A similar product is formed from aniline and 5-acetoxymercuri-3-nitro-salicylaldehyde.

**3-Chloromercuri-5-nitrosalicylal-aniline.**—Three g. of the aldehyde dissolved in 8 cc. of hot aniline and cooled gives an orange-red product which is insoluble and does not melt.

*Analyses.* Calc. for $C_{13}H_9O_3N_2ClHg$: Hg, 42.1. Found: 42.5, 42.8.

## Summary

1. Mercuration of salicylaldehyde by mercuric acetate gives mainly a dimercurated product with only small amounts of a monomercurated aldehyde.
2. The two nitro-salicylaldehydes give normal mercuration products.
3. The mercurated salicylaldehydes lose all their mercury when treated with potassium iodide, hydroxylamine or phenylhydrazine.
4. The mercurated salicylaldehydes form Schiff's bases with aromatic amines.

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# THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS. II

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Using the methods described by Brunel, Crenshaw and Tobin,[1] the additional alcohols, methylpropyl, diethyl, and dipropyl carbinols have now been purified, and additional specimens of several alcohols formerly investigated have been prepared.

The temperatures have now been followed during the distillations with the 12-junction, copper-constantan thermo-element and are, therefore, more reliable as determinations of the boiling points than those formerly obtained in the boiling-point apparatus subsequent to distillation.[2] In the case of the alcohols whose constants are redetermined, 2 of the boiling points now found are exactly the same; that of methyl-*iso*butyl carbinol, formerly given as only approximate, proves to have been 0.03° low; while that of *n*-propyl alcohol was 0.015° high.

As stated by Brunel, Crenshaw and Tobin, the junctions of the thermo-element were at first soldered, but later brazed. Only the hot junctions, however, were brazed, and at the beginning of the present work it was necessary to braze the cold junctions also. The fixed points were, therefore, redetermined with the following results (cold junctions at 0°): $Na_2SO_4.10H_2O$, transition point 32.384°, 15781 $\mu v$; $SrCl_2.6H_2O$, transition

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[1] Brunel, Crenshaw and Tobin, This Journal, **43**, 561 (1921).

[2] The use of the boiling point apparatus was necessary in the former work because the thermo-element was not installed until the distillation of the alcohols was completed.

point 61.341°, 30814$\mu v$; steam point, 100°, 52122$\mu v$; naphthalene, b. p., 216.61° at 736.80 mm., 123819$\mu v$. The equation now used for the thermoelement is based on the values for sodium sulfate, water and naphthalene, the value for sodium sulfate being substituted for that of strontium chloride formerly used, because we have been able to reproduce it more exactly. These values give $E = 469.856\ t + 0.55125\ t^2 + 0.0003761\ t^3$; but since this gives for the strontium chloride point 30809$\mu v$ instead of 30814$\mu v$ observed, constants were calculated for the equation recommended by Adams,[3] giving $E = 917.484\ t - 179314\ (1 - e^{-.000249731t})$. This gives for the strontium chloride point 30811$\mu v$, a little nearer to the observed value, and has been used in the present work.

The thermo-element has behaved, for the most part, satisfactorily, the e.m.f. for the steam point frequently coming within 1$\mu v$ of the accepted value; yet it has sometimes deviated more than this. The cause appears to lie in the variation in the potentiometer system, since the boiling points of other pure substances have usually fluctuated with the steam point. To avoid errors from this deviation, the steam point has been tested several times during each distillation and the deviation from the accepted value regarded as a correction to be applied to all readings. It now appears justifiable to consider some of the boiling points accurate to ±0.005°.

In order to detect low-boiling impurities as satisfactorily as possible, the final distillations have been started very slowly, usually at the rate of 2 or 3 drops a minute or even less, and statements as to the limits within which the substances distil imply as their lower limit the temperature at which the first drop distilled.

The installation of a new barometer has increased the reliability of the pressure readings. The densities and refractivities have been determined as formerly.

**Propyl Alcohol.**—On account of the apparent impossibility of purifying any fusel oil alcohol completely by distillation, this alcohol was converted into the solid propyl hydrogen phthalate; m. p., 54–55°. The alkyl hydrogen phthalates have been used by Haller[4] for the purification of methyl alcohol, and by Pickard and Kenyon[5] for the separation into optical isomers of numerous secondary alcohols. The following procedure gives excellent results.

A mixture of 200 g. (calc. 180 g.) of propyl alcohol, distilled once from lime, and 450 g. of phthalic anhydride is heated on the water-bath or over a free flame, avoiding overheating, for 3–4 hrs. until completely liquefied. The impure propyl hydrogen phthalate is poured into a solution of 120 g. of sodium hydroxide in 300 cc. of water mixed with considerable ice, with addition of phenolphthalein and more alkali, if necessary, to give an alkaline reaction. The resulting solution is diluted to about 2.5 liters, extracted thrice

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[3] Adams, *J. Washington Acad. Sci.*, **3**, 469 (1913).

