

show little effect upon critical concentration. The equivalent conductivity curve shows no break or a very doubtful one at the critical concentration, as expected for this type of polycyclic compound. Bile salts and sodium abietate, both shown to be colloidal electrolytes by freezing point measurements, give no break in the conductivity curve.^{5,6} The conductivity curve determined here ties in satisfactorily with the data given by Woodbury and Rosenblum,⁷ converted from 30 to 25° by assuming that the salt has the same temperature coefficient as that of the sodium ion.

The surface tension of these solutions is fairly low, but relatively independent of concentration and may easily result from small amounts of impurities.

(5) J. W. McBain and S. A. Johnston, *Proc. Roy. Soc. (London)*, **191A**, 129 (1942).

(6) I. M. Kolthoff and W. F. Johnson, *J. Phys. Chem.*, **50**, 440 (1946).

(7) D. T. Woodbury and C. Rosenblum, *J. Biol. Chem.*, **171**, 447 (1947).

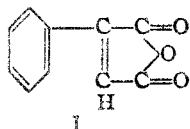
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIF.

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A Preparation of Phenylmaleic Anhydride

BY LEONARD E. MILLER, HARLOW B. STALEY AND D. J. MANN

Although phenylmaleic anhydride (I) was first isolated in low yield as a by-product in the synthesis of phenylmalic acid by the reaction of phenylsuccinic acid with bromine and phosphorus tribromide,¹ no satisfactory procedure for the preparation of (I) has been reported.



I

When phenylsuccinic anhydride is permitted to react with N-bromosuccinimide in the presence of a catalytic amount of benzoyl peroxide, phenylmaleic anhydride can be isolated in 57–64% yield.

The use of N-bromosuccinimide as a dehydrogenating agent for several hydroaromatic compounds has been reported recently by Barnes.²

Experimental³

Phenylsuccinic anhydride,⁴ m. p. 53–54°, was prepared in 78–84% yield from phenylsuccinic acid.⁵

Into a 500-ml., two-necked flask, equipped with a mechanical Hershberg stirrer (made of nichrome wire) and a condenser fitted with a drying tube, were placed 17.8 g. (0.1 mole) of N-bromosuccinimide, 8.8 g. (0.05 mole) of phenylsuccinic anhydride, 200 ml. of carbon tetrachloride

and 0.1 g. of benzoyl peroxide. The reaction mixture was heated under reflux with stirring for twenty-four hours, during which time the solution became bromine-red in color and a precipitate of succinimide formed. After the mixture was cooled to room temperature, the insoluble succinimide was separated on a filter and washed with several portions of hot benzene until the washes no longer gave a positive Baeyer test with potassium permanganate (about 150 ml. of benzene were required). When cool, the combined benzene and carbon tetrachloride solutions deposited an additional small quantity of succinimide which was separated. The clear solution was concentrated by distillation to a volume of 30 ml. and was then placed in a refrigerator for two hours. The crystals of phenylmaleic anhydride which formed were separated and recrystallized from dry acetone–petroleum ether (high boiling); yield 2.1–2.3 g., m. p. 119–120° (reported, 119–119.5°¹).

After the evaporation of the carbon tetrachloride filtrate to dryness under reduced pressure (water pump) in a two-bulb distillation apparatus, the residue was distilled under reduced pressure (1.0 mm.). At 60–70° a few drops of a yellow liquid were collected; this forerun was discarded. At 130–145° a yellow solid was collected. This material was recrystallized twice from dry acetone–petroleum ether (high boiling) (Norite) to give 2.1–2.3 g. of phenylmaleic anhydride, m. p. 119–120°. From the combined recrystallization filtrates, 0.8–1.0 g. of equally pure product was isolated. The total yield was 5.0–5.6 g. (57–64%).

The percentage yield was slightly lower (53–57%) when four times these amounts were used.

