(see above), is of the right order of magnitude and in the right direction to be caused by a change of Mg^{2+} to fourfold coördination in the glass. This does not indicate, however, whether *all* or part of the Mg^{2+} is in fourfold coördination, although the constant value obtained would seem to favor the former situation. Further evidence is found in the difference between the values for periclase (Mg^{2+} in sixfold coördination) and the MgO in spinel (Mg^{2+} probably in fourfold coördination).[10] The value of 0.64 for this difference can be attributed to the difference in coördination of the Mg^{2+} in the two compounds and also supports the view that *all* the Mg^{2+} is in fourfold coördination in glasses of diopside and enstatite compositions. Finally, it is to be expected that since Mg^{2+} is already in fourfold coördination in crystalline akermanite,[11] no change in molar refraction would occur in the glassy state. The data for akermanite bear this out and give values which show a distinctly smaller difference in the $R_{\text{glass}}-R_{\text{crystal}}$ value.

[10] E. J. W. Verway and E. L. Heilmann, *J. Chem. Phys.*, **15**, 174–180 (1947), have presented indirect evidence that the Mg^{2+} is in fourfold coördination, forming a "normal" spinel structure.

[11] B. E. Warren, *Z. Krist.*, **74**, 131–138 (1930).

"KISMET," HAZARIBAGH, INDIA RECEIVED MAY 28, 1949

Isophthalic and Terephthalic Acids[1]

BY PAUL G. SCHEURER[2] AND GENE M. LE FAVE[3]

Recently McBee and Frederick proved the structures of some chlorine substituted bis-(perfluoroalkyl)-benzenes by hydrolysis with 60–80% sulfuric acid,[4] following a procedure employed by Wertyporoch.[5] We felt that extending this method to a mixture of *m*- and *p*-bis-(trifluoromethyl)-benzenes made available through the work of McBee[6] would provide an excellent procedure for the preparation of iso- and terephthalic acids, particularly since bis-(trifluoromethyl)-benzenes are now commercially available as a mixture consisting of approximately 60% meta and 40% para isomers.[7]

Refluxing bis-(trifluoromethyl)-benzene with an excess of 80% sulfuric acid for several hours causes charring and does not give acceptable yields. Quantitative yields of the corresponding phthalic acids were obtained by reaction with 100% sulfuric acid and subsequent hydrolysis of the reaction product,[8] but long initiation periods were required and often large-scale reactions were controlled only with difficulty. However, a method was devised which proved entirely satisfactory. It has the very suitable advantage that only small amounts of hydrogen fluoride are evolved during the course of the reaction and may be conducted in an all-glass apparatus. Equimolar quantities of concentrated sulfuric acid and chlorosulfonic acid in slight excess were used; the reaction starts immediately upon heating and an even evolution of hydrogen chloride takes place throughout the reaction.

There appear to be two possibilities for the course of the reaction. The chlorosulfonic acid may react with the trifluoromethyl groups to give the partially substituted chloro compound with subsequent accelerated hydrolysis by the sulfuric acid,[9,10] or the sulfuric acid may act directly on the trifluoromethyl groups giving hydrogen fluoride and fluorosulfonic acid. The former will very probably be in equilibrium with the sulfuric acid[11]

$$HF + H_2SO_4 \longleftrightarrow FSO_3H + H_2O$$

However, under this equilibrium condition the chlorosulfonic acid will not be stable since it will react with the water formed giving hydrogen chloride and sulfuric acid, thereby shifting the equilibrium to the right and accounting for the evolution of hydrogen chloride and not hydrogen fluoride. Both mechanisms probably operate.

The acids formed upon pouring the reaction mixture into water were separated advantageously by virtue of their barium salts, the barium isophthalate being readily soluble in water while the terephthalate salt is quite insoluble in the same solvent. Of interest is that qualitative analysis of the acids showed that no chlorine was present indicating the superiority of hydrolyzing the fluorine compounds in lieu of the chlorine analog, which usually contains nuclear chlorine.

