

with Al_2O_3 these substances are much inferior as desiccating agents. Al_2O_3 is also more effective than H_2SO_4 . A tube filled with Al_2O_3 can be used for an indefinitely long period, if from time to time it is heated with a smoky flame while air, previously led through H_2SO_4 , is passed through it.

To replace the usual P_2O_5 tube used in connection with mercury pumps it appears particularly suitable, since the tube used need never be renewed. A small tube of P_2O_5 following the Al_2O_3 would serve to indicate when the Al_2O_3 needed reheating. Its uses in many investigations are obvious.

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CORRECTION.

The Connection between Electrical Conductivity and Loss of Electrons by Metals.—Dr. Falk has kindly called my attention to the fact that Sir William Ramsay, in his Faraday lecture (*J. Chem. Soc.*, **93**, 787), pointed out the connection between the ease with which metallic elements lose electrons and their properties as conductors. I regret that I should have overlooked this when writing the note which appeared in the May Journal (*THIS JOURNAL*, **34**, 664).

W. A. NOYES.

LONDON, June, 1912.

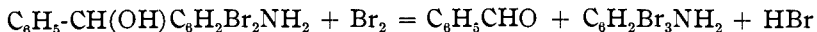
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE SPLITTING OF AMINOARYLCARBINOLS BY THE ACTION OF BROMINE.

BY LATHAM CLARKE AND RICHARD HARKNESS PATCH.

Received April 29, 1912.

It has been shown by Clarke and Esselen¹ that when 2,5-dibromo-4-aminobenzhydrol in chloroform solution is treated with bromine, a splitting takes place, whereby 2,4,6-tribromoaniline and benzaldehyde are produced:



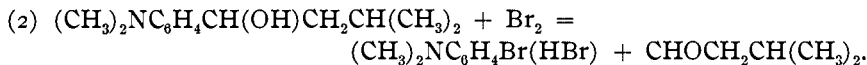
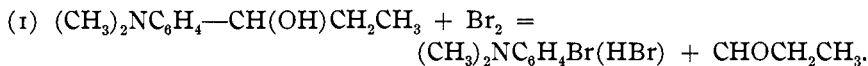
Since the publication of the above noted preliminary paper, Clarke and Esselen have found that with aminobenzohydrols, the reaction is a general one, and an account of this research will appear in the near future in *THIS JOURNAL*.

The present writers have extended this research to aminoarylcarginols containing an aliphatic residue and also to tertiary carbinols. The latter are of especial interest, for if tertiary carbinols are split in a manner analogous to the splitting of secondary carbinols, then the color bases of triphenylmethane dyes would be broken down to substituted bromoanilines and ketones, thereby giving a method for the exact proof of constitution.

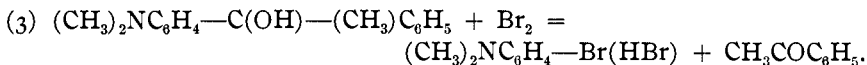
¹ *THIS JOURNAL*, **33**, 1135.

For the study of amino-aromatic aliphatic carbinols, we selected two compounds, on which to try the action of bromine, (1) ethyl-4-dimethylaminophenylcarbinol, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{—CH(OH)CH}_2\text{CH}_3$, and (2) isobutyl-4-dimethylaminophenylcarbinol, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{—CH(OH)CH}_2\text{CH(CH}_3)_2$.

Both these were found to undergo the splitting reaction with bromine, the first yielding the hydrobromide of *p*-bromodimethylaniline and propionic aldehyde, the second, the hydrobromide of *p*-bromodimethylaniline and isovaleric aldehyde.

