ever, as a result of the rapid decomposition of the sulfide at that temperature, the material could not be distilled successfully at atmospheric pressure. By repeated fractionation in packed columns at reduced pressure, the sulfide was recovered as a constant boiling, water-white, lachrymatory liquid; b.p. 62° (20 mm.); b.p. 82° (50 mm.); n^{20}_D 1.4826; d^{20}_4 1.1317.

Anal. Calcd. for $C_4H_6O_2S$: S, 27.14; neut. equiv., 59.07. Found: S, 26.68; neut. equiv., 58.41.

PHILLIPS PETROLEUM COMPANY
BARTLESVILLE, OKLAHOMA

Further Applications for Egloff's Boiling Point Equation. II

BY W. DAVID ENGLISH[1]

RECEIVED JANUARY 9, 1952

It was previously shown[2] that the equation derived by Egloff, *et al.*[3]

$$T = a \ln (n + b) + k$$

relating boiling points of hydrocarbons to their constitution is applicable to certain Group IV hydrides. In the equation, T is the boiling point in °K., n the number of atoms other than hydrogen, and a and b and k are empirical constants. k depends only on the structure of the molecule, while a and b do not vary with the structure, but are related to the Group IV element.

If the values of a and b previously reported for alkanes, silanes and germanes (Table VI) are plotted against the atomic weights of carbon, silicon and germanium smooth curves result. Extrapolation of the curves to the atomic weights of tin and lead gave values of a and b which were then substituted in the equation. When n was taken as 1, boiling points of stannane and plumbane were calculated (Table I). These values were about 18° higher than the observed values, the same discrepancy as was previously noted for methane,[3] silane[2] and germane.[2] A correction factor was introduced into the equation so that it read

$$T = a \ln (n + b) + k - \frac{18.0}{n^{\infty}}$$

The new term has the value of −18.0 when n = 1 and is 0 for any other value of n. In Table I there is a comparison of the boiling points calculated with the old and new forms of the equation and the observed values.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED BOILING POINTS FOR MH_4 COMPOUNDS

$$T = a \ln (1 + b) - 416.3 - \frac{18.0}{1}$$

Compound	Calcd. b.p. old eq., °K.	Calcd. b.p. new eq., °K.	Obsd. b.p., °K.	ΔT
Methane[a]	129.6	111.6	111.6	0
Silane[b]	179.0	161.0	161.6	+0.6
Germane[b]	202.1	184.1	183.0	−1.1
Stannane[c]	240	222	221	−1
Plumbane[d]	278	260	260	0

[a] Reference 3. [b] Reference 2. [c] Paneth, Haken and Rabinowitsch, *Ber.*, **57**, 1891 (1924). [d] Paneth and Rabinowitsch, *ibid.*, **58B**, 1138 (1925).

The correction factor is the equivalent of having a different k for compounds with the structure MH_4 compared to those with n-R-MH_3. The new k would equal −434.3. However, the extra term in the equation is more convenient than changing k.

Recent publication of physical properties of alkyl germanes (terminal Ge) alkyl stannanes (internal Sn) and disilyl alkanes (two terminal Si's) has made possible the calculation of Egloff equation constants for these families, Tables II, III, IV. The calculations were made using the k values derived by Egloff and determining a and b.

TABLE II

MONO-n-ALKYL GERMANES

$$T = 303.4 \ln (n + 7.0) - 416.3 - \frac{18.0}{n^{\infty}}$$

Compound	No. central atoms	T, °K.		ΔT
		Obsd.[a]	Calcd.	
Methylgermane	2	250	250	0
Ethylgermane	3	282.4	282.3	+0.1
n-Propylgermane	4	Above room temp.	311	...

[a] Teal and Kraus, THIS JOURNAL, **72**, 4706 (1950).

TABLE III

α,ω-DISILYL ALKANES

$$T = 342.2 \ln (n + 5.1) + k - \frac{18.0}{n_{\infty}}$$

Compound	No. central atoms	T, °K.		ΔT
		Obsd.[a]	Calcd.	
Normal compounds, k = −416.3				
Disilylmethane	3	299	299	0
1,2-Disilylethane	4	340	339	+1
2-Methyl compounds, k = −424.5				
1,1-Disilylethane	4	330	331	−1
1,2-Disilylpropane	5	368	367	+1

[a] English, Taurins and Nicholls, *Can. J. Chem.*, in press.

