collapsing. Trimming the upper edges of the cup gives a neater appearance.

To use such a dialyser it is nearly filled with the colloidal solution and suspended in a large vessel of pure water. Removal of ions is extremely rapid in spite of the fact that parchment is inferior as a membrane to goldbeater's skin. It is evident that with a given membrane the rate of dialysis is proportional to the effective surface of the membrane. In this form the bottom and sides of the cup are all effective.

The rate of dialysis may be doubled if two such cups are used, the smaller inside the larger. The inner cup holds pure water and the other the colloidal solution, while the combination of cups is hung in a larger vessel of pure water. This arrangement gives dialysing surface outside and inside the colloidal solution. The water may be changed as desired. It is quite possible that this simple method of making parchment cups may have been used by others but I have found no reference to it in the literature.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

SOME REACTIONS RESULTING IN THE CLEAVAGE OF POLYNUCLEAR AROMATIC COMPOUNDS.

BY E. P. KOHLER AND R. H. PATCH.

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In 1911 Clarke and Esselen[1] found that when bromine reacts with *p*-aminobenzhydrol the principal result is not a brominated hydrol but a mixture of two mononuclear compounds: benzaldehyde and a substitution product of aniline. They then studied the action of bromine on a number of derivatives of *o*- and *p*-aminobenzhydrol and found that all of these behaved in a similar manner. A typical reaction is represented by the equation

$$C_6H_5CHOHC_6H_2Br_2NH_2 + Br_2 = C_6H_5CHO + C_6H_2Br_3NH_2 + HBr.$$

All of the experiments of Clarke and Esselen were made with derivatives of diphenylcarbinol, but Clarke and Patch[2] subsequently extended the investigation to derivatives of triphenyl carbinol, and to amino alcohols that have aliphatic as well as aromatic groups. The results reported in this paper were obtained in continuation of that investigation.

That halogens occasionally replace an aliphatic side chain in aromatic compounds, or split diphenylmethane derivatives into mononuclear compounds has long been known. As early as 1845 Piria[3] found that

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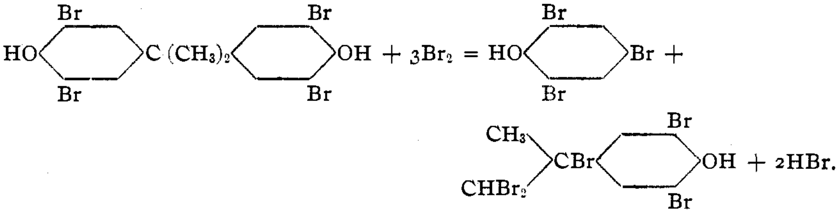
[1] THIS JOURNAL, 35, 1135 (1913); 36, 308 (1914).

[2] *Ibid.*, 34, 912 (1912).

[3] *Ann.*, 56, 47 (1845).

chlorine transforms *o*-hydroxybenzyl alcohol into trichlorophenol and Visser,[1] later, obtained a corresponding result with bromine. Since then isolated instances of a similar result have been recorded by various observers; but the only systematic investigations of the subject were made by Zincke[2] and by Auwers[3] in connection with their work on pseudo phenols. Zincke used alkylated diphenylmethane derivatives that had hydroxyl groups in the para position and found that bromine invariably splits these into mononuclear compounds. A typical case is illustrated by the equations



Auwers worked with *p*-dihydroxydiphenylmethane derivatives that had alkyl groups in the nucleus. He found that when these react with bromine the result is almost invariably a mixture of substitution and cleavage products. By comparing the behavior of five closely related substances he showed that the relative amount of cleavage depends upon the number and location of the alkyl groups in the diphenylmethane derivative.

