In the case of α-bromotetronic acid it appears that the bromine binds the electrons tightly enough to prevent inverse substitution, as indicated by the experiment with ferrous ions, but the carbon-bromine bond is sufficiently weak to permit rapid replacement of bromine with iodine.

It is interesting to note when a hydroxyl group[5] or an amino group[6,7] is attached to the α-carbon atom the compounds are good reducing agents. Thus we have the series

α-Iodotetronic acid—oxidizes iodide quantitatively
α-Bromotetronic acid—oxidizes iodide quantitatively. This is probably due to a rapid replacement of bromine by iodine
α-Chlorotetronic acid—oxidizes iodide only partially. This is probably due to a slow replacement of chlorine by iodine
Tetronic acid—does not oxidize iodide but reduces iodine to a slight extent forming α-iodotetronic acid
α-Hydroxytetronic acid—reduces iodine quantitatively
α-Aminotetronic acid—reduces iodine quantitatively

Summary

Ethyl α-iodoacetate and *sym*-iodoacetylacetone like α-iodotetronic acid oxidize iodide quantitatively to iodine, probably by inverse substitution. Ethyl α-iodoacetoacetate and α-iodotetronic acid oxidize ferrous to ferric ion, α-bromotetronic acid does not. Ethyl α-iodoacetoacetate contains 20% enol in the liquid state and 49% in absolute alcohol solution. α-Bromotetronic acid acts rapidly with bromine. The bromine titration method is not suitable for the accurate determination of the percentage of enol in the tetronic acids.

α-Chlorotetronic acid has been prepared. It does not oxidize iodide quantitatively to iodine. To account for the partial oxidation it is suggested that the iodide replaces chlorine to form some of the α-iodo compound which can oxidize iodide.

SAN FRANCISCO, CALIF. RECEIVED NOVEMBER 24, 1937

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[5] Micheel and Schulte, *Ann.*, **519**, 70 (1935).

[6] Wolff and Lüttringhaus, *ibid.*, **312**, 140 (1900).

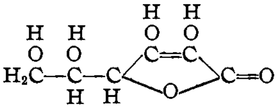
[7] Micheel and Mittag, *Z. physiol. Chem.*, **247**, 34 (1937).

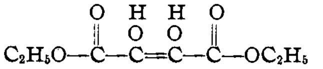
[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Dissociation Constants of Some Enols Related to *l*-Ascorbic Acid. Tetronic Acid, α-Chlorotetronic Acid, α-Bromotetronic Acid, α-Iodotetronic Acid, α-Hydroxytetronic Acid and Ethyl α-Iodoacetoacetate

BY W. D. KUMLER

l-Ascorbic acid has a *pKa* = 4.85 in alcohol-water solution and diethyl dihydroxymaleate has a *pKa* = 7.88 in the same solution.[1] These results are anomalous for the structure assigned to these compounds has nearly the same grouping about the ionizable hydrogen.





$\mathrm{C_2H_5O{-}C({=}O){-}C(OH){=}C(OH){-}C({=}O){-}OC_2H_5}$

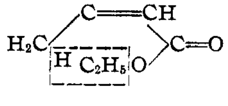
The work in this paper was undertaken to see whether or not other compounds containing the lactone ring found in *l*-ascorbic acid are strong acids and, if so, to investigate the cause of the high acid strength.

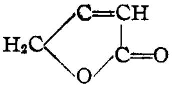
Five compounds containing this lactone ring were investigated. The hydrogen-ion concentrations of solutions of the partially neutralized acids were measured with a glass electrode and the dissociation constants were calculated. The results are given in Table I. The dissociation constant of ethyl α-iodoacetoacetate was measured. This and the dissociation constant for ethyl acetoacetate are included in the table.

TABLE I

	pKa	
α-Chlorotetronic acid	2.13 ± 0.013	
α-Bromotetronic acid	2.23 ± .005	
α-Iodotetronic acid	2.31 ± .005	
Tetronic acid	3.76 ± .003	
α-Hydroxytetronic acid	4.37 ± .02	
Ethyl α-iodoacetoacetate	7.0	
Ethyl acetoacetate	10.7	(Landolt–Börnstein)

If the formula for the ethyl acetoacetate molecule is written as follows, tetronic acid results when ethane is eliminated, and the oxygen of the ester group is attached to the methyl group.





