m.p. 147–148°, $[\alpha]_D$ −13.3°. (Lit.[12] gives 146–147°, $[\alpha]_D$ −13.8°.)

Anal. Calcd. for $C_{36}H_{54}O_2$: C, 83.34; H, 10.49. Found: C, 83.41; H, 10.43.

β-Sitosteryl 3,5-Dinitrobenzoate: Pale yellow plates from benzene–acetone, m.p. 211–213°, $[\alpha]_D$ −12.4°. (Lit.[12] gives 202–203°, $[\alpha]_D$ −10.4°.)

Anal. Calcd. for $C_{36}H_{52}O_6N_2$: C, 71.02; H, 8.61. Found: C, 71.28; H, 8.70.

Stigmasterol.—Fraction A, after two crystallizations from 95% acetone, was converted to the benzoate with pyridine–benzoyl chloride in the usual manner. After crystallization of the benzoate from acetone–benzene, the product was saponified. The free sterol, 0.05 g., was obtained as plates from 95% ethanol; m.p. 166–168°, $[\alpha]_D$ −46°. (Lit.[13] gives m.p. 168–169°, $[\alpha]_D$ −47.3°.)

Stigmasteryl Benzoate.—Plates from benzene–acetone, m.p. 158–161°, $[\alpha]_D$ −25°. (Lit.[13] gives m.p. 160.5–161.5°, $[\alpha]_D$ −24.5°.)

Acknowledgments.—The authors wish to thank the Engineering and Development Section of this Laboratory for supplying the dried potatoes, J. W. Garvin for extracting them, and T. Perlstein for obtaining the unsaponifiable extract. Carbon–hydrogen analyses were made by Kathryn M. Zbinden under the supervision of C. L. Ogg. The infrared spectra were obtained by C. S. Fenske under the supervision of C. R. Eddy.

(13) A. C. Ott and C. D. Ball, THIS JOURNAL, **66**, 489 (1944).

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The Rate of Pyrolysis of Di-(2-ethylhexyl) Sebacate[1]

BY EARL E. SOMMERS AND THOMAS I. CROWELL

RECEIVED JUNE 8, 1955

The rate of decomposition of liquid di-(2-ethylhexyl) sebacate, a synthetic lubricant, has been determined in the temperature range 261–304°. The results given in this paper supplement and confirm other recent studies of the kinetics and mechanism of ester pyrolysis.[2–4]

The reaction, which produced 2-ethylhexene-1, 2-ethylhexyl hydrogen sebacate and sebacic acid, was followed by titration for acid. Because of the high molar concentration of the pure liquid, decomposition of only 1% of the sample was adequate for a complete eight-sample run. Even in the first few tenths of a per cent. of its course, the reaction showed no induction period and was experimentally zero order, though the calculations were made assuming first-order kinetics. Neither concentrated sulfuric acid (1 mole per cent.) nor polished sheet copper catalyzed the reaction.

A plot of log k vs. $1/T$ (Fig. 1) is linear, and leads to an experimental activation energy of 47.1 kcal./mole. This result is comparable with the values 44.1 for cholesteryl acetate,[4] 39.2 for t-butyl propionate,[2] 38.1 for menthyl benzoate[3] and 45.8 for t-amyl acetate, calculated from the data of Menschutkin.[5] (The last three are vapor-phase decompositions.) The entropy of activation, −3.1 cal./deg.-mole, is compatible with a mechanism involving a cyclic transition state.[4,6]

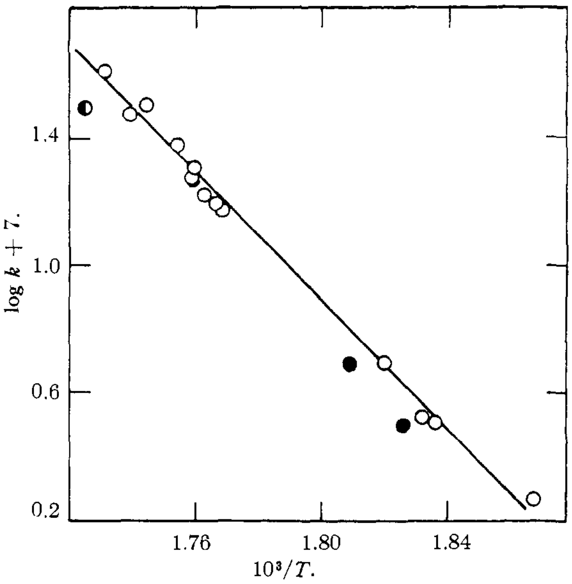

Fig. 1.—Variation of pyrolysis rate with temperature: ◐, Cu added; ●, H_2SO_4 added.

