vigorously for about 15 minutes and then more slowly for another 15 minutes, after which time the sodium hydroxide solution usually sucks back into the dry safety trap. After an additional 90 minutes of heating, the reaction mixture is cooled in an ice-bath and the product removed by filtration, washed twice with cold methanol and dried. The yield is 22.7 g. (80%). Some of the guanidinium iodides do not precipitate on cooling the reaction mixture, but do so after most of the solvent, water, acetone or methanol, is removed by distillation.

2-Cyclohexylamino-4,5-dihydroimidazole Picrate.—A quantitative yield of this compound precipitates immediately when a water solution of either the free base or its hydriodide is added to one molecular equivalent of picric acid dissolved in 95% ethanol.

2-Morpholinyl-3-benzenesulfonyl-4,5-dihydroimidazole.—2-Morpholinyl-4,5-dihydroimidazole hydriodide dissolved in a small quantity of water is treated without cooling with alternate portions of benzenesulfonyl chloride (1.5 equivalents) and 20% sodium hydroxide (3 equivalents). The mass of crystals which separates on slight cooling represents a quantitative yield and after recrystallization from water melts at 128–129°. Calcd. for $C_{14}H_{19}N_3O_3S$: H, 14.24. Found: N (Kjeld.), 14.09.

Summary

1. 2-Alkylamino-4,5-dihydroimodazoles are obtained in excellent yield by treating 2-methylmercapto-4,5-dihydroimidazoles with a primary or secondary amine.

2. The compounds are best isolated as their hydriodides and may be further characterized as picrates or benzenesulfonguanidides.

3. The free guanidines may be isolated from the hydriodides by treatment with excess alkali.

4. A study has been made of the effect of solvent, ratio of reactants and time on the yield.

WILLIAMSTOWN, MASS. RECEIVED JUNE 20, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Monomagnesium Derivatives of Dibromotoluenes

BY ALLEN S. HUSSEY AND JOHN R. DYER

The monomagnesium derivative obtained from the reaction of equimolar quantities of magnesium and 2,4-dibromoanisole has been shown to be a mixture of both isomers[1] contrary to previous reports.[2] One would expect the monomagnesium derivative of 2,4-dibromotoluene to consist of a similar mixture of isomers even though hydrolysis is reported to produce only 4-bromotoluene.[2]

We have investigated the monomagnesium derivatives of the four unsymmetrical dibromotoluenes, (2,3-, 2,4-, 2,5- and 3,4-), and have found all of them to be mixtures of both isomers. Ether solutions of the magnesium derivatives of each purified dibromotoluene were hydrolyzed with dilute acid and the products were examined for toluene, monobromotoluene and recovered dibromotoluene. The compositions of the several monobromotoluene fractions were determined by ultraviolet absorption. These results are summarized in Table I.

TABLE I

HYDROLYSIS OF MAGNESIUM DERIVATIVES OF DIBROMOTOLUENE

Dibromotoluene[a]	Toluene,[b] yield, %	Bromotoluene[b] Yield, %	Bromotoluene[b] Composition, %
2,3-	10–11	57–58[c]	91 ± 2 2-bromo
2,4-	11–12	73–74	70 ± 2 2-bromo
2,5-	12–14	76–78	70 ± 2 2-bromo
3,4-	9–13	58–62[c]	90 ± 2 3-bromo

[a] In all reactions, 2–3% of dibromotoluene was recovered. [b] Representative results of several experiments with each dibromotoluene. [c] *Ca.* 20% of high-boiling side-reaction product observed, presumably biphenyl compounds, but not identified.

The precision of the analysis of two of the monobromotoluene fractions is limited by the similarity of the absorption spectra of 2- and 3-bromotoluene. However, the precision can be increased considerably by making observations of the optical density of both of the pure monobromotoluene solutions and of the unknown solution simultaneously at the same wave length and slit-width setting of the spectrophotometer.[3]

The relative reactivities of bromine atoms in 2,4- and 3,4-dibromotoluene as determined in this way are consistent with what is already known about the activating effect of a methyl group. The steric effect of an adjacent methyl group is apparent in the case of 2,5-dibromotoluene, (where the bromine atom meta to the methyl group is predominately involved), and the pronounced steric effect when both methyl group and bromine atom are adjacent is apparent with 2,3-dibromotoluene.

Experimental[4]

Monobromotoluenes.—Samples of Eastman Kodak Co. monobromotoluenes were purified by washing with sulfuric acid, followed by three alternate fractional distillations and crystallizations. All three isomers distil at 74° at 19 mm. Other physical constants are given in Table II.

