the right, if it occurs at all, must be very slow and can play no significant part, if any, in the rapid reactions of the metal ketyls.[6]

Experimental Part

The Dissociation of Sodium Benzopinacolate into the Metal Ketyl in Liquid Ammonia.—In the experiments with liquid ammonia solutions, the aqueous acetic acid used by Bachmann was replaced by solutions of ammonium chloride or bromide in liquid ammonia. Under these conditions the ammonium salts function as strong acids, reacting instantaneously with the alkali metal compounds with formation of alkali metal halides. By means of trial experiments it was shown that benzopinacol was not decomposed by ammonium hydroxide, liquid ammonia or liquid ammonia solutions of ammonium or alkali metal halides.

The hydrolyses were carried out in the apparatus shown in Fig. 1. The metal ketyl solution was prepared in the reaction tube A. The ammonium halide was dissolved in the bath of liquid ammonia contained in the Dewar flask B and vigorously stirred with the stirrer E. By twisting the inlet tube C, which passed through a slip-joint, it was possible to snap it off at the capillary G. The metal ketyl solution was then forced through the openings into the bath under a slight pressure of ammonia vapor. The residue after evaporation of the ammonia was washed out with ether and water, and the benzopinacol was isolated from the ether extract. In a series of six experiments using 2 to 5 gram samples of ketone, 5 to 15% yields of benzopinacol were obtained (average 10.9%).

A crucial point in connection with these experiments is the fact that the sodium compound is capable of destroying the pinacol. This has been emphasized by Bachmann, who stated that the mixture must be run into the acid slowly in order to avoid accumulation of the sodium compound. Although the reaction between ammonium salts and the ammonia solutions of the sodium compound is extremely rapid, every effort was made to make the experiments with ammonia solutions as comparable with Bachmann's procedure as possible. Furthermore, additional experiments were carried out to make certain that none of the pinacol initially formed in the bath was subsequently destroyed. Weighed amounts of benzopinacol were added to the bath just before the solution of the sodium compound was run in. All of this pinacol was recovered in addition to the usual amount from the hydrolysis of the sodium compound.

Summary

1. It has been shown that sodium benzopinacolate is largely dissociated into the corresponding metal ketyl in liquid ammonia solution.

2. It has been shown that intermediate formation of the corresponding disodium compound plays no significant part, if any, in the rapid reactions of the metal ketyl.

3. It has been pointed out that the metal ketyls apparently exhibit more exceptional valence relationships than other tervalent carbon compounds.

PROVIDENCE, RHODE ISLAND RECEIVED JULY 24, 1934

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[6] This result is in agreement with the observations of Bachmann [THIS JOURNAL, **55**, 2828 (1933)], who was unable to detect any benzophenone in ether solutions of sodium benzopinacolate by the use of sodium phenyl.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

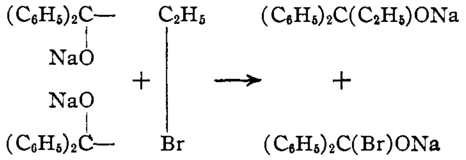
The Structure of Metal Ketyls. III. Mechanism of the Reactions with Alkyl Halides

BY CHARLES BUSHNELL WOOSTER AND WILLIAM E. HOLLAND

The reactions between alkyl halides and the metal ketyls ordinarily yield the corresponding ketone and alkyl carbinolate in approximately equimolecular proportions as may be illustrated by the following equation for the over-all reaction between ethyl bromide and sodium benzophenone.

$$2(C_6H_5)_2CONa + C_2H_5Br = NaBr + (C_6H_5)_2CO + (C_6H_5)_2C(C_2H_5)ONa \quad (1)$$

In order to account for the carbon alkylation, Schlenk[1] interpreted these transformations as trimolecular reactions in which the metal ketyl molecules, by virtue of their tervalent carbon atoms, cleaved the alkyl halide molecules and combined with the resulting fragments.



