

## Syntheses and Ultraviolet Spectra of Aromatic Azo Compounds. I. Bromo-methylazobenzenes

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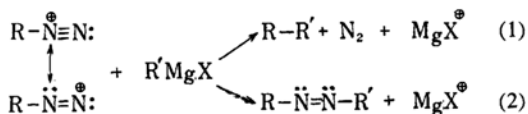
The reaction of Grignard reagents with aromatic diazonium salts was first investigated by Hodgson and Marsden<sup>1)</sup>, who found that the addition of the zinc chloride double salts of several diazonium chlorides to arylmagnesium bromides in refluxing dry ether gave azo compounds in low yields.

Oda and Nakano<sup>2)</sup>, on the other hand, reported that the zinc chloride double salt of benzenediazonium chloride reacted with alkyl- or arylmagnesium bromides in ether at 0°C to give 6~34% of the theoretical amount of alkyl- or arylbenzenes.

Curtin and Ursprung<sup>3)</sup> reinvestigated these reactions following the procedure of Oda et al. and observed that azo compounds were formed in 2~35% yields and no significant amounts

of biaryls, reported by Oda et al. to be products of these reactions, could be obtained. They postulated that small amounts of metal impurities might be contained in magnesium employed by Oda et al. which catalyzed the reaction in an abnormal way.

The formation of biaryl or azo compound in the reaction of Grignard reagent with diazonium ion may be represented by the following equations:



If the reaction proceeded according to 1, the same mole of nitrogen as biaryl R-R' should be evolved. But no significant amounts of nitrogen have been observed to evolve in these reactions in accordance with the observations of Curtin et al. Since azobenzenes initially formed by the reaction 2 might react further

1) H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, **1945**, 274.

2) R. Oda and K. Nakano, *Repts. Inst. Chem. Res., Kyoto Univ.*, **19**, 91 (1949); R. Oda, *Mem. Fac. Eng. Kyoto Univ.*, **14**, 195 (1952).

3) D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956).

TABLE I. BROMO-METHYLAZOBENZENES

No.	Compound	M.p., °C	Color	Found N, % (Calcd. for C <sub>13</sub> H <sub>11</sub> BrN <sub>2</sub> : N, 10.18%)	Yield*
I	2-Bromo-2'-methyl	88~89 <sup>a)</sup>	Red	10.10	64
II	2-Bromo-3'-methyl	44.5~45.5 <sup>b)</sup>	Orange red	9.99	40
III	2-Bromo-4'-methyl	60.5~61.5 <sup>c)</sup>	Red orange	10.03	60
IV	3-Bromo-2'-methyl	49 <sup>c)</sup>	Red orange	10.24	61
V	3-Bromo-3'-methyl	79~79.5 <sup>c)</sup>	Orange	10.23	52
VI	3-Bromo-4'-methyl	119.5 <sup>d)</sup>	Orange yellow	10.08	65
VII	4-Bromo-2'-methyl	53.5~54 <sup>c)</sup>	Red orange	10.14	42
VIII	4-Bromo-3'-methyl	81.5 <sup>c)</sup>	Orange	10.19	68
IX	4-Bromo-4'-methyl	153 <sup>a)</sup>	Brown orange	10.03	68
X	4-Bromo-2-methyl	73~73.5 <sup>b)</sup>	Red orange	9.97	73
XI	4-Bromo-3-methyl	68.5 <sup>b)</sup>	Yellow orange	10.35	74
XII	2-Bromo-4-methyl	43.5~44 <sup>c)</sup>	Red orange	10.20	65.6

a) Recrystallized from ethanol.

b) Distilled in vacuo and then recrystallized from methanol.

c) Distilled in vacuo and then recrystallized from dilute ethanol.

d) Recrystallized from ethanol containing a small amount of benzene.

\* Based on bromocompound used.

with excess Grignard reagent to yield hydrazobenzenes<sup>4)</sup> and their derivatives<sup>5)</sup>, it was suspected that the attack of Grignard reagents on azobenzenes might be responsible for the rather poor yields of azo compounds.

The present study was carried out for the purpose of applying the reactions of Grignard reagents with diazonium salts to the preparations of various azo compounds and always the excess of diazonium salts over Grignard reagents were used expecting better yields of azo compounds.

**General Procedure.**—The ethereal solution of tolylmagnesium bromide prepared from 1 mol. of bromotoluene and the excess of magnesium was added slowly with vigorous stirring to the suspension of 1.3~1.5 mol. of the zinc chloride double salt of bromobenzenediazonium chloride at a rate necessary to maintain refluxing. The resulting dark red mixture was stirred for an additional 60 min. at room temperature and then poured onto ice-cold dilute hydrochloric acid. The ether layer was separated and washed with water and dried. Evaporation of the ether gave a solid or oil, which crystallized upon standing. The crude bromo-methylazobenzenes thus obtained were recrystallized from alcohol or distilled in vacuo, followed by recrystallization from alcohol.

In the syntheses of 4-bromo-2-methylazobenzene (X), 4-bromo-3-methylazobenzene (XI) and 2-bromo-4-methylazobenzene (XII), phenyl magnesium bromide and the excess of the zinc chloride double salts of bromotoluene-diazonium chlorides were used.

