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

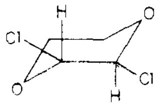
BY R. K. SUMMERBELL AND B. A. NELSON

RECEIVED JUNE 3, 1955

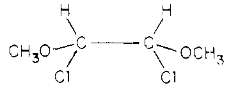
p-Dioxane has been chlorinated at reflux temperatures to give excellent yields[1] of a stable product, 2,3-dichloro-*p*-dioxane (I). The same product is obtained[2] when chlorine is added to *p*-dioxene, indicating a *trans* configuration for the chlorine atoms. The stability of the compound is in marked 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.), $n^{20}\text{D}$ 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).

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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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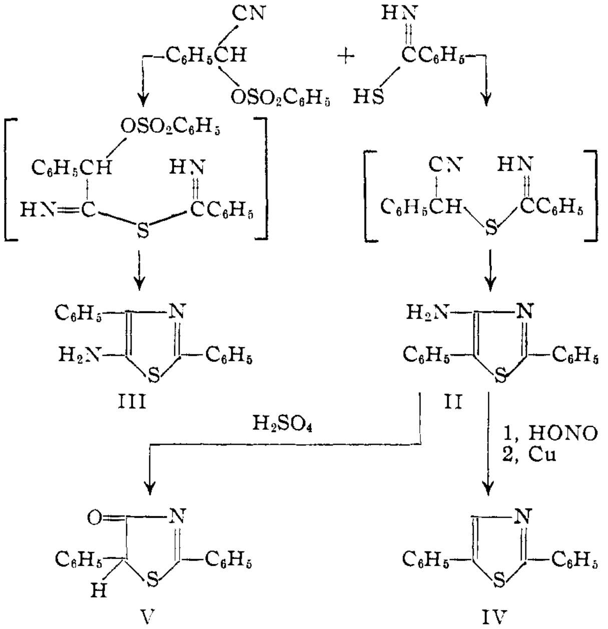
(1) Frick Chemical Laboratory, Princeton University, Princeton, N. J.

(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).

tion sequence may prove to be of interest for the synthesis of 2,5-diarylthiazoles; the only previously recorded synthesis of 2,5-diphenylthiazole involved the reaction of benzaminoacetophenone with phosphorus pentasulfide.[4]



In contrast to the extreme lability of the majority of previously prepared 4-aminothiazoles toward acid hydrolysis,[2,3,5–8] 4-amino-2,5-diphenylthiazole (prepared from the benzenesulfonic acid salt by treatment with ammonium hydroxide) proved to be remarkably stable and could be recovered unchanged after treatment with boiling alcoholic hydrochloric acid for ten minutes. It was converted in 95% yield to 2,5-diphenyl-4(5)-thiazolone (V) by heating under reflux with 40% sulfuric acid for ten hours.

Attempts to condense I with thioacetamide and α-phenylthioacetamide were unsuccessful, the only products isolated being ammonium chloride, ammonium benzenesulfonate and indefinite sulfur-containing oils.

Experimental

4-Amino-2,5-diphenylthiazole Benzenesulfonate.—A mixture of 5.46 g. (0.02 mole) of α-cyanobenzyl benzenesulfonate and 2.76 g. (0.02 mole) of thiobenzamide in 50 ml. of absolute ethanol was warmed on a steam-bath for about one minute to effect solution and then allowed to stand at 0° overnight. The yellow solid which had separated was collected by filtration, washed with cold absolute ethanol and recrystallized three times from absolute ethanol to give 3.02 g. (37%) of light yellow crystals, m.p. 198–199°.

Anal. Calcd. for $C_{15}H_{12}N_2S \cdot C_6H_6O_3S$: C, 61.4; H, 4.4; N, 6.8. Found: C, 61.7; H, 4.3; N, 6.9.

