

neutralized with sodium hydroxide. The insoluble layer was extracted with benzene, dried over calcium chloride and then distilled under reduced pressure. A total of 7.5 g. (75% yield) of the rearranged product was obtained; b. p. 96–98° (6 mm.);  $n_D^{20}$  1.4733. The substance gave a positive iodoform reaction, indicative of the  $-\text{COCH}_3$  group. Schiff's reagent required considerable time for a slight color change. When 0.5 g. of this material in 50 cc. of alcohol was refluxed for five hours with freshly prepared silver oxide, no acid was obtainable on working up the products. Crystallization of this material was a difficult matter but it was found that solidification set in after about two weeks at room temperature. Recrystallization of this product from petroleum ether yielded crystals which melted at 77–78°. Analysis was satisfactory for 2-acetyl-6-hydroxycamphane (IX).

*Anal.* (by M. Pollack). Calcd. for  $\text{C}_{12}\text{H}_{20}\text{O}_2$ : C, 73.41; H, 10.27. Found: C, 73.43; H, 10.03.

**Ozonization of 2-Acetyl-6-hydroxycamphane.**—Eighty cc. of carbon tetrachloride was used as solvent for 4.14 g. (0.021 mole) of (IX) and 62.3 liters of an 8–10% ozone mixture was run in during twenty hours. The ozonide was hydrolyzed by warming on the steam-bath with an equal volume of water. There was formed 0.040 mole of acidic material (97.0 cc. of 0.4170 *N* sodium hydroxide solution was required). The neutral aqueous solution was extracted twice with carbon tetrachloride, then concentrated and acidified with hydrochloric acid. A brown, viscous mass separated which, after three crystallizations from alcohol-water, yielded 2.8 g. (0.014 mole) of white, crystalline 6-hydroxy-2-camphanecarboxylic acid<sup>14</sup> (X), m. p. 221°.

*Neut. eq.* Calcd. for  $\text{C}_{11}\text{H}_{18}\text{O}_3$ , 198.2. Found: 198.8 (0.2649 g. required 12.20 cc. of 0.1091 *N* NaOH).

*Anal.* (semi-micro). Calcd.: C, 66.62; H, 9.15. Found:

(14) Houben, *Ber.*, 59, 2285 (1926), reported a melting point of 216–220°.

C, 66.62, 66.40; H, 9.07, 9.16. *Anal.* (macro, by M. Pollack). Found: C, 66.64; H, 9.02.

**Semicarbazone.**—This derivative, prepared in the usual manner from IX, melted at 202°. That it was the semicarbazide of 1-acetylcumene (VIII), rather than of IX, was shown by analysis. Evidently a dehydration process occurs during semicarbazone formation.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{21}\text{ON}_3$ : N, 17.88. Calcd. for  $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N}_3$ : N, 16.60. Found (Dumas): N, 17.84, 17.81.

### Summary

Rearrangement of ethynylcyclohexanol by hot formic acid yields 1-acetyl-1-cyclohexene, not cyclohexylideneacetaldehyde, since it is identical to the substance prepared from cyclohexene, acetyl chloride and aluminum chloride. Other evidence for the structure of the product is cited also.

No evidence could be found to support the statement in the literature that an isomeric aldehyde is produced from ethynylmethylphenylcarbinol by rearrangement with formic acid. Instead of  $\beta$ -phenylcrotonaldehyde, the product formed is acetophenone. The bulk of the product is a tar which probably arises *via* 2-phenylbutenone.

Ethynylbornyl alcohol, prepared from camphor, acetylene and sodium, undergoes rearrangement to 2-acetyl-6-hydroxycamphane. On oxidation, this substance yields 6-hydroxy-2-camphanecarboxylic acid. Improved directions are given for the synthesis of ethynylfenchyl alcohol.

