Lamb's[1] work, which showed that the dihydrate was decomposed by dehydration directly to HIO_4 without intermediate compounds. He also found that stronger dehydrating conditions in no instance gave the seven valent anhydride, but rather resulted in decomposition to I_2O_5.

The second stage in the fluorination was studied by allowing samples of the acid to react in a continuous stream of fluorine at room temperature. The remaining white solid was shown to be iodine pentoxide. It was a non-hygroscopic substance which failed to oxidize manganous ion to permanganate in solution containing sulfuric acid, and its water solution gave a white precipitate with silver ion. During the fluorination of a 2.310-g. sample of $HIO_4 \cdot 2H_2O$, the loss in weight was 0.613 g. This may be compared with the theoretical loss of 0.619 g. according to the equation

$$2HIO_4{\cdot}2H_2O \longrightarrow I_2O_5 + 5H_2O + O_2$$

Likewise this sample should yield a product with a total oxidation equivalent of 0.0608; the equivalency found iodometrically was 0.0607. Such a change to give iodine pentoxide is in accord with the findings of Lamb.[1]

The final stage of the fluorination was accomplished by an increase in temperature to about 250°. On so doing, the iodine pentoxide disappeared while a white solid condensed in a product receiving trap cooled by Dry Ice. This solid was determined to melt at $-8°$ to a colorless liquid which fumed in air. When a weighed sample of this liquid was treated with an acidified solution of potassium iodide and the liberated iodine titrated with standard sodium thiosulfate, an equivalent weight of 36.8 was found. This is in good agreement with the theoretical value of 36.9 for IF_5 (m. p. $-8°$, b. p. $+97°$).

The boiling point of the iodine pentafluoride was not determined as the reaction with the glass container was found to be too rapid above 30°. Such a behavior was also reported for IF_5 by Ruff and Braida.[2]

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(1) Arthur B. Lamb, *Am. Chem. J.*, **27**, 134 (1902).

(2) Otto Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **220**, 43–48 (1934).

DEPARTMENT OF CHEMISTRY AND
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The Esterification of Acylated α-Amino Acids

BY HEINRICH RINDERKNECHT AND CARL NIEMANN

Esters of the acylated α-amino acids or peptides are ordinarily prepared by the acylation of the α-amino acid or peptide ester or by the traditional acid catalyzed esterification of the acylated α-amino acid or peptide.[1] In seeking a more attractive procedure than either of the above it has been found that as with other carboxylic acids[2,3] certain of the acylated α-amino acids may be readily esterified by simply heating an alcoholic solution of the acid at approximately 180° in the absence of added catalyst. While this procedure appears to be useful for the esterification of many acylated α-amino acids it is to be anticipated that a number of acids will form products other than esters. For example with benzoyl-L-arginine the principal reaction product proved to be racemic 5-benzamidopiperidone-2.

Aside from convenience of the above method for the preparation of esters of acylated α-amino acids and carboxylic acids in general[3] it is one of the few procedures that can be used for the esterification of ketals of polyhydroxy acids such as 1;2,3;4-diisopropylidene-D-galacturonic acid.[4]

Experimental

Methyl Hippurate.—A solution of 18.0 g. of hippuric acid in 200 ml. of methanol under an initial pressure, at 25°, of 1000 lb./sq. in. of hydrogen was heated at 180–185° for ten hours. The reaction mixture was evaporated to dryness, the residue extracted with ether, the ethereal extract evaporated to dryness and the residue recrystallized from benzene to give 15.9 g. (82.5%) of methyl hippurate, m. p. 81–82°, uncor.

Benzoyl-DL-alanine Methyl Ester.—Benzoyl-DL-alanine (19.3 g.) in 200 ml. of methanol was heated at 180° for twelve hours. The reaction mixture was fractionally distilled and the distillate, b. p. 129–131° (0.15 mm.) was recrystallized from benzene to give 16.9 g. (91%) of benzoyl-DL-alanine methyl ester, m. p. 80–82°, uncor.

