neutralized with 20% aqueous sodium hydroxide until neutral to litmus. The mixture was then extracted with 20 ml. of chloroform and dried over anhydrous potassium carbonate. After the removal of the drying agent and solvent the residue was distilled. After collecting 2 g. of 4-methylpyrimidine there was obtained 3 g. (70%, based on recovered 4-methylpyrimidine) of a pale yellow liquid, b.p. 120–122° (30 mm.), n^{25}D 1.5145, d^{25}_4 1.0205.

Anal. Calcd. for $C_8H_{13}N_3$: C, 63.54; H, 8.66: N, 27.7. Found: C, 63.79; H, 8.46; N, 27.6.

Poly-4-vinylpyrimidine.—A sealed tube, previously evacuated at 10^{-5} mm., containing a mixture of 0.7 g. of 4-vinylpyrimidine, 0.0375 g. of 2,2'-azo-bis-isobutyronitrile and 7.5 ml. of dry toluene was heated on a steam-bath for four hours. A heavy viscous oil precipitated. After decanting the solvent, the oil was washed with 1 ml. of toluene and dissolved in 3 ml. of methanol and Norite was added. Upon removal of the Norite and addition of ether, a tan

amorphous precipitate appeared, 0.3 g., m.p. 127–142° dec. A molecular weight determination by the Rast method gave a value of 873. Analysis and molecular weight again indicated that catalyst fragments were present although less nitrogen was found in the polymer than was anticipated.

Infrared Absorption Spectra.—Infrared absorption spectra were determined with a Perkin–Elmer infrared spectrophotometer with no solvent. They were determined as liquids in a demountable cell using sodium chloride windows and no spacers.

BROOKLYN, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Reaction of o-Phenylenediamines with Carbonyl Compounds. III. Benzophenones and Dibenzyl Ketones[1]

BY ROBERT C. ELDERFIELD[2] AND VICTOR B. MEYER

The reaction of o-phenylenediamine with benzophenone and with dibenzyl, 4-methoxy- and 4-chloro-dibenzyl ketones has been studied. The presence of the substituents in the two latter ketones exerts a marked effect on the elimination of hydrocarbon in the reaction. Syntheses for unsymmetrically substituted dibenzyl ketones are described.

o-Phenylenediamine (I) and its mono-N-substituted derivatives have been shown to react with ketones, with the elimination of water, to give intermediate compounds which on heating split out hydrocarbons to yield benzimidazoles.[3,4] The structure of the intermediate, which is discussed in greater detail in the following paper, may be either that of a 2,2-disubstituted benzimidazoline or of a Schiff base.

The previous detailed investigation of the reaction[3] was limited almost exclusively to a study of the reaction between I and aliphatic ketones. The elimination reaction was shown to be catalyzed by strong bases and followed first-order kinetics either in the presence or absence of base. A mechanism based on elimination of the hydrocarbon as an anion was offered as providing a reasonable explanation for the observed facts.

Such a proposal, however, involves some inconsistencies. In the cases in which the alkyl groups in the ketone were unlike it was found that the group preferentially eliminated from the intermediate was the one more highly branched at the α carbon atom, e.g., isopropyl was eliminated in preference to n-propyl. If the departing group does indeed leave as a carbanion, then the observed order of ease of elimination is the reverse of what has been considered to be the order of stability of carbanions. Experimental proof for this order of stability has been provided recently.[5]

(1) The material here presented is taken from a dissertation submitted by Victor B. Meyer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Columbia University.

(2) University of Michigan, Ann Arbor, Michigan.

(3) R. C. Elderfield and J. R. McCarthy, THIS JOURNAL, **73**, 975 (1951).

(4) R. C. Elderfield and F. J. Kreysa, *ibid.*, **70**, 44 (1948).

(5) P. D. Bartlett, S. Friedman and M. Stiles, *ibid.*, **75**, 1771 (1953).

In order to secure additional information regarding the mechanistic details of the reaction and to extend its scope to include benzophenone and dibenzyl ketone derivatives the present investigation was undertaken.