Neither Zincke nor Auwers found a satisfactory explanation for this cleavage by bromine. Zincke inclined to the view that cleavage was due to the direct action of bromine upon the diphenylmethane derivative, and that the bromine substitution products were due to subsequent bromination of one of the cleavage products; but he also admitted that his facts could be interpreted equally well on the assumption that substitution in the alkyl groups was the primary process and that cleavage was due to the resulting hydrobromic acid. Auwers attributed cleavage to hydrobromic acid and, in support of this view, established the fact that no cleavage occurred when his substances were treated with bromine in the presence of enough potassium acetate to react with all of the hydrobromic acid formed by substitution. But Auwers could not explain the fact that no cleavage occurred when his substances were heated with hydrobromic acid instead of bromine.

The most significant fact brought to light by Clarke and Esselen, is the astonishing ease with which the amino derivatives of diphenylcarbinol undergo cleavage into mononuclear compounds under the influence of bromine. Zincke usually heated his substances with excess of bromine

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[1] *Arch. der Pharm.*, 235, 591 (1897).

[2] *Ann.*, 343, 76 (1905).

[3] *Ibid.*, 356, 175 (1907).

to 100° in sealed tubes. Auwers added bromine to boiling solutions of his compounds in glacial acetic acid. Clarke and Esselen found that the amino hydrols react rapidly at 0° in any indifferent solvent. In explanation, they attribute cleavage to a mechanism similar to that adopted by Hantzsch and Graf to account for the easy bromination of aromatic amines. They assume that bromine first combines with nitrogen to form a perbromide, and that this subsequently undergoes a series of rearrangements resulting in the cleavage products obtained.

$$C_6H_5CH(OH)C_6H_4N(CH_3)_2 + Br_2 = C_6H_5CH(OH)C_6H_4N(CH_3)_2Br_2 \longrightarrow$$
$$C_6H_5CH(OH)N(CH_3)_2Br.C_6H_4Br \longrightarrow C_6H_5CHO + HBr.N(CH_3)_2C_6H_4Br.$$

The results recorded in this paper show that the rapid, easy cleavage of hydrols is not confined to the action of halogens. Nitric acid, nitrous acid, and other reagents that are capable of forming substitution products by direct action upon aromatic compounds, split the hydrols in the same manner and with the same ease as do the halogens, and the substances that give a large proportion of cleavage products when treated with halogens, undergo an equally extensive cleavage under the influence of these reagents. Dimethylaminobenzhydrol and nitrous acid, for example, react almost quantitatively in accordance with the equation

$$C_6H_5CHOHC_6H_4N(CH_3)_2 + HNO_2 = C_6H_5CHO + H_2O + NOC_6H_4N(CH_3)_2.$$

The results also show that cleavage is not confined to hydrols that contain the amino or substituted amino groups. Any group that effectively promotes substitution in the nucleus of aromatic compounds will similarly promote cleavage in the case of hydrols. These groups are not, however, equally effective, and we have tried to find a quantitative expression for the relative effectiveness of different groups.

The reactions that may take place when a substance like dimethylaminobenzhydrol is treated with bromine are as follows:

I. Replacement of one or more hydrogen atoms in the α-position to the amino group by bromine.

II. Cleavage, both of the original substance, and of the substitution product formed in I.

III. Formation of an ether from two molecules of the hydrol—a process that readily takes place in the presence of small quantities of hydrobromic acid.

IV. Oxidation of the hydrol to the corresponding ketone.

Of the products formed in these reactions, only those resulting from cleavage are readily volatile with steam. By distilling with steam, oxidizing the aldehyde, and extracting and weighing the benzoic acid, it was generally possible to make a sufficiently accurate estimate of the amount of cleavage. These determinations warrant the following general statements:

I. Whenever the reaction takes place rapidly, so that for each molecule of hydroxyl compound one molecule of bromine or other suitable reagent disappears as fast as it is added, the result is almost exclusively cleavage and substitution. The groups whose presence in the para position leads to this result may be regarded as the most effective groups. When the reagent disappears more slowly and less completely, both cleavage and substitution diminish in favor of oxidation and ether formation. With hydrols that have a methyl group or a halogen atom in the para position, there is barely enough cleavage or substitution to be detected.

