stantially non-existent at temperatures above 350°. This conclusion is supported by thermodynamic data and calculations in references 8 and 9. (7) The material balances were found to be satisfactory (about 1% losses).

(8) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chem. Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1932.

(9) G. H. Burrows and C. Lucarini, This Journal, **49**, 1157 (1927).

Summary

1. The equilibrium constants for the system hydrindene-indene-hydrogen at temperatures between 375 and 525° have been determined.

2. The free energy equation for the reaction has been calculated.

3. A refractive index-composition equation for indene-hydrindene mixtures is given.

Edgewater, New Jersey Received June 9, 1949

NOTES

2,4- and 4,6-Dinitro- and Diamino-*m*-xylenes

By Roger Adams and A. S. Nagarkatti

There is no convenient method yet described for preparing pure 2,4- and 4,6-dinitro- or 2,4- and 4,6-diamino-*m*-xylenes. Because of the need for 2,4-diamino-*m*-xylene, a study of the separation of the mixed dinitro- and diamino-*m*-xylenes was undertaken.

When *m*-xylene is nitrated by means of nitric and sulfuric acids, a mixture of 2,4- and 4,6-dinitro-*m*-xylenes always results.[1,2,3] It has been reported that the two products may be separated by fractional crystallization from ethanol but this is difficult and unsatisfactory. The 4,6-dinitro-*m*-xylene is usually present in larger amounts. It is the less-soluble of the two and fractions can be obtained which consist mostly of this constituent. It is entirely impossible to obtain by this procedure the 2,4- isomer in any reasonable degree of purity. The pure 2,4-dinitro-*m*-xylene has previously been synthesized by nitration of 2-nitro-*m*-xylene.[4] The product from the nitration of *m*-xylene when crystallized from ethanol gives a crystalline material, usually with a melting point of 57-62°, which is not changed by further recrystallization.[2] It has now been found that by crystallization of this mixture from chloroform in which it is very soluble, a product results which, after two recrystallizations from the same solvent, melts sharply at 84°. About 10-15% of this product was obtained from the original mixture. This was characterized as pure 2,4-dinitro-*m*-xylene by reduction first with ammonium sulfide to 2-nitro-4-amino-*m*-xylene (m. p. 81°) and second by hydrogenation in presence of Raney nickel to 2,4-diamino-*m*-xylene (m. p. 65-66°). The diamine separated as an oil which by scratching was readily induced to crystallize. Upon one recrystallization from petroleum ether it was pure. This proved to be one satisfactory method for obtaining 2,4-diamino-*m*-xylene.

The 2,4- and 4,6-diamino-*m*-xylenes have been prepared previously by reduction (1) of the difficultly obtained dinitro compounds, (2) of the 2-nitro-4-amino-*m*-xylene[4] and 6-nitro-4-amino-*m*-xylene,[1] and (3) of 2,4-dinitro-3,5-dimethylbenzoic acid and of 2,6-dinitro-3,5-dimethylbenzoic acid, by means of tin and hydrochloric acid, with simultaneous loss of carbon dioxide.[5] Morgan[2] attempted the separation of the mixed diamines resulting from reduction of the mixture of dinitro-*m*-xylenes. Acetylation followed by crystallization then hydrolysis, crystallization of the diamine hydrochlorides, and finally fractional distillation of the free amines obtained from the salts gave a certain amount of 4,6-diamine in pure form but none of the pure 2,4-diamine.

A more simple separation of the mixed diamines has now been achieved. Catalytic reduction of the mixed dinitro compounds gave an oil which could not be induced to solidify. It was converted into the dihydrochlorides by addition of the required amount of concentrated hydrochloric acid. The solid dihydrochlorides have distinct differences in solubility in water and were separated by removal of successive amounts of solvent from the solution. The less-soluble material which crystallized first consisted of 2,4-diamino-*m*-xylene dihydrochloride; that obtained later proved to be 4,6-diamino-*m*-xylene dihydrochloride. Since the dihydrochlorides have high and unsharp melting points, fractions were made alkaline, the bases extracted with ether, dried and the melting points of the bases determined in order to follow the fractionation. About 10% of the mixture proved to be the 2,4-isomer which is in agreement with the amount found by separation of the two dinitro compounds by means of chloroform. To obtain the pure 2,4-dihydrochloride, one treatment more than for the 4,6-dihydrochloride was required ow-

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(1) Grevingk, *Ber.*, **17**, 2422 (1884).