TABLE II

PHYSICAL CONSTANTS OF MONOBROMOTOLUENES

	F. p., °C.	$n^{25}D$	d^{25}_4	(95% ethyl alc.) at 235	236	240	270 mμ
2-Bromo	−26.60	1.55375	1.4170	525	438	234	202
3-Bromo	−38.40	1.55025	1.4022	650	540	256	230
4-Bromo	+26.80	1.54864	1.3971	1254	...	512	397

2,3-Dibromotoluene.—2-Amino-3-bromo-5-toluenesulfonic acid[5] was prepared by adding 64 g. (0.4 mole) of liquid bromine over 2 to 3 hours to a vigorously stirred mixture of 200 cc. of carbon tetrachloride and 50 g. (0.27 mole) of 2-amino-5-toluenesulfonic acid[6] dissolved in 2500 cc. of water. The bulk of the water and carbon tetrachloride was removed under reduced pressure and 58 g. (80%) of crystalline product was collected by filtration.

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(1) Hussey and Wilk, THIS JOURNAL, **72**, 830 (1950).

(2) Paty and Quelet, *Bull. soc. chim.*, **11**, 505 (1944).

(3) This procedure was suggested by R. L. Burwell, Jr., L. G. Maury and R. B. Scott, who have used the same technique in analysis in the infrared; R. L. B., Jr., private communication.

(4) All m.p.'s corrected unless otherwise specified. Microanalyses by Miss Virginia Hobbs and Miss Joyce Sorensen.

(5) Wynne, *J. Chem. Soc.*, **61**, 1036 (1892).

(6) Nevile and Winther, *Ber.*, **13**, 1941 (1880).

Sodium 2,3-dibromo-5-toluenesulfonate was obtained from the above amine in 71% yield by the Sandmeyer procedure.[7] The addition of excess ammonia to a small sample of 2,3-dibromo-5-toluenesulfonyl chloride gave 2,3-dibromo-5-toluenesulfonamide,[8] m.p. 219.2–219.5°. *Anal.* Calcd. for $C_7H_7O_2BrNS$: N, 4.26. Found: N, 4.3.

Hydrolysis of the sulfonic acid to 2,3-dibromotoluene was only partly successful with sulfuric or phosphoric acid at 265° in a glass-lined bomb, but was effected at 275–290° with phosphoric acid and superheated steam in a steam distillation apparatus. The yield was poor (15–20%); b.p. 120.5° at 18 mm.

2,4-Dibromotoluene.—The reduction of 2-bromo-4-nitrotoluene,[8] m.p. 76.4–76.8°, with tin and hydrochloric acid gave 2-bromo-4-aminotoluene,[8] m.p. 23° (after distillation at 130–132° at 20 mm.), in 70% yield. The Sandmeyer procedure gave 64% of 2,4-dibromotoluene after one distillation at 102–105° at 11 mm.

3,4-Dibromotoluene.—The bromination of 385 g. (2.25 moles) of 4-bromotoluene with 240 g. (1.50 moles) of bromine was carried out in the presence of iron catalyst over 4 days at 25–40°.[9] Excess bromine was then destroyed with sodium bisulfite. In addition to 156 g. (42%) of 3,4-dibromotoluene (b.p. 122–124° at 19 mm.), there was recovered 203 g. of 4-bromotoluene, 23 g. (6%) of 2,4-dibromotoluene (b.p. 126–130° at 19 mm.) and 45 g. (18%) of 2,4,5-tribromotoluene,[8] m.p. 110.6–111.2°.

Purification of Dibromotoluenes.—The samples of dibromotoluene from above and a sample of Eastman Kodak Co. 2,5-dibromotoluene were purified to constant freezing point by two, or three, alternate fractional distillations and crystallizations. The physical constants are summarized in Table III.

TABLE III

PHYSICAL CONSTANTS OF DIBROMOTOLUENES

Dibromotoluene	B. p. °C.	B. p. Mm.	F. p., °C.	$n^{25.0}D$	d^{25}_4
2,3-	126–128	19	28.10	1.59835	1.8234
2,4-	103–104	11	− 9.70	1.59637	1.8176
2,5-	135–136	35	5.62	1.59984	1.8154
3,4-	123–124	19	−10.00	1.59787	1.8197

Reaction of Magnesium with Dibromotoluenes.—A solution of equimolar quantities (0.10–0.30 mole) of dibromotoluene and ethyl bromide[10] in 300–400 cc. of absolute ether was added with stirring over 2 hours to magnesium turnings equivalent to the total moles of organic bromides while the system was maintained under a stream of dry, oxygen-free nitrogen. The mixture was then refluxed for 2 hours longer, at which time nearly all of the magnesium had disappeared. The mixture was hydrolyzed in the cold with dilute sulfuric acid and the ether solution washed until neutral. The ether was removed and the product distilled to separate the toluene, monobromotoluene and dibromotoluene components.

