10°, micro b. p. 26–27°, $n^{20}\text{D}$ 1.3569. [c] Traces of yellow lower layer formed. [d] 0.6 cc. hydrocarbon residue boiling above 10°, micro b. p. 29°, $n^{20}\text{D}$ 1.3610. [e] $n^{20}\text{D}$ 1.3575. [f] Traces of permanent gases formed. [g] 20.6% of total *n*-butane charge isomerized to *i*-butane. [h] *i*-Butane charge. [i] The heart cut of this fraction was 30 × 10^{-4} mole, $n^{20}\text{D}$ 1.3548. [j] The complete column analysis was 9 × 10^{-4} mole low boiling material, 410 × 10^{-4} mole *i*-C_4H_{10}, 62 × 10^{-4} mole *n*-C_4H_{10}, 34 × 10^{-4} mole *i*-pentane, 24 × 10^{-4} mole boiling higher than *i*-pentane. [k] Propane. [l] Aluminum chloride. [m] Methyl chloride. [n] No *i*-butane; no alkylate. After removal of volatile products, 0.920 g. of a white to light amber solid remained, m. p. 24°, stable to pumping at 10^{-5} mm. [o] Ethyl bromide. [p] Light yellow solution. *Ca.* 0.3 cc. light orange lower layer developed at end of run. [q] Total distillate boiling above *n*-butane, $n^{20}\text{D}$ 1.3800. Traces of low boiling material. [r] Light yellow solution. [s] Traces of low boiling material; butane fraction 47.7% isomerized. [t] *Ca.* 0.5 cc. deep red lower layer formed. [u] The complete analysis was as follows: traces of CH_4, 140 × 10^{-4} mole C_2H_6, 80 × 10^{-4} mole C_3H_8, 82 × 10^{-4} mole *n*-C_4H_{10}, 185 × 10^{-4} mole *i*-C_4H_{10}, 130 × 10^{-4} mole *i*-C_5H_{12}, 95 × 10^{-4} mole C_6H_{14} and higher, $n^{20}\text{D}$ 1.3779.

Summary

In the presence of aluminum bromide, methyl and ethyl bromide will alkylate butanes to give substantial yields of pentanes and hexanes, respectively, as well as some higher paraffins. The occurrence of the alkylation reaction substantiates a prediction based on the mechanism of paraffin isomerization previously presented.

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NOTES

Trimethylchlorosilane

BY W. F. GILLIAM AND ROBERT O. SAUER

Taylor and Walden[1] have recently reported the successful preparation of trimethylchlorosilane by direct chlorination of trimethylsilane. We obtained this chlorosilane in January, 1941, by the reaction of methylmagnesium chloride with a mixture of methylchlorosilanes[2] in ether solution.

Experimental

429.5 g. of a methylchlorosilane mixture[3] (b. p. 68.0–70.1°; 57.8% Cl; 2.75 moles dimethyldichlorosilane and 0.50 mole of methyltrichlorosilane) was dissolved in one liter of anhydrous ether and added to a 5-liter, three-neck flask fitted with a stirrer, an addition funnel, and a condenser cooled by a bath of acetone and solid carbon dioxide. To this solution was slowly added 500 cc. of a 4.1 *M* solution of methylmagnesium chloride in ether; the magnesium chloride precipitated as a fine sludge. The ether solution was separated and the ether removed by distillation; fractional distillation of the residue in a column of 40 theoretical plates gave five fractions totaling 38.7 g. (0.35 mole) of trimethylchlorosilane. The higher boiling constituents contained 159.2 g. (1.23 moles) of dimethyldichlorosilane, and 30.8 g. of an intermediate fraction. These materials were analyzed by the hydrolysis of approximately 1-g. samples and the titration of the liberated acid with *N*/2 sodium hydroxide. A sample of trimethylchlorosilane collected at 57.0° (748 mm.) gave 32.5, 32.6% Cl (calcd., 32.64% Cl). The dimethyldichlorosilane distilled at 70.0° (757 mm.) and gave 54.8, 54.8% Cl (calcd., 54.95% Cl).