If the suggested mechanism for the elimination is correct, then it would be anticipated that when the reaction of I is carried out with appropriately substituted dibenzyl ketones an effect on the course of the elimination reaction due to the presence of electron attracting or electron donating substituents in the ketones should be apparent. This has been found to be so with two unsymmetrically substituted dibenzyl ketones.
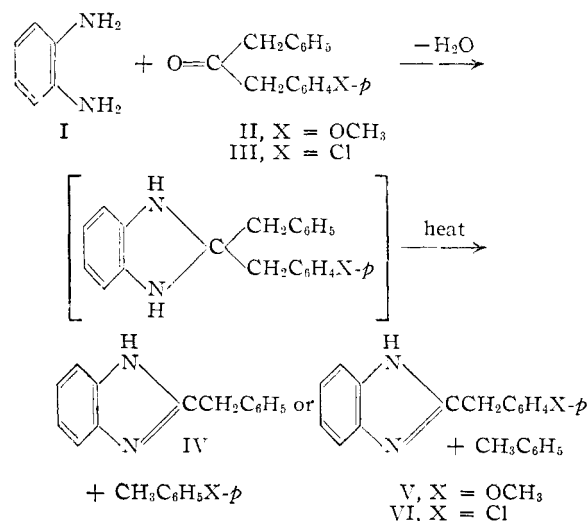
For exploratory purposes 4-methoxydibenzyl ketone (II) and 4-chlorodibenzyl ketone (III)

were chosen. The electron releasing methoxyl group *para* to the site of the reacting group has a σ-value of -0.268 and the similarly located electron withdrawing *para* chlorine has a σ-value of $+0.227$.[6]

Reaction of I with dibenzyl ketone paralleled those reported previously[3] except that the yield of 2-benzylbenzimidazole (IV) was higher (89%) when the intermediate was pyrolyzed at 225–250°. In addition to this high temperature decomposition several experiments were carried out in which the intermediate was heated at 150° for two hours in the presence of various additives. Under these conditions the intermediate alone (blank run) gave about 25% of IV. The yield was not appreciably affected by the addition of small amounts of I or of *p*-toluenesulfonic acid. Higher yields were obtained when di-*t*-butyl peroxide, the half-life of which is 1.3 hr. at 145°,[7] was added to the intermediate. In the presence of 6 mole per cent. of the peroxide the yield of IV was increased to 45%, and with 30 mole per cent. the yield was 64%. This observation raises the possibility that an alternate free radical-catalyzed mechanism may be operating, but a final decision on this point must await the outcome of further work. It has been reported[3] that addition of benzoyl peroxide did not affect the reaction of I and methyl ethyl ketone. However, the decomposition point of benzoyl peroxide is considerably below the temperature at which this particular elimination reaction occurs so that any peroxide catalysis may well have been missed in the earlier work.

When II was allowed to react with I at 225–230°, 80% of the theoretical amount of water was evolved and the residual benzimidazoles after the pyrolysis consisted of 65 mole per cent. of 2-(*p*-methoxybenzyl)-benzimidazole (V) and 35 mole per cent. of IV. The total yield of mixed benzimidazoles was 52%. A small amount of toluene (20%) and *p*-methoxytoluene was recovered from the volatile products of the reaction.

The results of the reaction of III with I were just the reverse of those obtained with II. Of the total mixture of benzimidazoles obtained (57%) 33 mole per cent. was 2-(*p*-chlorobenzyl)-benzimidazole (VI) and 67 mole per cent. was IV. Toluene (6%) and *p*-chlorotoluene (12%) were isolated from the volatile reaction products.

In interpreting these results the following assumptions have been made. In both reactions the benzimidazoles arise from similar intermediates (nothing is said about the structure of the intermediates at this time) as the result of similar thermal decompositions. Thus, if the reactions are of the same order, the ratio of the specific rate constants for the two reactions will be equal to the ratio of the products.[8] If the further assumption is made that the rate of elimination of the unsubstituted benzyl group in both of the reactions studied is substantially the same, *i.e.*, that it does

not depend on the substituent present in the second benzyl group of the ketone, then a tentative value for the reaction constant (ρ) may be calculated by use of the Hammett equation[9] in the form

$$\rho = \frac{\log k/k^0}{\sigma}$$

If k^0 is taken to be the rate constant for the elimination of the unsubstituted benzyl group and k as the rate constant for the elimination of the *para* substituted benzyl group, values for ρ of $+1.03$ and $+1.33$ are obtained from the methoxyl and chloro cases, respectively, giving an average value of $+1.2$.