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UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

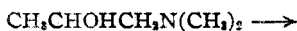
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Displacement-chlorination of Dimethylamino-propanol-2

BY N. I. WENDLER AND M. TISHLER

The reaction of methanesulfonyl chloride with dimethylaminopropanol-2 in an inert solvent was found to give rise to the *o*-mesylate hydrochloride (II) admixed to a greater or lesser extent with the hydrochloride of the propanolamine (I). The *o*-mesylate hydrochloride (II) could be obtained directly and in pure condition by conducting the reaction in a solvent mixture consisting of equal parts of chloroform and acetone.

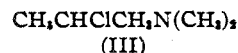
The *o*-mesylate hydrochloride was titrated with one equivalent of alkali and was converted thereby to the free ester base, characterized as its picrate. When heated above its melting point for a short time the *o*-mesylate hydrochloride was converted smoothly by internal displacement into dimethylamino-2-chloropropane (III). The latter was isolated and identified as its picrate.



(I)



(II)



(III)

Experimental

Dimethylaminopropanol-2 *o*-Mesylate Hydrochloride.—To a stirred solution of 10.5 g. of dimethylaminopropanol-2 in 25 cc. of chloroform at 0° was added portion-wise a solution of 12.5 g. of methanesulfonyl chloride in 25 cc. of chloroform. The homogeneous solution was treated with

(1) Alexander, *Ann.*, **258**, 67 (1890).

(2) Barnes, *This Journal*, **70**, 145 (1948).

(3) All m. p.'s and b. p.'s are uncorrected.

(4) Verkade and Hartman, *Rec. trav. chim.*, **52**, 945 (1933).

(5) "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1941, p. 451.

50 cc. of acetone and stored in the cold for twenty hours. During this time the *o*-mesylate hydrochloride crystallized. The crystals were collected, washed with cold 50% acetone-chloroform and dried in a vacuum desiccator over solid potassium hydroxide; yield 9.5–10 g. (40–45%), m. p. 126.5–128°. A small sample was recrystallized from acetone affording colorless micro-rhombs, m. p. 130–131°.

Anal. Calcd. for $C_8H_{10}O_2NSCl$: N, 6.44; Cl, 16.20; neut. equiv., 217.5. Found: N, 6.59; Cl, 16.10; neut. equiv., 226.

A sample of the *o*-mesylate hydrochloride was neutralized with aqueous potassium hydroxide at 0° and the oil which separated was extracted with ether-petroleum ether and dried over solid potassium hydroxide. The filtered solution was concentrated to dryness and the residue was converted to a picrate in ethyl acetate-ether solution. Recrystallization from ethyl acetate-ether afforded the picrate of the *o*-mesylate base as fine yellow needles, m. p. 90–91°.

Anal. Calcd. for $C_{12}H_{18}O_7N_4S$: C, 35.12; H, 4.39; N, 13.66; S, 7.81. Found: C, 35.39; H, 4.39; N, 13.67; S, 8.53.

Dimethylamino-2-chloropropane from *o*-Mesylate Hydrochloride.—*o*-Mesylate hydrochloride (II), 3.8 g., was sealed under vacuum in an ampule and heated in xylene vapor for four hours. The ampule was cooled. The contents were dissolved in an equal volume of water and treated with an excess of 50% aqueous potassium hydroxide solution. The oil which separated was extracted with petroleum ether, dried over solid potassium hydroxide and the solvent evaporated. The residue was converted to its picrate in ethyl acetate-ether solution and recrystallized from the same solvent as fine yellow needles, m. p. 101–103°. A mixed melting point with authentic picrate of dimethylamino-2-chloropropane was undepressed; yield 3.8–4.2 g. (70–75%).

Anal. Calcd. for $C_{11}H_{15}O_7N_4Cl$: Cl, 10.13; Found: Cl, 9.74.

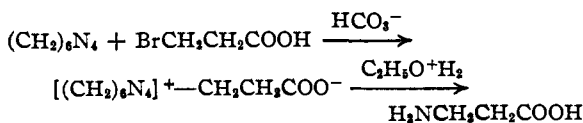
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RAHWAY, N. J.