The product obtained from 2,3- and 3,4-dibromotoluene contained a very much greater amount of high-boiling side-reaction product than was observed with the other two dibromotoluenes. Most of this distilled at 165–170° at 2 mm. Calculated as dibromobitolyl, this represented 19–21% of the starting material.

The monobromotoluene fractions thus obtained were washed with sulfuric acid and redistilled at 19 mm. (74–75°). Solutions of the several samples in 95% ethyl alcohol (approx. 2×10^{-3} *M*), were prepared and optical densities were measured at several wave lengths in the ultraviolet region using a Beckman ultraviolet spectrophotometer.

The precision of this determination was greatly improved by measuring simultaneously, at the same wave length and slit-width (0.5–1.0 mm.) setting of the instrument, the optical density of both of the pure monobromotoluene solutions and the unknown.[3] The molar extinction coefficients (ϵ) of the monobromotoluene samples were found to be as follows: from 2,3-dibromotoluene, 536 ± 2 and 447 ± 2 at 235 and 236 mμ, respectively; from 2,4-dibromotoluene, 318 ± 2 and 261 ± 2 at 240 and 270 mμ; from 2,5-dibromotoluene, 563 ± 2 and 466 ± 2 at 235 and 236 mμ; from 3,4-dibromotoluene, 282 ± 3 and 247 ± 2 at 240 and 270 mμ. These correspond to 91 ± 2% 2-bromotoluene, 70 ± 2% 2-bromotoluene, 70 ± 2% 2-bromotoluene and 90 ± 2% 3-bromotoluene, respectively.

Summary

The monomagnesium derivatives of four unsymmetrical dibromotoluenes have been found to be mixtures of both possible isomers. The relative amount of each isomer has been determined by hydrolysis and analysis of the resulting monobromotoluene mixture by ultraviolet absorption.

The physical constants of highly purified samples of 2-, 3- and 4-bromotoluene and 2,3-, 2,4-, 2,5- and 3,4-dibromotoluene are given.

EVANSTON, ILLINOIS

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(7) "Org. Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 282.

(8) Nevile and Winther, *Ber.*, **14**, 418 (1881).

(9) Miller, *J. Chem. Soc.*, **61**, 1023 (1892).

(10) Grignard, *Compt. rend.*, **198**, 625 (1934).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL CO. (INDIANA)]

Reaction of Isoalkanes and Olefin Precursors Catalyzed by Sulfuric Acid[1]

BY ROBERT F. MARSCHNER AND D. R. CARMODY

An electronic interpretation of the alkylation of alkanes is attractive,[2] and the electronic mechanism advanced by Schmerling[3] and Bartlett, Condon and Schneider[4] is quite acceptable when aluminum chloride is the alkylation catalyst. A consequence of this mechanism[3c] is the formation of alkylate by a *combination* of two isoalkane molecules

$$2\mathrm{C}_n \text{ isoalkane} + \mathrm{C}_m \text{ alkene} \longrightarrow \mathrm{C}_{2n} \text{ alkane} + \mathrm{C}_m \text{ alkane} \quad (1)$$

as well as by *addition* of isoalkane and alkene

$$\mathrm{C}_n \text{ isoalkane} + \mathrm{C}_m \text{ alkene} \longrightarrow \mathrm{C}_{(n+m)} \text{ alkane} \quad (2)$$

in which n and m are the number of carbons in the reagents. Although there is some evidence that eq. 1 occurs with sulfuric acid,[5–10] no studies with this catalyst as pertinent and convincing as those with aluminum chloride[3,4] have yet been reported. It will be observed, however, that equations 1 and 2

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(1) Presented in part before the Petroleum Division at the 109th Meeting of the American Chemical Society, Atlantic City, April, 1946.

(2) Whitmore, (a) THIS JOURNAL, **54**, 3274 (1932); (b) *Ind. Eng. Chem.*, **26**, 94 (1934); (c) *Chem. Eng. News*, **26**, 668 (1948).

(3) Schmerling, (a) THIS JOURNAL, **66**, 1422 (1944); (b) *ibid.*, **67**, 1778 (1945); (c) *ibid.*, **68**, 275 (1946).

(4) Bartlett, Condon and Schneider, *ibid.*, **66**, 1531 (1944).

(5) Birch, Dunstan, Fidler, Pim and Tait, *Ind. Eng. Chem.*, **31**, 1079 (1939).

(6) Waterman, Leendertse and Hesselink, *Rec. trav. chim.*, **58**, 1040 (1939).

(7) Birch and Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939).

(8) McAllister, Anderson, Ballard and Ross, *J. Org. Chem.*, **6**, 649 (1941).

(9) Pines and Ipatieff, THIS JOURNAL, **67**, 1631 (1945).

(10) Gibson, Cole and Matuszak, *ibid.*, **68**, 2728 (1946).