(2) Morgan, *J. Chem. Soc.*, **81**, 86 (1902).

(3) Ruggli, Zimmermann and Thouvay, *Helv. Chim. Acta*, **14**, 1250 (1931).

(4) Noelting, Braun and Thesmar, *Ber.*, **34**, 2242 (1901).

(5) Bamberger and Demuth, *ibid.*, **34**, 27 (1901).

ing to the presence of the former in small amounts. The separation is simple and not time consuming and provides a very satisfactory way to the two pure isomers. The pure 4,6-diamine is very readily obtained.

Since two good routes are available to the pure 2,4-diamine, the isolation and reduction of pure 2,4-dinitro-*m*-xylene as first described or the separation of the 2,4- from mixed diamines, selection of one over the other will depend on the particular composition of the nitrated *m*-xylene and on the quantity of 2,4-diamine desired.

Experimental

Isolation of Pure 2,4-Dinitro-*m*-xylene.—In 70 ml. of hot chloroform were dissolved 135 g. of the crude crystalline mixture of the dinitro isomers (m. p. 57–62°). This was cooled in ice. The crystals that separated as long broad plates were collected by filtration and dried (21 g.). The product sintered at 75° and melted at 81–83°. This was again crystallized from 20 ml. of chloroform. About 10 g. of solid was recovered (m. p. 82–84°). Another crystallization from 5 ml. of chloroform yielded 9.5 g. of product, m. p. 84°, and further crystallization did not effect a change in melting point. The mother liquor from the second crystallization was worked up and 9 g. more of the compound, m. p. 84°, was obtained.

This was characterized as 2,4-dinitro-*m*-xylene by reduction to the nitro amine and to the diamine. Reduction with hydrogen sulfide in warm ammoniacal solution yielded 2-nitro-4-amino-*m*-xylene which crystallized from water as golden yellow needles, m. p. 80–81°.

A suspension of 4.4 g. of the dinitro compound in 120 ml. of ethanol was hydrogenated over Raney nickel at room temperature and under a pressure of 1800 p.s.i. The theoretical amount of hydrogen was absorbed in ten to fifteen minutes. The colorless solution was filtered from the catalyst and the catalyst was washed with two 10-ml. portions of ethanol. The filtrates were combined and the ethanol was removed by distillation at reduced pressure (aspirator). The resulting viscous oil gave 3.4 g. (quantitative) of a solid on scratching with a glass rod. This was purified by crystallization from petroleum ether (b. p. 65–110°). There resulted 2.8 g. of colorless needles, m. p. 65–66°; dibenzoate, m. p. 227°; diformate, m. p. 219°.

Separation of 2,4-Diamino-*m*-xylene and 4,6-Diamino-*m*-xylene from a Mixture.—Reduction of 39.2 g. of a mixture of the dinitro isomers (m. p. 57–62°) was carried out as in the previous experiment. The temperature rose to 75° during reduction. The final product was a brownish oil weighing 28 g. After introduction of 40 ml. of concentrated hydrochloric acid, water was added until a clear solution resulted (total volume about 135 ml.). This was boiled with charcoal for fifteen minutes and filtered. Crystallization of the salt was carried out as follows: The solution was evaporated on a steam-bath until crystals began to appear. After cooling, the crystals that deposited were collected by filtration. Similar treatments with successive filtrates gave four more fractions. The fractions separated in this way weighed 11.2 g., (A); 3.4 g., (B); 11.5 g., (C); 12.0 g., (D); and 3.5 g., (E). A sample of (A) was dissolved in water, the solution made alkaline and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, filtered and the ether evaporated. An oil resulted. By similar treatment (B) also gave an oil. Fractions (C), (D) and (E) all gave a solid, m. p. 97–110°, which, when once crystallized from petroleum ether (b. p. 65–110°), had a sharp m. p. 104°. It was the pure 4,6-diamino-*m*-xylene. Fractions (A) and (B) were combined and crystallized again as described above. The solid which separated at first weighed 4 g. By decomposition, an oil resulted which would not crystallize, but upon dissolving in petroleum ether (b. p. 65–110°) crystals were deposited. After one recrystallization, the 2,4-diamino-*m*-xylene was pure (m. p. 65–66°).

