$$\Delta_n = (1/2) \sum_{i=1}^{n} (-1)^{i-1} /(i-1)! \qquad (7)$$

and

$$S_n = 1/2 \sum_{i=1}^{n} (n - i + 1)(-1)^{i-1}/(i-1)! \qquad (8)$$

When n is large, Δ_n represents the average number of isolated functional groups of either variety, X or Y, per substituent.[1] The series in (7) converges rapidly as n increases giving in the limit $\Delta_\infty = 1/2e$. That is, a fraction equal to $1/2e$, or 18.4%, of the functional groups is isolated at completion of the condensation.

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Some Heat Capacity Data for Gaseous 2,2,4-Trimethylpentane

BY MILO KIPERASH AND GEORGE S. PARKS

Recently Pitzer[1] has reported a single experimental value for the heat capacity at 423°K. and 1 atm. (constant pressure) of gaseous 2,2,4-trimethylpentane. On the basis of statistical calculations and with the guidance of this value he also has suggested the general equation

$$C_p = -227.3 + 110 \log T \qquad (1)$$

for the heat capacity of this hydrocarbon as a function of the absolute temperature.

Two years ago, in connection with some other work on organic compounds in the gaseous state, we likewise made five determinations of the molal heat capacity at 1 atm. pressure of gaseous 2,2,4-trimethylpentane. A "constant flow" method, briefly described elsewhere by Parks and Shomate,[2] was employed, and the uncertainty in the resulting data is probably within 1.5%. Our results lie between 442 and 458°K. and are given in the second column of Table I. For comparison the value of Pitzer is included parenthetically. Column 3 contains the corresponding values calculated by Pitzer's equation, from which our data differ on the average by 1.4%. In view of the facts this is a reasonable check.

In Column 4 appear C_p^0 values for the gas at zero pressure. These have been derived from the previous experimental results by use of Berthelot's equation of state ($C_p^0 = C_p - 81RPT_c^3/32P_cT^3$) and with the assumption of 25 atm. and

(1) Pitzer, THIS JOURNAL, 62, 1224 (1940).
(2) Parks and Shomate, J. Chem. Phys., 8, 429 (1940).

TABLE I
SOME HEAT CAPACITY DATA FOR GASEOUS 2,2,4-TRIMETHYLPENTANE
Units are cal. per degree per mole.

T, °K.	C_p (1 atm.) Expt.	Calc. eq. 1	C_p^0 Expt.	Calc. eq. 2
423	(61.6 ± 0.6)	61.6	(61.1)	60.3
442	63.8 ± 1.0	63.7	63.4	62.2
442	64.6 ± 1.0	63.7	64.2	62.2
448	65.6 ± 1.0	64.3	65.2	62.9
449	65.3 ± 1.0	64.4	64.9	63.0
458	66.7 ± 1.0	65.4	66.3	63.9

550° for P_c and T_c, respectively. The calculated values for C_p^0 in the last column have been obtained from Pitzer's general empirical equation for gaseous paraffins

$$C_p^0 = 5.65n - 0.62 + t(0.0111n + 0.0158) \qquad (2)$$

where n is the number of carbon atoms and t is the centigrade temperature.[3] While he suggests that this latter equation is probably applicable to branched paraffins as well as to the normal compounds, it apparently runs a little low in the case of this highly branched compound. In passing, we should note here that heat capacity values calculated for 2,2,4-trimethylpentane by the semi-theoretical methods of Bennewitz and Rossner[4] are of the order of 10 per cent. low, or more, as Pitzer likewise found in the case of their experimental determination on n-heptane.

(3) Pitzer, THIS JOURNAL, 63, 2413 (1941).
(4) Bennewitz and Rossner. Z. physik. Chem., B39, 126 (1938).

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STANFORD UNIVERSITY, CALIFORNIA

The Identification of Alcohols in Aqueous Solution

BY WILLIAM N. LIPSCOMB AND ROBERT H. BAKER[1]

The identification of an alcohol when it appears in aqueous solution as from the saponification of an ester usually involves its isolation by repeated distillation, salting out, and drying. Henstock[2] was able to avoid this time-consuming procedure by the use of the Schotten–Baumann reaction of p-nitrobenzoyl chloride at $-15°$.

We have found that the more satisfactory 3,5-dinitrobenzoates may be formed by slight modification of the Henstock procedure. The process involves adding alkali and sodium acetate to the aqueous solution of the alcohol and shaking it at

(1) Present address, Northwestern University, Evanston, Illinois.
(2) Henstock, J. Chem. Soc., 216 (1933).

0° with a hydrocarbon solution of 3,5-dinitrobenzoyl chloride.

