, which was named *cis*-3-bromocyclohexanecarboxylic acid. Either *cis*- or *trans*-3-hydroxycyclohexanecarboxylic acid (III and IV) reacts with aqueous hydrobromic acid at 100° to yield a mixture from which a higher melting acid, m.p. 167–168°, is isolated and is labeled *trans*.[3] However, current theory suggests that these conversions are displacement reactions which proceed with the inversion of the configuration of the carbon atom under attack, although inversion may be accompanied by varying degrees of racemization.[4] Consequently the designated configurations of the 3-bromo acids are probably inverted. The more probable configurational relationships are diagrammed below.

Furthermore, a neutralized alcoholic solution of the bromo acid, m.p. 67–68°, decomposes in a few minutes at the reflux temperature to yield the lactone I, whereas the higher melting acid is stable under the same conditions.[5] Only the latter acid forms a stable benzylammonium salt. These phenomena clearly demonstrate the participation of the carboxylate group in the decomposition of the salt of the lower melting bromo acid and therefore, in this acid, the carboxylate group must be *trans* to the bromo group, a configuration which permits the carboxylate group to displace the latter in a

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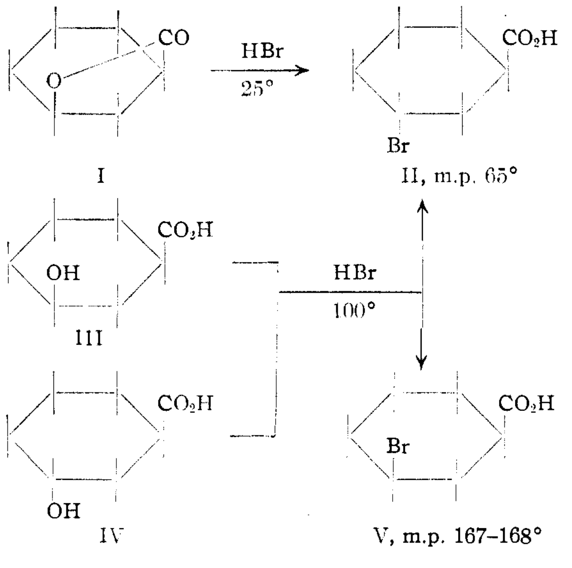
[1] Presented at the Southwestern Regional Meeting of the American Chemical Society, December, 1951.

[2] University of Arkansas, Fayetteville, Arkansas.

[3] W. H. Perkin, Jr., and G. Tattersall, *J. Chem. Soc.*, 482 (1907).

[4] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

[5] E. J. Boorman and R. P. Linstead, *ibid.*, 258 (1935).



one-stage process.[6] A comparison of the acidic dissociation constants of the bromo acids with the constants of the related hydroxy acids and the cyclohexanedicarboxylic acids provide further evidence of configuration. Clearly, dissociation constants reflect the relative orientation of the polar groups and the distance which separates them in a molecule.[7] Since the polarity of the bromo, the hydroxyl and the carboxylic acid groups is in the same direction (electron withdrawal from carbon) the relative acidities of *cis* and *trans* isomers should be in the same order.

The relative acidities (compared with cyclohexanecarboxylic acid) of the 3- and 4-substituted cyclohexanecarboxylic acids are given in Table I.[8] The configuration of the hydroxyacids[5,9] and the dicarboxylic[10,11] acids are well established. Apparently a *trans* 4-substituted acid is stronger than its isomer, a *cis* 4-substituted acid, whereas in the 3-series the *cis* acid is the stronger.

TABLE I

RATIO OF THE DISSOCIATION CONSTANTS ($K_{A_xB_0}$) OF SUBSTITUTED CYCLOHEXANECARBOXYLIC ACIDS

		$K_{A_xB_0}$			
Substituent	Solvent	*cis*-1,3	*trans*-1,3	*cis*-1,4	*trans*-1,4
CO_2H[a]	Water	4.3	2.8	2.4	3.6
OH[b]	Water	2.00	1.22	1.17	1.68
	Methanol	1.84	0.89	0.83	1.63
	Ethanol	1.82	0.92	0.87	1.44
Br	Methanol	2.47	<1.8	...	...
	Ethanol	2.71	<2.5	...	...

[a] R. Kuhn and H. Wasserman (*Helv. Chim. Acta*, 11, 50 (1928)) reports the dissociation constants of the acids. $K_{A_xB_0}$ was obtained by dividing them by 1.96×10^{-5}, K for cyclohexanecarboxylic acid in water at 25°, at an ionic strength of 0.1 (mainly sodium chloride). [b] Measurements to be reported by M. Kilpatrick and J. G. Morse.