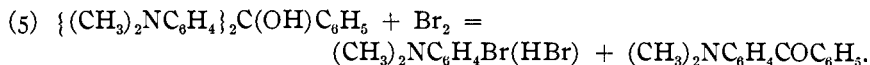
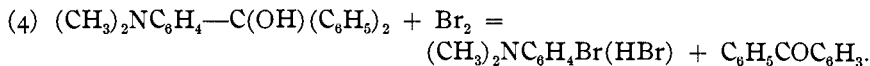


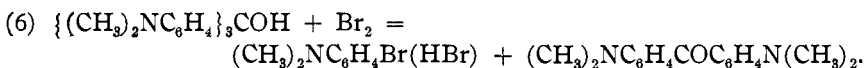
In the study of tertiary carbinols we first tried 4-dimethylaminodiphenylmethylcarbinol, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{—C(OH)(CH}_3)_2\text{C}_6\text{H}_5$. This, when treated in chloroform solution with two atoms of bromine, was broken down almost quantitatively to the hydrobromide of *p*-bromodimethylaniline and acetophenone.



We then turned our attention to the following series: (4) Dimethylaminotriphenylcarbinol, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{—C(OH)(C}_6\text{H}_5)_2$. (5) Tetramethyldiaminotriphenylcarbinol, $\{(\text{CH}_3)_2\text{NC}_6\text{H}_4\}_2\text{C(OH)C}_6\text{H}_5$. (6) Hexamethyltriaminotriphenylcarbinol, $\{(\text{CH}_3)_2\text{NC}_6\text{H}_4\}_3\text{COH}$. Number 5 will be recognized as the color base of malachite green and number 6 as the color base of crystal violet.

In the fourth case, the reaction with bromine took place; but only a relatively small quantity of benzophenone could be detected, although a fairly good yield of *p*-bromodimethylaniline was obtained. The greater part of the bromine appeared to be used up in converting the carbinol into fuchsondimethylium bromide. From numbers 5 and 6, *p*-bromodimethylaniline was isolated but in small yield; the expected ketones, however, could not be extracted from the reaction mixture. It is probable therefore that the reaction takes place in part, but most of the bromine seems to be used up here, in converting the color base into the dye, the bromo derivative corresponding to malachite green and crystal violet apparently being formed in the fifth and sixth cases respectively. The following reactions therefore take place to a certain extent with number 4, and to a lesser extent with numbers 5 and 6:





Experimental.

Ethyl-4-dimethylaminophenylcarbinol. *Preparation.*—This compound has been made by Sachs¹ from *p*-dimethylaminobenzaldehyde and two molecules of ethyl magnesium bromide, using ethyl ether as the reaction medium. We followed his directions.

The *p*-dimethylaminobenzaldehyde used was made according to the method described in Friedländer,² which consisted, in brief, in condensing dimethylaniline and sodium nitrobenzenesulfonate by means of formaldehyde in the presence of iron filings and hydrochloric acid, and subsequent splitting of the resulting benzylidene compound by sodium hydroxide. The aldehyde was recrystallized from water. Melting point 72–73°.

Sodium nitrobenzene sulfonate used in the above preparation was made by the process of Limpricht.³

Action of Bromine.—One and one-tenth grams of ethyl-4-dimethylaminophenylcarbinol were dissolved in a small amount of dry chloroform, and 0.35 cc. of bromine in chloroform was added; this was a slight excess over two atoms of bromine for each molecule of carbinol. After a few moments dilute sulfuric acid was poured into the reaction flask which was connected to a downward condenser, and steam passed through for about five minutes. The distillate which had a strong odor of propionic aldehyde was set aside. The mixture remaining in the flask was made alkaline, whereupon the steam distillation was resumed. The "milky" distillate had the strong characteristic odor of *p*-bromodimethylaniline. On standing crystals of the last mentioned compound separated out, were removed and recrystallized from 50% alcohol. The melting point of these crystals was 54°. Thus the formation of *p*-bromodimethylaniline was proved.

The first chloroform-water distillate mentioned above had now separated into two layers, the lower was removed and 0.5 gram of *p*-nitrophenylhydrazine⁴ was introduced in warm alcoholic solution. The resulting precipitate was recrystallized from hot ligroin, and yielded crystals melting at 123°, identical with the propylidene-*p*-nitrophenylhydrazone described by Dakin.⁵ This method seemed best for proving the presence

¹ *Ber.*, 38, 512.

² "Fortschritte der Theerfarben Fabrikation und verwandten Industriezweige," Bd. V, page 108.

