trode at temperatures as high as 40° for even the most precise work.

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.
RECEIVED AUGUST 24, 1938

The Preparation of *m*-Bromobenzaldehyde

BY FLOYD T. TYSON

For work in progress in this Laboratory it was necessary to prepare *m*-bromobenzalaminoacetal by the interaction of *m*-bromobenzaldehyde with aminoacetal. The *m*-bromobenzaldehyde was prepared by the reduction of *m*-nitrobenzaldehyde by stannous chloride and hydrochloric acid, followed by diazotization and conversion to bromobenzaldehyde by the Sandmeyer method as originally described by Einhorn and Gernsheim[1] and modified by Buck and Ide.[2] In these procedures, no attempt is made to isolate the intermediate *m*-aminobenzaldehyde from admixture with stannic chloride and hydrochloric acid.

Analysis of the *m*-bromobenzalaminoacetal yielded uniformly low results for halogen calculated as bromine and very high results for carbon and hydrogen. These analytical values were in accord with the assumption that much of the chloro compound was present with the bromo compound.

The *m*-bromobenzaldehyde used for the preparation of the impure *m*-bromobenzalaminoacetal was analyzed for halogen and the halogen calculated as bromine. The analytical values obtained were in agreement with the theoretical values for bromobenzaldehyde. However, analyses of the *m*-bromobenzaldehyde preparations for both chlorine and bromine proved the presence of both chlorine and bromine. The amounts of chlorine indicated a percentage of chlorobenzaldehyde ranging from 20 to 72 depending upon details of procedure.

Since *m*-nitrobenzaldehyde should be a convenient source for the preparation of pure *m*-bromobenzaldehyde, a procedure has been devised which will be published elsewhere, in which the presence of chlorides in the reaction mixture was avoided.

Experimental

The following table summarizes data obtained in the analysis of products resulting from the attempted preparation of pure *m*-bromobenzaldehyde from *m*-nitrobenzaldehyde as described in the literature. The preparations analyzed were fractionated; b. p. 92–97° (6 mm.).

TABLE I

Prepn.	Analyses, % Cl	Br	Calcd. % chlorobenzaldehyde present
1	18.17	11.86[3]	72.0
	18.31	11.57[4]	
2	5.11	34.50[3]	20.3
3	6.78	31.58[3]	26.9

Preparation No. 1 was made as described by Buck and Ide.[2] Preparation No. 2 was made as No. 1 except that the hydrobromic acid was added to the cuprous bromide mixture before mixing with the diazotized solution. Preparation No. 3 was made as described by Einhorn and Gernsheim.[1]

The analytical results reported in the following table were calculated on the erroneous assumption that the mixtures of silver chloride and bromide actually obtained in the analyses of preparations No. 1, 2 and 3 (Table I) were pure silver bromide. The satisfactory agreement with the values for *m*-bromobenzaldehyde may explain the fact that the preparations as recorded in the literature[1,2] were reported as essentially pure.

TABLE II

Prepn.	% Br found as assumed	% Br calcd. for *m*-bromobenzaldehyde
1	43.12	43.19
2	43.18	
3	43.25	

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[1] Einhorn and Gernsheim, *Ann.*, **284**, 141 (1894).

[2] Buck and Ide, *Org. Syntheses*, **13**, 30 (1933).

[3] Analyses made by the method of displacement of bromine from weighed silver chloride and bromide by chlorine as described in "Quantitative Analysis of Inorganic Materials," by N. Hackney, J. B. Lippincott, Philadelphia.

[4] Analysis made by the method of Baubigny [*Compt. rend.*, **136**, 1197 (1903)] as described by Hackney.[4]

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RECEIVED JULY 6, 1938

The Optical Rotation of a Grignard Reagent

BY FRANK C. WHITMORE AND BENJAMIN R. HARRIMAN

Frequent use is made of the Grignard reaction in preparing optically active compounds from optically active halogen compounds, but not to our knowledge has the rotation of an optically active Grignard reagent been measured previously. Porter[1] observed a very small rotation in an ethereal solution of methyl-*n*-hexylmagnesium

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[1] Porter, THIS JOURNAL, **57**, 1436 (1935).

bromide which he had prepared from active methyl-*n*-hexyl bromide. He ascribed this activity to unchanged bromide.

Since the position of the functional halogen atom relative to the asymmetric carbon atom determines the degree to which the product is racemic, we sought a halide in which the halogen was on the carbon atom next to the asymmetric carbon atom. Optically active 1-bromo-2-methylbutane, "active amyl bromide," was selected because it was prepared easily from the readily available optically active 2-methyl-1-butanol, which J. H. Olewine of this Laboratory has obtained by the fractionation of fusel oil through a 100-plate column.[2] Since the conversion of this bromide to another compound through the intermediate Grignard reagent gives a product which is only partly racemic, it was thought that rotation measurements on Grignard reagents made from this and similar halides might throw light on the mechanism of such racemizations and on the structure of the Grignard reagent itself. With this in mind a manipulative procedure for measuring the rotation of the Grignard reagent was evolved.

Obviously it was necessary to be assured of the absence of any excess halide. This could be done either by using an excess of magnesium or by removing the excess halide after the Grignard reagent was made. Grignard reagents were made by the first method under the most careful conditions for the exclusion of air and moisture, and a special polarimeter tube with optical Pyrex sealed-in windows was made to hold the volatile ethereal solution. However, what appeared to be finely dispersed magnesium rendered the solutions too dark for measurement.

The alternative method of using an excess of the optically active halide produced clear Grignard reagent solutions. Di-*n*-butyl ether (b. p. 141°) was used as the solvent so that the excess active amyl bromide (b. p. 120°) could be removed by distillation under reduced pressure. The Grignard reagent solution freed from excess halide was then transferred with a pipet to an ordinary polarimeter tube, in which measurement of its optical rotation readily was made. Specific rotations were calculated from data obtained by titrating the Grignard reagent with standard hydrochloric acid. Molecular rotations are given below as being non-committal as to the structure of the Grignard reagent. It is significant that the molecular rotation of the Grignard reagent was slightly greater than that of the active amyl bromide from which it was prepared.

The following is a typical run. Active 1-bromo-2-methylbutane, $[M]^{25}_{D}$ +5.06°, was prepared with phosphorus tribromide from active 2-methyl-1-butanol $[M]^{25}_{D}-4.35°$. Using an excess of this bromide with di-*n*-butyl ether as the solvent, the corresponding Grignard reagent was then prepared in the ordinary way. After distilling off the excess bromide under reduced pressure, a clear active Grignard reagent, $[M]^{25}_{D}$ +5.36°, was obtained.

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RECEIVED AUGUST 29, 1938

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(2) Olewine, THIS JOURNAL, **60**, 2569 (1938).