EVANSTON, ILLINOIS . RECEIVED OCTOBER 15, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

## The Removal of HX from Organic Compounds by Means of Bases. III. The Rates of Removal of Hydrogen Bromide from Substituted N-Bromobenzamides and their Relative Ease of Rearrangement in the Presence of Alkali. The Hofmann Rearrangement

BY CHARLES R. HAUSER AND W. B. RENFROW, JR.

According to the most generally accepted mechanism for the Hofmann rearrangement of a bromoamide in the presence of alkali,<sup>1</sup> hydrogen bromide is removed to form an unstable univalent nitrogen compound which undergoes the rearrangement to give an isocyanate. Since it is possible to isolate the alkali salts,  $(\text{RCONBr})\text{Na}$ , of certain bromoamides, the reaction apparently involves first, the

removal of the hydrogen as a proton, followed by the release of bromide ion and rearrangement of the molecule; this might be represented as follows

$$\text{RCONHBr} \xrightarrow{+\text{OH}^\ominus} \text{RCONBr}^\ominus \xrightarrow{-\text{Br}^\ominus} (\text{RCON}) \longrightarrow \text{RCNO}$$

We have taken the view that the rate determining step of this process is the release of bromide ion from the negative ion of the salt, and that the rearrangement, if it is a separate step, occurs rela-

(1) See especially Porter, "Molecular Rearrangements," The Chemical Catalog Co., New York, 1928, pp. 13–30.

tively rapidly as the molecule is stabilized.<sup>2</sup> On this basis the ease of rearrangement<sup>3</sup> of a bromoamide in the presence of alkali would be dependent upon the rate of removal of bromide ion. As a possible test for this hypothesis, a study has been made of the rates of decomposition of the sodium salts of a series of meta and para substituted bromobenzamides. It seemed reasonable to expect that if this view were correct then an inverse relationship should exist between the rates of decomposition of these salts and the dissociation constants of the corresponding carboxylic acids. Linear relationships have been reported recently between the rates of certain reactions and the dissociation constants of the corresponding acids.<sup>4</sup> An inverse relationship should be expected in the case of the bromoamide salts since, in their decomposition, bromine is released as a negative bromide ion, whereas, in the dissociation of an acid, hydrogen is removed as a positive ion, *i. e.*, as a proton; this relationship has been verified for certain meta and para substituted bromobenzamides.

### Experimental

**Preparation of Bromobenzamides.**—These compounds were prepared by a modification of the method by which Hoogewerff and van Dorp<sup>5</sup> prepared bromobenzamide and certain of its derivatives. Ten grams of pure, finely pulverized amide was added to 150 cc. of an ice-cold solution of sodium hypobromite, freshly prepared from 14.4 g. (0.09 mole) of bromine, and 9.0 g. (0.23 mole) of sodium hydroxide. After shaking for ten minutes, the mixture was filtered rapidly with suction into a cold solution of 9 cc. of glacial acetic acid in 25 cc. of water containing crushed ice. The bromoamide which precipitated was filtered off and washed thoroughly with water. The following conditions were found best for recrystallizing the various bromobenzamides used in this work. Bromobenzamide and the *p*-methyl derivative were dissolved in boiling chloroform, petroleum ether (b. p. 60–70°) added until

turbidity just disappeared, and the solution cooled; the *m*-bromo and *m*-chloro derivatives were dissolved in glacial acetic acid at 50–60°, water added until cloudiness just disappeared, and the solution cooled; the *m*-nitro derivative was dissolved in acetic acid at 80–85°, water or petroleum ether added and the solution cooled; the *p*-chloro derivative was recrystallized from hot (70–80°) 50% aqueous acetic acid, the *p*-nitro derivative from boiling glacial acetic acid, and the *o*-chloro derivative from a boiling mixture of two parts of carbon tetrachloride to one of chloroform. The *p*-methoxy derivative was dissolved in a 5% solution of sodium hydroxide containing ice, and filtered into dilute acetic acid and ice. The yields of pure products obtained were 40–70% of the theoretical quantities. They should be kept cold, away from light.