The yield of ester is affected rather critically by the temperature, the nature and concentration of the alkali, and to a lesser extent by the catalytic effect of sodium acetate. Preliminary experiments showed that it was necessary to dissolve the solid dinitrobenzoyl chloride in an inert solvent so as to keep it in a liquid phase during the course of the reaction. When ether is used for this purpose the melting points of the esters, with the exception of ethyl, are consistently low. This is true even when extreme care is taken to remove all alcohol from the ether and therefore must be due to cleavage of the ether. Benzene is satisfactory except for its high melting point and this is easily lowered by the addition of dry ligroin.

Although the yield of ethyl ester is greater at 0° than at room temperature, it is not necessary to employ the difficultly-maintained lower temperatures. The yield of ethyl ester is four times as great when formed in the presence of 5% sodium hydroxide as it is when a similar concentration of sodium carbonate is used, and weaker bases such as sodium bicarbonate give negligible yields of the ester. Increasing the concentration of sodium hydroxide in the reaction mixture at 0° increased the yield of ethyl ester as shown in Fig. 1. It is impractical to use concentrations of sodium hydroxide in excess of 20% because the reaction mixture becomes semi-solid and difficult to handle.
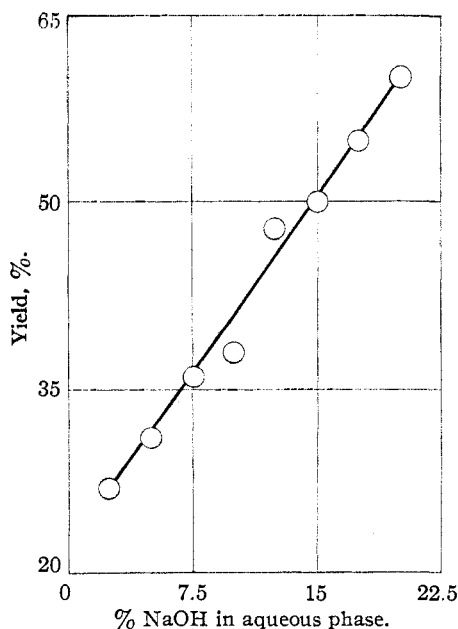

Fig. 1.

Reagent.—To 25 g. of 3,5-dinitrobenzoyl chloride is added 50 ml. of dry sulfuric acid-washed ligroin and the resulting solution is then diluted to 250 ml. with dry benzene.

Procedure.—One-half gram of sodium acetate crystals is dissolved in 10 ml. of a 5% aqueous solution of the alcohol, then 10 ml. of 40% sodium hydroxide is added and the solution cooled to 0°. Five ml. of the solution of 3,5-dinitrobenzoyl chloride in benzene–ligroin is then added and the mixture alternately shaken and placed in an ice-bath for one-half hour. The mixture is then transferred to a separatory funnel and extracted with 30 ml. of ether. The ether solution is washed with an equal volume of water, then 5% hydrochloric acid, and again with water. Evaporation of the solvent yields the crude derivative as recorded in Table I.

TABLE I

SUMMARY OF RESULTS

Alcohol	Crude ester, g.	Yield, %	M. p. of crude ester, °C.	M. p. in lit.,[a] °C.
Methyl	0.09[b]	17	94–96	107
Ethyl	.27	52	90–91	93
n-Propyl	.37	67	72–73	74
Isopropyl	.10	18	117–118	122
n-Butyl	.37	64	62–63	64
s-Butyl	.06	10	72–73	75
Isobutyl	.30	52	83–84	86
t-Butyl	.01	1		142
Allyl	.22	42	40–41	48

[a] Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1940, p. 185. [b] Obtained only after three successive additions and shakings with the acid chloride solution.

Sterols. CXXVI. Sapogenins. LII. The Structure of the Side Chain of Sarsasapogenin. The Identification of the Acid Obtained by the Haloform Reaction on the Dibasic Acid from the Potassium Permanganate Oxidation of Anhydrosarsasapogenoic Acid

BY RUSSELL E. MARKER AND ANTHONY C. SHABICA

We have repeated the experiment of Fieser and Jacobsen[1] on the hypohalite oxidation of the dibasic acid (II)[2] obtained by the permanganate oxidation of anhydrosarsasapogenoic acid (I).[3] We obtain an acid which corresponds with that of Fieser and Jacobsen.[1] We find, however, that it is the known 3(β)-hydroxy-etio-bilianic acid ($C_{19}H_{30}O_5$) (III) and not the C_{25} acid suggested by them. Although the analyses might fit either

(1) Fieser and Jacobsen, THIS JOURNAL, **60**, 2753 (1938).
(2) Marker and Rohrmann, ibid., **61**, 2072 (1939).
(3) Marker, Shabica and Turner, ibid., **63**, 2274 (1941).