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[1] Kumler and Daniels, THIS JOURNAL, **57**, 1929 (1935).

It is a very surprising fact that two molecules differing so little in structure should have dissociation constants differing by ten million fold.

We will consider the factors that affect acid strength to see if any of them can account for the ten million fold increase in the dissociation constant, which results from this ring closure. The negativity of substituted groups, or atoms, is a common factor influencing acid strength, but this factor cannot be the cause in this case, for no groups have been substituted, and the negative groups are the same in the two compounds.

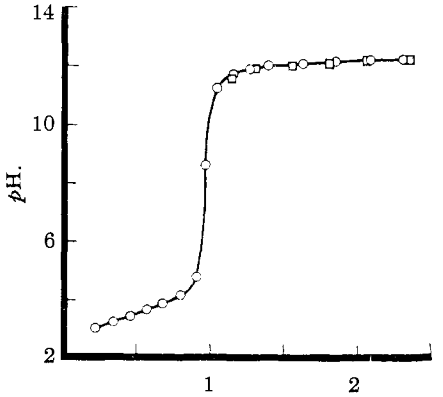


Fig. 1.—○, Tetronic acid; □, benzoic acid.

The ring structure of tetronic acid enables a group to act on the ionizable hydrogen from two directions—clockwise and counterclockwise about the ring. The double action of each of the groups would tend to increase the acid strength of the compound. However, the magnitude of this effect must be small, for chlorophenols are not very strong acids. Also, the dissociation constants of the monosaccharides are not abnormally large compared with the dissociation constants of alcohols.

Another possibility is that the lactone ring opens and the acidity is due to a carboxyl hydrogen. The acids that are obtained from the salts, however, have molecular weights that correspond to the lactone structure. If the hydroxy acid structure exists, the equilibrium must be very rapid and favor the lactone structure in acid, and the open structure in basic, solution. That the opening of the lactone ring is not responsible for the acidity is shown by three lines of evidence.

If the ring opens, the first dissociation constant would be due to the carboxyl group and the compounds would have a second dissociation constant due to the enol hydroxyl group. This second dissociation constant would be small due to the acid weakening effect of the negative charge on the ion. A hydrogen electrode was used for investigating the possibility of a second dissociation constant, because of the limitation of the glass electrode at low hydrogen-ion concentration. The bromo and iodo substituted tetronic acids gave inconsistent results with the hydrogen electrode, probably because of their own oxidizing action. Tetronic acid behaved normally and consequently was used in looking for the second dissociation constant. The curve for tetronic acid was compared with that of an acid known to be monobasic, namely, benzoic acid. The second dissociation constant would be evident by causing the curve for tetronic acid to fall below that for benzoic acid when between one and two equivalents of base had been added. The graph shows that the points fall virtually on the same line, thus showing that tetronic acid does not have a second dissociation constant. *l*-Ascorbic acid, in contrast to tetronic acid, does have a second dissociation constant.

It seems then that the first dissociation constant of *l*-ascorbic acid and of tetronic acid cannot be due to an opening of the ring, for in that case both compounds would have a second dissociation constant. With the first hydrogen coming in both cases from enol hydroxyl groups *l*-ascorbic acid has the possibility of a second dissociation constant from the other enol hydroxyl. Tetronic acid, however, has but one enol hydroxyl and consequently only one dissociation constant.

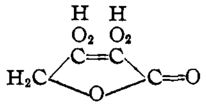
The analysis of the sodium salts of tetronic, α-bromotetronic and α-iodotetronic acids gives further evidence on the structure of the ions. If the ring opens the molecular weights of the salts will be increased by one molecule of water. To each acid was added the theoretical amount of a solution of sodium hydroxide. The solutions were dried in a vacuum desiccator over calcium chloride at room temperature, and after two days the salts were analyzed by decomposing the compounds with sulfuric acid and weighing the sodium sulfate. Heating while drying was avoided to eliminate the possibility of converting any salts of hydroxy acids back to the lactone. The results show the salts to have the lactone structure.