For analysis the bromobenzamides were dissolved in glacial acetic acid, excess potassium iodide added, the solution diluted with water to about 150 cc., and the liberated iodine titrated with sodium thiosulfate to the starch-iodide end-point. The analytical data for the bromobenzamides used in this work are given in Table I. These compounds melted with decomposition. Their approximate melting or decomposition points are given in Table I. These values were determined by immersing samples in a bath which was previously heated to within 5–10° of these temperatures and gradually heating the bath in the usual manner.

**Products of Reactions of Bromobenzamides with Alkali.**—Bromoamides readily dissolve in sodium hydroxide to form sodium salts<sup>1,6</sup> which release bromide ion and undergo rearrangement to isocyanates. In the presence of alkali, the latter are hydrolyzed to primary amines. Bromoamides may also undergo hydrolysis to form the corresponding acids. These reactions may be represented by the following scheme.

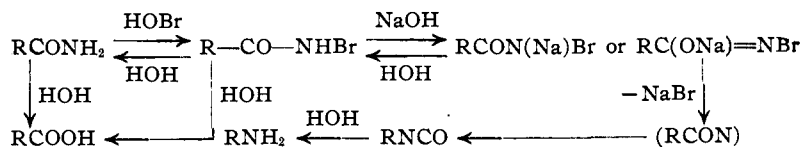


TABLE I  
ANALYTICAL DATA AND MELTING POINTS OF SUBSTITUTED BROMOBENZAMIDES

| Substituent               | M. p. (dec. T), °C. | Active bromine, % |       |
|---------------------------|---------------------|-------------------|-------|
|                           |                     | Calcd.            | Found |
| <i>p</i> -CH <sub>3</sub> | 131–133             | 37.34             | 37.13 |
| <i>o</i> -Cl              | 104–105             | 34.09             | 33.90 |
| H                         | 129–131             | 39.96             | 39.72 |
| <i>p</i> -Cl              | 170–174             | 34.09             | 34.05 |
| <i>m</i> -Br              | 122–126             | 28.65             | 28.34 |
| <i>m</i> -Cl              | 102–105             | 34.09             | 34.00 |
| <i>o</i> -NO <sub>2</sub> | 170–176             | 32.62             | 32.38 |
| <i>m</i> -NO <sub>2</sub> | 173–176             | 32.62             | 32.44 |
| <i>p</i> -NO <sub>2</sub> | 198–202             | 32.62             | 32.30 |

At 30° in the presence of a large excess of alkali, the yields of amine obtained from the bromobenzamides studied in this investigation, with the exception of the nitro derivatives, were 90% or better, whereas the yields of the corresponding acids were less than 5% (see Table IV). The meta and para nitro derivatives, however, gave 25 and 46% yields of the corresponding acid, those of the

(2) In this connection see especially, Whitmore, *THIS JOURNAL*, **54** 3281 (1932); Wallis and Whitmore, *ibid.*, **56**, 1427 (1934).

(3) Jones and co-workers<sup>1</sup> assumed that the ease of rearrangement of this type is dependent upon the tendency for the radical R, in the univalent nitrogen derivative, to exist as a free radical, and they presented certain evidence to support this hypothesis. Recently, Wallis and co-workers [*THIS JOURNAL*, **55**, 1701, 2598 (1933)]; and Bell, *J. Soc. Chem. Ind.*, **52**, 584 (1933)], have presented evidence that R does not actually exist as a free radical during the Hofmann rearrangement.

(4) (a) Hammett and Pfluger, *THIS JOURNAL*, **55**, 4079 (1933); Hammett, *Chem. Rev.*, **17**, 125 (1935); (b) Dippy and Watson, *J. Chem. Soc.*, 436 (1936).

