[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE BROMO-ALPHA-NAPHTHOLS AND THE ORIENTATION OF CERTAIN CLASSES OF DISUBSTITUTED NAPHTHALENE DERIVATIVES

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The orientation of 1,5, 1,6, 1,7 and 1,8 disubstituted naphthalene derivatives has almost always been assigned by relating the given compound to one of the corresponding dichloro-naphthalenes[2] the structures of which depend in turn on the 1,5, 1,6 and 1,7-chloronaphthols obtained by Erdmann and Schwechten[3] by the Erdmann ring closure from the *o*-, *m*- and *p*-bromo-β-benzal-propionic acids, respectively. The 1,8-chloronaphthol is unknown but since three of the four above mentioned dichloro-naphthalenes are of known orientation, that of the 1,8-dichloro-naphthalene follows by the principle of exclusion.

Inasmuch as most of the commonly occurring groups are replaceable by the *chloro* and *hydroxyl* groups, this method is applicable to a very large number of compounds.[4] There is, however, no very direct method by which substituted naphthoic acids and their derivatives may be related to the chloro-naphthols and the writer in a recent study of the orientation of naphtholactone[5] was able to solve the difficulty by using as a reference substance a *bromo*-naphthol in place of the usual chlorine analog. The 1,5-bromonaphthol was synthesized from *o*-bromophenyl-paraconic acid by the Erdmann method and related to the 1,5-hydroxynaphthoic acid (and, consequently, to the 1,8-hydroxynaphthoic acid and naphtholactone) by replacement of the bromine atom by the *carboxyl* group by means of the Grignard reaction.[6] Further, by oxidation of the Grignard reagent the *dihydroxy* derivative was formed and thus this compound also was brought into relation with the 1,5-bromonaphthol.

The feasibility of turning this into a general method was at once apparent. It is clear from the foregoing example that by use of the bromonaphthols in place of the chloronaphthols, it becomes an easy matter to determine the orientation of the corresponding hydroxynaphthoic acids and di-

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[1] National Research Fellow in Chemistry. This work was begun at the University of Minnesota.

[2] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Veit and Company, Leipzig, **1903**, 2^2, p. 331.

[3] Erdmann and Schwechten, *Ann.*, **260**, 75 (1890).

[4] It should be noted, however, that inasmuch as the usual methods for effecting these replacements involve somewhat drastic means such as fusion with alkali or high temperature reactions, the determination of orientation in this way is open to objection.

[5] Fuson, THIS JOURNAL, **46**, 2779 (1924).

[6] For this purpose the hydroxyl group was, of course, suitably "protected," the 1,5-methoxy-bromonaphthalene being used.

hydroxy-naphthalenes as well as of their numerous derivatives. The hitherto unknown 1,6- and 1,7-bromonaphthols have, accordingly, been prepared from the *m*- and *p*-bromophenyl-paraconic acids, respectively. This gives us five of the seven possible monobromo derivatives of α-naphthol all of which are of known orientation. They are the 1,5 (m. p., 137°), 1,6 (m. p., 129–130°) and 1,7 (m. p., 105.5–106.5°), prepared by the above method, the 1,8 (m. p., 60–61°) prepared by Meldola and Streatfeild[7] the orientation of which follows by the law of exclusion and the 1,4 (m. p., 127–128°) likewise of known orientation.[8]

It should be pointed out that this series of compounds can be used wherever the chloronaphthols are applicable as well as in the cases cited above.

If these bromonaphthols could be obtained in sufficiently large quantity, they would serve admirably as starting materials in the synthesis of many substances, particularly the 1,7 and 1,8 derivatives, which are unknown or can be made only with great difficulty. It is, therefore, desirable to find some means of increasing the yields in the Erdmann ring closure and the problem is being investigated from this point of view.