	Equiv. wt. from sodium present	Theoretical equiv. wt. for lactone structure
Tetronic acid	123.5	122.0
α-Bromotetronic acid	199.5	200.9
α-Iodotetronic acid	243	248

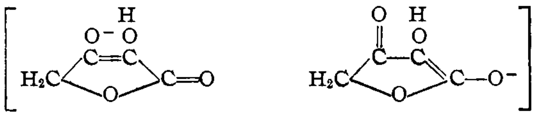
The *p*-nitrobenzyl ester of α-bromotetronic acid gives further evidence on the structure. The analysis of this ester shows that the compound is not a carboxylic ester. The ester is not acidic, which also rules out the carboxylic ester structure.

All three lines of evidence, namely, the absence of a second dissociation constant in tetronic acid, the analysis of the sodium salts of tetronic, α-bromotetronic and α-iodotetronic acids, and the behavior of an ester of α-bromotetronic acid, indicate that the high acid strength of these compounds is not due to an opening of the lactone ring.[1a]

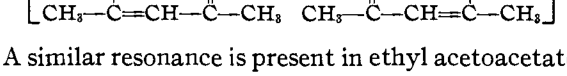
Resonance is another factor that must be considered as a possible explanation. Although from our present knowledge of resonance there seems no *a priori* reason why acids of the tetronic type should have much more acid strengthening resonance than those of the diethyl dihydroxymaleate or ethyl acetoacetate type, nevertheless there are several lines of evidence that point to a large amount of resonance in the tetronic type acids. Micheel and Schulte[2] have obtained evidence that the strongly acid hydroxyl in hydroxytetronic acid is on carbon 3 and not carbon 2.



On a basis of the negativity or acylous character of the groups, hydroxyl on carbon 2 should be the strong acid because it has on one side the acylous $=\overset{|}{C}-O-H$ group and on the other side the acylous $-\overset{O}{\overset{\|}{C}}-O$ group, while the hydroxyl on carbon 3 has on one side the acylous $=\underset{|}{C}-OH$ group but on the other the non-acylous $H_2C\langle$ group. The most likely resonance structure, however, presents a different picture. The ion formed as a result of dissociating hydrogen from the hydroxyl on carbon 3 would have two forms of nearly the same energy



which would stabilize the ion and make the acid strong. It is not possible to write similar resonances for the ion found by dissociating the hydrogen from the hydroxyl on carbon 2 without producing extremely improbable configurations. The fact that the hydrogen from the OH group on carbon 3 is the strong acid hydrogen is good evidence that the above type of resonance is largely responsible for the high acidity of these compounds. This resonance distributes the negative charge on the ion between two oxygen atoms and is analogous to the resonance that gives acidity to the enolic form of 1,3-diketonic substances in general. For example, in the enol form of acetylacetone, which has a *Ka* of 1.3 × 10^{-5}, the following resonance is present



$$\left[CH_3-\overset{O^-}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3 \quad CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{O^-}{\overset{|}{C}}-CH_3\right]$$

A similar resonance is present in ethyl acetoacetate but now the presence of an oxygen in the ester group disturbs this resonance, consequently ethyl acetoacetate is considerably weaker than acetylacetone. When ring closure takes place in ethyl acetoacetate the dissociation constant of the resulting tetronic acid is greater than that of

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[1a] The solution used for investigating the possible second dissociation constant of tetronic acid was approximately 0.06 molar—a concentration ample for the detection of a dissociation constant around 10^{-11} to 10^{-12}. The second dissociation constant of *l*-ascorbic acid [*pKa* 11.51, Kumler and Daniels, THIS JOURNAL, **57**, 1929 (1935)] was measured with a hydrogen electrode in a solution approximately 0.03 molar.

That the hydrogen electrode does not reduce tetronic acid and thus prevent the detection of the second dissociation constant is indicated by two lines of evidence. First, the e. m. f. as the hydrogen was bubbled through the solution was constant. If reduction took place the e. m. f. would change with time. The e. m. f. previously was observed to be constant for *l*-ascorbic acid—a substance much more easily reduced than tetronic acid. We recently have measured the first dissociation constant of *l*-ascorbic acid with the glass electrode and obtained the same value (within the experimental error) that we formerly obtained with the hydrogen electrode. If reduction had occurred with the hydrogen electrode the value with the glass electrode would have been different. Second, tetronic acid was made by the reduction of α-bromotetronic acid with sodium amalgam—a method that would not have been successful if tetronic acid were easily reduced. Clutterbuck, Raistrick and Reuter, *Biochem. J.*, **29**, 300 (1935), have made γ-methyltetronic acid by reducing α-bromo-γ-methyltetronic acid with hydrogen and palladium—a procedure that likewise would not have been possible if the tetronic acid structure were easily reduced.