The relative amounts of cleavage and substitution depend upon the character of the "bridge;" under conditions under which a given benzhydrol derivative gives principally cleavage products, the corresponding diphenylmethane derivative undergoes but little cleavage, while the corresponding ketone will give only substitution products.

II. The efficiency of different groups in promoting cleavage is represented by the following series, in which the most effective comes first: $(CH_3)_2N$, HO, CH_3O, CH_3, Br.

III. Substituents in the *o*-position to these groups invariably diminish the relative amount of cleavage and with all but the most effective, diortho substitution stops it altogether.

These facts show that cleavage and replacement of hydrogen are similar processes, promoted equally by the same groups, hindered in the same way, therefore the result of the same mechanism.

I. Experiments with Amino Compounds.

***p*-Dimethylaminobenzhydrol and Bromine.**—The reaction between these substances in chloroform has been described by Clarke and Esselen. For the purpose of determining the influence of the solvent we compared the results obtained in chloroform with those obtained in glacial acetic acid, and in dilute hydrochloric acid. We found that the products are the same in all cases, but that, possibly owing to salt formation, the reaction goes more slowly in the acid solvents. We also examined the behavior of the hydrol towards concentrated hydrobromic acid. For this purpose a solution of the hydrol in hydrobromic acid (sp. gr. 1.78) was allowed to stand in a glass stoppered bottle for 11 days, then diluted with water and neutralized. A faint odor of benzaldehyde was perceptible, but the usual procedure did not give enough benzoic acid even for a melting-point determination. Cleavage, therefore, is not due to hydrobromic acid.

***p*-Dimethylaminobenzhydrol and Nitrous Acid.**—A dilute aqueous solution of sodium nitrite was added, very gradually, to a solution of five grams of the hydrol in 12.5 cc. of concentrated hydrochloric acid and 25 cc. water, that was cooled to 0°. The nitrous acid disappeared as fast as formed and none could be detected in the solution with starch-iodide paper until slightly more than one equivalent of sodium nitrite had been added. The solution at first turned orange, then deposited an orange-colored precipitate. This soon disappeared, however, and as more nitrite was added a yellow crystalline deposit took its place and oily drops of benzaldehyde collected on the surface of the liquid. As soon as free nitrous acid appeared in the solution, the precipitate was filtered off, washed with alcohol containing hydrochloric acid, dried, and weighed. The crude salt melted at 173–174°. As the melting point of pure nitrosodimethyl aniline hydrochloride is 177°, this was nearly pure salt and the 3.45 g. obtained show 94% of cleavage. The salt was decomposed with a solution of potassium carbonate, the base recrystallized and identified as nitrosodimethyl aniline—a brilliant green solid melting at 85–86°.

***p*-Dimethylaminobenzhydrol and Nitric Acid.**—The experiments with nitric acid were carried out in glacial acetic acid or, in specified cases, without use of solvent. The reaction was invariably accompanied by the evolution of oxides of nitrogen indicating oxidation by nitric acid. Experiments with benzhydrol showed that cold, concentrated nitric acid does not oxidize hydrols to benzoic acid. Any benzoic acid obtained in the reaction between substituted hydrols and nitric acid must therefore be due to the intermediate formation of benzaldehyde by cleavage. The oxidation of these hydrols with cold neutral permanganate also stops when the hydrol has been oxidized to the corresponding ketone. For these reasons it was not necessary to isolate the benzaldehyde first and then oxidize it to benzoic acid. A more accurate value for the amount of cleavage was obtained, in some cases, by diluting the reaction mixture with water, neutralizing with soda, oxidizing with permanganate in the cold, removing the oxides of manganese with sulfur dioxide, and finally extracting and weighing the resulting benzoic acid.