[4] Haller, *Compt. rend.*, **114**, 1326 (1892).

[5] Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

with ether, warmed a little, and freed from ether by an air current. It is then acidified with hydrochloric acid, 200 cc. of chloroform is added, the lower layer separated, and the aqueous layer extracted twice more with small quantities of chloroform. The combined chloroform solution is rather viscous and is best dried by warming gently and shaking vigorously with anhydrous magnesium sulfate, which cakes together so that filtration is avoided.

The chloroform is distilled, with an air current at the end, and before the ester solidifies (crystallization is sluggish) 180 cc. of dry ether is added. This solution will crystallize in a freezing mixture with just about the right amount of mother liquor for convenient filtration. The ester is pulverized and allowed to stand until free from the odor of ether, saponified by addition of an excess of conc. aqueous sodium hydroxide, the alcohol distilled and the substance separated from water by potassium carbonate.

Two lots of alcohol so prepared were free from the odor of foreign substances but, upon distillation after drying with lime, acquired a strong odor of aldehyde which increased with further boiling. The distillate gave a heavy mirror with silver oxide. This reminds one of the marked instability noted by Michael, Scharf and Voigt[6] in particularly pure *iso*butyl bromide, and of the apparent easy oxidation of pure ethyl alcohol. The propyl alcohol was all combined distilled once under diminished pressure from *p*-nitro-phenylhydrazine, and then twice from a little sulfuric acid. This gave an excellent product, although it was probably contaminated with traces of nitrogen compounds which prevented further oxidation.

When dried with lime, 82% distilled within 0.019° on the first distillation. The correct boiling point appeared to be 96.960° at 754 mm., or $b_{760}$ = 97.175° (0.36° per cm.). The best boiling portion was collected in 2 fractions with identical densities; $d_4^{15} = 0.79985$; $n_{25}^{D} = 1.3834, 1.3835$.

***iso*Propyl Alcohol**.—Acetone was purified by boiling with permanganate, then dried with calcium chloride and cupric sulfate. Several weeks' standing with the latter is necessary. The boiling point was found on 2 successive days to be 55.96° and 55.97° at 757.00 mm. The variation with pressure appears to be about 0.39° per cm., which gives as $b_{760}$, 56.08–56.09°.[7] Only that portion boiling within 0.01° was reduced to alcohol in the apparatus previously described. The alcohol (650 g.) all distilled within 0.1° on the first distillation, 82% distilling within 0.002° at 82.028° at 753.04 mm.; $b_{760}$ = 82.258 (0.33° per cm.); $d_4^{25}$, 0.78084; $n_{25}^{D}$, 1.3747.

***sec*-Butyl Alcohol**.—Methylethyl ketone was purified with permanganate. After a few fractionations, the best boiling portion was left standing with cupric sulfate for 4 months, when nearly all distilled within 0.005°; $b_{755.00}$, 79.370°.[8] The alcohol obtained by reduction of this ketone

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[6] Michael, Scharf and Voigt, THIS JOURNAL, **38**, 655 (1916).

[7] The best previous determination of the b. p. of acetone appears to be that of Timmermans, *Proc. Roy. Soc. Dublin*, **13**, 330 (1912), who found 56.10± .01° after drying with $P_2O_5$.

[8] The variation of b. p. with pressure appeared, from rather inadequate observations, to be 0.40° per cm., as found by Marshall, *J. Chem. Soc.*, **89**, 1375 (1906). This gives $b_{760}$, 79.57°, as found by him.

gave, after two distillations, 249 g. collected within 0.01°. On redistillation, all of this boiled within 0.22°, 82% within 0.02°, and 72% within 0.005°; $b_{754.67}$, 99.337°; or $b_{760}$, 99.529 (0.36° per cm.); $d_4^{25}$, 0.80235.

**Methyl-*iso*butyl Carbinol.**—Two lots of this substance prepared as formerly, were fractionated at pressures varying from 748 to 760 mm.; $b_{760}$, 131.85°; $d_4^{25}$, 0.80245, 0.80248; $n_{25}^{D}$, 1.4089, 1.4090.

**Methylpropyl Carbinol.**—This was prepared by reduction of the ketone, the latter being prepared by passing a mixture of acetic and butyric acids in the molecular ratio 3:1 over thorium oxide at 450°, as described by Senderens.[9] The particular impurity to be avoided was diethyl carbinol, whose boiling point is close to that of methylpropyl carbinol. Part of the butyric acid used was made by oxidation of *n*-butyl alcohol, and should have been free from propionic acid. During the war, however, some ketone was made from commercial butyric acid. This was subjected to a prolonged series of fractionations, and the portion eventually boiling within about 1.5° separated into several fractions of which only the higher, which should have contained valeric rather than propionic acid, were used.[10] The methylpropyl carbinol proved to be easily purified by fractionation; 363 g. boiling within 0.01° was obtained for a final distillation. All of this distilled within 0.23°, 95% within 0.17°, and 85% within 0.005°; $b_{754.00}$, 119.275°. The best boiling portion was collected in two fractions with $d_4^{25}$, 0.80484, 0.80482; $n_{25}^{D}$, 1.4043. No accurate values are reported in the literature.