$$\begin{matrix} (C_6H_5)_2C- & & C_2H_5 & & (C_6H_5)_2C(C_2H_5)ONa \\ | & & | & & \\ NaO & + & | & \longrightarrow & + \\ NaO & & | & & \\ | & & | & & \\ (C_6H_5)_2C- & & Br & & (C_6H_5)_2C(Br)ONa \end{matrix} \quad (2)$$

$$(C_6H_5)_2C(Br)ONa \longrightarrow (C_6H_5)_2CO + NaBr \quad (3)$$

There are a number of reasons for questioning the validity of this hypothesis. It is difficult to understand why the sodium atom in the metal ketyl molecule would not react directly with alkyl halides, for it is highly reactive toward iodine, oxygen, sulfur, carbon dioxide and hydrolytic reagents. Furthermore, the extraordinary cleavage power attributed by Schlenk to the tervalent carbon atom is not exhibited by any

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[1] Schlenk and Weickel, *Ber.*, **44**, 1182 (1911).

other type of tervalent carbon compound. Triphenylmethyl does not cleave ethyl bromide and although the formation of addition compounds between esters and triphenylmethyl might conceivably be regarded as the first step in an incompleted cleavage, it is significant that these esters react but very slowly with liquid ammonia solutions of the metal ketyls and the products obtained are not analogous to those yielded by alkyl halides. Instead, the reaction appears to consist of hydrolysis of the metal ketyl by the products of ammonolysis of the esters.

It is evident from the nature of the reaction products that one molecule of ethyl bromide reacts with two molecules of the metal ketyl. This might involve a single trimolecular reaction as assumed by Schlenk (Equation 2), *or* two successive reactions: a primary reaction between ethyl bromide and one molecule of the ketyl yielding an intermediate product, and a secondary reaction between this intermediate product and another molecule of the ketyl. According to the first hypothesis, the relative proportions of the reaction products should be independent of the relative proportions of the ketyl and the alkyl halide and of the speed with which the latter are permitted to interact. On the other hand, the second hypothesis permits a variation in the proportions of the reaction products as the result of any influence tending to speed up the primary reaction at the expense of the secondary reaction. *Experiments based on this criterion have decisively confirmed the second hypothesis.*

When sodium benzophenone is decomposed by the slow addition of ethyl bromide, benzophenone may be obtained in yields as high as 99% of the theoretical in accordance with Equation 1, but if an excess of ethyl bromide is added rapidly with vigorous stirring to the metal ketyl, the yields of benzophenone may be reduced to as low as 20%. The experimental errors involved in determining the yield of benzophenone were not greater than 3.5% and it has also been shown that the reduced yields of benzophenone cannot be ascribed to partial polymerization of the ketyl to pinacolate, or to reaction between ethyl bromide and Schlenk's hypothetical precursor of the benzophenone, *i. e.*, $(C_6H_5)_2C(Br)ONa$. Accordingly, these results can only signify that *the benzophenone is formed in a secondary reaction* which was curtailed by the rapid decomposition of the ketyl with ethyl bromide. Rewriting the formula of the ketyl as $C_{13}H_{10}ONa$ to avoid prejudice regarding its structure, the process may be expressed by Equations 4 and 5.

$$C_{13}H_{10}ONa + C_2H_5Br = NaBr + (C_{15}H_{15}O) \qquad (4)$$

$$(C_{15}H_{15}O) + C_{13}H_{10}ONa = (C_6H_5)_2CO + (C_6H_5)_2C(C_2H_5)ONa \qquad (5)$$

When excess ethyl bromide was quickly dispersed in the solution by stirring, the ketyl was consumed so rapidly in reaction 4 that reaction 5 was largely eliminated, resulting in very reduced yields of ketone. The fate of the excess of the radical $C_{15}H_{15}O$ under these conditions is not yet known, it may polymerize, disproportionate or react with the solvent, but it does not produce any benzophenone. Evidence regarding the structure of this radical will be presented in a subsequent paper.

Experimental Part

The Action of Ethyl Bromide on Triphenylmethyl.—Triphenylmethyl was prepared from 3.00 g. of triphenylmethyl chloride and 0.23 g. of sodium in liquid ammonia as described by Kraus and Kawamura[2] and treated with 1 cc. of ethyl bromide. The solution was stirred, but no change was observed in the course of an hour. About 10 cc. of toluene was added and the ammonia was allowed to evaporate. After the toluene solution had attained room temperature it was treated with an additional 2 cc. of ethyl bromide, but again no change was observable. The yellow solution was then decolorized by passing a stream of dry oxygen through it and the toluene was subsequently removed by steam distillation. The solid residue was washed with ether and after crystallization from hot benzene melted with characteristic suddenness at 191–192° to an orange-red liquid. The 1.84 g. of triphenylmethyl peroxide obtained in this way represents a yield of 66.1%. Since the yield is usually[3] no more than 63–69%, it is evident that no appreciable quantities of triphenylmethyl reacted with the ethyl bromide to form triphenylmethyl bromide and triphenylpropane.