The reaction between *p*-dimethylaminobenzhydrol and nitric acid[1] was carried out with 5 g. of hydrol, dissolved in 30 g. of glacial acetic acid, and 20 g. of nitric acid (sp. gr. 1.50) added, the mixture being cooled with running water both while the acid was added and afterwards as long as heat was given off. Oxidation of the product, which had a strong odor of benzaldehyde, with permanganate gave 0.65 g. of benzoic acid—showing 28% cleavage. Owing to the ease with which the hydrols are oxidized to ketones by nitric acid, the proportion of cleavage products is smaller than with other reagents.

Ethyl Ether of *p*-Diethylaminobenzhydrol and Bromine.—According to the mechanism that Clarke and Esselen proposed to account for the splitting of carbinols, no cleavage would be expected in the case of ethers. The ether we used was made by the method of Willstätter.[2] A test

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[1] See Zincke, *Ann.*, **362**, 203 (1908); Pinnow, *Ber.*, **27**, 3163 (1894).

[2] *Ber.*, **39**, 3765 (1906).

with ethyl magnesium bromide showed that it was free from hydrol, but it rapidly decolorized bromine, and at least a third of it was split in the usual way. The products identified were benzaldehyde and *p*-bromodimethyl aniline. Special search was made for ethyl bromide, but neither this nor ethyl alcohol could be detected among the products, hence the fate of the ethyl group remains unknown. The results are inconclusive, because, as usual, some replacement of hydrogen by bromine occurred and therefore some hydrobromic acid was formed. Although every precaution was taken to avoid the presence of water, it is possible that the hydrobromic acid transformed some of the ether into diethylaminobenzhydrol, and that this was responsible for the cleavage products.

Ethyldi-(4-dimethylaminophenyl) Carbinol, $(C_2H_5)((CH_3)_2NC_6H_4)_2COH$, was prepared by the action of ethylmagnesium bromide on Michler's ketone. As the ketone is sparingly soluble in ether, and too vigorous reaction readily leads to the formation of an ether in place of the carbinol, the procedure adopted was as follows: A solution of the ketone in pure, dry benzene was dropped, slowly, into an ethereal solution that contained an excess of ethyl magnesium bromide, and was cooled in a freezing mixture. Each drop of the ketone solution produced an orange-colored precipitate that redissolved on shaking. The mixture was allowed to stand at the ordinary temperature for 36 hours, then poured into excess of iced sulfuric acid. A part of the product remained in the ether-benzene layer which deposited it in crystalline form on evaporation. The remainder dissolved in the acid, from which it was recovered by neutralization with ammonia in the presence of ammonium chloride. The carbinol was purified by recrystallization from a mixture of benzene and ligroin. The yield was 92 g. from 100 g. of ketone—82% of the calculated quantity.

Calc. for $C_{19}H_{26}ON_2$: C, 76.51%; H, 8.72%. Found: C, 76.02%; H, 8.37%.

The substance is sparingly soluble in ligroin and cold ether, readily in boiling ether and other common organic solvents. It melts at 118°.

Reaction with Bromine.—A solution of 8 g. of bromine in chloroform was added to a solution of 14.9 g. of the carbinol in the same solvent. Reaction took place immediately but there was no evidence of an intermediate addition product. The residue left after evaporating the chloroform in a current of air was made alkaline with sodium hydroxide and distilled with steam. The distillate contained 6.7 g. of *p*-bromodimethyl aniline, melting at 54°, showing that cleavage in this case amounted to at least 67%. All attempts to get the second product of the reaction in pure condition, or in the form of some crystalline derivative failed.

Naphthyl-(4-dimethylaminophenyl) Carbinol and Bromine.—Pure carbinol, prepared by the method of Sachs,[1] was dissolved in chloroform and this solution treated with a slight excess of bromine in the same solvent.

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[1] *Ber.*, 38, 516 (1905).

