treated with hydrobromic acid. An over-all yield of 19% was obtained for the bromo-acid. A considerable amount of a high boiling fraction which solidified upon cooling was also isolated. This material was identified as adipic acid by its melting point and neutral equivalent. Marvel and co-workers[3] prepared ε-bromocaproic acid in an over-all yield of approximately 40% by the treatment of δ-phenoxybutyl bromide with ethyl malonate and subsequent decomposition of the diethylphenoxybutyl malonate with hydrobromic acid.

Several unsuccessful attempts were made to isolate the ε-caprolactone from the oxidation step. The excess peroxide was destroyed by the addition of sodium bisulfite and the solution extracted with ether. The ether was evaporated and the residue subjected to vacuum distillation. A violent explosion occurred. This behavior did not parallel the results of Westerfeld who was able to isolate δ-valerolactone. Two subsequent experiments only served to confirm the original observation.

Experimental

To a solution of 600 ml. of 2 N NaOH was added alternately with continuous stirring, 114 g. of redistilled cyclohexanone with 300 ml. of 30% hydrogen peroxide (Merck Superoxol). The temperature of the oxidation mixture was held at 45°. Water was distilled from the reaction mixture under diminished pressure until a white pasty residue was formed.

The crude reaction product was treated with 100 ml. of 48% hydrobromic acid solution followed by the slow addition of 100 ml. of concd. sulfuric acid. After gentle refluxing for 3 hours the reaction mixture was diluted with one liter of water and extracted 5 times with ether. Upon evaporation of this ethereal extract 43.6 g. of ε-bromocaproic acid was obtained. It distilled completely at 142–143° (11 mm), m.p. 32.5°. The acid was recrystallized from petroleum ether. *Anal.* Calcd. for $C_6H_{11}O_2Br$: Br. 40.9. Found: Br, 40.3.

(3) Marvel, *et al.*, THIS JOURNAL, **46**, 2841 (1924); **49**, 1831 (1927).

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Positive Halogens from Trifluoroacetyl Hypohalites[1]

BY ALBERT L. HENNE AND WILLIAM F. ZIMMER

CF_3COOBr and CF_3COOI are a source of positive bromine and iodine, respectively, as shown by the fact that they halogenate toluene in the ring in marked preference to or even to the exclusion of the side chain. They are conveniently made by adding the stoichiometric amount of bromine or iodine to a solution of silver trifluoroacetate in an organic solvent: (1) $CF_3CO_2Ag + X_2 \rightarrow AgX \downarrow + CF_3CO_2X$ and (2) $CF_3CO_2X + CH_3C_6H_5 \rightarrow CF_3CO_2H + CH_3C_6H_4X$. Discoloration is a convenient measure of the reaction progress. Trifluoroacetic acid is recoverable.

The positive character of the halogen in these hypohalites is similar to that of the bromine in perfluorinated N-bromosuccinimide $CO(CF_2)_nCONBr$.[2]

(1) A. L. Henne, Am. Chem. Soc., Chicago Meeting, Sept., 1950, Abstracts p. 10L.

(2) A. L. Henne and W. F. Zimmer, *ibid.*, p. 11L; and THIS JOURNAL, **73**, 1103 (1951).

In both cases, the positive halogen "hangs" from a polarizable atom attached to one or two strongly electronegative perfluoroacetyl groups.

Other acyl hypohalites should, and do show a similar property, but to a smaller extent (CH_3CO_2-Br) or in a less convenient form (CCl_3CO_2Br). The solubility of silver trifluoroacetate in organic solvent is of great practical help, and the resistance of the CF_3CO_2 ion to decarboxylation[3] minimizes the importance of the so called Hunsdiecker or Simonini reactions, with formation of CF_3X. Specifically,[4] the reaction $CF_3CO_2Ag + I_2 \rightarrow CO_2 + CF_3I + AgI$ does not occur appreciably below 100°.

A private communication[5] reports that "CF_3CO_2X halogenates benzenic derivatives such as phenol, aniline and benzoic acid in the expected positions." These experiments confirm the ability of X to act in a positive form, yet have no opportunity to show that it does so in preference to acting in atomic form.