The Action of Esters on Metal Ketyls.—A solution of monosodium benzophenone in liquid ammonia prepared from 3.33 g. of the ketone and 0.42 g. of the metal was treated with 5 cc. of ethyl carbonate. No change in the appearance of the blue solution was observed for some time. After the mixture had stood overnight it was evident that a slow reaction was taking place for the color was greatly diminished in intensity although not yet completely discharged. Another experiment using 1.00 g. of ketone and 0.131 g. of sodium and a large excess of methyl acetate led to similar results. When the color of the metal ketyl had completely disappeared the ammonia was allowed to evaporate, the residue treated with water and ether and the ethereal extract dried and evaporated. The resulting residue was dissolved in alcohol and treated with hydroxylamine hydrochloride as subsequently described. Benzo-

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[2] Kraus and Kawamura, THIS JOURNAL, **45**, 2758 (1923).

[3] Schmidlin, "Das Triphenylmethyl," Verlag Ferdinand Enke, Stuttgart, 1914, p. 90.

phenone oxime was obtained and identified by its melting point. The material insoluble in aqueous alkali after treatment with hydroxylamine was obtained in crystalline form by precipitation from alcoholic solution with concentrated aqueous ammonium chloride. After drying, this precipitate melted at 68°. The melting point remained unchanged after crystallization from petroleum ether and the substance was identified as benzohydrol by a mixed melting point. No evidence of any diphenylmethylcarbinol was observed. These facts indicate that even the slow reaction observed between methyl acetate and sodium benzophenone does not proceed directly, but only through ammonolysis of the ester.

Determination of Benzophenone in Reaction Mixtures.—It has been pointed out previously[4] that the organic products of the reaction between ethyl bromide and monosodium benzophenone are obtained as an uncrystallizable oil from which even the amounts of ketone and carbinol necessary for identification were obtained with difficulty. Earlier investigators[1] discouraged by this fact have studied the metal ketyls derived from phenyl biphenyl ketone and dibiphenyl ketone in order to obtain decomposition products with higher melting points.

However, it has been found that a satisfactory semi-quantitative method for determining the benzophenone content of the reaction mixtures could be based on the separation of the ketone in the form of its oxime. The sample containing about one gram of benzophenone was dissolved in 12 cc. of alcohol, treated with 8 cc. of potassium hydroxide solution (1:2.17 by weight) and 4 cc. of hydroxylamine hydrochloride solution (1:3 by weight) and the mixture boiled gently under a reflux condenser for thirty minutes. The mixture was then diluted with about 200 cc. of normal potassium hydroxide solution[5] and the impurities which separated were removed by filtration if solid, or by extraction with petroleum ether (b. p. 60–70°) if liquid. In some instances both petroleum ether extraction and filtration were found necessary. The petroleum ether extract was washed repeatedly with normal potassium hydroxide solution until the wash liquors no longer gave a precipitate when neutralized with dilute sulfuric acid. The benzophenone oxime was then precipitated from the clear alkaline solution by acidifying slightly with dilute sulfuric acid. After the precipitate had been allowed to coagulate, it was collected in a glass crucible of the Gooch type with a sintered glass filter plate and dried in an oven at 110° to constant weight. One hour of heating was found to be sufficient for samples containing about one gram of benzophenone, but larger samples required a proportionately longer time. It is not advisable to prolong the heating any more than necessary as the oxime will volatilize slowly. For this reason it is also well to heat the crucible on a watch glass rather than in a covered beaker. In a series of seven experiments employing samples of pure benzophenone the conversion of the ketone to oxime involved an average experimental error of 1.3 ± 0.6%. In another series of six experiments using mixtures of benzophenone and diphenylethylcarbinol containing from 1.0045 to 1.4140 g. of the ketone the average experimental error was 1.9% and the limits were 0.1 and 3.3%. Although when the purified carbinol is used it may be separated from the oxime solution by filtration, extraction with petroleum ether was employed to test the suitability of this procedure.

