

With olefins the dimerization observed by Bockemüller<sup>5</sup> in the case of tetrachloroethylene was confirmed and also established for trichloroethylene. The products obtained may be termed *dimer addition products*, and it is assumed that in compounds of this type the fluorine atoms are in the 1,4-positions. Chlorine fluoride was formed in the reaction mixtures and substitution and addition products resulting from its action were isolated. Chlorine fluoride seems to add normally to ethylenic compounds without the formation of dimers since no monofluorobutane derivatives were found. In fact, the formation of dimer addition products from simple olefins appears to be a type of reaction peculiar to fluorine among the halogens.

### Summary

The reactions of some simple chlorinated ali-

phatic organic compounds with fluorine have been studied. Using pure fluorine, charring was not observed in any case and reactions were easily controlled. The types of reaction observed were: substitution of hydrogen attached to saturated carbon; substitution of hydrogen attached to double bonded carbon; addition to ethylenic bonds; dimerization of saturated molecules by removal of two hydrogens; dimerization of ethylene derivatives accompanied by the addition of two fluorine atoms; secondary reactions due to the presence of chlorine fluoride.

The reaction conditions used and results obtained are discussed briefly. Essentially "non-ionic" conditions prevailed and the hypothesis was advanced that radical type mechanisms of reaction in which the fluorine molecule is split symmetrically are of greatest significance.

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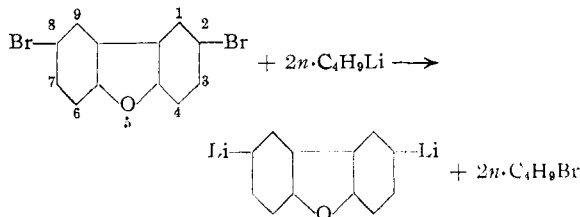
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Halogen-Metal Interconversion with *m*- and *p*-Bromodimethylanilines<sup>1</sup>

BY HENRY GILMAN AND IRVING BANNER

The two chief transformations which resulted when an organolithium compound reacted with a nuclear-brominated aryl-alkyl or diaryl ether were: (1) metalation or replacement of a nuclear hydrogen by lithium<sup>2</sup> and (2) halogen-metal interconversion or the replacement of nuclear halogen by lithium.<sup>2,3</sup> The metalation occurred when the halogen was *para* to the ether linkage; and halogen-metal interconversion took place when the halogen was *ortho* to the ether linkage. Subsequently<sup>4</sup> it was shown that it was not necessary to have bromine *ortho* to an ether linkage to have a halogen-metal interconversion, for 2,8-



(1) This is paper XXVIII in the series of relative reactivities of organometallic compounds. The preceding paper is THIS JOURNAL, **61**, 1513 (1939).

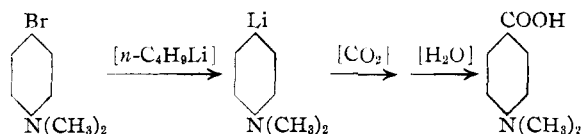
(2) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Wittig and co-workers, *Ber.*, **71**, 1903 (1938), and **72**, 89 (1939); Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939).

(3) Gilman, Cheney and Willis, *ibid.*, **61**, 951 (1939).

(4) Gilman, Willis and Swislowky, *ibid.*, **61**, 1371 (1939).

dibromodibenzofuran and *n*-butyllithium gave an excellent yield of 2,8-dibenzodifurylenedilithium. When bromine is *meta* to the ether linkage as in 3-bromodibenzofuran, both metalation and interconversion probably occur, for the acids isolated subsequent to carbonation were 3-dibenzofuran-carboxylic acid and 4-dibenzofuran-carboxylic acid.<sup>4</sup> The reaction with 1-bromodibenzofuran, in which the bromine is also *meta* to the ether linkage, is exclusively interconversion.<sup>5</sup> Actually, as the accompanying paper<sup>6</sup> on methoxy-halogenodibenzofurans illustrates, interconversion is the predominant reaction of bromo ethers.

We are reporting at this time the reaction of *n*-butyllithium with *m*- and *p*-bromodimethylanilines. Reaction was to be expected because of the related activating effects of dialkylamino and alkoxy groups. In each case a halogen-metal interconversion took place.



Unlike the case with *p*-bromoanisole, there was

(5) Unpublished studies.

(6) Gilman, Swislowky and Brown, THIS JOURNAL, **62**, 348 (1940).

no evidence of significant nuclear metalation. The reaction may prove of synthetic value with amines having nuclear halogen, as already has been demonstrated with halogenated carbazoles.<sup>5</sup>

Not only does *p*-bromodimethylaniline react differently from *p*-bromoaniline toward *n*-butyllithium, but it also undergoes a different reaction with another metalating agent, mercuric acetate. Whitmore<sup>7</sup> obtained a 74% yield of *N,N*-dimethyl-4-bromo-2-acetoxymercurianiline by treating *p*-bromodimethylaniline with mercuric acetate in alcohol at low temperatures for several days.