³ *Ann.*, 177, 62.

⁴ Made according to Bamberger and Kraus' method (*Ber.*, 29, 1834) from *p*-nitraniline. The latter was very kindly furnished us by Cassella & Co., to whom we wish to express our thanks.

⁵ *J. Biol. Chem.*, 4, 237.

of propionic aldehyde, as the boiling point of the free aldehyde is low (49°) and as obtained was mixed with water and chloroform.

Isobutyl-4-dimethylaminophenylcarbinol. Preparation.—The directions of Sachs¹ were followed in the synthesis of this carbinol. One molecule of *p*-dimethylaminobenzaldehyde was treated with two molecules of isobutyl magnesium bromide, using ether as the reaction medium.

Action of Bromine.—Four grams of this carbinol dissolved in 20 cc. of dry chloroform were treated with 3.1 grams bromine (2 atoms) in chloroform solution. After a few moments the major part of the chloroform was evaporated by means of a stream of cold air—the odor of isovaleric aldehyde was very noticeable during this process—to the residue water slightly acidulated with sulfuric acid was added, the mixture was transferred to a flask and distilled with steam for about five minutes. The distillate separated into two layers; the lower consisted of a small amount of chloroform containing isovaleric aldehyde in solution, but since there was not enough material for a separation by distillation, it was converted into the *p*-nitrophenylhydrazone by treatment with a strong alcoholic solution of *p*-nitrophenylhydrazine. The hydrazone was purified by recrystallization from petroleum ether. Melting point 107 – 108° . Dakin² gives the melting point 109 – 110° .

Subst. 0.1360 g.; N_2 , 22.2 cc. at 17° and 751.5 mm.

Calculated for $C_{11}H_{14}N_2Br$: N, 19.09. Found: N, 18.72.

The residue from the above steam distillation was rendered alkaline with sodium hydroxide and again distilled with steam. The "milky" distillate yielded white flaky crystals on standing, which were recrystallized from 50% alcohol. The crystals then melted at 54° , and the substance was therefore *p*-bromodimethylaniline.

Calculated for $C_8H_{10}NBr$: Br, 39.99. Found: Br, 40.30.

4-Dimethylaminodiphenylmethylcarbinol. Preparation.—This compound has been made by H. Fecht,³ who obtained it, however, only as an oil. Our method which is given herewith yielded a white crystalline compound melting at 67° .

p-Dimethylaminobenzophenone was prepared from benzanilide, dimethylaniline and phosphorus oxychloride.⁴ The yield was good and the compound was sufficiently pure after two crystallizations from alcohol.

Sixty grams of carefully dried *p*-dimethylaminobenzophenone dissolved in dry benzene were added to an ethereal solution of methyl magnesium iodide, made by dissolving 12.8 grams of magnesium turnings in 76 grams of methyl iodide mixed with ether. The resulting organo-magnesium

¹ Ber., 40, 4364.

² Loc. cit.

³ Ber., 40, 3902.

⁴ Friedländer, Loc. cit., Bd. I, page 44.

compound was allowed to stand over night. Next day, the orange reddish colored solution was decomposed with ice, dilute hydrochloric acid and ammonium chloride, the temperature all the time being kept at about 0° . The benzene-ether layer was removed and the aqueous portion made alkaline with ammonia, the temperature still being maintained at 0° . A finely divided white precipitate was thrown down, which on standing became flaky crystalline in structure; this was the chief portion of the carbinol. The benzene-ether solution was dried over anhydrous sodium sulfate, and evaporated, giving a mixture of brownish crystals and an oil, which later solidified; the mixture was recrystallized from petroleum ether. This was also the carbinol. The total yield was excellent.