This result is understandable in terms of current concepts of the stereochemistry of substituted cyclohexanes.[12,13] Thus the stronger acid for each pair is that isomer which can have both groups in the "equatorial" positions, *e.g.*, the 1,3-*cis* and 1,4-*trans*. And although the center of the dipole of a "polar" substituent is closer than that of an "equatorial" substituent to the ionizable proton of an "equatorially" placed carboxylic acid group, the orientation of the "polar" dipole is less favorable for the detachment of the proton. And the orientation factor is dominant here.

The substituted cyclohexanecarboxylic acids under consideration are stronger acids than cyclohexanecarboxylic acid. The acidity of the higher melting 3-bromo acid (m.p. 167–168°) is greater by a factor of 2.47 in methanol. Because of the instability of the lower melting acid in hydroxylic solvents, only an upper limit (< 1.8 in methanol) can be placed upon its relative acidity but it is unquestionably a weaker acid than the higher melting bromo acid. These data are again consistent with the assignment of the *cis* configuration to the bromo acid, m.p. 167–168°, and the *trans* configuration to the lower melting isomer.

Experimental

Preparation of the Higher Melting Acid (m.p. 167–168°). —The isomeric 3-bromocyclohexanecarboxylic acids were prepared in the manner described by Boorman and Linstead.[5] After it was recrystallized from benzene it had the properties: m.p. 167–168°; neutralization equivalent weight, 207.1 (calcd. 207.1).

Preparation of the Lower Melting Isomer (m.p. 65°).[6]—The lower melting isomer, m.p. 65°, was obtained from the reaction, at room temperature, of the lactone of 3-hydroxycyclohexanecarboxylic acid with hydrogen bromide in an aqueous solution saturated at 0°. It was purified by recrystallization from petroleum ether, b.p. 60–80°; neutralization equivalent weight, 206.6 (calcd. 207.1).

The acid (90 mg.) decomposed when it was stirred with water (15 ml.) for three hours at room temperature. An analysis of the solution showed 0.44 milliequivalent of acid and 0.42 milliequivalent of halogen. This indicates that the decomposition products are largely the lactone and hydrogen bromide.

Benzylammonium Salt of *cis* 3-Bromocyclohexanecarboxylic Acid.—This salt was prepared by combining a solution of the bromo acid in anhydrous ether with an equivalent quantity of benzylamine also dissolved in ether. It was recrystallized from ethyl acetate and was obtained in the form of white needles, m.p. 125–126°. The bromo acid, m.p. 167–168°, was regenerated from the salt in an acidified aqueous solution. *Anal.*[14] Calcd. for $C_{14}H_{20}O_2NBr$: N, 4.46; Br, 25.4. Found: N, 4.28; Br, 25.7.

Dissociation Constants.—The dissociation constants of the bromo acids were measured by an e.m.f. method which has been described previously.[15] The acids were not measured in water because of the limited solubility in that solvent. However, anhydrous methanol and ethanol were satisfactory media. The dissociation constant of the higher melting isomer was measured accurately but the dissociation constant of the lower melting isomer is approximate because its ready solvolysis caused an apparent increase of acidity with time. Nevertheless, an upper limit for its acidity can be stated with confidence and an approximation of its true value was obtained by an extrapolation of the acidity of the solution to the zero time of mixing. The ionization con-

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[6] (a) P. D. Bartlett and P. N. Rylander, THIS JOURNAL, **73**, 4275 (1951); (b) D. W. Wujciak, R. L. Feller and J. F. Lane, *ibid.*, **73**, 2392 (1951).

[7] J. G. Kirkwood and F. A. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

[8] The 2-substituted acids are not included because of the probable occurrence of proximity effects.

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[10] S. Boeseken and A. E. J. Peek, *Rec. trav. chim.*, **44**, 841 (1925).

[11] W. H. Mills and G. H. Keats, *J. Chem. Soc.*, **147**, 1373 (1935).

[12] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[13] H. A. Smith and F. P. Byrne, *ibid.*, **72**, 4406 (1950).

[14] Elementary analysis was performed by the Micro-Tech Laboratory, Skokie, Illinois.

[15] J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 454 (1941).

stants relative to cyclohexanecarboxylic acid are given in Table I.

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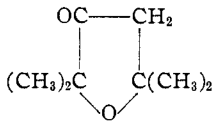
The Dehydration of 4-Hydroxy-2,2,4,5,5-pentamethyltetrahydrofuran (Acetylene Studies, Part VI)[1]

By Max Sulzbacher and Ernst D. Bergmann

Received January 26, 1953

When II, the product of the reaction between 4-keto-2,2,5,5-tetramethyltetrahydrofuran (I) and methylmagnesium iodide, is dehydrated, a compound of the expected composition $C_9H_{16}O$ is obtained. Apart from the normal formulas, III, IV, the structure V is possible for this compound. Indeed, V has been proposed by Bouveault and Locquin,[2] as the same substance is also formed by acid dehydration of 2,3,5-trimethylhexane-2,3,5-triol (VI).

