(Methylthio)triphenylsilane(II) is cleaved by phenyllithium to give tetraphenylsilane in a reaction analogous to the well-known cleavages of siloxanes by organometallic reagents.

$$(C_6H_5)_3SiSCH_3 + C_6H_5Li \longrightarrow (C_6H_5)_4Si + CH_3SLi$$

No observable reaction was noted between the lithium salt of triphenylsilanethiol (I) and iodobenzene, chlorotrimethylsilane, or chlorotriphenylsilane.

EXPERIMENTAL[9]

Preparation of the intermediate lithium salt of triphenylsilanethiol (I). To a stirred suspension of 0.62 g. (0.0193 g.-atom) of sulfur in 25 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution of triphenylsilyllithium[8] prepared by the cleavage of 5.0 g. (0.00965 mole) of hexaphenyldisilane with excess lithium. During the addition, some heat was given off, and the solution became almost black in appearance. When the addition was complete, Color Test I[10] was negative, indicating that the triphenylsilyllithium had reacted completely.

Solutions of I prepared in this manner were used in the following three reactions.

Reactions of intermediate I. A. With methyl iodide. Excess methyl iodide was added to a solution of I prepared in the manner described. The dark color of the solution was discharged, and heat was evolved. The tetrahydrofuran was strip distilled. The resulting oil was fractionated to give 4.05 g. (76%) of crude (methylthio)triphenylsilane, b.p. 145–150° (0.06 mm.), which solidified on standing. Recrystallization from petroleum ether (b.p. 60–70°) gave 3.07 g. (52%) of pure product, m.p. 83–84°.

Anal. Calcd. for $C_{19}H_{18}SSi$: Si, 9.15. Found: Si, 9.33, 9.28.

B. With benzyl chloride. To a solution of I prepared in the manner described was added excess benzyl chloride. The dark color of the solution was discharged over a period of about 30 min. The tetrahydrofuran was stripped off. Distillation of the residual oil gave 3.33 g. (45%) of crude (benzylthio)triphenylsilane (III), b.p. 172–177° (0.015 mm.). Two recrystallizations from petroleum ether (b.p. 60–70°) gave 2.7 g. (36%) of crystals, m.p. 92–94°.

Anal. Calcd. for $C_{25}H_{22}SSi$: Si, 7.33. Found: Si, 7.08, 7.27.

C. With benzoyl chloride. Addition of 3.05 g. (0.0217 mole) of benzoyl chloride to a solution of I, prepared in the manner described, resulted in a fast exothermic reaction. The tetrahydrofuran was stripped off the almost clear solution. The resulting oil was distilled to give 4.48 g. (59%) of crude (benzoylthio)triphenylsilane (IV), b.p. 183–189° (0.01 mm.). Recrystallization from anhydrous petroleum ether (b.p. 60–70°) gave 2.75 g. (36%) of yellow needles, m.p. 128–129°. The infrared spectrum of the product showed a normal carbonyl absorption peak at 5.9 μ.

Anal. Calcd. for $C_{25}H_{20}OSSi$: Si, 7.08. Found: Si, 7.10, 6.87.

Cleavage of (methylthio)triphenylsilane (II) *by phenyllithium.* To a stirred solution of 2.0 g. (0.00653 mole) of II in 20 ml. of ether was added 32 ml. of an ethereal solution containing 0.00978 mole of phenyllithium. The reaction mixture was hydrolyzed with water and filtered to give 1.97 g. (89%) of tetraphenylsilane, m.p. 233–235°, identified by a mixed melting point with an authentic specimen. The filtrate smelled strongly of a sulfur compound, presumably methyl mercaptan.

Acknowledgment. This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Dr. V. A. Fassell and Mr. R. Kniseley for obtaining the spectra.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

---

[9] Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Temperatures are uncorrected.

[10] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Consecutive Rate Constants for Saponification of the Isomeric Diethyl Phthalates

CHARLES A. BURKHARD[1] AND ROBERT E. BURNETT

Received November 25, 1959

In our recent publication[2] the saponification and acid-catalyzed hydrolysis of the diethyl phthalates and methoxyphthalates were reported. The rates of saponification of the individual ester groups in diethyl 2- and 5-methoxyisophthalates were calculated by the method of Frost and Schwemer.[3] Unfortunately, the tables in the Frost and Schwemer publication did not include time ratios for values of k_1/k_2 greater than 10.0, where k_1 and k_2 are, respectively, the rate constants for the consecutive saponification of first one and then the remaining carbethoxyl group of the diester molecule. This made it necessary to obtain by tedious calculation and interpolation the value of k_1/k_2 for diethyl 5-methoxyisophthalate which is greater than 10.0.

A computer program has been written[4] to extend broadly the tables of Frost and Schwemer, and thereby greatly facilitate the calculation of the consecutive or separate rate constants from a much wider range of experimental data. By using the new extended tables obtained from the computer program together with our previous experimental results,[2] it has been possible to calculate k_1 and k_2 for the saponification of the diethyl esters of the isomeric phthalic acids, and to recalculate those for 2- and 5-methoxyisophthalic acids. The recalculation of k_1 and k_2 for the latter two methoxy compounds has revealed that the constants initially reported[2] are one-half the true values.

---

[1] Present address: Locomotive & Car Equipment Department, General Electric Company, Erie, Pa.

[2] C. A. Burkhard and R. E. Burnett, *J. Am. Chem. Soc.*, **80,** 341 (1958).

[3] A. A. Frost and W. C. Schwemer, *J. Am. Chem. Soc.*, **74,** 1268 (1952).