There is a possibility that the ester may have a different structure than the free acid or its salt. For instance, the alkyl group sometimes goes to carbon when sodium ethyl acetoacetate is esterified. This may occur with this compound. It is, however, extremely unlikely in the process of making the ester from sodium α-bromotetronate that any rearrangement other than this can occur. For the salt to have a hydroxy carboxylic acid structure and the ester to have a lactone structure would involve replacement of the sodium with the R group, a shifting of the R group to the enolic oxygen where it replaces the enolic hydrogen, the splitting out of water from this hydrogen and the alcoholic hydroxyl group and a final ring closure. This involves a series of reactions which is highly improbable considering the positions of the various groups in the molecule.

Since the only possibility of impurities in the salts was the amount of water present (assuming that the sodium hydroxide and the original acids were pure, which was the case) there did not seem to be any advantage in recrystallizing them. In the case of sodium α-bromotetronate a sample was recrystallized from 95% alcohol before analysis. The following result was obtained: equiv. wt., 202.4, 202.0; theoretical equiv. wt. for the lactose structure, 200.9.

[2] Micheel and Schulte, *Ann.*, **519**, 70 (1935).

acetylacetone. Professor G. E. K. Branch has suggested two possibilities to account for the effect of ring closure on the resonance. First, the ring closure may nullify the normal resonance weakening effect of the oxygen of the ester group. In this case the resonance would give tetronic acid a Ka of about 10^{-5} and the negativity of the additional oxygen, plus the double action around the ring, would be sufficient to bring the Ka up to the observed value of 1.7×10^{-4}. Second, the ring closure may introduce a new resonance which in some way allows the third oxygen atom to assist in carrying the negative charge on the ion.

The dissociation constant of tetronic acid is 1.7×10^{-4} and that of hydroxytetronic acid is 4×10^{-5}. Replacing a hydrogen by an hydroxyl group in this case decreases the strength of the acid. Substituting a hydroxyl or an —OR group for a hydrogen normally increases the strength of the acid except in those cases where the hydroxyl or —OR group either interferes with an acid strengthening resonance or introduces an acid weakening resonance. Examples are: benzoic $Ka = 6.6 \times 10^{-5}$ and *p*-hydroxybenzoic $Ka = 2.9 \times 10^{-5}$,[3] phenylboric acid $Ka = 1.97 \times 10^{-10}$ (in 25% alcohol), and *p*-phenethylboric acid $Ka = 6.08 \times 10^{-11}$,[4] (in 25% alcohol). The fact that hydroxytetronic acid is less than one-fourth as strong as tetronic acid indicates that resonance is a factor of major importance in determining the acidity of the compound.

That the hydroxyl group does increase the strength of these acids when it is placed in the molecule in a position where it does not interfere with the resonance in the ring is shown by a comparison of the dissociation constant of *l*-ascorbic acid $Ka = 7 \times 10^{-5}$ with that of hydroxytetronic acid $Ka = 4 \times 10^{-5}$. Thus the introduction of two hydroxyl groups on a side chain about doubles the dissociation constant of the acid. The increase in strength resulting therefrom is roughly comparable to that brought about by introducing two hydroxyl groups in like positions with respect to a carboxyl group.

