activity × 8[7]:3,300 cts./min./mg. barium carbonate) was reduced with 8.7 g. (0.228 mole) of lithium aluminum hydride following the procedure of Nystrom and Brown.[8] The benzyl alcohol was obtained in a yield of 21.1 g. (85.5%), b. p. 114–115° (32 mm.).

Methylene-labeled Benzyl Chloride.—In an all-glass apparatus closed with a calcium chloride tube, 10.3 g. (6.6 cc., 0.075 mole) of phosphorus trichloride was added to 21.1 g. (0.195 mole) of benzyl alcohol (prepared above) at zero degrees. The mixture was allowed to stand at room temperature for thirty minutes and at 50° for one hour. The excess phosphorus trichloride was removed and the benzyl chloride distilled, b. p. 60–61° (12 mm.), yield 21.8 g. (88.1%).

Methylene-labeled Phenylacetic Acid.—Benzylmagnesium chloride was prepared from 21.8 g. (0.172 mole) of methylene-labeled-benzyl chloride and 4.2 g. (0.172 atom) of magnesium turnings. The Grignard reagent was carbonated at −5° with gaseous carbon dioxide and the reaction mixture processed in the usual manner. The phenylacetic acid was recrystallized from petroleum ether, m. p. 76–77° (cor.), yield, 17.3 g. (74%), specific activity × 8:3,300 cts./min./mg. barium carbonate.

β-Methylene-labeled β-Phenethyl Alcohol.—Phenylacetic acid (11.1 g.) was reduced with lithium aluminum hydride as above and β-phenethyl alcohol was obtained in a yield of 8.5 g. (85.6%), b. p. 114° (9 mm.).

β-Methylene-labeled β-Phenethyl Chloride.—β-Phenethyl alcohol (8.5 g.) was allowed to react with 4.8 g. of phosphorus trichloride in the normal manner and the chloride was received in a yield of 3.3 g. (33.8%), b. p. 55° (2 mm.).

β-Methylene-labeled β-Phenylpropionic Acid.—β-Phenethylmagnesium chloride was prepared from 3.3 g. of β-phenethyl chloride (prepared above) and 0.63 g. of magnesium and the Grignard reagent carbonated with gaseous carbon dioxide, yield 1.82 g. (51.5%), m. p. 48–49°, specific activity × 9:3,300 cts./min./mg. barium carbonate.

Decarboxylation Procedure.—A mixture of 0.25 g. of the acid and 0.25 g. of the catalyst and 5 cc. of quinoline was heated for forty minutes in a salt-bath. The reaction mixture was flushed continuously with nitrogen and after the heating the aeration continued for one hour at room temperature. The evolved carbon dioxide was collected in 50 cc. of 0.14 *M* barium hydroxide. The barium carbonate was collected by filtration under nitrogen and the precipitate washed with water, alcohol and ether and dried at 110°. The yields varied from 40–80%.

All samples of barium carbonate were regenerated to carbon dioxide and reprecipitated to check for radioactive impurities. In all cases, a constant specific activity was obtained.

Radioactivity Determination.—The procedure of Dauben, Reid and Yankwich[9] was employed for sample preparation and counting.

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[7] This value was obtained by combustion of a microsample of the ester, precipitation of the carbon dioxide as barium carbonate and counting the barium carbonate. To correct for the dilution of activity in the compound, the observed specific activity was multiplied by eight.

[8] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

[9] Dauben, Reid and Yankwich, *Anal. Chem.*, **19**, 828 (1947).

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Reaction of Thiophenealdehyde Derivatives with Maleic Anhydride

BY WERNER HERZ[1]

The present note describes the reaction of two derivatives of 2-thiophenealdehyde with maleic anhydride. Parallel reactions of benzylidene[2] and furfurylidene[3] derivatives have been reported previously.

Experimental

Thiophenealdehyde-1-maleylphenylhydrazone.—A solution of 3 g. of thiophenealdehyde phenylhydrazone[4] in 20 ml. of ether was treated with 1.8 g. of maleic anhydride. The solution was warmed until solution of the anhydride occurred. The crude product which separated after standing overnight was washed with ether and weighed 4.5 g. Several recrystallizations from ethanol raised the m. p. of the yellow needles to 119–120°.