The Yield of Benzophenone in the Reaction between Ethyl Bromide and Sodium Benzophenone.—Considerable experimentation was required to develop a suitable apparatus for studying the influence of rapid stirring on the reaction, under complete exclusion of air and moisture. The design finally adopted comprised a liquid ammonia reaction tube equipped with inlet and outlet tubes for ammonia, a side tube for the introduction of solids, a dropping funnel for the introduction of liquids and a mechanical stirrer of the centrifugal type. The ammonia inlet tube was led down outside the reaction tube and attached at the bottom in order to leave room for the stirrer inside the reaction tube. This stirrer was fitted with a mercury seal constructed of Pyrex glass which differed from the usual design only in that the rotating tube could be fitted by means of a ground joint into the mercury reservoir, thus excluding the pressure of the external atmosphere. Accordingly, by connecting the mercury reservoir to the outlet of the reaction tube, the pressure in the latter could be varied as desired without displacing the mercury in the reservoir.

The procedure was as follows. The sodium was first weighed out under "Nujol" and then an equivalent quantity of benzophenone was placed in the reaction tube. The rotating tube was set on the ground joint and the mercury reservoir connected with the outlet of the reaction tube, which was then alternately evacuated and swept out with ammonia gas several times, after which the sodium was placed in the side tube and the reaction tube again evacuated and swept out. Then it was surrounded with a bath of liquid ammonia in a Dewar flask and dry ammonia was condensed on the ketone. The sodium was added piece by piece from the side tube and the solution stirred with a stream of ammonia gas until the reaction was complete. Then the pressure in the reaction tube was adjusted to equal that of the atmosphere, the mercury reservoir was disconnected from the outlet of the reaction tube, the rotating tube was raised to free it from its seat in the ground joint and an excess of ethyl bromide was run in through the dropping funnel under a slight air pressure.

In one series of experiments the stirrer was allowed to remain idle and the ammonia inlet was shut off during the addition of ethyl bromide so that the mixture was agitated as little as possible. Under these conditions several minutes elapsed before the blue color of the metal ketyl disappeared entirely. In the second series, the stirrer was set in motion just before the addition of the ethyl bromide and the mixture was stirred vigorously until the reaction was complete, which required less than one minute under these conditions. The liquid ammonia was finally allowed to evaporate and the benzophenone content of the residue determined. In some experiments the reaction tube was washed out with ether and water, the ether extract separated, evaporated and the residue analyzed. In others the analysis was carried out directly on the residue in the reaction tube to ensure against loss, but these variations produced no significant differences in the final results.

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(4) Wooster, THIS JOURNAL, **50**, 1388 (1928).

(5) If the mixture is diluted with water some of the benzophenone oxime is liberated from its potassium salt by hydrolysis and is precipitated with the impurities. The use of normal potassium hydroxide solution effectively prevents this hydrolysis.

The results obtained in the two series of experiments may be summarized as follows. In the first series of six experiments the average yield of benzophenone was 94.0% of the theoretical calculated on the basis of Equation 1 and the limits of variation were 99.3 and 88.3%. In the second series of five experiments the average yield was but 32.3% (limits 44.7 and 19.9) so that there was an average difference in the yields under the two conditions of 61.7%. Since it is practically impossible to reproduce exactly the rate of diffusion of the ethyl bromide in the reaction mixture, it is not reasonable to expect very close agreement between all the experiments in a given series. However, since the difference between the lowest value in series one and the highest value in series two is 43.6%, there can be no doubt that when the decomposition of sodium benzophenone is sufficiently rapid, the yield of ketone is very significantly reduced.