(5) Hoogewerff and van Dorp, *Rec. trav. chim.*, **8**, 173 (1889); see also, *ibid.*, **6**, 373 (1887). In agreement with our results these workers have shown that the potassium salts of *m*- and *p*-nitrobromobenzamides are more stable than the salt of bromobenzamide.

amines being correspondingly smaller. The relatively low yields of amines obtained in these cases may be explained by the fact that the rate of rearrangement of these compounds is greatly retarded by the presence of the nitro group (see Table IV), whereas the rate of hydrolysis is probably accelerated. It is of interest that the rearrangement apparently has a higher temperature coefficient than the hydrolysis. A 90% yield of *p*-nitroaniline was obtained when *p*-nitrobromobenzamide was dissolved in alkali solution at the temperature of the boiling water-bath (96–100°), whereas a yield of amine of only 48% was obtained at 30°. This point should be considered in the preparation of amines by this reaction.

The yields of amine and acid given in Table IV have been determined under the conditions used in the rate measurements described below. These products were isolated according to the following procedure.

The pure bromoamide (0.005 mole) was dissolved in 100 cc. of 1.0 molar carbonate-free sodium hydroxide solution at 30 ± 0.02°, and kept at this temperature until the mixture no longer contained active bromine. In order to convert any unchanged isocyanate into primary amine, the mixture was acidified with hydrochloric acid and heated on the water-bath for an hour. It was then cooled and extracted with three 25-cc. portions of ether. Organic acid mixed with a very small amount of neutral tarry material was obtained from the dried<sup>6</sup> ether extracts by evaporation of the solvent. The primary amine was obtained from the aqueous solution by making it alkaline and extracting it with three portions of ether. Liquid amines were isolated as their hydrochlorides by passing dry hydrogen chloride into their dried ether solutions. The organic acids and solid amines were identified by their melting points and in most cases by mixed melting points with authentic specimens.

**Relative Stabilities of the Sodium Salts of Bromobenzamides.**—Van Dam and Aberson<sup>7</sup> have studied the rate of decomposition of bromobenzamide in various concentrations of alkali. With an equivalent of alkali a colored precipitate formed within a short time, interfering with the titration; benzoylphenylurea was isolated from the reaction mixture. Under these conditions we have been able to obtain a yield of aniline of only 30% of the theoretical amount. Van Dam and Aberson<sup>7</sup> showed that in the presence of an excess of alkali the rate was dependent not only on the concentration of bromobenzamide but also on that of the alkali, being approximately proportional to the concentration of alkali when twenty to forty equivalents of the latter to one of the bromoamide were used.<sup>8</sup> We have obtained 94–95% yields of aniline using 10, 20 or 40 equiva-

(6) Anhydrous calcium sulfate (Drierite) was used.

(7) Van Dam and Aberson, *Rec. trav. chim.*, **19**, 318 (1900); Van Dam, *ibid.*, **18**, 408 (1899).

(8) It does not seem possible that this alkali effect could be due only to a shift in the equilibrium of the acid-base reaction between the bromoamide and alkali. Further studies in this connection are planned.

lents of alkali to one of bromobenzamide. In this investigation therefore, the rates of decomposition of substituted bromobenzamides were determined in the presence of a large excess (20 to 1) of alkali, using the same molar concentrations of reactants in all cases.

The course of the reaction of a 0.05 molar bromoamide solution in 1.0 molar sodium hydroxide at 30 ± 0.02° was followed by titrating samples for active bromine in the usual manner. Since the reaction is first order with respect to the bromoamides, velocity constants have been calculated from the first order rate of reaction equation

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

where *t* is in minutes. Two sets of measurements have been made with each bromoamide, the data and velocity constants with a representative compound being given in Table II. The average values of velocity constants *K*, calculated for 25–95% decomposition of the bromoamides are arranged in decreasing order in Table IV. With the exceptions of the *p*-methoxy and the nitro derivatives, these values are reproducible to within 1–3%. Under the conditions used the *p*-methoxy compound<sup>9</sup> decomposed too rapidly (95% within five minutes) to measure accurately. The values of *K* calculated for the *o*-, *m*- and *p*-nitro derivatives were not constant but increased steadily from 0.00105–0.00174, 0.000556–0.000988 and 0.000823–0.000974, respectively. Mean values are recorded in Table IV merely to illustrate their relative stabilities. It is to be noted that in these cases considerable hydrolysis occurred.