TABLE IV

POLYALKYL STANNANES

$$T = 324.7 \ln (n + 6.3) + k - \frac{18.0}{n^{\infty}}$$

Compound	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
Normal compounds, k = −416.3				
Dimethylstannane	3	308[a]	308	0
2-Methyl compounds, k = −424.5				
Trimethylstannane	4	332[b]	331	+1
Dimethylethylstannane	5	363[c]	363	0

[a] B.p. 35°, Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947). [b] B.p. 60°, Kraus and Greer, *ibid.*, **44**, 2629 (1922); b.p. 59°, Finholt, Bond, Wilzbach and Schlesinger, *ibid.*, **69**, 2692 (1947). [c] B.p. 90°, Bullard and Vingee, *ibid.*, **51**, 892 (1929).

By using the values of a and b previously derived for polyalkyl silanes[2] together with k's found by Egloff for 3- and 4-methyl compounds,[3] it was possible to calculate the boiling points of methyldiethyl- and methyldipropylsilane (Table V) to ±1°. This increases to four the number of structural constants (k) shown to apply to other Group IV hydrides as well as hydrocarbons.

The root mean square deviation for the compounds tabulated is ±0.71°, almost the same value as was found in the previous paper.

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[1] Defence Research Chemical Laboratories, Ottawa, Ont., Canada.

[2] W. D. English and R. V. V. Nicholls, THIS JOURNAL, **72**, 2764 (1950).

[3] G. Egloff, J. Sherman and R. B. Dull, *J. Phys. Chem.*, **44**, 730 (1940).

TABLE V

POLYALKYL SILANES

$$T = 322.0 \ln (n + 5.0) + k - \frac{18.0}{n^{\infty}}$$

Compound	No. central atoms	T, °K. Obsd.[a]	T, °K. Calcd.	Δ
3-Methyl compounds, $k = -422.9$				
Methyldiethylsilane	6	350	349	+1
4-Methyl compounds, $k = -424.6$				
Methyldipropylsilane	8	400	401	−1

[a] Price, THIS JOURNAL, 69, 2600 (1947).

In Table VI are listed the various values of a and b found in this and previous work. Except for the already mentioned regularities of a and b for compounds containing only one Group IV element, no systemization has yet been possible.

TABLE VI

COMPARISON OF a AND b

Type of compound	a	b
n-Alkanes[a]	323.7	4.4
Silanes[b]	395.8	3.5
Germanes[b]	446.1	3.0
Stannane	482.0	2.9
Plumbane	520.6	2.8
Monoalkyl silanes[b] (terminal Si)	321.1	5.2
Polyalkyl silanes[b] (internal Si)	322.0	5.0
α,ω-Disilyl alkanes (two terminal Si's)	342.2	5.1
Monoalkyl germanes (terminal Ge)	303.4	7.0
Polyalkyl stannanes (internal Sn)	324.7	6.3

[a] Reference 3. [b] Reference 2.

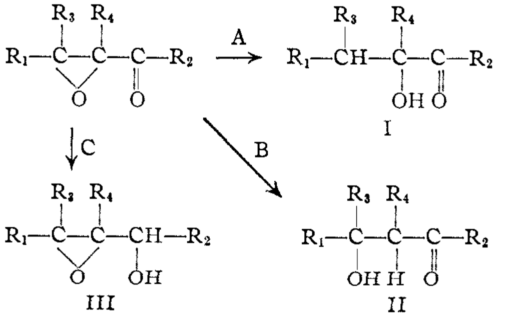
DIVISION OF ORGANIC CHEMISTRY
MCGILL UNIVERSITY
MONTREAL, P.Q., CANADA

Reduction of Benzalacetophenone Oxide

BY WERNER HERZ

RECEIVED JANUARY 26, 1952

Although the catalytic reduction of α-ketoepoxides may theoretically take three different paths,



and several such reductions have been reported,[1] systematic studies to determine the influence of catalyst or solvent on the mode of hydrogen addition have not been undertaken until recently. In the aliphatic–aromatic series, Temnikova and coworkers[2] have studied the reduction of benzalacetone oxide and several of its homologs. When R_1 = phenyl, R_2 = methyl or ethyl, R_3 and R_4 = H, use of platinum black or nickel–platinum favors path C and eventually leads to a glycol. When R_1 = phenyl, R_2 and R_4 = methyl, use of platinum black resulted in path A. On the other hand, in all experiments reported so far, path A was favored when the Russian workers used a nickel–palladium catalyst.

