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.

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Reduction of Benzalacetophenone Oxide

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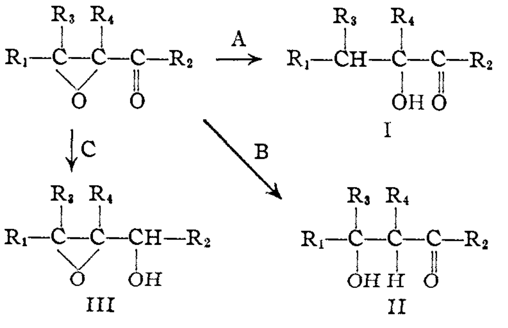
Although the catalytic reduction of α-ketoepoxides may theoretically take three different paths,



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.

phenylpropiophenone reported in the literature is 65–66°.[8]

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.61; H, 6.23. Found: C, 79.67; H, 6.12.

The 2,4-dinitrophenylosazone, recrystallized from ethyl acetate, melted at 233–234°.

Anal. Calcd. for $C_{27}H_{20}N_8O_8$: N, 19.17. Found: N, 19.39.

Further reduction of the acyloin in ethanol solution, using platinum oxide as catalyst, gave the diol of m.p. 84° described below in 85% yield.

Platinum Oxide–Ethanol.—Two moles of hydrogen was taken up. The residual sirup solidified on stirring with petroleum ether and chilling, weight 3.1 g. Evaporation of the petroleum ether gave 1.8 g. of an oil from which 217 mg. of the osazone of α-hydroxy-β-phenylpropiophenone was obtained on treatment with dinitrophenylhydrazone. The solid gave 2.1 g. of needles, m.p. 79.5–81°, after one recrystallization from benzene–ligroin; further crystallizations raised the m.p. to 84° but resulted in considerable losses. Periodic acid titration[9] indicated that all fractions, including those from the mother liquors, consisted exclusively of 1,2-diol.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 79.15; H, 6.82.

Benzoyl chloride in pyridine gave the dibenzoate in 75% yield, m.p. 157° from much ethanol.

Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.79; H, 5.54. Found: C, 80.27; H, 5.39.

The diacetate was prepared with acetic anhydride in pyridine and melted at 71–72°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.04; H, 6.46. Found: C, 73.59; H, 6.46.

Saponification of 1.1 g. of the dibenzoate regenerated 0.52 g. (90%) of the 1,2-diol, m.p. 84–84.5°. Periodic acid oxidation of the diol in methanol solution gave an oil which was converted to a mixture of dinitrophenylhydrazones. Chromatography over alumina (solvent benzene, eluent benzene–ether) led to the separation of the dinitrophenylhydrazones of benzaldehyde and phenylacetaldehyde in 85 and 82% yield, respectively.

Repetition of the work of Trevoy and Brown[10] who recently reported that a diol identical with that of Levy and Dvoleitzka-Gombinska[8] was obtained by lithium aluminum hydride reduction of benzalacetophenone oxide led to the isolation in 77% yield of an unsharply melting product, m.p. 72–80°, whose 1,2-diol content was only 80%. From this material we obtained the dibenzoate of m.p. 157° in 50% yield; and on saponification the diol of m.p. 84°.

Other Solvent–Catalyst Combinations.—Platinum oxide in ethyl acetate and acetic acid, palladium–charcoal in ethanol, ether, ethyl acetate and acetic acid, Raney nickel in ethanol, ether and ethyl acetate gave oily or solid diol mixtures which usually could be converted to 50–80% of crystalline material melting in the range 65–73°. Frequently a small amount of pure diol of m.p. 84° separated from the mother liquors of the first recrystallization on standing. Each time a solution of 1 g. of the mixture in 25 ml. of benzene was chromatographed through a column of 30 g. of alumina and developed with benzene, benzene–ether (4:1), benzene–ether (1:1) and ether. Ordinarily several eluate fractions yielded material melting sharply at 84° after recrystallization from petroleum ether, together with much lower melting material.

The diastereoisomer of m.p. 128° was isolated only from the oil obtained by reduction of benzalacetophenone oxide in ethanol with Raney nickel. Several fractions obtained after chromatography over alumina (solvent benzene, eluate benzene–ether) and crystallization from petroleum ether melted above 110°; these were combined and fractionally crystallized until the melting point remained constant at 128°. Periodic acid oxidation of this material, weight 73 mg., resulted in the characteristic odor of benzaldehyde.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 78.77; H, 7.00.

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Complex of Polysilicic Acid with N-Diethylaniline Hydrochloride

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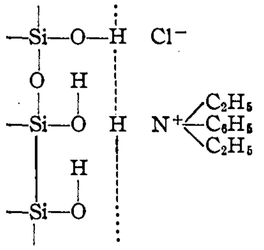
Kirk[1] first reported that complexes of polysilicic acid with electron donor compounds such as ethers and amides can be isolated from aqueous solution by a salting-out technique. It might therefore be expected that polysilicic acid might similarly combine with an amine to form an addition compound corresponding to a substituted ammonium salt of polysilicic acid. However, it has now been found that the complex salted out of a solution containing polysilicic acid and diethylaniline hydrochloride, contains silica combined with the amine hydrochloride rather than with the amine. Since the nitrogen atom in the amine salt does not possess a free pair of electrons, it is evident that the association of this salt cannot involve the formation of a hydrogen bond between the nitrogen atom and the hydrogen of polysilicic acid. In this complex, the relationship of the components might be represented by the following scheme, in which the electronegative chlorine, oxygen and nitrogen atoms are associated through hydrogen bonds.



This suggestion as to possible structure is purely speculative, but is offered in the hope that it will stimulate further investigation of this interesting system.

In the following experiments, polysilicic acid, made from sodium silicate, was permitted to polymerize in acidic aqueous solution, then diethylaniline hydrochloride was added, giving a homogeneous, clear aqueous solution. When the solution is then saturated with sodium chloride, the complex of polysilicic acid and diethylaniline hydrochloride separates either as a viscous second liquid phase or as a white precipitate, depending upon the degree of polymerization of the polysilicic acid. Neither polysilicic acid nor diethylaniline hydrochloride alone can be salted out of solution by this procedure.

Experimental

Preparation of Polysilicic Acid.—A solution of sodium silicate, 1.715 molar with respect to SiO_2, was first prepared

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[8] A. McKenzie, G. Martin and H. G. Rule, *J. Chem. Soc.*, **105**, 1583 (1915); E. P. Kohler and R. H. Kimball, THIS JOURNAL, **56**, 729 (1934); C. Prévost and A. Sommière, *Bull. soc. chim.*, [5] **2**, 1151 (1935); P. Julian, E. W. Meyer, A. Magnani and W. Cole, THIS JOURNAL, **67**, 1203 (1945).

[9] E. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 361.

[10] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[1] J. S. Kirk, U. S. Patents 2,408,654 and 2,408,656 (1946).