Velocity constants for the sodium salts of bromobenzamide and of *p*-methyl- and *m*-chlorobromobenzamides have been measured at two or three temperatures, and the heats of activation

TABLE II  
RATES OF DECOMPOSITION OF *m*-CHLOROBROMOBENZAMIDE  
(0.05 *M*) IN 1.0 *M* NaOH AT 30°

| Run no. 1  |   |                      | Run no. 2  |   |                      |
|------------|---|----------------------|------------|---|----------------------|
| Time, min. | Cc. Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 0.02 <i>N</i> | <i>K</i>             | Time, min. | Cc. Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 0.02 <i>N</i> | <i>K</i>             |
| 0          | 44.60   | 0.00621 <sup>a</sup> | 0          | 47.85   | 0.00528 <sup>a</sup> |
| 12.75      | 41.19   | .00573               | 14         | 44.45   | .00555               |
| 37.75      | 35.92   | .00571               | 35         | 39.40   | .00565               |
| 63.25      | 31.08   | .00571               | 65         | 33.15   | .00567               |
| 100.75     | 25.07   | .00571               | 111        | 25.50   | .00566               |
| 130.75     | 21.13   | .00571               | 169        | 18.40   | .00566               |
| 309.25     | 7.60  | .00571               | 221        | 13.70   | .00566               |
|            | Average   | .00571               |            | Average   | .00566               |

<sup>a</sup> Not averaged.

(9) This was the most unstable compound prepared. A product 90% pure was used for an approximate rate determination.

calculated. The results are given in Table III. It can be seen that the heat of activation for the *p*-methyl derivative is about one thousand calories less than that for bromobenzamide, whereas the value obtained for the *m*-chloro derivative is 400 cal. greater; this latter difference might be within the experimental error. This phase of the problem is being studied further.

TABLE III

HEATS OF ACTIVATION OF THE SODIUM SALTS OF BROMOBENZAMIDE AND CERTAIN OF ITS DERIVATIVES

| Derivative       | $T_1$ | $K_1$ | $T_2$ | $K_2$  | $Q$                 |
|------------------|-------|-------|-------|--------|---------------------|
| <i>p</i> -Methyl | 30    | 0.138 | 20    | 0.0301 | 27,000              |
| <i>p</i> -Methyl | 20    | .0301 | 11.5  | .00741 | 27,300              |
| Bromobenzamide   | 30    | .0461 | 20    | .00942 | 28,200 <sup>a</sup> |
| <i>m</i> -Chloro | 45    | .0536 | 30    | .00569 | 28,600              |

<sup>a</sup> From the data reported by Van Dam and Aberson for bromobenzamide the heat of activation of 28,700 cal. has been calculated; see ref. 7.

It can be seen from Table IV that the rates of decomposition of the salts of the meta and para substituted bromobenzamides at 30°, and pre-

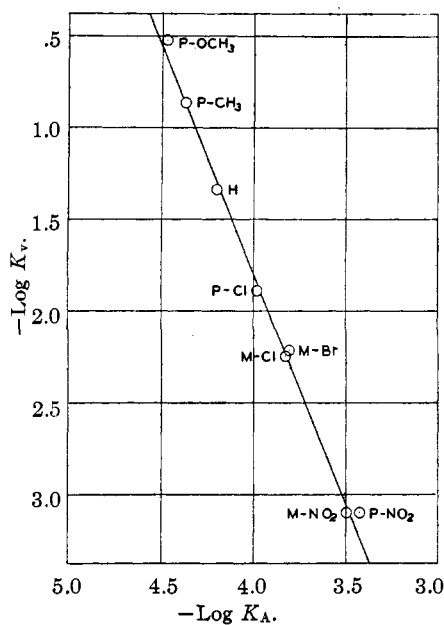


Fig. 1.

sumably their ease of rearrangement,<sup>10</sup> are in general in the inverse order to the dissociation constants of the corresponding carboxylic acids.<sup>11</sup> When the logarithms of the rate constants<sup>12</sup> are

(10) This does not necessarily mean that the ease of rearrangement of the corresponding univalent nitrogen compounds, if they have an independent existence, would be in the same order; see note 3.