Experimental

Reaction Products.—Commercial diester (98–99%) was heated in a flask at about 300° for 3 hours. The volatile distillate was identified as a branched-chain octene by its physical constants, b.p. 120–121°, d^{20}_4 0.7318, n^{26}_D 1.4120, and assumed to be 2-ethylhexene-1. When the residue in the flask was cooled, sebacic acid precipitated (m.p. after recrystallization from aqueous nitric acid, 133–133.5°; m.p. of N-benzylamide, 165°).

To obtain the monoester, the heating of the diester was carried out for a somewhat shorter time at 280°. The liquid was taken up in ether and extracted with 5% sodium hydroxide. After the extract was washed several times with ether and acidified with dilute hydrochloric acid, an oil separated, which was purified by redissolving in sodium hydroxide and repeating the washing and precipitation. The following analytical data showed the oil to be a fairly pure sample of 2-ethylhexyl hydrogen sebacate: neutral equivalent 93% of theoretical; saponification equivalent 98% of theoretical; calcd. for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.79; H, 10.44.

Kinetics. Method A.—The diester was heated in a 500-ml. flask supplied with a reflux condenser, a magnetic stirrer and a mercury regulator which controlled the Glas-Col heater. Samples were withdrawn by a special pipet. **Method B.**—Sealed Pyrex tubes containing about 1 g. of diester were immersed in a Wood metal thermostat. They were removed at intervals and quenched in cold water before opening.

In both methods, the temperature was observed by means of a Chromel-P Alumel thermel The reference junction was maintained at 0°. The samples were titrated in 95% ethanol with 0.1 M aqueous potassium hydroxide and 1–2 drops of 0.1% phenolphthalein. Duplicate samples were taken in all cases, and except when darkly colored, showed good agreement.

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[1] From the M.S. thesis of Earl E. Sommers, University of Virginia, 1953. This work was done under the financial sponsorship of the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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[3] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 1715 (1953).

[4] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **75**, 2118 (1953).

[5] N. Menschutkin, *Ber.*, **15**, 2512 (1882).

[6] C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938); E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950); R. T. Arnold, G. G. Smith and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

The results are given in Table I. The agreement between methods A and B indicates that the pyrolysis is a homogeneous, liquid-phase reaction.

TABLE I

RATE OF PYROLYSIS OF DI-(2-ETHYLHEXYL) SEBACATE

Temp., °C.	Method	10^7 *k*, sec.$^{-1}$
261.6	A	1.87
271.4	A	3.29
272.7	A	3.42
276.4	B	4.85
292.1	B	15.6
292.6	B	16.5
294.1	B	17.5
295.1	B	21.6
295.2	A	19.3
295.3	B	20.1
296.0	B	25.3
299.6	B	34.3
301.5	B	31.7
304.5	B	43.5
274.5	A (H_2SO_4)	3.14
279.5	A (H_2SO_4)	5.00
306.2	A (Cu)	33.3

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1,2-Dichloro-1,2-dimethoxyethane

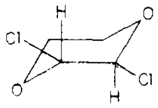
BY R. K. SUMMERBELL AND B. A. NELSON

RECEIVED JUNE 3, 1955

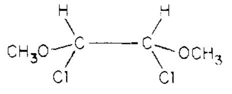
p-Dioxane has been chlorinated at reflux temperatures to give excellent yields[1] of a stable product, 2,3-dichloro-*p*-dioxane (I). The same product is obtained[2] when chlorine is added to *p*-dioxene, indicating a *trans* configuration for the chlorine atoms. The stability of the compound is in marked contrast to that of monochloro-*p*-dioxane[2] and of 2,5-dichloro-*p*-dioxane,[3] both of which deteriorate rapidly on standing at room temperature.