Experimental Part

The *m*- and *p*-bromophenyl-paraconic acids were prepared from the corresponding bromobenzaldehydes and succinic anhydride by the method of Fittig and Jayne[9] previously used by the writer in the preparation of the *ortho* compound.[5] From them the 1,6 and 1,7-bromonaphthols were prepared by distillation in the usual way.[10]

***m*-Bromophenyl-paraconic Acid.**—This compound differed from the *ortho* and *para* isomers in that it did not "melt" when boiled with water (see *para* compound below) and was, therefore, much more easily purified. It crystallized from water in yellowish leaflets which after repeated recrystallization melted at 164–165°, yield, 12 g. from 40 g. of the aldehyde, or 20%. On oxidation with an acid solution of potassium permanganate it gave *m*-bromobenzoic acid.

Anal. Subs., 0.1716: AgBr, 0.1138. Calcd. for $C_{11}H_9O_4Br$: Br, 28.04. Found: 28.22.

***p*-Bromophenyl-paraconic Acid.**—The acid first separated as a yellow liquid which solidified on standing. Attempts to purify it by converting it into the insoluble barium *p*-bromophenyl-itamalate and by treatment with carbon disulfide were ineffectual. The following method of purification was worked out. The acid was dissolved in a minimum quantity of boiling water from which, on cooling, it began to separate as an oil which settled to the bottom of the vessel carrying with it nearly all of the impurity. The warm solution which still contained a large part of the acid was decanted from the oily layer and allowed to cool. The acid separated in colorless crystals which after repeated recrystallization in the above manner melted at 140–140.5°; yield, 50–60%.

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[7] Meldola and Streatfeild, *J. Chem. Soc.*, **63**, 1058 (1893).

[8] Reverdin and Kauffmann, *Ber.*, **28**, 3054 (1895).

[9] Fittig and Jayne, *Ann.*, **216**, 100 (1883).

[10] See Fittig and Erdmann, *Ber.*, **16**, 43 (1883).

Anal. Subs., 0.2872: AgBr, 0.1886. Calcd. for $C_{11}H_9O_4Br$: Br, 28.04. Found: 27.95.

1,6-Bromonaphthol.—This compound dissolved readily in hot water from which it separated slowly in the form of long, fibrous needles; m. p., 129–130°; yield, 0.3 g. from 4 g. of the paraconic acid, or about 10%.

Anal. Subs., 0.1384: AgBr, 0.1162. Calcd. for $C_{10}H_7OBr$: Br, 35.85. Found: 35.73.

1,7-Bromonaphthol.—This naphthol crystallized from hot water in cotton-like masses which slowly turned dark when exposed to light. It resembled the 1,6-isomer very closely, having a marked phenolic odor and giving a deep purple color when treated with ferric chloride solution; m. p., 105.5–106.5°.

Anal. Subs., 0.1665, 0.2040: AgBr, 0.1417, 0.1735. Calcd. for $C_{10}H_7OBr$: Br, 35.85. Found: 36.20, 36.19.

Summary

1. *M*- and *p*-bromophenylparaconic acids have been prepared and from them by the Erdmann ring closure the 1,6 and 1,7 bromonaphthols, respectively.

2. The five known monobromo derivatives of α-naphthol have been listed and their usefulness as reference substances in orientation work has been pointed out.

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THE PREPARATION OF HYDROCARBONS BY THE REACTION BETWEEN ALKYL SULFONATES AND ORGANOMAGNESIUM HALIDES

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Introduction

Many methods are available in organic synthesis for the preparation of hydrocarbons. However, syntheses involving the preparation of unsymmetrical hydrocarbons are generally somewhat indirect.[1] A number of these indirect methods have a circumscribed utility for several reasons: they often involve the use of expensive materials, some of the reactions used may be unreliable in the determination of structure and the yields are frequently rather low.

The Grignard reagent (RMgX) has long been used in a wide variety of direct and indirect[2] syntheses for the preparation of hydrocarbons. Recently, Gilman and Hoyle[3] reported on the preparation of hydrocarbons

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[1] Maihle has reviewed recently methods for the preparation of hydrocarbons; *J. usines gaz.*, **48,** 34 (1924); *C. A.*, **18,** 1464 (1924).

[2] In particular, Clarke and co-workers, *Am. Chem. J.*, **39,** 572 (1908), etc., who prepared a number of isomeric paraffin hydrocarbons by indirect methods.

[3] Gilman and Hoyle, THIS JOURNAL, **44,** 2621, 2969 (1922).