Anal. Calcd. for $C_{15}H_{12}N_2O_3S$: C, 59.99; H, 4.03; neut. equiv., 300. Found: C, 59.95; H, 4.09; neut. equiv., 301.

Under the same conditions pyrrolealdehyde phenylhydrazone on treatment with maleic anhydride yielded golden-yellow needles which decomposed immediately on exposure to air and could not be recrystallized satisfactorily.

N-*p*-Tolylmaleamic Acid.—A solution of 1.8 g. of thiophenealdehyde *p*-toluidine[5] in 15 ml. of ether on treatment with 1.2 g. of maleic anhydride gave yellowish-green needles, m. p. 201° with gas evolution after recrystallization from ethanol, which did not depress the m. p. of authentic N-*p*-tolylmaleamic acid.[6]

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[2] La Parola, *Gazz. chim. ital.*, **64**, 919 (1934); **65**, 624 (1935).

[3] Herz, THIS JOURNAL, **67**, 1854 (1945).

[4] Biedermann, *Ber.*, **19**, 636 (1886).

[5] Hantzsch and Witz, *ibid.*, **35**, 841 (1901).

[6] Dunlap and Phelps, *Am. Chem. J.*, **19**, 492 (1897).

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The Heat Capacity of Organic Vapors. VI. Acetone[1]

BY BEN T. COLLINS,[2] CHARLES F. COLEMAN AND THOMAS DE VRIES

The work reported in this paper is a continuation of a program for measuring the heat capacity of organic vapors. The heat capacity and heat of vaporization of acetone has been measured at 1 atm., at temperatures from near its boiling point to 150°.

Experimental and Results

Two sets of determinations are reported. Those of set I were made with a reverse-flow calorimeter and auxiliary equipment previously described[3]; those of set II, with the apparatus and by the procedure described in the preceding paper.[4]

The values obtained for the heat capacity are presented in Table I and Fig. 1. The latter also shows the value 22.5 cal./mole/degree at 137°, reported by Bennewitz and Rossner,[5] and a line drawn through the calculated values of C_p at 1 atm. by Dobratz.[6] Other values reported in the literature are 20.1 and 21.7 for the temperature

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[3] De Vries and Collins, THIS JOURNAL, **63**, 1343 (1941).

[4] Coleman and De Vries, *ibid.*, **71**, 2839 (1949).

[5] Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 125 (1938).

[6] Dobratz, *Ind. Eng. Chem.*, **33**, 759 (1941).

TABLE I

HEAT CAPACITY OF ACETONE

Set I, Reverse-Flow Calorimeter, 760 mm.

t, °C.	61	75	90	105
T, °K.	334	348	363	378
c_p, cal./g./degree	0.375	0.374	0.380	0.384
C_p, cal./mole/degree	21.8	21.7	22.1	22.3
t, °C.	120	135	155	165
T, °K.	393	408	428	438
c_p, cal./g./degree	0.390	0.398	0.416	0.420
C_p, cal./mole/degree	22.7	23.1	24.2	24.4

Set II, Direct-Flow Calorimeter, 760 mm.

t, °C.	59.4	74.6	99.1	149.4
T, °K.	332.6	347.8	372.3	422.6
c_p, cal./g./degree	0.376	0.374	0.380	0.406
C_p, cal./mole/degree	21.8	21.7	22.0	23.6

ranges 26 to 110° and 27 to 179° by Wiedmann,[7] and 23.9 for the range 129 to 233° by Regnault.[8]

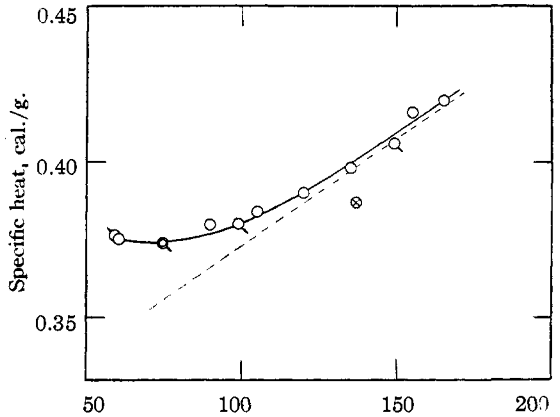

Fig. 1.—Specific heat of acetone: O, set I; ⚲, set II; ⊗, Bennewitz; - - - -, Dobratz.