Another sample of trimethylchlorosilane[3] upon careful fractional distillation in a column of 50 theoretical plates gave three consecutive fractions having the following properties: (a) b. p. 57.6–57.7° (760 mm.); d^{27}_{27} 0.8538; % Cl, 32.58, 32.59, 32.59; (b) b. p. 57.7° (760 mm.)-57.3° (749 mm.); d^{27}_{27} 0.8536; % Cl, 32.57, 32.56, 32.57; (c) b. p. 57.7° (760 mm.); d^{27}_{27} 0.8536, 0.8538; % Cl, 32.55, 32.57.

The vapor density of trimethylchlorosilane indicates this compound to be slightly associated at 100°. The result obtained by the Dumas method was 5.091 g./l. (S. T. P.) corresponding to a molecular weight of 114 (calcd., 108.6).

The molecular weight of this compound was also determined cryoscopically in cyclohexane (determined freezing point constant, 207). The following results show trimethylchlorosilane to exist as the dimer in this solvent at 6° (maximum concentration of solute, 0.3%): mol. wt., 223, 205, 216, 212 (calcd. for the dimer, 217.2).

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(1) Taylor and Walden, THIS JOURNAL, **66**, 842 (1944).

(2) Gilliam, Liebhafsky and Winslow, *ibid.*, **63**, 801 (1941).

(3) Mr. W. J. Scheiber of this Laboratory kindly provided and distilled these materials.

The Solubility of Potassium Iodide in Sodium Hydroxide Solutions at 20°

BY H. DARWIN KIRSCHMAN[1] AND RICHARD POMEROY[1]

In former articles[2] we have presented the results of studies on the solubility of potassium iodide in potassium hydroxide solutions and of sodium iodide in sodium hydroxide solutions at 20°. The present paper extends these studies to the iodide of potassium in solutions of sodium hydroxide from 0 to 16.5 *N*.

The results of our measurements are presented in Table I and Fig. 1.

Experimental

The solutions were equilibrated and analyzed as previously described except that the concentration of iodide was determined by titration with standard silver nitrate solution using eosine as an adsorption indicator. Equilibrium was more rapidly established than in the case of sodium iodide in sodium hydroxide solutions but less

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(1) 117 East Colorado St., Pasadena 1, Calif.

(2) (a) Kirschman and Pomeroy, THIS JOURNAL, **65**, 1695 (1943); (b) Pomeroy and Kirschman, *ibid.*, **66**, 178 (1944).

TABLE I

SOLUBILITY AND DENSITY DATA AT 20°

NaOH, moles/liter	KI, moles/liter	Density, g./ml.
0.00	6.09	1.716
0.95	5.48	1.674
1.34	5.26	1.661
2.57	4.58	1.624
3.60	4.06	1.597
4.77	3.53	1.573
5.04	3.44	1.568
5.20	3.35	1.564
6.78	2.75	1.543
7.77	2.42	1.532
8.68	2.18	1.531
10.06	1.81	1.526
10.80	1.67	1.530
13.45	1.29	1.540
16.22	1.03	1.569
16.50	1.03	1.583

rapidly than with potassium iodide in potassium hydroxide solutions. The solid phase in equilibrium with solution 16.22 *N* in alkali was washed free from solution and dried. Analysis of the crystals gave 76.07% iodine (calcd. for KI 76.45%). The crystals were optically isotropic.