It has been shown in a previous paper[6] that about 15% of the metal ketyl is associated to the corresponding pinacolate in liquid ammonia. Thus if all of the pinacolate reacted with ethyl bromide to yield products other than benzophenone, the maximum reduction in the yield of ketone due to this influence would be 15%, which is quite inadequate to account for the results observed.[7]

According to Schlenk's hypothesis, the free ketone results from decomposition of a bromoalcoholate, $(C_6H_5)_2C(Br)ONa$. It is conceivable that conditions which favored the reaction of this intermediate with ethyl bromide

$$(C_6H_5)_2C(Br)ONa + C_2H_5Br = NaBr + (C_6H_5)_2CBrOC_2H_5 \quad (6)$$

might prevent its spontaneous decomposition to ketone, but it is very unlikely that any of the observed reduction in yield of ketone was actually due to this effect. The reaction product, α-bromobenzohydryl ethyl ether, has not been prepared in the pure condition, but there is considerable evidence to indicate that if it does not decompose spontaneously with formation of benzophenone, it would certainly react with alkaline solutions of hydroxylamine to give benzophenone oxime. For instance, Straus and Blankenhorn[8] have obtained the analogous α-chlorobenzohydryl methyl ether in the form of its mercuric chloride double compound and found that it is readily decomposed with formation of benzophenone on treatment with solvents containing a hydroxyl group. Furthermore, bromination of benzohydryl ethyl ether yields a product which forms benzophenone oxime on treatment with an alkaline solution of hydroxylamine.

Bromination of Benzohydryl Ethyl Ether.—An ethereal solution of benzohydryl ethyl ether did not react with bromine in the cold, when heated or when exposed to the light of a 1000-watt bulb. After evaporation of most of the solvent ether, reaction was induced by illuminating the mixture with a mercury vapor lamp. One portion of the reaction product (0.580 g.) yielded 0.311 g. of benzophenone oxime. If the bromination product actually contained α-bromobenzohydryl ethyl ether, the yield of oxime corresponds to 0.459 g. of the bromo ether or 79% of the sample. However, an attempt to obtain benzophenone diethyl acetal by treating a second portion of the bromination product with sodium ethylate was unsuccessful. No further attempts were made to isolate or characterize the bromo ether because of the probability that it had been pyrolyzed by the heat of the mercury vapor lamp to ethyl bromide and benzophenone. A blank experiment demonstrated that the original benzohydryl ethyl ether was incapable of yielding any benzophenone oxime on treatment with alkaline hydroxylamine.

Ethoxyl Content of the Reaction Residue.—The hypothetical side reactions, under discussion, which might reduce the yield of benzophenone, all involve the formation of ethoxyl compounds: benzopinacol mono- or diethyl ether or α-bromobenzohydryl ethyl ether. Accordingly, the petroleum ether extract obtained during the benzophenone determination in one experiment in which the ketyl was prepared from 3.8220 g. of ketone was evaporated to dryness on a water-bath and the ethoxyl content of the residue was determined by the method of Zeisel.[9] The amount of silver iodide obtained was 0.8130 g. and since numerous experiments have shown that ethyl alcohol seldom can be removed completely

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[6] Wooster, THIS JOURNAL, **56**, 2436 (1934).

[7] It is probable that the pinacolate reacts with ethyl bromide by first dissociating into the metal ketyl. Direct reaction between the pinacolate and ethyl bromide might be expected to give pinacol ethers (mono- or di-ethyl) or free pinacol. Reaction of the pinacolate in the latter sense would not affect the yield of ketone as determined, for when benzopinacol is treated with hydroxylamine hydrochloride and potassium hydroxide it forms benzophenone oxime in accordance with the equation

$$(C_6H_5)_2COHCOH(C_6H_5)_2 + NH_2OH{\cdot}HCl + KOH = 2H_2O + KCl + (C_6H_5)_2CHOH + (C_6H_5)_2CNOH$$

[8] Straus and Blankenhorn, *Ann.*, **415**, 232–256 (1918).

[9] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1932, p. 206.

from residues by evaporation on a water-bath, this figure is significant only as a limit, indicating the maximum amount of ethoxyl compounds which could have been formed from the metal ketyl in this experiment. If all the silver iodide resulted from cleavage of benzopinacol monoethyl ether or α-bromobenzohydryl ethyl ether to ethyl iodide, the result could account for a reduction in the yield of benzophenone from the theoretical 100 to 67.1%, but not to 19.9% as was actually observed in this experiment. By attributing the silver iodide to cleavage of benzopinacol diethyl ether, it is only possible to account for a reduction in the yield of benzophenone to 83.5%. This result proves conclusively that the reduction in the yield of benzophenone can be explained only by the fact that it is formed in a secondary reaction which was curtailed by the rapid decomposition of the ketyl with ethyl bromide.[10]

Summary

It has been shown that the reaction between metal ketyls and alkyl halides does not follow the course suggested by Schlenk. The ketone which is regenerated results from a secondary reaction between a product of the primary reaction and a second molecule of the ketyl. When the ketyl is consumed with sufficient rapidity in the primary reaction, the secondary reaction may be greatly curtailed, resulting in very reduced yields of ketone.

