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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.

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

Fluorinated Derivatives of Methane Bearing Phenyl Groups

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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).

however, in both cases another phenomenon appears, namely, susceptibility to hydrolysis, and the by-products are therefore benzophenone and triphenylcarbinol, respectively. As could be expected, this tendency is much more marked in the latter case than in the former. It should be added, however, that the decomposition of benzyl fluoride does not yield an alcohol, any more than that of benzal fluoride an aldehyde.

Efforts to synthesize phenylfluoromethanes by the Friedel-Crafts method (in order to avoid difficulties similar to those previously reported) invariably were disappointing, and caused this method to be abandoned; the reasons are illustrated in the case of dichlorodifluoromethane and benzene. In the presence of aluminum chloride, a very lively reaction takes place, but hydrogen fluoride is evolved in preference to hydrogen chloride; consequently the final products no longer contain any fluorine; moreover, the reaction is so vigorous that more benzene molecules are linked than desired, and the main products are therefore triphenylchloromethane and the substances obtained from its decomposition, namely, triphenylmethane and triphenylcarbinol. Friedel and Crafts reactions involving other fluorochlorides were tried and always gave the same disappointing results.

Preparation of Diphenyldifluoromethane.—The synthesis of diphenyldifluoromethane was carried out successfully by the interaction of diphenyldichloromethane and antimony trifluoride in the presence of a very small quantity of bromine (the latter is not indispensable). This mixture is heated rapidly in an oil-bath at about 140° until it is liquefied completely. This indicates that all the antimony fluoride has been transformed into antimony chloride; further heating is then not only superfluous but actually harmful. The antimony salt is washed out by means of concentrated hydrochloric acid; in order to facilitate the washing and decantation, it is convenient to add some carbon tetrachloride, because the density of diphenyldifluoromethane is only slightly higher than unity. After the washing, decanting and drying have been completed, the carbon tetrachloride is removed by distillation at atmospheric pressure; then the remaining product is subjected to fractionation at reduced pressure. This yields the expected product first, and a residue of very pure benzophenone. The amount of tar is quite small.

The new derivative, diphenyldifluoromethane, has been characterized as follows: it boils at 125° at 10 mm.; at atmospheric pressure the boiling point is approximately 260°, but decomposition occurs, and benzophenone can be found in the distillate, while noticeable etching of the glass takes place. The melting point is -1.9 to $-1.8°$, the density d^{20}_4 is 1.1614, and the refractive index for the D line of sodium is n^{20}_D 1.53786. From these constants the molecular refraction is computed as 54.985; subtracting from this value the customary increments for carbon, hydrogen and double bonds results in an atomic refraction of 1.07 for each fluorine atom. This value compares favorably with 1.024 in benzyl fluoride, 1.013 in benzal fluoride and 0.996 in benzotrifluoride. The analysis by the Parr bomb method indicates 17.8% fluorine instead of 18.6% calculated, a good result for this method of analysis.[6]

This new compound is considerably more stable than benzal fluoride and considerably less so than benzotrifluoride. As is true of all fluorine compounds, it is more sensitive to acids than to alkalies. An idea of the order of magnitude can be gained by the following experiments, in which 2 cc. of the compound was heated at 100° for five hours with 0.1 *N* hydrochloric acid or potassium hydroxide. Benzal fluoride yields 0.13 g. of hydrofluoric acid in the first case and 0.084 g. in the second; diphenyldifluoromethane yields 0.0054 g. and 0.0024 g., respectively; benzotrifluoride is not affected.

Summary

Diphenyldifluoromethane has been synthesized and described fully. A comparison of its properties with those of other phenylated fluoromethanes affords an explanation of the erratic behavior of the latter. The introduction of a phenyl group decreases the stabilizing effect which CF_2 or CF_3 groups have on aliphatic compounds.

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[6] Henne and Renoll, THIS JOURNAL, 59, 2436 (1937).