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

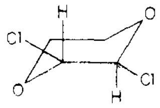
BY R. K. SUMMERBELL AND B. A. NELSON

RECEIVED JUNE 3, 1955

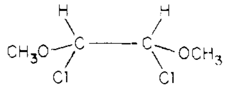
p-Dioxane has been chlorinated at reflux temperatures to give excellent yields[1] of a stable product, 2,3-dichloro-*p*-dioxane (I). The same product is obtained[2] when chlorine is added to *p*-dioxene, indicating a *trans* configuration for the chlorine atoms. The stability of the compound is in marked 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.

[2] R. K. Summerbell and L. N. Bauer, THIS JOURNAL, **57**, 2364 (1935).

[3] L. A. Bryan, W. M. Smedley and R. K. Summerbell, *ibid.*, **72**, 2206 (1950).

[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).

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).