In connection with our studies of the chlorinated dioxanes, it occurred to us that the closely related compound, 2,3-dimethoxyethane, should also be examined. Under the same conditions that dioxane gives excellent yields of a stable product, this compound gave poor yields of an unstable product, 2,3-dichloro-2,3-dimethoxyethane (II). The structure of II was proved by hydrolysis to glyoxal and by reaction with phenylmagnesium bromide to yield hydrobenzoin dimethyl ether.

The instability of II is doubtless due to the possible free rotation about the carbon–carbon bond which readily permits a hydrogen atom to assume a *trans* position to the chlorine atom on the vicinal carbon atom, making possible the easy elimination of hydrogen chloride. A similar favorable relationship of the hydrogen and chlorine atoms in the *trans*-2,3-dichloro-*p*-dioxane (I), would be prevented by the ring structure.



I



II

Experimental

1,2-Dimethoxymethane.—2-Methoxyethanol was treated with methyl sulfate and aqueous sodium hydroxide in the usual manner.[4] The product was purified by refluxing seven hours with 1 *N* hydrochloric acid, separated by the use of solid sodium hydroxide, and dried by distillation from sodium; b.p. 84.5–85° (749 mm.), $n^{20}{}_D$ 1.3798, $d^{20}{}_{20}$ 0.864, *MR* calcd. 23.88 (found 23.87).

1,2-Dichloro-1,2-dimethoxyethane.—Dry chlorine was passed through 125 g. (1.4 moles) of 1,2-dimethoxyethane for ten hours. The temperature was gradually raised to 125° as the reaction products accumulated. Distillation at 4 mm. yielded some unchanged starting material, 23.7 g. material (b.p. 45–65°), which was collected in three fractions, and a tarry residue. The crystals that separated from all three fractions upon cooling were crystallized from dry ether; yield 12 g. (7.5%), m.p. 68–71°, b.p. 48–50° (4 mm.).

Anal. Calcd. for $C_4H_8O_2Cl_2$: Cl, 44.65; mol. wt., 158.98. Found: Cl, 42.63, 43.71; mol. wt., 159.8.

The colorless crystals decomposed readily in air, liberating hydrogen chloride. They reacted with potassium iodide in acetone to liberate iodine. Hydrolysis followed by treatment with phenylhydrazine yielded glyoxal osazone, m.p. 168–171° (lit. m.p. 168–170°). Treatment of 5 g. (0.03 mole) with excess phenylmagnesium bromide (0.25 mole) yielded 1 g. (13%) of the dimethyl ether of hydrobenzoin, m.p. 139–141° (lit. m.p. 140–142°).[5]

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[1] J. Boeseken, F. Tellegen and P. Henriquez, *Rec. trav. chim.*, **50**, 909 (1931), and numerous others. Yields of 90% are routinely obtained in our laboratory.

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[4] P. H. Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., New York, N. Y., 1935, p. 481.

[5] J. Irvine and J. Weir, *J. Chem. Soc.*, **91**, 1390 (1907).

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The Synthesis of 4-Amino-2,5-diphenylthiazole

BY E. C. TAYLOR, JR.,[1] J. A. ANDERSON AND G. A. BERCHTOLD

RECEIVED MAY 31, 1955

The versatility of α-cyanobenzyl benzenesulfonate (I) as a reagent for the synthesis of 4-aminothiazoles by condensation with thioureas[2] and dithiocarbamates[3] has been described recently. It was of interest as a logical extension of this work to investigate the reaction of I with thioamides in an attempt to prepare the difficultly available 2-aryl- and 2-alkyl-4-aminothiazoles. Our results are described briefly below.

The condensation of α-cyanobenzyl benzenesulfonate (I) with thiobenzamide gave the benzenesulfonic acid salt of a compound $C_{15}H_{12}N_2S$, which could have been either the expected 4-amino-2,5-diphenylthiazole (II) or the isomeric 5-amino-2,4-diphenylthiazole (III), depending on the mode of ring closure. That the product was actually II was established by diazotization and reduction to the known 2,5-diphenylthiazole (IV). This reac-

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[1] Frick Chemical Laboratory, Princeton University, Princeton, N. J.

[2] E. C. Taylor, Jr., J. Wolinsky and H. H. Lee, THIS JOURNAL, **76**, 1866 (1954).

[3] E. C. Taylor, Jr., J. Wolinsky and H. H. Lee, *ibid.*, **76**, 1870 (1954).