Properties.—This carbinol crystallizes from petroleum ether in beautiful transparent prisms, melting at 67° . It is easily soluble in the common organic solvents, with the exception of ligroin and petroleum ether. Insoluble in water. On exposure to the air it turns to a yellowish color, and then to a deep purplish red. With this carbinol strong sulfuric acid gives a greenish yellow color; both strong and dilute hydrochloric acid produce a greenish yellow color. Concentrated nitric acid produces an amber color; on addition of water, a bright red solid was precipitated, which gradually turned brown red on standing. Glacial acetic acid gives a light canary yellow color, which rapidly deepens, and slowly changes over to a cherry red. In dilute acetic acid, the substance is soluble when hot, and on cooling separates in beautiful white needles.

Calculated for $C_{16}H_{19}ON$: C, 79.62; H, 7.88.

Found: C, 79.13; H, 7.54.

Action of Bromine.—Eight grams of this carbinol in dry chloroform solution were treated with a chloroform solution of 5.4 grams bromine (2 atoms). After a few moments, the chloroform was evaporated by a stream of air, the residue mixed with 150 cc. of dilute sulfuric acid, transferred to a flask and distilled with steam. From the distillate, an oil separated out which was acetophenone. The yield was 2.8 grams, about 70% of the theoretical. A small amount (0.4 gram) was dissolved in alcohol and a dilute acetic acid solution of 0.5 gram *p*-bromophenylhydrazine was added, which formed the corresponding hydrazone of acetophenone. This was recrystallized from petroleum ether. Melting point, $111-112^{\circ}$. (Freer¹ gives $112-113^{\circ}$.)

Calculated for $C_{14}H_{13}N_2Br$: Br, 27.68. Found: Br, 28.02.

The acid residue from the above distillation was made alkaline with sodium hydroxide and distilled with steam again. From the distillate crystals of *p*-bromodimethylaniline separated. These were recrystallized from 50% alcohol. Melting point, 54° . The yield was 4 grams.

¹ *Am. Chem. J.*, 21, 30.

Calculated for $C_8H_{10}NBr$: Br, 39.99. Found: Br, 40.18.

Dimethylaminotriphenylcarbinol. Preparation.—The most convenient way to prepare this carbinol is by means of the Barbier-Grignard reaction, using phenyl magnesium bromide and *p*-dimethylaminobenzophenone. The organo-magnesium compound derived from 20 grams of *p*-dimethylaminobenzophenone dissolved in benzene and two molecules of phenylmagnesium bromide (from 28 grams of bromobenzene and 4.3 grams magnesium turnings), in ether solution, were allowed to stand over night. Ice and aqueous tartaric acid solution were added, the benzene-ether layer removed and distilled with steam to remove excess of bromobenzene. The residue containing the desired carbinol was recrystallized from an ether-ligroin mixture (containing two parts of ether to one of ligroin). Melting point $92-93^\circ$.¹

Action of Bromine.—A chloroform solution of dimethylaminotriphenylcarbinol was treated with the requisite amount of bromine—two atoms—for the splitting reaction. The solvent was then evaporated by a stream of air, the reddish oily residue transferred to a flask, made alkaline and distilled with steam. *p*-Bromodimethylaniline was isolated from the distillate, but the amount was small. Remaining in the distillation flask was still the major part of the above mentioned residue. This was extracted with ether, the extract dried with potassium carbonate and evaporated. We did not succeed in isolating any benzophenone from this very impure product, so we attempted to prepare its oxime by treatment with hydroxylamine.

We were able to isolate a compound melting not sharply at $135-137^\circ$, which was without doubt the oxime of benzophenone, although the melting point of the pure substance is 140° . Thus a certain amount of the carbinol is split, but a large part remains unchanged. The mechanism is probably that the carbinol for the most part by the action of bromine is converted to the fuchsondimethylimonium bromide, and this of course would not be further affected by bromine.

Tetramethyldiaminotriphenylcarbinol and hexamethyltriaminotriphenylcarbinol were also treated in chloroform solution with bromine. In each case, a small amount of *p*-bromodimethylaniline was obtained, but no ketone could be isolated. The bromine apparently converted almost all the carbinol into the dyes or fuchson derivatives.

These carbinols will be investigated further, and the research will be extended to many related carbinols.

CAMBRIDGE, MASS., April 24, 1912.

¹ Baeyer also gives these figures (*Ber.*, 37, 2857).