In any event, the susceptibility of the elimination reaction to changes in electron density produced by varying the substituents in the *para* position of one of the benzyl groups appears to be roughly of the same order of magnitude as the effect of varying the *meta* and *para* substituents of benzoic acids on their ionization constants ($\rho = +1.000$) and is in the same direction as the latter reaction when the over-all reaction is viewed from the standpoint of the elimination reaction rather than of the formation of benzimidazoles. Whether the reaction constant (ρ) so derived reflects a real physical situation, and additional data required to furnish a reliable, accurate value for this constant, must await the results of further work which is currently underway.

We have also investigated in more detail the reaction of I with benzophenone, *p*-methoxy- and *p*-nitrobenzophenone. When the reaction of I and benzophenone was carried out under the conditions previously described[3] (heating the mixture in pseudocumene at 180–190° for 12 hours) which had been reported to give a 20% yield of 2-phenylbenzimidazole, none of the benzimidazole was obtained. Rather a 31% yield of benzhydrylidene-*o*-phenylenediamine (VII, X = H)[10] was obtained. Hydrolysis of an aliquot of the final reaction mixture led to the recovery of benzophenone to the extent of 95% of the original ketone taken. The logical explanation for the earlier results is that the solvent, pseudocumene, had escaped during the heating period with attainment of a resultant higher reaction temperature. It has now been found that direct heating of a mixture of benzophenone and I at 250–280° for 50 hours gave 44% of 2-phenylbenzimidazole along with benzene and water. Pyrolysis of the intermediate (VII, X = H) at 270–280° for 43 hours also gave 36% of the benzimidazole and 13% of pure benzene. The reaction may thus be represented by the sequence


VII, X = H, *p*-OCH₃, *p*-NO₂
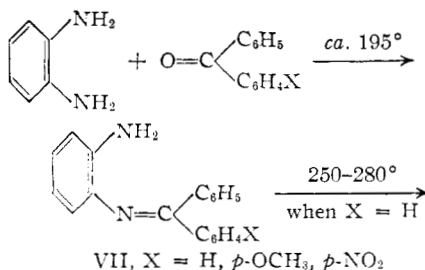
(6) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 188. These σ-values were derived from the ionization constants of the benzoic acids.

(7) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948).

(8) S. G. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1085.

(9) Reference 6, p. 186.

(10) Evidence for the structure assigned to this substance is presented in the following paper.
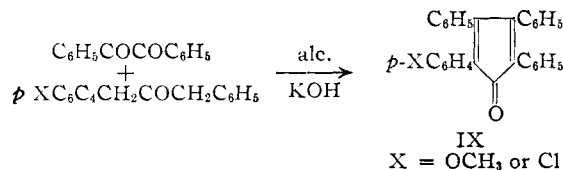
$$\text{(structure)} \quad CC_6H_5 \quad + \quad C_6H_6$$
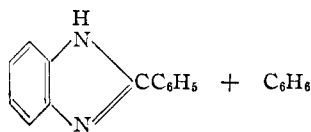
When VII (X = either p-OCH$_3$ or p-NO$_2$) was heated under comparable conditions extensive carbonization took place and at lower temperatures no elimination was noted.

From the results obtained, particularly with the dibenzyl ketones, there seems to be no reason to reject the over-all mechanism proposed for the reaction.[3] However, as discussed in the following paper, the structure of the intermediate when dibenzyl ketone is involved is so complex that the rate controlling step in the over-all reaction may well be one other than that involving elimination of hydrocarbon. Further work is underway to clarify this point.

Since the unsymmetrically substituted dibenzyl ketones represent previously undescribed types[11] an exploration of various reactions leading to the compounds was made. p-Methoxybenzylmagnesium chloride (VIII) and phenylacetamide in boiling toluene gave no material boiling in the range expected for II. The cadmium compound[12] prepared from VIII was unstable, even at 0°, and decomposed rapidly with precipitation of metallic cadmium. Performic acid hydroxylation[13] of 3-anisyl-1-phenylpropene[14] to the glycol and dehydration of the latter by boiling dilute sulfuric acid[15] did indeed give the desired ketone, but the product was of prohibitively poor quality and contained other neutral materials boiling in the same range.