4-Amino-2,5-diphenylthiazole.—A mixture of 6.15 g. of 4-amino-2,5-diphenylthiazole benzenesulfonate and 50 ml. of aqueous ammonia (1:1) was shaken for about five minutes and the yellow solid then collected by filtration, washed with water and dried; yield 3.74 g. (99%), m.p. 103.5–104.5°.

Anal. Calcd. for $C_{15}H_{12}N_2S$: C, 71.1; H, 5.2; N, 11.1. Found: C, 71.3; H, 4.9; N, 10.9.

2,5-Diphenylthiazole.—One gram of 4-amino-2,5-diphenylthiazole was dissolved in a mixture of 30 ml. of ethanol and 15 ml. of concentrated hydrochloric acid. The solution was cooled to 0° and 4 ml. of a 20% solution of sodium nitrite added. After the mixture had stood for one hour, 0.1 g. of powdered copper was added and the solution was warmed to 50°. It then was filtered and the filtrate evaporated to about 20 ml. and cooled. The crystals which separated were recrystallized twice from absolute ethanol to give 0.27 g. (29%) of 2,5-diphenylthiazole, m.p. 103–104°. The reported melting point for 2,5-diphenylthiazole is 103–104°.[4]

Anal. Calcd. for $C_{15}H_{11}NS$: C, 75.9; H, 4.7; N, 5.9. Found: C, 76.0; H, 4.5; N, 5.8.

2,5-Diphenyl-4(5)-thiazolone.—A mixture of 3.78 g. of 4-amino-2,5-diphenylthiazole and 80 ml. of 40% sulfuric acid was heated under reflux for ten hours. The yellow product started separating from the hydrolysis mixture after about one hour. The cooled mixture then was filtered and the collected solid washed well with water and recrystallized from absolute ethanol to give 3.62 g. (95%) of bright yellow crystals, m.p. 215–215.5°.

Anal. Calcd. for $C_{15}H_{11}ONS$: C, 71.1; H, 4.4; N, 5.5. Found: C, 71.2; H, 4.6; N, 5.5.

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[5] W. Davies, J. A. Maclaren and L. R. Wilkinson, *J. Chem. Soc.*, 3491 (1950).

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The Synthesis of N-Methyl-3-cyano-4-methoxy-6-pyridone, a Structural Isomer of Ricinine

BY E. C. TAYLOR, JR.,[1] ALDO J. CROVETTI AND HARVEY M. LOUX

RECEIVED MAY 31, 1955

During the course of a program concerned with the chemistry of pyridine-N-oxides, which recently has led to a new synthesis of the alkaloid ricinine (I),[2] we had occasion to prepare for comparison purposes a hithertofore unknown structural isomer of this alkaloid. The condensation of diethyl acetonedicarboxylate with ethyl orthoformate and ammonia was carried out according to the method of den Hertog[3] to give ethyl 4,6-dihydroxynicotinate (II), which was converted to the corresponding amide III with anhydrous ammonia in a sealed steel bomb at 150°. Treatment of III with a mixture of phosphorus oxychloride and phosphorus pentachloride effected chlorination and simultaneous dehydration to give 4,6-dichloronicotinonitrile (IV) in an overall yield of 67%, based on II. An alternative and lengthier route to IV has been described by den Hertog.[4]

Sodium methoxide in methanol converted IV in 94% yield to 4,6-dimethoxynicotinonitrile (V), which was isomerized with methyl iodide in a sealed tube in 93% yield to N-methyl-3-cyano-4-methoxy-6-pyridone (VI), a structural isomer of ricinine. The structure of the product was confirmed by hydrolysis with concentrated hydrochloric acid to N-

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

[2] E. C. Taylor, Jr., and Aldo J. Crovetti, THIS JOURNAL, **77**, in press.

[3] H. J. den Hertog, *Rec. trav. chim.*, **65**, 129 (1946).

[4] H. J. den Hertog, J. C. M. Schogt, J. de Bruyn and A. de Klerk *ibid.*, **69**, 673 (1950).