boiling point of 2,2′-dimorpholinodiethyl ether as given by Sand.[10] The picrate melted at 177°. A picrate prepared from known 2,2′-dimorpholinodiethyl ether melted at 175°[11] and a mixture of the two picrates melted at 175°.

Table II gives a summary of the compounds obtained. The percentage yields are based upon the amount of 4-morpholineëthanol used.

TABLE II

	Grams	Yield, %
Water	..	..
Morpholine	15.4	12
β-4-Morpholineëthanol	29.0	22
1,2-Dimorpholinoethane	7.2	6
2,2′-Dimorpholinodiethyl ether	8.2	6
Acetylene	..	..

4-Morpholinoethyl Chloride with Alcoholic Potassium Hydroxide.—To 13.4 g. (0.09 mole) of 4-morpholinoethyl chloride was added 9.2 g. of potassium hydroxide in 9 cc. of water and 66 cc. of absolute alcohol. After heating on a steam-bath for two hours, the solution was cooled and diluted with 50 cc. of water. The alcohol was removed by distillation using a fractionating column. The aqueous solution was extracted with ether, the ether extract dried over solid sodium hydroxide and the ether removed by distillation. The residual liquid distilled at 93–97° (14 mm.) and was redistilled at 200–201° (uncor.) at atmospheric pressure. The yield was 11 g. (77%). Since this boiling point corresponds to that of 4-morpholinoethyl ethyl ether, a picrate was prepared. It melted at 102° and a mixture with some unknown 4-morpholinoethyl ethyl ether picrate[12] melted at 102°.

(10) Sand, *Ber.*, **34**, 2906 (1901).
(11) Mason and Malkiel, THIS JOURNAL, **62**, 1449 (1940).

Summary

4-Morpholineëthanol was dehydrated by passing the vapors through a tube containing activated aluminum oxide at 270–280°. In addition to water, the products isolated were acetylene, morpholine, 1,2-dimorpholinoethane, 2,2′-dimorpholinodiethyl ether and unreacted 4-morpholineethanol. A further attempt to prepare N-vinyl morpholine by treating 4-morpholinoethyl chloride with alcoholic potassium hydroxide yielded only 4-morpholinoethyl ethyl ether.

(12) Mason and Block, *ibid.*, **62**, 1446 (1940).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

Arylsulfonyl Ureas

BY EDWARD H. COX AND SAMUEL M. RAYMOND, JR.

A search of the literature reveals that only two reactions for the preparation of arylsulfonyl ureas have been reported. Billeter[1] prepared benzenesulfonyl urea by the action of ammonia on benzenesulfonyl isocyanate, which was prepared from benzenesulfonyl chloride and silver cyanate. No yields are recorded for any of the reactions leading to the final product. The reaction of acid chlorides and silver cyanate gives only fair yields and is so highly exothermic as to require careful attention.[2]

Much earlier Cleve[3] reported the preparation of two sulfonyl urea derivatives of naphthalene, by the action of potassium cyanate on the aminonaphthalene sulfonamides. The compounds were apparently impure products, and neither experimental details nor analyses are given.

We attempted some methods of preparing arylsulfonyl ureas without success. The hydrolysis of benzenesulfonyl guanidine[4] by barium hydroxide solution produced benzenesulfonamide while the original guanidine was recovered after treatment with boiling hydrochloric acid. From analogy in the pyrimidine series[5] we subjected benzenesulfonyl methylisothiourea to boiling hydrochloric acid. Methyl mercaptan and benzenesulfonamide were produced.

McKee[6] has reported that when phenyl methylisourea was heated with hyrochloric acid, phenylurea and methyl chloride were produced. We have applied this reaction with success in the preparation of arylsulfonyl ureas. When the arylsulfonyl ethylisoureas are treated with hydrochloric acid, the arylsulfonyl ureas are produced in good yields.

Experimental Part

The procedure for the preparation of the following arylsulfonyl ureas, with but slight changes, is the same as that given for benzenesulfonyl urea. The melting points and analyses for both the isoureas and ureas are given in tabular review. It is recommended that the starting material,

(1) Billeter, *Ber.*, **37**, 694 (1904).
(2) Communication from Professor A. J. Hill, Yale University.
(3) Cleve, *Ber.*, **21**, 3266, 3273 (1888).
(4) Ackermann, *Z. physiol. Chem.*, **47**, 366 (1906).
(5) Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 394 (1907).
(6) McKee, *ibid.*, **26**, 230 (1901).

cyanamide, be desiccated for several days over phosphorus pentoxide before using.

Ethylisourea Hydrochloride.—This compound was prepared, with modifications, by the procedure of Stieglitz and Noble.[7] Dry hydrogen chloride was passed into a solution of 10 g. of cyanamide in 100 cc. of absolute ether until no more precipitate came down. The cyanamide dihydrochloride was filtered, washed with ether and stored in a desiccator over phosphorus pentoxide. The yield was 95%.