Here also we could secure no evidence that an intermediate addition product was formed at low temperatures. After the solution had stood at the ordinary temperature for a few minutes, the excess of bromine and the solvent were removed in the usual way. The residue was poured into water containing enough acid to combine with any amine present and distilled with steam. The distillate, which held a yellow oil in suspension, was extracted with chloroform. The resulting chloroform solution, when diluted with alcohol and digested with a solution of *o*-nitrophenylhydrazine in dilute acetic acid, deposits a hydrazone in bright red needles melting at 179–180°. The analysis showed that this was the nitrophenylhydrazone of naphthoic aldehyde.

Calc. for $C_{17}H_{13}O_2N_3$: N, 14.4%. Found: N, 14.8%.

The residue left in the distilling flask was made strongly alkaline and again distilled with steam. The crystals that separated from the distillate were *p*-bromodimethyl aniline, melting at 54°. As the object of this experiment was the detection of any intermediate compound that might be formed, the relative amount of cleavage products was not determined.

Methylphenyl-(3-bromo-4-dimethylaminophenyl) Carbinol, $(CH_3)(C_6H_5)[C_6H_3(Br)N(CH_3)_2]COH$ was made by adding 30 g. of finely powdered bromodimethylaminobenzophenone to a cooled solution obtained by dissolving 4.7 g. magnesium in an ethereal solution of 30 g. of methyl iodide. The mixture was allowed to stand overnight at the ordinary temperature, then poured into a separatory funnel containing cracked ice, ammonia, and ammonium chloride. The ethereal layer, after drying over anhydrous potassium carbonate and evaporation, left an oil. As this could not be induced to crystallize it was transformed into the oxalate by shaking the ethereal solution with a concentrated aqueous solution of oxalic acid. The oxalate separated in colorless crystals that were washed with water and ether. A bromine determination showed that these were pure oxalate.

Calc. for $C_{18}H_{20}O_5NBr$: Br, 19.51%. Found: Br, 19.45%.

The free base was liberated by shaking the pure oxalate with excess of potassium hydroxide, but the product purified in this way likewise was an oil that would not crystallize. Owing to the ease with which it loses water, it could not be distilled under diminished pressure. It was therefore dried and used without further attempt at purification.

Reaction with Bromine.—The reaction was carried out at —10° with 5 g. of carbinol dissolved in chloroform, the bromine being added until it was plainly in excess. The product was poured into dilute sulfuric acid and distilled with steam. The distillate contained 1 g. acetophenone, showing that 53% of the carbinol had undergone cleavage, as compared with 70% obtained in the case of the corresponding bromine-free compound.

Methylphenyl-(3-bromo-4-dimethylaminophenyl) Carbinol and Nitrous Acid.—The behavior of this substance is in sharp contrast with that of dimethylaminobenzhydrol. When a solution of sodium nitrite was added to a solution of the hydrol in hydrochloric acid, free nitrous acid appeared in the solution before a third of one equivalent had been introduced and no acetophenone or other cleavage product could be detected. The bromine in the *o*-position to the dimethylamino group evidently stops cleavage by nitrous acid as effectively as substituents in this position stop the introduction of a nitroso group in the *p*-position of amines.[1]

II. Experiments with Hydroxyl and Methoxyl Compounds.

***p*-Hydroxybenzhydrol and Bromine.**—As the hydrol is sparingly soluble in chloroform the reaction in this case was carried out in glacial acetic acid. It took nearly 6 atoms of bromine to produce a permanent color and about 3 hours to complete the reaction. The acid was then neutralized with soda and the resulting liquid distilled with steam. The distillate contained benzaldehyde, which was removed with bisulfite, and tribromophenol, which was identified by making a mixed melting-point determination with a sample on hand. The residue left after the steam distillation was crystallized from benzene. It separated in white needles that melted, with decomposition at 164°.

Calc. for $C_{13}H_{10}O_2Br_2$: Br, 44.69%. Found: Br, 44.5%.