Experimental

A mixture of 60 g. of chlorosulfonic acid, 50 g. of concentrated sulfuric acid, and 53.5 g. (0.25 mole) of bis-(trifluoromethyl)-benzene was heated in a flask fitted with a reflux condenser and the usual hydrogen chloride trap until the reaction commenced and only intermittently thereafter. After the evolution of hydrogen chloride had ceased, the reaction mixture was cautiously poured with stirring into ice-water, the resultant precipitate filtered, washed thoroughly with cold water, and finally dissolved in 500 ml. of warm water containing 27 g. of sodium carbonate and 3 g. of Norit. This solution was then filtered, 130 g. of barium chloride dihydrate added, and refiltered. The filtrate was neutralized, the precipitate collected, washed, and recrystallized from methanol. The isophthalic acid thus obtained weighed 30 g. (55.5%) based on the weight of the starting material. It melted at 347–349°.

Anal. Calcd. for $C_8H_6O_4$: C, 57.83; H, 3.63. Found: C, 57.99; H, 3.71.

The insoluble barium salt of terephthalic acid was washed and neutralized, the precipitated terephthalic acid collected and washed thoroughly with cold water by suspension, stirring and refiltration, finally drying in the oven at 100°. It weighed 21 g. (39%) and sublimed

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[1] Paper III of the Series entitled, "Some Reactions of the Trifluoromethyl Group in the Benzotrifluoride Series."

[2] The Graduate School, The Ohio State University, Columbus, Ohio.

[3] J. I. Holcomb Research Fellow, 1948–1950.

[4] McBee and Frederick, THIS JOURNAL, **71**, 1490 (1949).

[5] Wertyporoch, *Ann.*, **493**, 1536 (1932).

[6] See Murray, Beanblossom and Wojcik, *Ind. Eng. Chem.*, **39** 302 (1947).

[7] Hooker Electrochemical Company, Niagara Falls, N. Y.

[8] Le Fave, THIS JOURNAL, **71**, 4148 (1949).

[9] Kracker and Herrlein, U. S. Patent 2,119,882 (June 7, 1938).

[10] E. Spreckels, *Ber.*, **52B**, 317 (1919).

[11] Traube, *ibid.*, **46**, 2525 (1913).

around 300°. The dimethyl ester, prepared in the usual manner, melted at 66–67°.

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The Silver Salt Degradation of *t*-Butylacetic Acid

BY WALTER T. SMITH, JR., AND ROBERT L. HULL

The conversion of the silver salt of a carboxylic acid by bromine to an alkyl or aryl bromide with one less carbon atom has been regarded[1] as a reaction proceeding by way of a free radical mechanism. The isolation of an inactive bromide from the decarboxylation of the silver salt of optically active α-ethylcaproic acid[2] has been cited as evidence for this mechanism. Other work[3,4,5] has indicated that the isolation of an inactive bromide from an optically active silver salt may not be significant. Arcus, Campbell and Kenyon[4] found that optically active α-phenylethyl bromide is racemized in carbon tetrachloride by bromine in the presence of silver bromide. These same workers also found that decarboxylation of silver (+)-α-phenylpropionate yields (+)-α-phenylethyl bromide with inversion of configuration.

It was of interest to carry out the degradation of the silver salt of *t*-butylacetic acid, since, if the intermediate formed is a carbonium ion it would rearrange and give *t*-amyl bromide rather than neopentyl bromide. When such a reaction was carried out, neopentyl bromide was isolated in 62% yield (based on *t*-butylacetic acid consumed.) The product was identified by physical constants and by conversion to *t*-butylacetanilide by treatment of the neopentylmagnesium bromide with phenyl isocyanate. The absence of *t*-amyl bromide in the neopentyl bromide was shown by a negative test with alcoholic silver nitrate.

The formation of neopentyl bromide by the degradation of silver *t*-butylacetate is in keeping with a free radical mechanism and indicates that the silver salt degradation does not proceed *via* a carbonium ion mechanism.