**Diethyl Carbinol.**—This was also prepared from the ketone. At the time this was prepared, only commercial propionic acid was available. Since this contained both acetic and butyric acids, the best precaution that could be taken to avoid formation of methylpropyl ketone was to take care that the lower fractions which might contain acetic acid should not be sent through the catalytic apparatus at the same time with the higher fractions which might contain butyric acid.

Of the 188 g. obtained for a final distillation, although the total boiling point range was nearly 1°, 70% distilled within 0.006°; $b_{754.00}$, 115.40°; $d_4^{25}$, 0.81542; $n_{25}^{D}$, 1.4077. Timmermanns[11] gives $b_{760}$, 115.35°.

**Dipropyl Carbinol.**—This also was prepared from the ketone. The latter was prepared from several lots of butyric acid, some of which must

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[9] Senderens, *Bull. soc. chim.*, [4] **5**, 480, 916 (1909).

[10] The freezing point of all of the butyric acid used was close to —6°. According to Faucon, *Ann. chim. phys.*, [8] **19**, 95 (1910), a butyric acid-water mixture containing 4.7 molecular per cent. of water freezes at —6°. If we assume that this is the concentration of propionic and valeric acids in the material used, we should have had, in the mixture converted into ketone, a ratio of 4.7 mols. of foreign acid, mostly valeric rather than propionic, to 400 mols. of acetic and butyric acids. The amount of diethyl ketone formed should have been negligible.

[11] Timmermanns, *Bull. soc. chim. Belg.*, **27**, 334 (1913); *Chem. Centr.*, **1914**, I, 618.

have been rather impure. Prolonged fractionation failed to give a constant boiling product. A quantity of 311 g. was subjected to a final distillation. Although 92.5% distilled within 0.13°, only 58% could be obtained within an interval of 0.056°. The correct boiling point appears to be 155.00 ± 0.04° at 750 mm. The best two fractions had $d_4^{25}$, 0.81303, 0.81287; $n_{25}^D$, 1.4177, 1.4178.

TABLE I

RESULTS

| Compound | B.p. °C. | $p$ Mm. | $d_4^{25}$ | $n_{25}^D$ |
|---|---|---|---|---|
| Acetone | 56.085 ± .01 | 760 | .... | .... |
| Methylethyl ketone | 79.370 ± .01 | 755 | .... | .... |
| *n*-Propyl alcohol[a] | 97.175 ± .01 | 760 | 0.7998 | 1.3834 |
| *iso*Propyl alcohol[b] | 82.258 ± .005 | 760 | .7808 | 1.3748 |
| *sec*-Butyl alcohol[c] | 99.529 ± .005 | 760 | .8023 | 1.39495 |
| Methylpropyl carbinol | 119.275 ± .01 | 754 | .80483 | 1.4043 |
| Diethyl carbinol | 115.40 ± .01 | 754 | .8154 | 1.4077 |
| Methyl-*iso*butyl[d] carbinol | 131.85 ± .01 | 760 | .80245 | 1.40895 |
| Dipropyl carbinol | 155.00 ± .04 | 750 | .8129 | 1.4178 |

[a] Former values, 97.19°, 0.7997, 1.3833.
[b] Former values, 82.26°, 0.7808, 1.3749.
[c] Former values, 99.53°, 0.80229, 1.39495.
[d] Former values, 131.82°, 0.8025 1.40895.

The values of $d_4^{25}$ quoted under (a) and (c) were incorrect in the former paper, due to an error in calculation. They are correctly given here. The values of $d_4^{25}$ for *iso*butyl alcohol also were incorrect. The most probable value should read 0.79763.

The change of boiling point with pressure is not known with certainty for 4 of the compounds in Table I. This can, however, be estimated with only slight error from the principle of Crafts [*Ber.*, **20**, 709 (1887)]. The values for $b_{760}$ so calculated follow, the increment in degrees per millimeter being indicated; methylethyl ketone, 79.57° (0.040); methylpropyl carbinol, 119.50° (0.038); diethyl carbinol, 115.63° (0.038); dipropyl carbinol, 155.42° (0.042).

## Summary

The thermo-element used by Brunel, Crenshaw and Tobin has been recalibrated. Several additional alcohols, together with acetone and methylethyl ketone, and additional specimens of 4 of the alcohols formerly investigated have been prepared. The table records our most reliable values for the physical constants of these compounds. The probable accuracy of the boiling points is indicated in the table. The error in the densities should not exceed 0.0001 except in the case of dipropyl carbinol; that in the refractivities is probably 0.0001.

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