This substance was identified as 3,5-dibromo-4-hydroxybenzhydrol, which had previously been obtained by Zincke from 3,5-dibromo-4-hydroxydiphenylmethane.[2]

All of the products were isolated in this case, and by weighing these it was possible to determine the relative amounts of cleavage and substitution with considerable accuracy. We found that the result depends to some extent upon the rate with which the bromine is added; when it was added very slowly the cleavage products represent 33% of the hydrol used. This was increased to 42% when all of the bromine was added at once.

Anisalcohol and Bromine.—Anisalcohol dissolved in chloroform readily reacts with bromine. There is some replacement of hydrogen by bromine, but even at −15° a considerable part of the alcohol undergoes cleavage into *p*-bromoanisol, formaldehyde, and hydrobromic acid. The hydrobromic acid transforms some of the alcohol into *p*-methoxybenzylbromide and water which accumulates on top of the chloroform solution. By allowing the reaction to proceed in the presence of excess of finely divided mercuric oxide it was possible to remove the hydrobromic acid as fast as formed. This prevented the formation of methoxybenzylbromide,

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[1] *Monatsh. Chem.*, 19, 627 (1898).

[2] *Ann.*, 334, 367 (1904).

but the cleavage into bromanisol and formaldehyde took place as before. Cleavage is therefore not due to hydrobromic acid but to bromine.

***p*-Methoxybenzhydrol,** $(CH_3OC_6H_4)(C_6H_5)CHOH$.—The alcohol was obtained by Busch[1] when he added sodium nitrite to the hydrochloride of methoxybenzhydrylamine. As anisic aldehyde can be obtained in quantity we undertook to make it by treating the aldehyde with phenyl magnesium bromide in the usual way. Twenty-seven grams of aldehyde gave 20 g. of a mixture of solid products. By repeated recrystallization from ligroin the mixture was separated into the desired alcohol and a less soluble substance that crystallized in colorless needles melting at 120°. This proved to be *p*-methoxybenzhydryl ether.

Calc. for $C_{28}H_{26}O_3$: C, 81.95%; H, 6.34%. Found: C, 82.2%; H, 6.2%.

As the Grignard reaction always gave a mixture, we subsequently tried the reduction of methoxybenzophenone with sodium amalgam and found this the most satisfactory method of preparation. Excess of sodium amalgam was added to a solution of the ketone in alcohol, the mixture allowed to stand overnight, then boiled for six or seven hours and finally poured into a large quantity of water and allowed to stand until the oil had solidified. The solid was recrystallized from ligroin. It separated in large transparent needles that melted at 60° (Busch 58°).

***p*-Methoxybenzhydrol and Bromine.**—The reaction was carried out in chloroform. As the bromine was added, the solution assumed a pink color similar to that of the solid addition product which is obtained when bromine is added to anisic aldehyde. The color soon disappeared, however, hydrobromic acid appeared and a liquid collected in the solution. Benzaldehyde and *p*-bromoanisol were obtained as cleavage products, and the usual method of procedure showed about 20% of the possible amount of cleavage.

***p*-Methoxybenzhydrol and Nitric Acid.**—About 7.5 g. of nitric acid were added gradually to a cooled solution of 4 g. of the hydrol in 10 cc. of glacial acetic acid and the mixture allowed to stand for several days. In this case the product was poured into water and the volatile constituents separated by distillation with steam. The distillate contained benzaldehyde, which was oxidized to benzoic acid and extracted with soda, and *p*-nitroanisol which was identified by comparison with a sample on hand. The pasty residue left in the distilling flask was extracted with naphtha. This dissolved most of it, leaving a small quantity of a colorless solid. The naphtha on evaporation deposited faintly red crystals melting at 55–6°, identified as slightly impure hydrol. The solid, insoluble in naphtha was recrystallized from 80% alcohol, which deposited it in pale yellow needles melting at 104°. The analyses show that this is nitromethoxybenzhydrol, $(CH_3O)(NO_2)C_6H_3CHOHC_6H_5$.