(11) In this connection it should be mentioned that certain hydroxy bromobenzamide derivatives are very unstable. McCoy, *Am. Chem. J.*, **21**, 116 (1899); see also ref. 7.

(12) See note (c) Table IV.

TABLE IV

RATES OF DECOMPOSITION OF SUBSTITUTED BROMOBENZAMIDES (0.05 M) IN 1.0 M NaOH AT 30° AND YIELDS OF PRODUCTS OBTAINED

| Substituent                 | Monomolecular constant $K$ | $K_A$ of RCOOH <sup>a</sup> × 10 <sup>4</sup> | Percentage yields<br>Amine | Percentage yields<br>Acid |
|-----------------------------|----------------------------|---|----------------------------|---------------------------|
| <i>p</i> -CH <sub>3</sub> O | 0.3 <sup>b</sup>           | 3.38  | ....                       | ....                      |
| <i>p</i> -CH <sub>3</sub>   | .138                       | 4.24  | 98                         | Trace                     |
| <i>o</i> -Cl                | .0533                      | (114.)  | ....                       | ....                      |
| H                           | .0461                      | 6.27  | 95                         | 2                         |
| <i>p</i> -Cl                | .0130                      | 10.5  | 94                         | 5                         |
| <i>m</i> -Br                | .00615                     | 15.4  | 90                         | 4                         |
| <i>m</i> -Cl                | .00569                     | 14.8  | 92                         | 3                         |
| <i>o</i> -NO <sub>2</sub>   | .0013 <sup>c</sup>         | (700.)  | ....                       | ....                      |
| <i>m</i> -NO <sub>2</sub>   | .0008 <sup>c</sup>         | 32.1  | 70                         | 25                        |
| <i>p</i> -NO <sub>2</sub>   | .0008 <sup>c</sup>         | 37.6  | 48                         | 46                        |

<sup>a</sup> The dissociation constants listed here, with the exception of the one for *o*-nitrobenzoic acid, have been taken from the recent papers of Dippy and co-workers, see note 13.

<sup>b</sup> An approximate value for the constant. In qualitative agreement with our results, Van Dam has previously reported that in the presence of potassium hypobromite, *p*-methoxybenzamide is decomposed more readily than benzamide; see ref. 7. <sup>c</sup> Not a constant; an average value only.

plotted against the logarithms of the dissociation constants of the corresponding acids an approximately linear relationship is exhibited as shown in Fig. 1; the equation for the straight line is  $\log K_v = -11.81 - 2.50 \log K_A$ . The dissociation constants used here are the thermodynamic values recently reported by Dippy and co-workers.<sup>13</sup> If the values given in the "International Critical Tables" are used, the discrepancy between the *m*-chloro and *m*-bromo derivatives disappears but, on the whole, the linear relationship is not quite as good as that represented in Fig. 1.

It is considered that these results are in agreement with the hypothesis that the ease of rearrangement of a bromoamide in the presence of alkali is dependent upon the ease of release of bromide ion from the negative ion of the salt. It can be seen from Table IV that the *o*-chloro and *o*-nitro derivatives are more unstable than would be anticipated from the dissociation constants of the corresponding acids; however, such lack of agreement between theory and experiment with ortho substituted compounds has been observed in other cases.<sup>14</sup>

(13) Dippy and co-workers, *J. Chem. Soc.*, 1888 (1934); 343 (1935); 645 (1936).