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An Application of the Delépine Reaction to β -Bromopropionic Acid

BY N. L. WENDLER

A modification of the Delépine reaction¹ has been applied to β -bromopropionic acid for its conversion to β -alanine. A quaternary betaine-complex was formed between β -bromopropionic acid and hexamethylenetetramine according to a method applied by Schubert² to iodoacetic acid. This complex was subsequently decomposed by hydrochloric acid in ethanol to afford β -alanine in good yield and high state of purity.



Experimental

To a solution of 5 g. of β -bromopropionic acid³ in 15 cc. of water and 10 cc. of ethanol was added 2.74 g. of sodium bicarbonate. After neutralization was complete, a solution of 4.57 g. of hexamethylenetetramine in 10 cc. of water was added and the resulting solution allowed to

stand at room temperature for fifteen hours. At the end of this time, 50 cc. of ethanol was added to the point of faint turbidity followed by scratching, whereupon voluminous crystallization of colorless needles of the betaine-complex ensued. The crystals were chilled in ice for one to two hours and filtered, 9 g. A second crop afforded 0.5 g. yielding a total of 9.5 g. of material.

The betaine-complex (9.5 g.) was treated with 120 cc. of ethanol and 15 cc. of concentrated hydrochloric acid and refluxed for fifteen hours. The mixture was concentrated to dryness *in vacuo* at 50° and the residue extracted with several portions of ethanol. The filtered extract was concentrated to dryness and the residue boiled under reflux with 50–75 cc. of water for one-half hour. The cooled aqueous solution was treated portion-wise with an excess of silver oxide with stirring to remove chloride ion and subsequently filtered, and the filtrate saturated with hydrogen sulfide gas. The precipitated silver sulfide was removed by centrifugation followed by filtration. The colorless solution was concentrated *in vacuo* to a volume of a few cc. and diluted with ethanol to the point of crystallization. After chilling and filtering there was afforded 2.5 g. (85%) of β -alanine, m. p. 199–200° dec. A mixed melting point with known material was undepressed.

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Explosive Properties of Metal Amines¹

BY W. R. TOMLINSON, K. G. OTTOSON AND L. F. AUDRIETH

The literature contains numerous references to the explosive nature of certain coordination compounds, but no generalization has thus far been formulated in which an effort has been made to relate chemical composition of such coordination compounds to explosive character. The experimental evidence which is presented below, together with information gleaned from the literature, demonstrates that metal compounds containing (a) coordinated ammonia and related nitrogen-containing donor molecules, and (b) coordinated and/or ionic groups of an oxidizing nature such as perchlorate, chlorate, nitrate, nitrite (or nitrate- and nitro-groups), will decompose violently under various conditions. As is known to be the case among substances classed as explosives, the sensitivity of various coordination compounds to impact, to friction, and to heat will vary widely; nevertheless, some of these same compounds can be caused to detonate when properly initiated. For this reason, due caution should be exercised in the preparation, handling and storage of compounds falling within the categories defined above.

It is significant that "metal nitrates with molecular ammonia" have been incorporated in explosive compositions containing ammonium nitrate as the principal ingredient.² Metallic chlorates and perchlorates containing coordinated hydrazine³ have been found to be brisant and sensitive explosives. Other coordination compounds reported

(1) Publication of the material contained in this paper has been approved by the Ordnance Department of the United States Army.

(2) Cook, Davis and Lawson (to E. I. du Pont de Nemours and Co.), British Patent 544,582; *cf. Chem. Abstracts*, 36, 6804 (1942).

(3) Friederich and Vervoort, *Z. ges. Schiess.-Sprengstoffw.*, 21, 49, 65, 84, 103, 123, 143 (1926).

(1) Delépine, *Compt. rend.*, 120, 501 (1895).

(2) Schnbert, *J. Biol. Chem.*, 116, 444 (1936).

(3) "Organic Syntheses," Vol. IV, p. 25.