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[1] *J. prakt. Chem.*, [2] 77, 20 (1905).

Calc. for $C_{14}H_{13}O_4N$: C, 64.9%; H, 5.0%. Found: C, 64.8%; H, 4.4%; C, 64.6%; H, 4.6%.

In this case all of the hydrol could be accounted for; the sole products of the reaction were: a nitro derivative of the hydrol formed by substitution, and benzaldehyde and *p*-nitroanisol resulting from cleavage. As a part of the hydrol did not participate in the reaction it is not possible to calculate the extent of cleavage with accuracy, but the amount of benzoic acid obtained showed that it must have been considerable. Somewhat different results were obtained when the hydrol was added directly to the carefully cooled nitric acid. The substances formed were the same as those obtained in the presence of acetic acid, but the principal product was the nitro hydrol resulting from substitution.

The Ethyl Ether of Methoxybenzhydrol, $C_6H_5(CH_3OC_6H_4)CHOC_2H_5$, was made by treating anisic aldehyde with phenyl magnesium bromide as described in the preparation of methoxybenzhydrol. The mixture was boiled for an hour, then cooled in a freezing mixture and treated with acetyl chloride that had been freed from hydrochloric acid by distillation with diethylaniline. A vigorous reaction took place and was completed by warming on a steam bath for half an hour. The mass was then poured into iced acid, and the solution distilled with steam for a short time to remove solvent, bromobenzene and diphenyl. This left a gummy solid—presumably of acetyl compound—which was boiled with alcohol for three or four hours, and finally distilled under diminished pressure. Most of the product distilled at 258–260° under a pressure of 25 mm.

Calc. for $C_{16}H_{18}O_2$: C, 79.3%; H, 7.4%. Found: C, 78.9%; H, 7.4%.

The ether was obtained as a pale yellow oil that did not solidify at —17°.

Reaction with Bromine.—This ether, like that of dimethylaminobenzhydrol, reacted with bromine as readily as the hydrols. The product was first distilled from a water bath to remove the chloroform used as solvent and then under diminished pressure to separate the cleavage products from those due to substitution. The chloroform gave iodoform when shaken with iodine and potassium hydroxide, showing the presence either of alcohol or ethyl bromide, probably the latter because the chloroform that was used was free from alcohol and precautions were taken to avoid the presence of water. The vacuum distillation gave benzaldehyde and *p*-bromoanisol as cleavage products. The amount of cleavage, calculated from the weight of *p*-bromoanisol obtained, was slightly under 10%.

The Ethyl Ether of *p*-Methoxybenzhydrol and Nitric Acid.—The reaction was carried out like that with the hydrol itself and it gave the same products. About 10% of the substance appeared in the form of cleavage products; but as the substitution product that was obtained was the nitro hydrol, it is evident that the ether was decomposed at some stage in the process and it was not possible to determine whether this preceded or followed cleavage.

3-Bromo-4-methoxybenzhydrol, $C_6H_5[C_6H_3(Br)(OCH_3)]CHOH$, was made by adding bromo anisic aldehyde to phenylmagnesium bromide in ethereal solution and allowing the mixture to stand in the cold. The resulting magnesium compound was decomposed with iced ammonium chloride, the volatile substances removed by distillation with steam and the residue recrystallized from naphtha or 50% alcohol. It is readily soluble in all organic solvents except petroleum ether and naphtha, and melts at 79°.

Calc. for $C_{14}H_{13}O_2Br$: Br, 27.3%. Found: Br, 27.2%.

The reaction with bromine was carried out at the ordinary temperature and the amount of benzaldehyde that was formed was determined in the usual way. This showed only about 7.5% of cleavage. The bromine in the *o*-position to the methoxyl group therefore greatly reduces, but does not entirely prevent, cleavage.

