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.

character of these soap systems. In comparing one of these systems, sodium stearate–*n*-heptane, with that employing a homologous solvent, cetane, as is used in the study of Doscher and Vold, one would expect a similar or an even greater resemblance. However, inspection shows that these two systems differ widely from each other, both qualitatively and quantitatively. One feature common to both sets of data is the observation of phase islands, although they, too, differ considerably in size and location in the heptane and in the cetane system. These phase islands are reminiscent of similar features observed in aqueous systems, and are correspondingly designated in analogy with these systems by Doscher and Vold.

In the course of a study of the system sodium stearate–cetane by various methods in these laboratories it was desired to resolve, if possible, the inconsistent character of the two published phase diagrams of the soap in paraffinic solvents. Certain concentrations of the sodium stearate–cetane system were studied in sealed capillaries by means of the polarizing microscope, and also by visual inspection of larger samples in sealed glass cells. Special care was taken in the preparation, purification, and drying of the sodium stearate, which is notoriously difficult to obtain pure and dry. By prolonged evacuation of the sample at 150 to 180° it was possible to obtain reproducible results in differential thermal analysis of the soap; thermal analysis is a sensitive criterion of purity of many organic compounds.

The samples were thoroughly mixed, heated well past their t_i-points, and slowly brought back to room temperature. The t_i-points were then observed as the temperature was raised, *i.e.*, as the system changed from anisotropic to isotropic under crossed polarizers. The rate of heating was usually about 0.5 to 1° per minute except when the temperature came within about 20° of the expected transition. Then the heating rate was reduced and the observation of the transition was made repeatedly, the temperature sometimes being kept almost constant for several hours to ensure equilibrium conditions. Mechanical mixing by means of a magnetic plunger was used during these observations. The change in the reverse direction, *i.e.*, isotropic to anisotropic, was found to give poor reproducibility because of supercooling. In spite of careful examination it was not possible to detect any indication of phase islands in our observations.

The t_i-points observed optically as described are given in the table, and it is apparent that our observations differ substantially from those of Smith as well as from those of Doscher and Vold. In general these values are higher than the corresponding values obtained by Doscher and Vold, as taken from their published phase diagram.[1] Only at the higher soap concentrations do their values seem to coincide with the values presented in this work. Our experience with the difficulties of drying and maintaining dry samples of sodium stearate leads us to the suggestion that small traces of water may have been present in the samples reported in the literature. The effect of water on depression of t_i-points is indeed remarkable; the addition of as little as 0.17% water was found to depress by 48° the t_i-point of the anhydrous sample containing 9% soap. In addition, visual study indicated a profound difference between samples with water and those without, in their appearance and behavior on heating.[4]

It is difficult for the present to answer the question whether the existence of phase islands, independent of the nature of the hydrocarbon component, is also traceable to the presence of water. The phase diagrams reported by Doscher and Vold and by Smith do bear a great resemblance to aqueous systems.

A more detailed paper on this subject, consisting chiefly of a study of this system by differential thermal analysis, is in preparation.

Our thanks are due Messrs. R. J. Moore and E. R. White of Shell Development for the preparation and purification of the organic compounds.

OPTICAL OBSERVATIONS OF THE t_i TEMPERATURES FOR THE SYSTEM SODIUM STEARATE–CETANE

Sodium stearate content, % wt.[a]	t_i, °C. This work	t_i, °C. Doscher and Vold	t_i, °C. H_2O added
2	167	167	
9	215	180	165 (0.17%)
18	220	182	
30	240	240	161 (1.66%)
50	248	249	226 (0.65%)
67	259	253	
71	255	255	
100	282	280	

[a] These values have been rounded off to the nearest integer and are within ±0.3% of the Na Stearate concentration.

Since the writing of this note, a paper by A. S. C. Lawrence[5] has lent support to the thesis that traces of water may have influenced the systems described.

(4) Ref. 1, p. 1.

(5) Lawrence, *J. Phys. Coll. Chem.*, **52**, 1504 (1948).

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The Reduction of Bromic Acid by Hydrobromic Acid in the Presence of Hydrogen Peroxide

BY H. A. YOUNG

The net reaction for the reduction of bromic acid by hydrogen peroxide may be written[1]

$$BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + H_2O \qquad (1)$$

Bray and Davis also concluded that the rate of the reaction could be expressed as the sum of two terms, the more important of which, after some

(1) Bray and Davis, THIS JOURNAL, **52**, 1427 (1930).