A comparison of the increment given to the acid strength of tetronic acid by the substitution of halogens with that given to acetic acid by the halogens shows that the halogens increase the strength of tetronic acid less than they increase the strength of acetic acid.

$$\frac{Ka\ \alpha\text{-Chlorotetronic acid}}{Ka\ \text{Tetronic acid}} = 43$$
$$\frac{Ka\ \alpha\text{-Bromotetronic acid}}{Ka\ \text{Tetronic acid}} = 34$$
$$\frac{Ka\ \alpha\text{-Iodotetronic acid}}{Ka\ \text{Tetronic acid}} = 28$$
$$\frac{Ka\ \text{Chloroacetic acid}}{Ka\ \text{Acetic acid}} = 85$$
$$\frac{Ka\ \text{Bromoacetic acid}}{Ka\ \text{Acetic acid}} = 76$$
$$\frac{Ka\ \text{Iodoacetic acid}}{Ka\ \text{Acetic acid}} = 39$$

That the low increment is not indigenous to enol–keto compounds is shown by a comparison of the Ka of ethyl acetoacetate with that of ethyl α-iodoacetoacetate.

$$\frac{Ka\ \text{Ethyl}\ \alpha\text{-iodoacetoacetate}}{Ka\ \text{Ethyl acetoacetate}} = 5000$$

In this case as in the case of most enol–keto compounds the substitution of halogen for hydrogen will have two effects: it will change the percentage of enol and change the Ka of the enol form. Since the keto form is non-acidic, an increase in the percentage of enol will have the effect of increasing the over-all dissociation constant of the acid. The two effects can be distinguished by calculating the dissociation constants of the enol forms.[1] This reduces the ratio

$$\frac{Ka_{\text{enol}}\ \text{Ethyl}\ \alpha\text{-iodoacetoacetate}}{Ka_{\text{enol}}\ \text{Ethyl acetoacetate}} = 73$$

to a value a little less than three times the increment obtained by substituting iodine in tetronic acid. Although the determination of the percentage of enol in tetronic acid and α-iodotetronic acid is inconclusive[5] the evidence points to a high percentage of enol in both compounds. Consequently there is probably not enough difference in the percentage of enol to affect greatly the ratio of the dissociation constants. It is interesting to note that a substitution of iodine in ethyl acetoacetate both increases the percentage of enol (by about 4-fold) and increases the dissociation constant of the enol form by 73-fold. A comparison of the ratio

$$\frac{Ka\ \alpha\text{-Iodotetronic acid}}{Ka\ \text{Ethyl}\ \alpha\text{-iodoacetoacetate}} = 50{,}000$$

with the ratio

$$\frac{Ka\ \text{Tetronic}}{Ka\ \text{Ethyl acetoacetate}} = 10{,}000{,}000$$

shows that ring closure has much less effect on the dissociation constant after iodine has been substituted for hydrogen. This is further evidence

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[3] Branch and Yabroff, THIS JOURNAL, **56**, 2568 (1934).

[4] Branch, Yabroff and Bettman, *ibid.*, **56**, 937 (1934).

[5] Kumler, *ibid.*, **60**, 857 (1938).

that resonance is a major factor in determining the acid strength of these compounds.

Experimental

The dissociation constants were calculated assuming the relations $pH = -\log (H^+)$ and

$$Ka = \frac{(H^+)\left[(Na^+) + (H^+) - \frac{Kw}{(H^+)}\right]}{M - \left[(Na^+) + (H^+) - \frac{Kw}{(H^+)}\right]}$$

where M is the total concentration of undissociated acid and salt. The dissociation constants are thus neither classical dissociation constants in terms of concentrations nor thermodynamic dissociation constants in terms of activities. They approximate the "acidity constants" defined by Brönsted.[6] The pH of the solutions of the acids at $^1/_3$, $^1/_2$ and $^2/_3$ neutralization with sodium hydroxide were measured with a Coleman Model 3A Glass electrode. The measurements were made at 25 ± 0.5°. The pKa values given are an average of the separate values obtained at $^1/_3$, $^1/_2$ and $^2/_3$ neutralization and the errors given are the average errors A where $A = \pm\Sigma v/n\sqrt{n}$.

In looking for a possible second dissociation constant in tetronic acid a Bunker type hydrogen electrode, saturated calomel cell, Leeds and Northrup type K potentiometer and Leeds and Northrup type C galvanometer were used.