3,5-Dibromo-4-hydroxybenzhydrol was also treated both with bromine and with concentrated nitric acid but we could get no evidence of cleavage with either reagent.

Phenyltolylcarbinol and Bromine.—Thirty grams of bromine were added to a solution of 60 g. of the carbinol in 150 cc. of chloroform. The reaction started immediately, heat was given off and a heavy liquid began to accumulate below the chloroform. The reaction soon became slower and, although less than one equivalent of bromine had been added, some remained after the mixture had stood for three days, but this rapidly disappeared when the solution was exposed to sunlight. The lower layer was found to be a saturated solution of hydrobromic acid in water. After this had been removed enough additional bromine was added to bring the total amount to one equivalent. This was decolorized very rapidly on exposure to sunlight, but no more water was formed. The mixture was then distilled with steam. The first portions of distillate had the odor of benzaldehyde, indicating some cleavage, but the amount was extremely small. The latter distillates contained a colorless oil that solidified on standing. The solid was found to be unchanged carbinol. From the nonvolatile residue ether extracted a solid that after recrystallization melted at 105°. The analyses show that this was phenyltolyl carbinyl ether.

Calc. for $C_{28}H_{28}O$: C, 88.9%; H, 6.9%. Found: C, 88.7%; H, 7.0%.

The remainder of the product was an oily mixture of halogen compounds that decomposed when distilled under diminished pressure. These results indicate that when the group in the para position is no more effective than an alkyl group, bromine, in the cold, and in the dark, oxidizes a part of the hydrol to the ketone and transforms the rest into the ether.

CAMBRIDGE, MASS.

CRYSTALLINE β-METHYL FRUCTOSIDE AND ITS TETRACETATE.[1]

BY C. S. HUDSON AND D. H. BRAUNS.

Received March 20, 1916.

In a previous article[2] several methods for the preparation of tetracetyl fructose were described and it was shown that the action on fructose of acetic anhydride containing $ZnCl_2$ gives the best result and yields about 36% of the theory. This easily prepared crystalline tetracetate is a convenient material from which to start the preparation of various fructose derivatives and in the article mentioned its conversion to α-pentacetyl fructose was described. We have now sought to use it in the preparation of a monomethoxy derivative of fructose, and have applied to it the method of methylation with methyl iodide and silver oxide which was devised by Purdie.[3] Although this method has been applied with good success to the preparation of methylated derivatives of many of the sugars, particularly by Irvine and his co-workers, fructose has never yielded but two pure derivatives. Purdie and Paul[4] prepared tetramethyl fructose in crystalline form, and Irvine and Hynd[5] obtained a crystalline monomethyl fructose by the methylation of fructose diacetone and showed that the methoxy group in it is attached to the terminal carbon atom farthest from the ketonic carbon. Our results show that Purdie's method of methylation succeeds excellently with fructose tetracetate and gives almost a quantitative yield of pure crystalline tetracetyl monomethoxy fructose, the acetyl groups of the tetracetate not being affected by the methyl iodide of neutral reaction. The substance crystallizes very well from petroleum ether in long prismatic needles. Its saponification with barium hydroxide has yielded a crystalline monomethoxy fructose which does not reduce Fehling's solution until after hydrolysis by acid. This reaction differentiates the substance from Irvine and Hynd's monomethoxy fructose, which reduces strongly, and proves that our crystalline material is *methyl d-fructoside*. On the probable assumption that it is a γ-cyclo derivative, its constitution is

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[1] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

[2] THIS JOURNAL, 37, 2736 (1915).

[3] "A General Review of Purdie's Reaction," by Charles Robert Young, Memorial Volume of Scientific Papers of St. Andrews University, 500th Anniversary.

[4] *J. Chem. Soc.*, 91, 289 (1907).

[5] *Ibid.*, 95, 1220 (1909).