The heat of vaporization at 1 atm. (56.5°) found from the determinations of set II is 119.5 cal./g., 6940 cal./mole. This value is lower than that tabulated in the "International Critical Tables,"[9] which is 124.5 cal./g.

The precision of the calorimetric data and the agreement between the two sets are good at the lower temperatures. The accuracy at 100° and lower is considered to be about 1%, as confirmed by check determinations with benzene.[4] At the higher temperatures the precision of the set I determinations was poorer. The accuracy of the 150° value of set II is probably within 2%.

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(7) Wiedmann, *Wied. Ann.*, **2**, 195 (1877).

(8) Regnault, *Me. del' Acad.*, **26**, 1 (1862).

(9) "International Critical Tables," Vol. V. McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 138.

On Erickson's Melting Point Formula for Straight-Chain Dicarboxylic Acids

BY LEO F. EPSTEIN

Erickson[1] has recently published a curious iterative empirical formula for the centigrade melting point T_n of a straight chain dicarboxylic acid containing $(n + 2)$ carbon atoms, *viz.*

$$T_n = 100\,d_n + 80 \qquad (1)$$
$$d_n = (0.095)^{0.85\,d_{n-1}} \qquad (2)$$

with the initial value $d_2 = 0.873$. By numerical calculation, carried up to $n = 30$, he finds that as n approaches infinity, $d_\infty \rightarrow 0.43$ and $T_\infty \rightarrow 123°$. This formulation is, so far as is known, the first time that an empirical function has been found which reproduces the odd-even oscillatory nature of the dicarboxylic acid melting points. Other substances[2] (*e. g.*, the fatty acids) also exhibit this peculiar behavior, for melting points and other physical properties (*e. g.*, aqueous solubilities).

This note is intended as a guide in fitting an Erickson-type formula to other data, by pointing out the limitations in the choice of constants, and by showing how the limiting value of the sequence can readily be computed without calculating all the intermediate values.

It follows from (2) that

$$d_n = \underbrace{C^{C^{C^{\cdot^{\cdot^{\cdot^{C^{C^{d_2}}}}}}}}}_{\ldots\ldots(n-2)C\text{'s}} \qquad (3)$$

with $C = (0.095)^{0.85} = 0.13523$ in the present case. Then

$$d_\infty = C^{C^{C^{C^{\cdot^{\cdot^{\cdot}}}}}} \qquad (4)$$

with an infinite number of terms, provided that C has a value such that the sequence converges. It is obvious that when $C = 0$, $d_\infty = 0$ and when $C = 1$, $d_\infty = 1$. By inspection, (4) can be written $d_\infty = C^{d_\infty}$. To establish the range of values of C for which a finite limit exists, consider the transcendental equation for d_∞, obtained by taking logarithms in (4)

$$d_\infty = \ln d_\infty / \ln C \qquad (5)$$

by writing $y_1 = x$ and $y_2 = \ln x/\ln C$, it will be seen that the sequence converges and $d_\infty = x$ exists when $y_1 = y_2$. Plotted against x, y_1 is a straight line with a unit slope through the origin; and y_2 is minus infinity at the origin, and increases monotonically, crossing the $y = 0$ line when $x = 1$, for all values of C. These two curves will

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(1) John G. Erickson, THIS JOURNAL, **71**, 307 (1949).

(2) J. F. Norris, "The Principles of Organic Chemistry," 3rd ed., McGraw-Hill, New York, N. Y., 1931, p. 142.