The bromo-methylazobenzenes prepared by this method were shown in Table I. They are all new compounds except 4-bromo-4'-methylazobenzene (IX)<sup>6)</sup> and 4-bromo-3-methylazobenzene (XI)<sup>7)</sup>, which showed no depression of their melting points on admixture with a respective authentic specimen prepared according to the literature.

Electronic absorption spectra were measured in an alcoholic solution. The maxima of the absorption spectra of bromo-methylazobenzenes were listed in Table II. It can be seen that the K-bands of bromo-methylazobenzenes shift

TABLE II. WAVELENGTHS AND INTENSITIES OF ELECTRONIC ABSORPTION MAXIMA (IN ETHANOL)

	K-band		R-band	
	$\lambda$ , m $\mu$	$\epsilon_{\max}$	$\lambda$ , m $\mu$	$\epsilon_{\max}$
I	329	14400	465	420
II	324	15700	455	430
III	333	19550	456	460
IV	327	18700	454	510
V	321	19900	446	670
VI	329	22300	442	570
VII	332	22800	456	590
VIII	328	24600	446	460
IX	333	26100	441	570
X	333	26600	457	610
XI	327	25600	445	530
XII	331	18900	456	450

6) 4-Bromo-4'-methylazobenzene was synthesized by D. Bigiavi et al., *Gazz. chim. ital.*, **57**, 557 (1927), by the condensation of *p*-nitroso-toluene and *p*-bromoaniline.

7) 4-Bromo-3-methylazobenzene was prepared by the bromination of 3-methylazobenzene or by the condensation of 5-amino-2-bromotoluene and nitrosobenzene. J. Burns et al., *J. Chem. Soc.*, **1928**, 2932.

4) H. Franzen and W. Deibel, *Ber.*, **38**, 2716 (1905).5) E. Bamberger and M. Tichvinsky, *ibid.*, **35**, 4179 (1902).

towards a longer wavelength than unsubstituted azobenzene ( $\lambda_{\max}$  318 m $\mu$ ,  $\epsilon_{\max}$  = 20900 in alcohol) especially when methyl or bromine is in ortho or para positions. On the other hand, the molecular extinction coefficients ( $\epsilon_{\max}$ ) became larger when methyl or/and bromine was situated in ortho, meta and para positions, in this order.

### Experimental

Ultraviolet absorption spectra were measured by a Hitachi EPU 2 type spectrophotometer using a 1 cm. quartz cell.

**Preparation of the Zinc Chloride Double Salt of Diazonium Chloride.**—The mixture of 1 mol. of amine and 3~4 mol. of hydrochloric acid (1:1) was diazotized at 0°C with sodium nitrite dissolved in a small amount of water. To the resulting solution of diazonium chloride was added a cold saturated solution of zinc chloride (200 cc.) with stirring, when the zinc chloride double salt of diazonium chloride was separated out. After being allowed to stand in ice water for some time with occasional stirring, the double salt was filtered by suction and washed several times with a little ice-cold alcohol and then with ether. The double salt was spread in air and then dried in vacuum desiccator. The yield was excellent in most cases.

A few examples of the preparation of the zinc chloride double salt of diazonium chloride was shown below.

Thirty two grams of 2-amino-5-bromotoluene were added to 100 cc. of dilute hydrochloric acid (1:1), and the resulting suspension of the amine hydrochloride was diazotized at 0°C. A saturated solution of zinc chloride (about 40 cc.) was added to the diazotized solution with stirring. The yield of the double salt was 40 g. or 98% of the theoretical. In the same manner, from 17.2 g. of *p*-bromoaniline was obtained 28.0 g. (95% yield) of the double salt, and from 17.2 g. of *m*-bromoaniline was obtained 28.3 g. of the double salt.

**Preparations of Bromo-methylazobenzenes.**—Twelve bromo-methylazobenzenes were prepared following the general procedure described above.

An example is given below in the preparation of 2-bromo-2'-methylazobenzene (I).

Seventeen grams of the zinc chloride double salt of *o*-bromobenzenediazonium chloride and 150 cc. of dry ether were put in a 300 cc. flask equipped with an efficient stirrer, a reflux condenser and a dropping funnel. A Grignard solution prepared from 7 g. of *o*-bromotoluene and 1.3 g. of magnesium in ether and diluted to about 40 cc. with dry ether was introduced from the dropping funnel to the suspension of the diazonium salt with vigorous stirring over a period of 15 min. without external cooling. Exothermic reaction occurred and gentle reflux continued for some time after all the Grignard solution was added. The mixture was diluted to double its volume with ether and shaken with cold dilute hydrochloric acid and then with water, dried over calcium chloride and evaporated to give the red crystals, which were recrystallized from ethanol with a small amount of decolorizing charcoal. The yield of 2-bromo-2'-methylazobenzene was 7 g. or 64% of the theoretical amount based on *o*-bromotoluene.

### Summary

1) Twelve bromo-methylazobenzenes have been synthesized by the reactions of Grignard reagents with zinc chloride double salts of diazonium compounds. Ten of them are new compounds.

2) The ultraviolet absorption spectra of bromo-methylazobenzenes have been measured and some regularities of the absorption maxima have been observed in them.

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