Preparation of Compounds

Ethyl α-Iodoacetoacetate, α-Iodotetronic Acid, α-Chlorotetronic Acid.—The methods used in preparing these compounds were described in previous papers.[5,7]

α-Bromotetronic Acid.—This compound was prepared using the method of Wolff and Schwabe[8] with slight modifications. Some 200 g. of Eastman ethyl acetoacetate was placed in a one-liter three-necked flask and immersed in an ice-water bath. An equal volume of dry diethyl ether was placed in the flask and 492 g. of N. F. bromine was added over a period of about two hours while the solution was stirred with a mechanical stirrer. The solution was permitted to stand overnight, then washed twice with an equal volume of ice water and thoroughly dried over calcium chloride. No attempt was made to purify the ethyl α,γ-dibromoacetoacetate. The product was then placed in a Claisen flask and heated in an oil-bath at 120–130° and under a pressure of about 15 mm. for three hours. The contents of the flask were then cooled to about 0° and filtered. The resulting solid was washed with ether and recrystallized from ethyl acetate. The mother liquor was returned to the flask, heated, filtered and recrystallized as previously. This was repeated until further heating did not produce an appreciable amount of α-bromotetronic acid. Usually three heatings were carried out on each batch. In case the acid after recrystallization was colored it was boiled in ethyl acetate with activated charcoal and recrystallized. The product obtained was a white solid; m. p. 183° with decomposition; literature 183° with decomposition; yield about 100 g.

Anal. Calcd. for $C_4H_3O_3Br$: equiv. wt., 178.9; Br, 44.6. Found: equiv. wt., 179; Br, 44.2.

Tetronic Acid.—The method of Wolff and Schwabe[8] was used in preparing tetronic acid; 30 g. of α-bromotetronic acid was dissolved in the smallest possible amount of a concentrated solution of sodium carbonate, cooled to zero degrees and 400 g. of 4% sodium amalgam added in about 50-g. portions while a stream of carbon dioxide was bubbled through the solution. After five or six hours the contents were acidified with strong sulfuric acid (1:1 water), care being taken not to add too great an excess, and the solution extracted with about 25 volumes of ether. The ether was distilled off and the solid recrystallized by dissolving in the smallest amount of hot absolute alcohol and adding petroleum ether thereto. White needles were obtained; m. p. 141°, literature 141°; yield 50%.

Anal. Calcd. for $C_4H_4O_3$: equiv. wt., 100. Found: equiv. wt., 100.

α-Hydroxytetronic Acid.—This compound was synthesized using the method of Micheel and Jung:[9] twenty grams of benzoyl ethyl glycolate[10] was placed in a 500-ml. three-necked flask fitted with a mechanical stirrer and a condenser; 50 ml. of benzene was added and dry nitrogen was conducted through the solution; 5 g. of potassium was added in small amounts and the flask was heated for three hours in an oil-bath maintained at about 100°. The mixture was acidified with a little more than the calculated amount of sulfuric acid (1:10 water). The water layer was then pipetted off and evaporated *in vacuo* at about 35° under carbon dioxide. The solid was extracted with ethyl acetate, and most of the ethyl acetate evaporated *in vacuo* under carbon dioxide. Crystals were obtained from the resulting thick liquid by letting it stand on a porous plate in an atmosphere of carbon dioxide. The solid was recrystallized from ether and petroleum ether; colorless crystals, m. p. 152°, literature m. p. 153°; yield 0.5 g.

Anal. Calcd. for $C_4H_4O_4$: equiv. wt., 116.0. Found: equiv. wt., 116.5.

p-Nitrobenzyl α-Bromotetronate.—The method of Reid[11] for preparing p-nitrobenzyl esters was used. One gram of α-bromotetronic acid was dissolved in 5 ml. of 1.1078 normal sodium hydroxide solution. Ten ml. of 95% ethyl alcohol and 1 g. of p-nitrobenzyl bromide was added. The solution was refluxed for two hours on a steam-bath, then cooled in ice and the crystals that separated were filtered on a Büchner funnel, washed with 63% alcohol and then with water. The product was recrystallized twice from 95% ethyl alcohol, m. p. 177°.

Anal. Calcd. for $C_{11}H_8O_5NBr$: Br, 25.5. Found: Br, 25.3.

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(6) Brönsted and King, *Z. physik. Chem.*, **130**, 700 (1927).

(7) Kumler, THIS JOURNAL, **60**, 855 (1938).