The 2,4-diamino-*m*-xylene dihydrochloride, which resulted from evaporation of a solution of (A) and (B), was recrystallized thrice from water, m. p. 317–320°.

Anal. Calcd. for $C_8H_{12}N_2 \cdot 2HCl$: C, 45.95; H, 6.75; N, 13.41. Found: C, 45.71; H, 7.05; N, 13.93.

The 4,6-diamino-*m*-xylene dihydrochloride (Fraction E) was crystallized thrice from water, m. p. 300–303°.

Anal. Calcd. for $C_8H_{12}N_2 \cdot 2HCl$: C, 45.95; H, 6.75; N, 13.41. Found: C, 45.97; H, 6.84; N, 13.39.

Satisfactory melting points for the dihydrochlorides can be obtained only by introducing the melting point tube into the bath previously heated at 295–300°. 4,6-Diamino-*m*-xylene was characterized by its dibenzoyl (m. p. 258°) and diformyl (m. p. 182–183°) derivatives.

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Identity of a Substance Isolated from *Cassia reticulata* Willdenow with that Isolated from *Cassia alata* L.

BY MARJORIE ANCHEL

In a recent publication[1] the isolation of unidentified "pale yellow crystals" from the leaves of *Cassia reticulata* Willdenow was mentioned in a footnote. While the structure of this compound has not yet been established, its identity with a substance obtained from the leaves of *Cassia alata* L. by Nazario and Hauptmann[2] is apparent from the following data.

			"Pale yellow crystals"	Compound of Nazario and Hauptmann
Analysis, %	Carbon		60.16	60.10
	Hydrogen		2.95	2.82
Melting point, °C.			330–340 dec. uncor.	335-336
Diazomethane product	Analysis, %	Carbon	61.93	62.23
		Hydrogen	3.94	3.63
		OCH_3	19.21	Mol. wt. 318
		Sapn. eq.	...	160.9
	Melting point, °C.		182.5–183	187

These figures agree well with the empirical formula $C_{15}H_8O_7$ (C, 60.01; H, 2.69) for the original compound, and $C_{17}H_{12}O_7$ (C, 62.18; H, 3.63; OCH_3, 18.91; mol. wt., 328) for a dimethylated product.

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(1) Anchel, *J. Biol. Chem.*, **177**, 169 (1949).

(2) Private communication from Dr. Hauptmann; see THIS JOURNAL, **72**, 1492 (1950).

THE NEW YORK BOTANICAL GARDEN
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Erythrina Alkaloids. XVII. Tetrahydroerysovine

BY KARL FOLKERS AND FRANK KONIUSZY

The minimum curarizing dose of erysopine hydrochloride and of erysodine hydrochloride as determined by intralymphatic injection in frogs was found to be 4 and 10 mg./kg., respectively.[1] Hydrogenation of these two alkaloids to give tetrahydroerysopine[2] and tetrahydroerysodine[2,3] re-

(1) Unna and Greslin, *J. Pharmacol.*, **80**, 55 (1944).

(2) Koniuszy, Wiley and Folkers, THIS JOURNAL, **71**, 875 (1949).

(3) Prelog, Wiesner, Khorana and Kenner, *Helv. Chim. Acta.*, **32**, 453 (1949).