Cyanamide dihydrochloride, 23 g. (0.2 mole), and cyanamide, 8.4 g. (0.2 mole), were suspended in 70 cc. (1.2 mole) of absolute alcohol and heated in a pressure bottle for one hour at 55–65°. One-half of the alcohol was removed at the water pump and 150 cc. of absolute ether was added. An oil which first appeared soon solidified into a white crystalline mass. The weight of the crystals of ethylisourea hydrochloride was 40 g. (80%).

Benzenesulfonyl Ethylisourea.[8]—The best yields of this compound were obtained in the following manner: to a mixture of 10 g. (0.08 mole) of ethylisourea hydrochloride and 14 g. (0.08 mole) of benzenesulfonyl chloride in 50 cc. water, was added a solution of 6.4 g. (0.16 mole) of sodium hydroxide in 30 cc. of water. The reaction mixture was kept cold in an ice-bath and stirred during the addition of the alkaline solution. One-third of the alkaline solution was added and the reaction mixture was set aside until it showed acid to litmus. The second third was added likewise. The reaction mixture remained permanently alkaline after the third portion of alkali was added. After standing in the cold for twenty-four hours the reaction mass was filtered and washed with cold water. The crude air-dried product weighed 11.7 g. (65%). It crystallized from dilute alcohol in fine colorless plates and melted at 101°.

(7) Stieglitz and Noble, *Ber.*, **38**, 2243 (1905).

(8) Basterfield and Whelan, THIS JOURNAL, **49**, 3179 (1927).

Benzenesulfonyl Urea.—The benzenesulfonyl ethylisourea, 5 g., was covered with 25 cc. of concentrated hydrochloric acid. The isourea dissolved almost immediately as the hydrochloride. The flask containing the solution was immersed in a boiling water-bath for five minutes. The solution was then cooled in an ice-bath and the product filtered and washed. The dried product weighed 4.3 g. (practically quantitative). It crystallized from alcohol as fine white needles and melted at 169°.[9]

TABLE I

ARYLSULFONYL ETHYLISOUREAS, Ar—SO_2N=$C(OC_2H_5)$-NH_2

Ar	M. p., °C.	Formula	Nitrogen, % Calcd.	Found	
Benzene	101	$C_9H_{12}O_3N_2S$	12.27	12.17	12.17
p-Toluene	79	$C_{10}H_{14}O_3N_2S$	11.56	11.53	11.41
α-Naphthalene	145	$C_{13}H_{14}O_3N_2S$	10.06	10.11	9.84
Arylsulfonyl ureas, Ar—$SO_2NHCONH_2$					
Benzene	169	$C_7H_8O_3N_2S$	13.98	13.94	13.91
p-Toluene	192	$C_8H_{10}O_3N_2S$	13.08	13.01	12.95
α-Naphthalene	211	$C_{11}H_{10}O_3N_2S$	11.19	11.17	11.16

Summary

Some unsuccessful methods for the preparation of arylsulfonyl ureas have been mentioned.

The successful procedure was that of the hydrolysis of the corresponding arylsulfonyl ethylisourea by means of concentrated hydrochloric acid.

p-Toluenesulfonyl and α-naphthalenesulfonyl ethylisoureas, and *p*-toluenesulfonyl and α-naphthalenesulfonyl ureas have not been previously described in the literature.

(9) Billeter, *Ber.*, **37**, 694 (1904).

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Carcinogenic Hydrocarbons. IV. The Bromination of Hydrindene and a Briefer Synthesis of Cholanthrene[1]

BY WILLIAM F. BRUCE

One of the intermediates in the preparation of cholanthrene by the method of Fieser and Seligman[2] is 4-bromohydrindene, which they obtained from *o*-bromocinnamic acid. We have investigated the possibility of preparing this intermediate more directly by bromination of commercial hydrindene. Both of the possible nuclear monobromohydrindenes are formed in the bromination. The physical properties of these two compounds are too much alike to permit from available physical data alone a conclusion concerning the nature of the mixture.

We therefore employed the oxidation method which v. Braun[3] used for the determination of the isomers from the bromination of tetralin. The mixture of bromohydrindenes was oxidized and the relative amounts of 3-bromo and 4-bromophthalic acid were determined by esterification under conditions which do not affect the sterically hindered carboxyl group of the 3-bromo com-

(1) Previous paper, Bruce and Todd, THIS JOURNAL, **61**, 157 (1939). For previous studies of the bromination of hydrindene, see Perkin and Revay, *J. Chem. Soc.*, **65**, 251 (1894); Meyer and Meyer, *Ber.*, **51**, 1583 (1918); Borsche and Pommer, *ibid.*, **54**, 102 (1921).

(2) Fieser and Seligman, THIS JOURNAL, **57**, 2174 (1935).

(3) Von Braun, Braunsdorf, Engelbertz, E. Hahn, G. Hahn, Hainbach, Kredel and Larbig, *Ber.*, **56**, 2332 (1923).