Carbobenzoxy-DL-alanine Methyl Ester.—A solution of 22.3 g. of carbobenzoxy-DL-alanine in 200 ml. of methanol heated at 180° for twelve hours was fractionally distilled and the fraction, b. p. 129–131° (0.2 mm.), recrystallized from ligroin to give 13.3 g. (59%) of carbobenzoxy-DL-alanine methyl ester, m. p. 49–50°, uncor.

Anal. Calcd. for $C_{12}H_{15}O_4N$: C, 60.8; H, 6.3; N, 5.9. Found: C, 61.0; H, 6.5; N, 5.6.

Attempted Esterification of α-Benzoyl-L-arginine.—α-Benzoyl-L-arginine (27.6 g.) in 200 ml. of methanol was heated at 170° for fifteen hours, the reaction mixture filtered (ppt. 7.0 g.), the filtrate evaporated to dryness and the residue recrystallized from hot water to give 8.5 g. (39%) of 5-benzamido-piperidone-2, m. p. 183–184°, insoluble in aqueous acid and alkali, soluble in hot water and ethanol.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.1; H, 6.4; N, 12.8. Found: C, 66.4; H, 6.7; N, 12.5. The benzamidopiperidone was hydrolyzed with 20% hydrochloric acid and the dipicrate of DL-ornithine, m. p. 198–199°, isolated from the hydrolysate. A solution of α-benzoyl-L-nitroarginine in methanol heated at 170° for seventeen hours gave 68% of 5-benzamido-piperidone-2, m. p. 183–184°.

Methyl Benzoate—Fractional distillation of a solution of 12.2 g. of benzoic acid in 200 ml. of methanol previously heated at 185° for fifteen hours gave 12.2 g. (90%) of methyl benzoate, b. p. 83° (12 mm.).

Methyl Lactate.—A solution of 12.0 g. of freshly distilled lactic acid, b. p. 78° (0.1 mm.), in 250 ml. of methanol heated at 170° for fourteen hours upon fractional distillation gave 9.6 g. (69%) of methyl lactate, b. p. 143–145°.

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(1) E. Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Protein," Julius Springer, Berlin (1906, 1923).

(2) W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd ed., Longmans, London, 1948, p. 100.

(3) Private communication from Prof. Homer Adkins, University of Wisconsin, Madison.

(4) C. Niemann, unpublished data.

Attempted Esterification of Gallic Acid.—Gallic acid monohydrate (9.4 g.) in 250 ml. of methanol was heated at 200° for fourteen hours, the solution evaporated to dryness and the residue recrystallized from benzene to give 6.2 g. (98%) of pyrogallol, m. p. 129–130°, uncor.

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An Approximate Method for the Determination of Active Halogens

BY JOHN R. SAMPEY, ANNE B. KING AND BARBARA C. BLITCH

The observation of Wanscheidt[1] that sodium bromide precipitates when 9-bromofluorene is dissolved in an acetone solution of sodium iodide has been made the basis for an approximate determination, within one or two per cent., of this active halogen in a mixture of bromofluorenes. Data are given to show that the method is applicable to two other compounds containing active halogen, namely, phenacyl bromide and benzyl bromide.

Analyses of 9-Bromofluorene, Phenacyl Bromide and Benzyl Bromide.—Samples (1.0000 g.) of the halogen compounds are dissolved in 20.00 ml. of a saturated solution of sodium iodide in acetone, and are filtered after standing several hours at 25°. Sodium bromide starts separating immediately upon solution of the halogen compounds, but in the case of 9-bromofluorene, if the sample stands too long, large amounts of difluorenyl precipitate; if this does occur, the difluorenyl and sodium bromide may be weighed together, and then the latter may be washed out with water; another weighing gives the amount of sodium bromide present before washing. The sodium iodide adhering to the sodium bromide after the filtration is readily washed out with 60 ml. of acetone; tests are made on the last washings for iodide ion (nitrous acid test). A correction is made for the solubility of the sodium bromide in the acetone. The sodium bromide is filtered and dried at 110°.