The infrared spectrum of the dehydration product is compatible only with formula V. Whilst it does not show any sign of double bond absorption in the 1620–1700 cm.$^{-1}$ region, the following bands were observed: 980 cm.$^{-1}$ (optical density d = 0.6) cyclobutane[3]; 1099 cm.$^{-1}$ (d = 0.3) isopropyl; 1175 cm.$^{-1}$ (d = 0.8) superposition of the isopropyl and the tetrahydrofuran absorption.[4] The chemical properties of the compound $C_9H_{16}O$ are in accord with formula V. It could not be hydrogenated catalytically to 2,2,4,5,5-pentamethyltetrahydrofuran at ordinary temperature and pressure, and did not decolorize bromine in carbon tetrachloride.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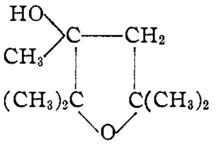
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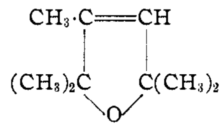
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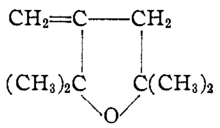
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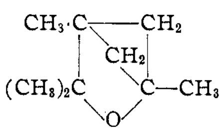
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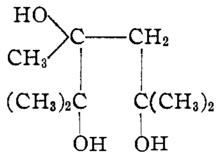
VI

Experimental

I was prepared in quantitative yield from 1,1,4,4-tetramethyl-2-butyne-1,4-diol and aqueous mercuric sulfate,[5-7] b.p. 150° (760 mm.).

4-Hydroxy-2,2,4,5,5-pentamethyltetrahydrofuran (II).—The reaction of I with 2 moles of methylmagnesium iodide[6] gave II in 63% yield; from diisopropyl ether, m.p. 77°.[8]

Dehydration to V.—The mixture of 80 g. of II and 100 g. of freshly fused and finely ground potassium hydrogen sulfate was heated for six hours at 120°. The liquid product was distilled directly, dried and fractionated; b.p. 132°, yield 68 g. (96%), $d^{27.5}_{4}$ 0.820 (literature 0.826).

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.4. Found: C, 77.0; H, 11.5.

The infrared spectrum was measured in the 950–1200 cm.$^{-1}$ region in carbon disulfide solution (0.015 g. plus 1 cc. of solvent), in the 1600–1700 cm.$^{-1}$ region in carbon tetrachloride (0.016 g. plus 1 cc. of solvent); cell thickness 0.5 mm.[9]

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[2] L. Bouveault and R. Locquin, *Ann. chim.*, [8] **21**, 414 (1910).

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[4] H. Tschamler and H. Voetter, *Monatsh.*, **83**, 302 (1952). See also G. M. Barrow and S. Searles, This Journal, **75**, 1175 (1953).

[5] G. Dupont, *Compt. rend.*, **152**, 1486 (1911).

[6] G. Dupont, *Ann. chim.*, [8] **30**, 536 (1913).

[7] H. Richet, *ibid.*, [12] **3**, 317 (1948).

[8] G. Dupont, *Compt. rend.*, **154**, 601 (1912).

[9] We are greatly indebted to Dr. S. Pinchas, Optics Department, Weizmann Institute of Science, Rehovoth, for the determination of the spectrum.

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cis- and *trans*-Tropine (Tropanol)[1]

By Pierre F. Smith[2] and Walter H. Hartung[3]

Received March 5, 1953

Recent papers establish the stereochemical structure of the tropine (tropanol) isomers,[4-6] namely, that in tropine the hydroxyl group and N-methyl bridge are *trans* and that in ψ-tropine they are *cis*. We now submit additional experimental evidence confirming these conclusions.

A study of models suggested that the structure with the –OH and >NCH$_3$ groups in close proximity might be expected, owing perhaps to hydrogen bonding, to exhibit greater pK values in aqueous solution and less change in pH upon titration. Our results, obtained from the titration of 20.00-ml. portions of 0.050 N solutions of the isomeric tropines (purified by sublimation *in vacuo*) with 0.0613 N hydrochloric acid, are summarized in Fig. 1. The pK values at 25°, as estimated from the half neutralization points, are 2.98 for tropine and 3.67 for ψ-tropine. The greater value for ψ-tropine is suggestive of intramolecular hydrogen bonding and therefore a configuration of the –OH *cis* to the >NCH$_3$ group.

Tropine, refluxed for ten minutes with benzoyl chloride in a 1:8 molar ratio, yielded 84.5% of tropine benzoate hydrochloride. ψ-Tropine, identically treated, yielded 79.2% of ψ-tropine benzoate hydrochloride. Regrettably limited amounts of materials did not permit further study of the reactivity of the –OH groups in the isomeric alcohols.

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[1] Experimental work performed at the University of Maryland.

[2] Rutgers University, Newark, N. J.

[3] University of North Carolina, Chapel Hill, N. C.

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