At the present time we wish to report the results of a study carried out on benzalacetophenone oxide (R_1 and R_2 = phenyl, R_3 and R_4 = H). The catalysts used were platinum oxide, 5% palladium–charcoal and Raney nickel (W-2), the solvents being alcohol, ether, ethyl acetate and acetic acid. Regardless of catalyst and solvent the mode of hydrogen addition invariably followed path A. In the case of one catalyst–solvent combination (platinum oxide–ether) the reduction stopped after the uptake of one molecule of hydrogen and a compound of type I, α-hydroxy-β-phenylpropiophenone, was isolated. More usually, however, reduction proceeded further and led to the formation of a glycol, 1,3-diphenylpropane-1,2-diol.

The identification of this compound was complicated by the fact that it may exist in two diastereoisomeric modifications which are difficult to separate. Since the melting points (84 and 128°) differed considerably from the melting point of recorded preparations,[3] the structure of the form, m.p. 84°, was proved by periodate oxidation and its homogeneity was established by conversion to the dibenzoate by hydrolysis. Only a small amount of the higher-melting form was isolated in pure form; however, its analysis and the results of periodic acid oxidation agreed with the assumption that it is a diastereoisomer of the lower-melting compound.

Acknowledgment.—We wish to thank the Research Corporation for a grant in support of this work.

Experimental[4]

Apparatus and Methods.—Reductions were carried out in a Parr low pressure hydrogenator at 2–3 atmospheres pressure. Five grams of benzalacetophenone oxide[5] was dissolved in 125 ml. of solvent with warming if necessary, the catalyst was added (0.2 g. of platinum oxide, 0.25 g. of 5% palladium–charcoal, one teaspoonful of Raney nickel[6]) and the mixture was shaken until hydrogen uptake ceased. The solvent was removed by evaporation at reduced pressure, repeated stirring of the viscous residue with petroleum ether and chilling usually caused crystallization although from certain runs only a sirup was obtained.

Platinum Oxide–Ether.—Reduction ceased after a volume of hydrogen corresponding to one mole had been taken up. Crystallization of the solid residue from much petroleum ether (b.p. 30–60°) yielded 3.3 g. of chunky crystals, m.p. 65–65.5°, which gave a positive test with Malaprade[7a] and Brady[7b] reagent. The melting point of α-hydroxy-β-

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(1) (a) A. E. Bradfield, A. R. Penfold and J. L. Simonsen, *J. Chem. Soc.*, 2744 (1932); (b) E. Wedekind and K. Tettweiler, *Ber.*, **64**, 1796 (1931); (c) J. Reese, *ibid.*, **75**, 384 (1942); (d) Pl. A. Plattner, H. Heusser and A. B. Kulkarni, *Helv. Chim. Acta*, **31**, 1822 (1948); (e) R. Adams and W. Herz, THIS JOURNAL, **71**, 2551 (1949).

(2) T. I. Temnikova and V. F. Martynov, *Zhur. Obshchei Khim.*, **15**, 499 (1945); T. I. Temnikova and V. A. Kropachev, *ibid.*, **18**, 692 (1948); **19**, 2069 (1949); **21**, 501 (1951).

(3) J. Levy and Dvoleitzka-Gombinska, *Bull. soc. chim.*, [4] **49**, 1765 (1931). report 63–64° as the m.p. of a product obtained from the corresponding dibromide by conversion to the diacetate followed by hydrolysis. P. Ruggli and A. H. Lutz, *Helv. Chim. Acta*, **30**, 1070 (1947), obtained a product of m.p. 65–66° by catalytic reduction of phenyl benzylglyoxal.

(4) All melting points are uncorrected. Analyses by the Clark Microanalytical Laboratory, Urbana, Illinois.

(5) E. P. Kohler, N. R. Richtmyer and W. F. Hester, THIS JOURNAL, **53**, 205 (1931).

(6) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

(7) (a) R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 115; (b) *ibid.*, p. 97.