[4] C. A. Burkhard, *Ind. Eng. Chem., in publication.*

The new and recalculated values for separate rate constants, and the ratio of k_1/k_2, for the saponification of the five esters are given in Table I.

TABLE I

RATES OF SAPONIFICATION OF DIETHYL ESTERS, 25°. INITIAL CONCENTRATION = 0.025 mole/l.

Diethyl ester	$k_1 \times 10^4$	$k_2 \times 10^4$	k_1/k_2
	l. mole^{-1} sec.$^{-1}$		
2-Methoxyisophthalate, Run 1	45.6	9.31	4.90
Run 2	46.4	9.46	4.90
5-Methoxyisophthalate	89.7	7.40	12.11
Phthalate	13.2	2.65	4.97
Isophthalate, Run 1	82.2	6.07	13.55
Run 2	79.7	5.88	13.55
Terephthalate,[a] Run 1	153	7.10	21.72
Run 2	157	7.20	21.72

[a] Crystals separated from the reaction mixture.

In a previously reported study[5] of the rate of saponification of diethyl phthalate in 91% ethanol a value of $k_1/k_2 = 2.5$ was obtained at 40.° Wegscheider[6] reported a ratio of about 2 for k_1/k_2 at 25°. In the present work the ratio (4.97) was found to be about double those originally reported. As has been noted[7] already the rate of saponification for the isomeric phthalates increases in the order diethyl phthalate, diethyl isophthalate, and diethyl terephthalate, the last being the fastest. The major increase is evidenced in the rate for the saponification of the first ester group, k_1. While attack on the first ester linkage in all five diesters, Table I, is enhanced, to varying extents through the influence of the second ester group, the much lower value of k_1 for the phthalate ester suggests a shielding effect brought about by the proximity of the bulky ethyl group. In the acid-catalyzed hydrolysis of these same esters,[2] the over-all k for diethyl phthalate is again noticeably lower than the others.

In the aliphatic series,[3] *e.g.*, in the saponification of diethyl adipate in dilute aqueous solution at room temperature, the values of k_1/k_2 indicate that the second ester group saponifies at a rate several times slower than the first group. Westheimer[8] attributes such effect to the electrostatic repulsion between the attacking hydroxyl ion and the monoethyl adipate anion. Since, under the conditions of saponification presently used (Table I) the rate constant for the saponification of ethyl benzoate was found[2] to be 6.3×10^{-4} l. mole^{-1} sec.$^{-1}$, which is close to the k_2 values in Table I, the electrostatic repulsion effect of the monoethyl phthalate anions would seem to be of lesser importance than the accelerating influence of the second ester group previously mentioned (indicated by the high k_1 values).

The position effect of the methoxyl groups in the substituted isophthalates on the saponification rate of the first ester linkage appears to be normal. The values for k_1 in Table I agree with the previously observed structural relations in that saponification is slightly faster when the methoxyl is *meta* and slower when *ortho* to the ester groups.

With the exception of the references cited for phthalate, the k_1 and k_2 values, and their ratios, for the isomeric esters had hitherto not been reported.

EXPERIMENTAL

The diethyl esters were purified by distillation in a Podbielniak spinning-band column or by recrystallization: diethyl phthalate, n_D^{20} 1.5021; diethyl isophthalate, n_D^{20} 1.5071; and diethyl terephthalate, m.p. 44°.

Saponification procedure. Reaction mixtures (100 ml.) containing 0.05 equiv. per l. of ethyl ester and of sodium hydroxide in 85% by weight ethanol were prepared. In each case 0.005 equiv. of ester and 40.6 ± 0.2 g. of aqueous ethanol (85% by weight ethanol) were weighed in 250-ml. glass-stoppered flasks and placed in a water bath maintained at 25 ± 0.1°. At the start of a reaction 50 ml. of 0.1*N* alcoholic sodium hydroxide (85% by weight ethanol), also adjusted to 25°, was added by pipet to the ester solution. To effect solution the flask was swirled in the bath for about 2 min. Zero time was taken at half the delivery time of the 50-ml. pipet. During a run at least five 10-ml. aliquots of reaction mixture were taken out at intervals and added to 15 ml. of 0.1*N* aqueous hydrochloric acid which had been cooled in ice to stop the reaction. Sampling time was taken when half the aliquot had been delivered into the acid. The resulting acid solution was promptly titrated with 0.1*N* aqueous sodium hydroxide to a greenish-blue end-point with bromothymol blue. It was established by direct titration of each of the five dibasic acids under consideration that in all cases both carboxyl groups are determined quantitatively under the analytical conditions employed. Duplicate saponification runs gave satisfactory checks.

GENERAL ELECTRIC RESEARCH LABORATORY
THE KNOLLS,
SCHENECTADY, N. Y.

---

(5) G. Semerans, *Gazz. chim. ital.*, **65**, 252 (1935).

(6) R. Wegscheider and W. Von Amann, *Monatsch*, **36**, 549 (1915).

(7) E. Kivinen and E. Tommila, *Suomen Kemistilehti*, **14B**, 7 (1941); *Chem. Abstr.* **36**, 21.

(8) See *Advanced Organic Chemistry* by G. W. Wheland, John Wiley and Sons, Second Ed., p. 440; also F. H. Westheimer, W. A. Jones, and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

Electronic Effects in the Gomberg Reaction[1]

HAROLD WEINGARTEN

Received December 14, 1959

When benzene competes with chlorobenzene or nitrobenzene for phenyl radicals in a Gomberg reaction the substituted benzene reacts more rapidly.[2] If the phenyl radical is substituted by an electron

---

(1) Presented at the 135th Meeting of the American Chemical Society at Boston, Mass., April 1959, Abstr., p. 47–O.

(2) D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 2994 (1952).