(14) In this connection it is of interest to note that although the calculated dipole moments of *m*-, and *p*-chlorobenzoic acids can be correlated with their dissociation constants, apparently no correlation is found in the case of *o*-chlorobenzoic acid; dipole moment calculations seem to indicate that the latter should be weaker than benzoic acid, whereas actually it is much stronger; see Smallwood, *This Journal*, **54**, 3048 (1932); see also ref. 4b.

The writers wish to thank Dr. Douglas G. Hill for suggestions on the kinetics of these reactions.

### Summary

1. The rates of decomposition of the sodium salts of a series of substituted bromobenzamides have been measured at 30°.

2. The rates of decomposition of the sodium salts of bromobenzamide and of *m*-chloro- and *p*-methylbromobenzamides have been measured at two or three temperatures and their heats of activation calculated.

3. It has been found that the relative rates of decomposition of certain meta and para substituted bromobenzamides at 30°, and presumably their relative ease of rearrangement in the pres-

ence of alkali, are inversely related to the dissociation constants of the corresponding carboxylic acids.

4. These results are considered to be in agreement with the hypothesis that the ease of rearrangement of a bromoamide in the presence of alkali is dependent upon the ease of release of bromide ion from the negative ion of the alkali salt.

5. It has been found that in the presence of excess alkali at 30°, *p*-nitrobromobenzamide gives approximately as much *p*-nitrobenzoic acid by hydrolysis as *p*-nitroaniline by rearrangement; at 96–100°, however, a 90% yield of *p*-nitroaniline is obtained.

DURHAM, N. C.

RECEIVED AUGUST 12, 1936

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

## Studies on Lignin and Related Compounds. XXVI. The Properties of Spruce Lignin Extracted with Formic Acid

BY GEORGE F. WRIGHT AND HAROLD HIBBERT

The recent publications by Freudenberg and co-workers<sup>1</sup> and by Staudinger and Dreher,<sup>2</sup> in which they describe the extraction of spruce wood meal with formic acid, anticipate a current investigation in this Laboratory. Although this study is not yet complete it seems advisable to present a preliminary account of the work.

Considerable doubt exists as to the reliability of any known extraction process for isolating *unchanged* lignin from wood, and it seems preferable to consider an extractant as the first reagent in a series of reactions intended to prove structure. As one of a series of such extractants, so regarded, it has been found that boiling formic acid removes from resin- and soluble-carbohydrate-free spruce wood meal 17% of its weight in the form of methoxyl-containing material. Because of partial demethoxylation this process yields lignins of comparatively low methoxyl content (12–14%) but it possesses the advantages of: (a) rapidity and convenience of extraction, and (b) isolation of extracts readily soluble in many organic solvents. Thanks to this ease of solubility, it has been found possible to effect a separation of the isolated lignin into five fractions by precipitation of chloroform, acetone and

aqueous acetone solutions into ether and also petroleum ether (Table I). This fractionation is undoubtedly incomplete; indeed, subsequent experiments show that the fractions are still complex. Nevertheless, examination of these partially separated products shows a definite trend in chemical and physical properties undoubtedly characteristic of the individual substances that comprise the isolated mixture called lignin.

The behavior of two functional groups has been examined in this study, namely, (a) reactions of the hydroxyl and (b) reactions of the carbonyl group. The suitable solubility of formic acid lignin has permitted the use of the Grignard machine<sup>3</sup> for simultaneous determination of both groups. These analyses have been supplemented by appropriate methoxylations and tosylation. The results (Table I) show two interesting facts: (i) the native lignins contain small amounts of non-enolizable carbonyl groups; (ii) the more soluble, and therefore simplest, fractions, have *higher hydroxyl* and *lower methoxyl* values than their more complex, insoluble analogs. This decrease in hydroxyl value with decreasing solubility suggests that increasing aggregation of

(1) Freudenberg, Janson, Knopf and Haag, *Ber.*, **69**, 1415 (1936).

(2) Staudinger and Dreher, *ibid.*, **69**, 1729 (1936).

(3) Kohler, Stone and Fuson, *THIS JOURNAL*, **49**, 3181 (1927); Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930).