Experimental

Preparation and Degradation of Silver *t*-Butylacetate.—The silver salt of *t*-butylacetic acid was prepared by dissolving 41.5 g. (0.36 mole) of *t*-butylacetic acid in excess dilute ammonium hydroxide. The excess ammonia was boiled off and an aqueous solution of 61.2 g. (0.36 mole) of silver nitrate was added. The solution was cooled and the silver salt was collected by filtration and washed with water, methanol, and petroleum ether (28–38°). It was then dried in an oven at 110° for twelve hours and then in a desiccator over Drierite for an additional twelve hours; yield of dry silver *t*-butylacetate, 77.8 g. (97%).

In a 200-ml. round-bottom flask, surrounded by an ice bath, was placed 44.6 g. (0.20 mole) of silver *t*-butylacetate. A solution of 32.0 g. (0.20 mole) of bromine in 25 ml. of nitrobenzene was added slowly with shaking over a period of about twenty minutes. A slow evolution of gas was noted. After all the bromine solution had been added, the reaction mixture was removed from the ice-bath and allowed to warm to room temperature. As the temperature rose, the evolution of gas became more vigorous. When the evolution of gas had ceased, the reaction mixture was placed on a steam-bath and heated for two hours. The mixture was cooled, 25 ml. of ether was added, and the silver bromide was removed by filtration. The ethereal filtrate was washed in turn with 25 ml. of 5% sodium sulfite solution and 25 ml. of 5% sodium carbonate solution.

From the acidified washings there was obtained 7.6 g. of *t*-butylacetic acid boiling at 180–190°.

The ethereal solution was dried over calcium chloride and the ether was evaporated on a steam-bath. The resulting liquid was distilled at reduced pressure; the portion boiling below 80° (20 mm.) weighed 15.1 g. This portion was then fractionated at atmospheric pressure to give 12.6 g. (62% yield based on *t*-butylacetic acid consumed) of neopentyl bromide, b. p. 104–109°, n^{20}_{D} 1.4369, d^{20}_{4} 1.258. It gave no precipitate with alcoholic silver nitrate or sodium iodide in acetone.[6]

Conversion of the bromide to the Grignard reagent and treatment with phenyl isocyanate gave *t*-butylacetanilide, m. p. 130–131°, a mixed melting point with *t*-butylacetanilide prepared from *t*-butylacetyl chloride and aniline was 130–131°.

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[1] Price, "Mechanism of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, New York, N. Y., 1946, p. 55.

[2] Arnold and Morgan, THIS JOURNAL, **70**, 4248 (1948).

[3] Doering and Farber, *ibid.*, **71**, 1514 (1949).

[4] Arcus, Campbell and Kenyon, *J. Chem. Soc.*, 1510 (1949).

[5] Bell and Smyth, *ibid.*, 2372 (1949).

[6] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

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The Phase Behavior of the System Sodium Stearate–Cetane

BY F. H. STROSS AND S. T. ABRAMS

There are few studies of phase diagrams of the anhydrous system: fatty acid soap–organic solvent, in the literature. Recent work includes a paper by Doscher and Vold[1] on the system sodium stearate–cetane, carried out by means of the polarizing microscope, and the work by G. H. Smith[2] on sodium stearate–aromatic, naphthenic and paraffinic compounds of low molecular weight, done by visual observations of evacuated glass cells under polarized light. While Smith's diagrams for various hydrocarbon types resemble each other remarkably, especially with regard to the large exaltation of the t_i-point[3] at 25–30% solvent concentration, the sodium stearate–cetane system studied by Doscher and Vold is of a very different character. Thus Smith's systems with low molecular weight solvents (C_6 to C_8) of widely differing chemical nature resemble each other to such an extent that Smith constructed a generalized phase diagram sodium stearate–hydrocarbon from which one may conclude that the nature of the hydrocarbon has little influence upon the qualitative or even the quantitative

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[1] Doscher and Vold, *J. Coll. Sci.*, **1**, 299 (1946).

[2] G. H. Smith, *J. Am. Oil Chem. Soc.*, XXIV, 353 (1947); also thesis, Stanford, 1947.

[3] The t_i-point is the temperature at which the optically anisotropic jelly and isotropic liquid are in equilibrium.