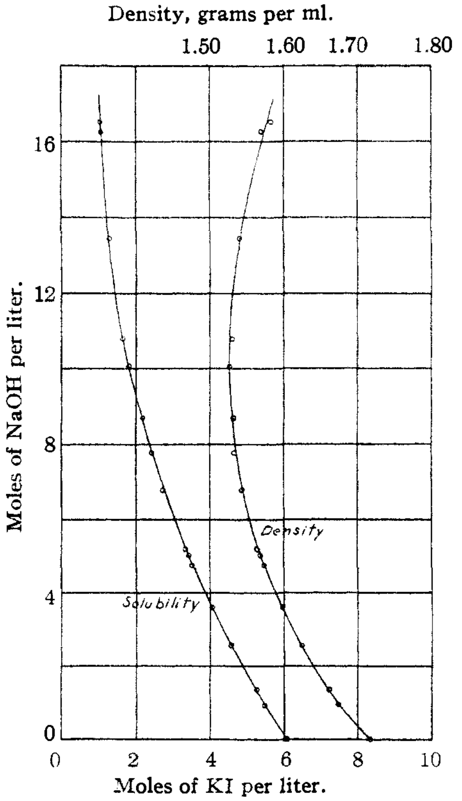

Fig. 1.

These observations, and the apparent continuity of the curves, indicate that potassium iodide was the only solid iodine compound in equilibrium with the solutions. The accuracy of the results is estimated to be 0.5%.

CONTRIBUTION FROM THE
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Isolation of Quercitrin and Quercetin from Goldenrod Material

BY JOHN D. GUTHRIE, ROBERT T. O'CONNOR, MACK F. STANSBURY AND THEODORE R. SAVICH

Quercitrin (3,3′,4′,5,7-pentahydroxyflavone-3-rhamnoside) and its aglucone, quercetin, were isolated from the acetone extractives of goldenrod, *Solidago leavenworthii*, T. and G. Since 15 to 20% of the dry goldenrod material, chiefly leaves, was soluble in acetone, a large quantity of material was available as a by-product from the acetone–benzene extraction process for obtaining rubber from goldenrod.

Experimental

Quercitrin.—Goldenrod leaf material that had been dried in a tray drier at 65° was ground to pass a 40-mesh screen, extracted with acetone in a Soxhlet-type metal extractor for forty-eight hours and the acetone removed from the extract by distillation. Quercitrin was isolated by extraction of the green, gummy material with 0.25 *N* sodium hydroxide, acidification of the extract with acetic acid, centrifugation, neutralization of the supernatant liquid with sodium hydroxide solution and precipitation of the quercitrin with lead acetate. After decomposition of the lead precipitate with hydrogen sulfide, some of the quercitrin was found in the filtrate and some adsorbed on the lead sulfide precipitate, from which it could be eluted with acetone. The quercitrin was purified by crystallization from dilute acetone. In a typical experiment 1.7 g. was obtained from 25 g. of the acetone-extractives. A solution in 95% ethanol had absorption maxima at 2600 and 3500 Å.

Anal. Calcd. for quercitrin, dry, $C_{21}H_{20}O_{11}$: C, 56.3; H, 4.7. Found after drying *in vacuo* at 170°, C, 56.2; H, 4.5.

The aglucone was obtained by hydrolysis of the quercitrin. Its absorption maxima were at 2560 and 3720 Å. in 95% ethanol.

Anal. Calcd. for quercetin, $C_{15}H_{10}O_7$: C, 59.6; H, 3.3. Found: C, 59.1; H, 3.4.

The hydrolyzate gave the Rosenthaler test for rhamnose and yielded the osazone of rhamnose. After recrystallization from dilute pyridine and dilute methanol, it melted at 184–185° (cor.); mixed melting point 184–185° (cor.). Nitrogen: found, 16.33; calcd., 16.36.

Quercetin.—Goldenrod leaf material that had been dried at 65° was extracted in a large jacketed extractor by percolation with acetone at 50° for twenty-four to thirty-six hours. After recovery of the acetone by distillation, the extractives were melted by heating to about 140° and poured into cans. Quercetin was isolated from 47 kg. of the green, gummy acetone-extractives by extraction with boiling water, hydrolysis of the quercitrin in the hot water extract by adding sulfuric acid in the amount of 1% and heating. The crude product which separated weighed 4.3 kg. and contained about 58% quercetin. It was purified by solution in alcohol, precipitation with water, recrystallization from 80% alcohol, and fractional precipitation from acetone with petroleum ether. The yield of purified quercetin was 780 g.