Experimental

Iodination of Toluene.—CF_3CO_2Ag[4] (55 g. or 0.25 mole) dissolved in toluene (120 g.) was added dropwise to a slurry of iodine (63.5 g. or 0.25 mole) in toluene (125 g.). Reaction with heat evolution, silver iodide precipitation and formation of CF_3CO_2H fumes was instant. AgI was decanted. Trifluoroacetic acid and the excess of toluene were distilled off. Tolyl iodide (46 g. or 0.21 mole) n^{20}D 1.6005 was then collected about 210°; this is an 84% yield. A small amount was oxidized with chromic acid to give iodobenzoic acid, which after one crystallization from benzene melted at 269–270°, correct for *p*-iodobenzoic acid.

Bromination of Toluene.—A solution of bromine (80 g. or 0.36 mole) in carbon tetrachloride was added to CF_3CO_2Ag (80 g. or 0.36 mole) and toluene (33.1 g. or 0.36 mole) in carbon tetrachloride. Stirring and cooling were maintained throughout the reaction. Working up was as above. Distillation gave tolyl bromide (45 g. or 73%) at 179–181°. A small amount of this was converted to its Grignard derivative and the latter carbonated to methylbenzoic acid; after one crystallization from water, a m.p of 176–178° was observed which denoted *p*-methylbenzoic acid.

Bromination of Methylnaphthalene.—Bromine (32 g. or 0.20 mole) was added in 90 minutes to an ether solution of β-methylnaphthalene (28.5 g. or 0.20 mole) and CF_3CO_2Ag (44.2 g. or 0.20 mole) with constant stirring and cooling in a water-bath. After filtration of AgBr, the filtrate was brown and could not be bleached by a bisulfite wash. Distillation at reduced pressure gave: β-methylnaphthalene, 4.8 g., b. 116–120° (16 mm.), intermediate, 1.3 g., b. 120–140° (16 mm.); α-bromo-β-methylnaphthalene, 26.7 g., b. 107–115° (1.0 to 1.5 mm.); higher boiling fraction, 1.3 g., b. 115–140° (1.0 to 1.5 mm.); residue, 5.4 g. The third fraction (26.7 g. or 0.121 mole) is a 60.5% conversion, or a 77.1% net yield when fraction 1 is taken into count. A small amount of this was converted to its Grignard derivative and carbonated; after one crystallization from benzene, the reaction product melted at 126–127°, denoting β-methyl-α-naphthoic acid.

Testing of Acetyl Hypoiodite.—Silver acetate was mechanically dispersed in an excess of toluene containing an equimolecular amount of iodine; the reaction was slow and required gentle heating to proceed to completion. During the working up, extensive decomposition was observed, with liberation of iodine. The yield of tolyl iodide was only 47.5%, mostly the para-isomer as shown by oxidation to low grade *p*-iodobenzoic acid.

Testing of Trichloroacetyl Hypoiodite.—Preparation of silver trichloroacetate proved inconvenient, light sensitive and beset with silver chloride formation. The reaction was then tried by placing CCl_3CO_2H in an excess of toluene, stirring with silver oxide until neutralized and adding an

(3) I. Auerbach, F. Verhoek and A. Henne, *ibid*, **72**, 299 (1950).

(4) A. L. Henne and W. G. Finnegan, *ibid.*, **72**, 3806 (1950).

(5) R. N. Haszeldine, The University, Cambridge, England.

equivalent solution of iodine in toluene. No more than half the expected amount of iodine reacted; the silver precipitate was heavier than computed, and contained silver chloride. Decomposition with iodine evolution ,occurred during distillation; no tolyl iodide was obtained; a small, charred iodine colored residue remained.

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Heat Capacity of the Furfuryl Alcohol–Aniline System[1]

BY E. W. HOUGH,[2] D. M. MASON AND B. H. SAGE

The isobaric heat capacities of furfuryl alcohol–aniline mixtures in the liquid phase at compositions from 0.0 to 1.0 weight fraction furfuryl alcohol were determined at bubble-point pressure in a stainless steel bomb calorimeter. Six sets of heat capacity measurements were made for compositions of approximately 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 weight fraction furfuryl alcohol in the temperature ranges 50 to 175, 30 to 115, 25 to 100, 30 to 95, 30 to 95,

Experimental.—A description of the equipment and techniques employed is available.[3,4,5] A stainless steel bomb calorimeter with a volume of approximately 1 liter was suspended by small wires within a vacuum jacket. An electrical heater was used to raise the temperature of the calorimeter and contents. The temperature was established within 0.002° by means of a platinum resistance thermometer. The liquid sample within the calorimeter was agitated by a small centrifugal impeller. (The energy measurements were made in watt-seconds and were converted to gram calories by the relation: 1 thermochemical calorie = 4.1840 abs. joules.)