### Experimental Part

**Preparation of *o*- and *m*-Bromodimethylanilines.**—These bromodimethylanilines were prepared by customary reactions but in yields somewhat higher than those reported.<sup>8</sup>

To a mixture of 100 g. (0.58 mole) of *o*-bromoaniline and 100 cc. of water, contained in a 1-liter, three-necked flask provided with a mechanical stirrer, was added three equivalents (219 g.) of methyl sulfate in the following manner. One equivalent of the methyl sulfate was added with stirring and the mixture allowed to stand until homogeneity was reached. The contents were then carefully neutralized with a 25% solution of potassium hydroxide, during which cooling was effected in an ice-bath. The second equivalent of methyl sulfate was then added and the process repeated, except that a slight excess of base was added. Finally, the third equivalent was added, and the mixture was allowed to stand for one hour after stirring. The alkaline mixture was extracted with ether, and the ethereal extracts were washed with water, dried over potassium carbonate and then distilled at 100–101° (12 mm.). The yield was 81.5 g. or 70%.

The *m*-bromodimethylaniline was prepared in a related manner from 100 g. (0.58 mole) of *m*-bromoaniline and 219 g. of methyl sulfate. The yield of product distilling at 118–119° (8 mm.) was 63 g. or 54%. The melting point of the picrate (134–135°) agreed with that described in the literature.<sup>8</sup>

Pure *p*-bromodimethylaniline was obtained by recrystallization of a commercial product from alcohol. All samples of the bromodimethylanilines were shown to be free of primary and secondary amines. Houben and co-workers<sup>9</sup> have shown that some *N*-ethylanilines when treated first with ethylmagnesium iodide to form  $-N-(C_2H_5)(MgI)$  types, and then with carbon dioxide at 225° for twenty-four hours, undergo nuclear carboxylation.

***m*-Bromodimethylaniline and *n*-Butyllithium.**—A solution of 8 g. (0.04 mole) of *m*-bromodimethylaniline in 50 cc. of ether was added to a filtered solution of 0.055 mole of

*n*-butyllithium.<sup>10a</sup> The reaction was carried out in a nitrogen atmosphere and in a flask provided with a mechanical stirrer. After refluxing for twenty hours, the mixture was cooled, and then carbonated by adding it jet-wise to solid carbon dioxide.<sup>10b</sup>

The resulting mixture was extracted thoroughly with a 5% potassium hydroxide solution. The ether layer was washed with a little water and the washings combined with the aqueous layer.

The aqueous layer was concentrated, made slightly acidic with acetic acid, and then exhaustively extracted with an ether-chloroform mixture. After drying the ether-chloroform solution over sodium sulfate, the solvents were removed by distillation. The brownish oily residue was crystallized from water to yield 1.7 g. or 26% of *m*-dimethylaminobenzoic acid melting at 150–150.5°. The melting point reported<sup>11</sup> is 151°. The acid was derivatized by preparing the methyl ester hydrochloride, which melted at 175–176°.<sup>12</sup>

The yellowish ether layer yielded 1.1 g. of an as yet unidentified oil distilling between 90–115° (13 mm.).

In a check experiment, the yield of *m*-dimethylaminobenzoic acid was 32%, and the yield of oil from the ether solution was 1.3 g.

***p*-Bromodimethylaniline and *n*-Butyllithium.**—A reaction mixture of 8 g. (0.04 mole) of *p*-bromodimethylaniline in 50 cc. of ether and 0.055 mole of *n*-butyllithium in ether was refluxed for twenty hours, then carbonated, and worked up by the general procedure described for *m*-bromodimethylaniline. The yield of *p*-dimethylaminobenzoic acid (m. p. 240–241°) was 41%, and the compound was derivatized as the methyl ester<sup>13</sup> (m. p. 102°). From the ether layer was obtained an unidentified oil distilling between 100–130° (20 mm.). This oil did not yield a picrate of *p*-bromodimethylaniline, a compound which forms readily from pure reactants in ethanol and melts at 140–141°.

In a check experiment, the yield of *p*-dimethylaminobenzoic acid was 56%, and the yield of oil from the ether extracts was 1.5 g.

Experiments were not carried out with either *m*- or *p*-bromodimethylaniline to establish optimal conditions for the halogen-metal interconversion. However, it is highly probable that the yields can be improved by reducing the time of refluxing with the *n*-butyllithium. In this connection, it is interesting to note that forty seconds are sufficient to give a 23% interconversion in the reaction between 4-bromodibenzofuran and *n*-butyllithium in ether.

### Summary

A halogen-metal interconversion takes place in the reaction of *m*- and *p*-bromodimethylanilines with *n*-butyllithium to give *m*- and *p*-dimethylaminophenyllithiums, respectively.

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(7) Whitmore, *THIS JOURNAL*, **41**, 1846 (1919); see, also, Whitmore, Cade and Leucks, *ibid.*, **51**, 1952 (1929).

(8) For *o*-bromodimethylaniline, see Auwers, *Ber.*, **40**, 2530 (1907); and von Braun, *ibid.*, **49**, 1105 (1916). For *m*-bromodimethylaniline, see Wurste and Scheibe, *ibid.*, **12**, 1818 (1879); Vorländer and Siebert, *ibid.*, **52**, 287 (1919); Hodgson and Wignall, *J. Chem. Soc.*, 1144 (1927).

(9) Houben and co-workers, *Ber.*, **42**, 3729, 4488 (1909).

(10) (a) Gilman, Zoellner and Selby, *THIS JOURNAL* **54**, 1957 (1932); (b) Gilman and Van Ess, *ibid.*, **55**, 1258 (1933).

(11) Griess, *Ber.*, **6**, 587 (1873).

(12) The melting point of methyl *m*-dimethylaminobenzoate hydrochloride reported by Cumming, *Proc. Roy. Soc. (London)*, **A78**, 103 (1906), is 175–177°.

(13) Bischoff, *Ber.*, **22**, 343 (1889).