TABLE I

ANALYSES OF 9-BROMOFLUORENE, PHENACYL BROMIDE AND BENZYL BROMIDE

Compound	Sample, g.	NaBr ppt., g.	NaBr dissolved, g.	Sum, g.	%
9-Bromofluorene	1.000	0.407	0.003	0.410	97
9-Bromofluorene	1.000	.406	.003	.409	97
Phenacyl bromide	1.000	.501	.003	.504	97
Phenacyl bromide	1.000	.508	.003	.511	99
Benzyl bromide	0.907	.540	.003	.543	99
Benzyl bromide	1.285	.774	.003	.777	100

Solubility of Sodium Bromide in Acetone.—A correction must be applied for the solubility of sodium bromide in the acetone used. Column 4 of Table I gives the solubility of sodium bromide in the particular sample of acetone used in these analyses; other samples of reagent grade acetone dissolved as much as 0.119 g. of the salt; agitation of this moist sample of acetone with anhydrous calcium chloride reduced the amount of sodium bromide to less than 10 mg. on a second solubility determination. The solubility of sodium bromide in any sample of reagent grade acetone is determined by suspending 1.000-g. samples of the salt in 20.00-ml. portions of the acetone saturated with sodium iodide; to ensure solution, the flasks are placed on a shaking machine for several hours; the solutions are run through Gooch filters, and the adhering sodium iodide is washed out with 60 ml. of the same acetone used in making the solution.

The solubility of sodium bromide in acetone changes little with change in temperature. When the temperature is raised from 25 to 41°, the solubility decreased only two or three milligrams over that recorded in Column 4 of Table I. Sodium iodide shows a more marked decrease in solubility at elevated temperatures, for when a saturated solution of this salt in acetone is refluxed, large amounts of sodium iodide separate, and then on cooling redissolve.

The effect of changes in relative humidity on the solubility of sodium bromide in acetone has been noted. The acetone solutions were cooled to 0° and the samples were filtered slowly in an atmosphere in which the relative humidity was 95; under these conditions the solubility of sodium bromide increased five to six milligrams over that found by rapid filtration on a day in which the relative humidity was 40. The same quantities of salt and acetone were used as in previous runs. These effects of wide changes in humidity do not alter the usefulness of this approximate method for the determination of active halogens in the three classes of compounds analyzed in Table I.

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[1] A. Wanscheidt, *Ber.*, **59**, 2092–2100 (1926).

The Exaggerated Effect of Iodine as Carrier in the Bromination of Fluorene

BY JOHN R. SAMPEY AND ANNE B. KING

Discovery of the Exaggerated Effect of Iodine.—In an attempt to relate the rate of bromination to the intensity of the irradiation in the photobromination of fluorene the observation was made that a considerable amount of bromine disappeared regardless of the illumination. This led to experiments in the dark in which 10 cc. of a 1 molar solution of bromine in carbon disulfide was added to 0.01 mole of fluorene in 20 cc. of the same solvent. The reaction was stopped by adding potassium iodide solution after which the liberated iodine was titrated. The results were surprising. In 5 runs the bromination was 8 to 10% in one-half minute, in 3 runs, 8 to 11% in three minutes and in 2 runs, only 11 to 13% in ten minutes. Tests showed that none of the bromine had entered the side chain. The first supposition was that the fluorene contained an easily brominated impurity. To test this, samples of fluorene from three different sources were recrystallized repeatedly, vacuum distilled and sublimed. All three showed 8 to 11% bromination in one-half and three minute periods. This surprising result was finally traced to the effect of the iodine that was liberated on the addition of the potassium iodide solution. For a part of the time during the shaking, fluorene, bromine and iodine were present in the carbon disulfide solution. This led to a study of the effect of iodine on the bromination of fluorene.