The apparatus was calibrated[6] by measurements with water for which accurate thermodynamic data are available. The volume of the gas phase was less than 2.5% of the total volume of the calorimeter, and therefore simplifying assumptions in the calculations of the heat capacity from the thermal data are justified at temperatures below 100°.[3]

The furfuryl alcohol and aniline were purified by fractional distillation at reduced pressure in an Oldershaw column. The mixtures were prepared by weighing the constituents and mixing them before introduction into the calorimeter.

Results.—Smoothed values of the isobaric heat capacity of the furfuryl alcohol–aniline system are shown in Table I for compositions from 0.0 to 1.0 weight fraction in the temperature

TABLE I

SMOOTHED VALUES OF ISOBARIC HEAT CAPACITY OF FURFURYL ALCOHOL-ANILINE SYSTEM AT BUBBLE POINT

Composition, weight fraction furfuryl alcohol	Isobaric heat capacity, cal./g., °C.							
	40°	60°	80°	100°	120°	140°	160°	180°
0.00	0.503	0.511	0.520	0.528	0.536	0.544	0.552	0.561
.10	.502	.511	.520	.529	.537	...	...	...
.20	.501	.511	.521	.530	.539	...	...	...
.30	.501	.512	.522	.531	.541[a]	...	...	...
.40	.501	.512	.523	.533	.544[a]	...	...	...
.50	.501	.512	.524	.536	.547[a]	...	...	...
.60	.501	.513	.526	.538	.551[a]	...	...	...
.70	.501	.514	.528	.542	.555[a]	...	...	...
.80	.501	.516	.531	.547	.561[a]	...	...	...
.90	.501	.517	.535[a]	.552[a]	.568[a]	...	...	...
1.00	.501	.519	.538[a]	.557[a]	.576[a]	...	...	...

[a] These values are extrapolated.

TABLE II

SMOOTHED VALUES OF DENSITY OF FURFURYL ALCOHOL-ANILINE SYSTEM AT BUBBLE POINT

Composition, weight fraction furfuryl alcohol	Density, g./ml.								
	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.	70°C.	80°C.	90°C.
0.00	1.033[a]	1.023[a]	1.014[a]	1.006	0.9966	0.9874	0.9785	0.9692	0.9602
.10	1.043	1.034	1.025	1.016	1.007	0.9976	0.9885	0.9794	0.9704
.20	1.054	1.045	1.036	1.027	1.017	1.007	0.9989	0.9898	0.9808
.30	1.065	1.056	1.046	1.038	1.028	1.019	1.009	1.000	0.9909
.40	1.076	1.066	1.057	1.048	1.038	1.029	1.020	1.010	1.001
.50	1.086	1.077	1.068	1.059	1.049	1.039	1.030	1.020	1.011
.60	1.097	1.088	1.078	1.069	1.060	1.050	1.040	1.031	1.021
.70	1.108	1.099	1.090	1.080	1.071	1.061	1.051	1.042	1.038
.80	1.120	1.110	1.101	1.091	1.082	1.072	1.062	1.053	1.044
.90	1.131	1.122	1.112	1.102	1.093	1.084	1.074	1.064	1.055
1.00	1.143[a]	1.133[a]	1.124	1.114	1.105	1.095	1.086[a]	1.076[a]	1.067[a]

[a] These values are extrapolated.

and 30 to 65°, respectively. The density of these mixtures was determined for atmospheric pressure at 5, 40, and 70°. The refractive index of these mixtures was determined at 25°.

range from 40 to 180°. In Fig. 1 the data are presented graphically and, for comparison, literature

(1) This paper presents the results of one phase of research carried out for the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. W-04-200-ORD-1482 sponsored by the U. S. Army Ordnance Department.

(2) Stanolind Oil and Gas Company, Tulsa, Oklahoma.

(3) B. H. Sage and E. W. Hough, Anal. Chem., 22, 1304 (1950).

(4) W. P. White, "The Modern Calorimeter," The Chemical Catalog Co., New York, N. Y., 1928.

(5) N. S. Osborne, H. F. Stimson and E. F. Fiock, Nat. Bur. Standards, J. Res., 5. 411 (1930).

(6) B. H. Sage and W. N. Lacey, Trans. Am. Inst. Min. and Met. Engrs., 136, 136 (1940).