(10) The referee to whom this paper was submitted inquired, "why the authors have omitted discussion of the reaction $(C_6H_5)_2CONa + C_2H_5Br = NaBr + (C_6H_5)_2CO + C_2H_5—$ which is in all probability strongly exothermic. The ethyl groups formed could then react with the ketyl to give the carbinolate or if present in higher concentration might be expected also to react . . . with . . . benzophenone to give an ether."

As this thought may also occur to other readers it seems advisable to point out that the chief objection to this hypothesis is that it implies that the ketone is formed in the primary reaction, whereas the evidence in this paper shows that it results from a secondary reaction. The referee's mechanism suggests that the yield of benzophenone might be *increased* when the secondary reaction is largely eliminated (by rapid decomposition of the ketyl), but does not account for the *reduced* yield actually observed, for even if all of the ethyl radicals which were unable to combine with a ketyl radical reacted with the benzophenone to form, for instance, the ethyl ether of diphenylethylcarbinol, the yield of free benzophenone would still equal that required by Equation 1. As a matter of fact, the results of the ethoxyl determination described above show that in at least one case not more than 16.5% of the ketyl molecules were converted into ethoxyl compounds.

Finally, to the extent that the referee's mechanism may be considered to imply that the reaction between sodium benzophenone and ethyl bromide should be identical with the reaction between sodium and a mixture of benzophenone and ethyl bromide, this mechanism is essentially that of Schmidlin which has been discussed in a previous paper of this series [Wooster, THIS JOURNAL, **51**, 1856 (1929)].

PROVIDENCE, RHODE ISLAND RECEIVED JULY 25, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Certain Methoxychalcones and Methoxybenzal-β-coumaranones from Methoxyacetophenones and Nitrobenzaldehydes[1]

BY DONALD PRICE[2] AND MARSTON TAYLOR BOGERT

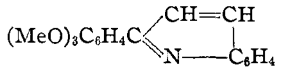
In continuance of our studies of the connection between chemical constitution and tinctorial properties in various groups of dyes,[3] we have carried out some experimental work in the field of the chalcones and structurally related benzal-β-coumaranones (1-benzal-2(1)-benzofuranones). The present paper records the synthesis of the compounds required and incidental observations. A subsequent paper will report the tinctorial properties of these products and discuss the apparent influence of chemical constitution upon these properties.

2,3,4-Trimethoxyacetophenone was condensed with *o*-, *m*- and *p*-nitrobenzaldehyde, in the presence of alkali, and the resulting nitrochalcones were reduced with stannous chloride and hydrochloric acid in glacial acetic acid solution

(I) $(MeO)_3C_6H_2COCH_3 + OCHC_6H_4NO_2 \longrightarrow$

(II) $(MeO)_3C_6H_2COCH{=}CHC_6H_4NO_2 \xrightarrow{+H_2}$

(III) $(MeO)_3C_6H_2COCH{=}CHC_6H_4NH_2 \xrightarrow{-H_2O}$

(IV) 

$(MeO)_3C_6H_4C\begin{cases} CH{=}CH \\ \quad | \\ N{-}C_6H_4 \end{cases}$

The aminochalcones (III) were obtained readily in the case of the *m*- and *p*-derivatives. As was expected, however, reduction of the *o*-nitrochal-

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(1) Presented at the Washington Meeting of the American Chemical Society, March 27, 1933, before the Division of Dye Chemistry. Based upon the Dissertation submitted by Donald Price, 1929, in partial fulfilment of the requirements for the Ph.D. degree in the Faculty of Pure Science, Columbia University, and to which the reader is referred for further details.

(2) Du Pont Fellow at Columbia University, 1928–1929.

(3) See Bogert and Allen, THIS JOURNAL, **49**, 1315 (1927), where references to earlier publications also are given.