(8) Wolff and Schwabe, *Ann.*, **292**, 231 (1896).

(9) Micheel and Jung, *Ber.*, **66B**, 1291 (1933).

(10) The author is indebted to Professor T. C. Daniels for the sample of benzoyl ethyl glycolate and to Mr. Leslie Beretta for assisting in the preparation of the α-hydroxytetronic acid.

(11) Reid, THIS JOURNAL, **39**, 124 (1917).

The author wishes to thank Professor G. E. K. Branch for several valuable discussions during the course of the work.

Summary

The dissociation constants of tetronic acid, α-chlorotetronic acid, α-bromotetronic acid, α-iodotetronic acid, α-hydroxytetronic acid and ethyl α-iodoacetoacetate have been determined. The tetronic acids are all stronger acids than acetic acid and considerably stronger than the ethyl acetoacetate compounds from which they may be considered to be derived.

Ethyl acetoacetate by ring closure and the elimination of ethane would give tetronic acid, an acid ten million times as strong as the original ethyl acetoacetate. Three possibilities are considered to explain this great difference, namely, negativity, double action around the ring, and an opening of the lactone structure, but each is discarded. It is suggested that resonance is the explanation. Three lines of evidence point to a large amount of acid strengthening resonance in these compounds. The resonance structures account for the observation that the hydroxyl on the β-carbon atom contains the strong acid hydrogen while other factors affecting acidity are unable to account for this fact. Resonance accounts for the observation that hydroxytetronic acid is considerably weaker than tetronic acid.

SAN FRANCISCO, CALIF. RECEIVED NOVEMBER 24, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Methane Bearing Phenyl Groups

BY ALBERT L. HENNE AND HENRY M. LEICESTER

The synthesis of diphenyldifluoromethane was undertaken and carried out because it had been discovered that dimethyldifluoromethane[1] was exceedingly easy to prepare and had proved to be a very stable substance; it was thus hoped that diphenyldifluoromethane would be equally easy to make and would be a very stable, high boiling liquid, practically inert to chemical agents; this hope was also enhanced by the known qualities of benzotrifluoride,[2] as well as of $CH_3CF_2CH_3$ and $CCl_3CF_2CCl_3$.[1] However, experimental results fulfilled these expectations in part only and showed that the reasoning based on analogies was quite inadequate, as it did not take enough account of the influence of the phenyl groups; this error of judgment was partly due to the fact that in benzotrifluoride the adverse influence of the phenyl group is masked by the extraordinarily high stability of the CF_3 group, a factor which had not been appreciated before.

Other derivatives of methane bearing fluorine and one or several phenyl groups have been prepared and described briefly by different authors, specifically: benzyl fluoride was prepared by Ingold and Ingold,[3] who were particularly impressed by the fact that it loses hydrofluoric acid; benzal fluoride was prepared by van Hove,[4] who was much concerned with the difficulty of its preparation; triphenylfluoromethane was synthesized by Blicke,[5] who particularly noticed its easy hydrolysis as compared with the previously mentioned compounds. Reported in complete ignorance of each other, these characteristics (which have now been verified) first appeared to be erratic, but became quite understandable when the behavior of diphenyldifluoromethane was learned and taken into account.

The instability of benzyl fluoride is due to a tendency to lose hydrofluoric acid, but though a loss of acid usually yields an ethylenic derivative, it occurs here not within the molecule, but between two distinct molecules, and results in the formation of a clear polymer $[-CHPh-]_n$. The same reaction explains the difficulties in the synthesis of benzal fluoride, where acid elimination also takes place between two different molecules, and polymerization occurs, though to a smaller extent. In marked contrast, the syntheses of diphenyldifluoromethane and triphenylfluoromethane are not attended by polymerization, since it is impossible to lose hydrofluoric acid within the molecule, or between two molecules;

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(1) Henne and Renoll, THIS JOURNAL, **59**, 2434 (1937).

(2) Swarts, *Bull. acad. roy. Belg.*, 389 (1920).

(3) Ingold and Ingold, *J. Chem. Soc.*, 2249 (1928).

(4) Van Hove, *Bull. acad. roy. Belg.*, 1074 (1913).

(5) Blicke, THIS JOURNAL, **46**, 1515 (1924).