Encouraging results were obtained when benzylcadmium reagent was treated with phenylacetyl chloride; the yield of crude dibenzyl ketone was only 20% but the quality was good.[16] Although detailed development of the reaction was not done, by following certain details given in the experimental part rigorously, pure II was prepared in 60% yield and pure III in 72% yield from benzylcadmium reagent and the appropriate phenylacetyl chloride. Like dibenzyl ketone they are low melting crystalline solids and were charac-

$$C_6H_5COCOC_6H_5$$
$$+ \quad \xrightarrow[\text{KOH}]{\text{alc.}}$$
$$p\ XC_6C_4CH_2COCH_2C_6H_5$$

IX
X = OCH$_3$ or Cl

terized by conversion to the high-melting, nearly black "tetracyclones" by condensation with benzil.[17] The "tetracyclones" (IX) not only served to characterize the ketones but also provided direct proof of their structures.

Experimental[18,19]

4-Chlorodibenzyl Ketone (III).—A solution of benzylmagnesium chloride[20] prepared from 101 g. (0.8 mole) of benzyl chloride in ether was transferred through a glass wool plug from unreacted magnesium by nitrogen pressure into a 3-liter flask equipped with a Hershberg stirrer and thermometer and protected by a calcium chloride tube leading to a mercury trap (U-tube). The solution was diluted with 300 ml. of absolute ether and cooled in an icebath. With vigorous stirring, 147 g. (0.8 mole) of anhydrous cadmium chloride was added over 15 minutes, the temperature being held below 10°. Forty-five minutes after the salt had been added the grayish-green suspension showed a very weak positive test for the Grignard reagent with the Michler ketone; after 75 minutes the mixture was a greenish-yellow creamy suspension. A solution of 63.0 g. (0.33 mole) of p-chlorophenylacetyl chloride, b.p. 107–109° at 5 mm., in 150 ml. of absolute ether was added over ten minutes during which the temperature was held below 5°. The system was flushed with nitrogen and cooling and stirring were continued for six hours. The mixture was hydrolyzed by cautious addition of 450 ml. of 10% sulfuric acid. The ether layer was separated and the aqueous layer was extracted with three 100-ml. portions of ether. The combined ether extracts were washed successively with water, 5% sodium bicarbonate solution, water and saturated sodium chloride solution. After removal of the solvent, the residue (94 g.) was distilled under reduced pressure. After a forerun (10 g.) consisting largely of dibenzyl, the entire fraction boiling above 145° at 0.3 mm. was collected. The crude ketone, amounting to 70 g. (86%), was a viscous pale yellow oil, n^{27}D 1.576, d^{20}_4 1.17, which readily crystallized on cooling. Recrystallization from hexane (1050 ml.) gave 46.5 g. of fine white needles, m.p. 40–41°. Concentration of the mother liquor gave an additional 12 g., m.p. 40–41°; the total yield was 72%.

Anal. Calcd. for C$_{15}$H$_{13}$ClO: C, 73.6; H, 5.4; Cl, 14.5. Found: C, 73.8; H, 5.2; Cl, 14.4.

The ketone was stored in the refrigerator under nitrogen until used.

In another run under similar conditions but in which only one-half the molar proportion of organocadmium reagent specified above was used 33% of the acid chloride was recovered as the acid. The yield of purified ketone was 40% or 60% based on unrecovered acid chloride.

When the ethereal solution of the organocadmium reagent prepared as above was refluxed, an exothermic decomposition occurred accompanied by the separation of metallic cadmium.

Condensation of 4-Chlorodibenzyl Ketone with Benzil. The "Tetracyclone" (IX, X = Cl).—To a warm solution of 490 mg. (0.002 mole) of V and 460 mg. (0.0022 mole) of benzil in 3.5 ml. of absolute ethanol was added 0.35 ml. of alcoholic potassium hydroxide solution (1 g. of base in 5 ml. of absolute ethanol). The mixture, which immediately turned deep red, was refluxed for 15 minutes, cooled to 0° filtered and the fine "black" crystals were washed with cold ethanol. The "tetracyclone" (663 mg., 79%) was recrystallized from 16 ml. of 1:2 benzene–absolute ethanol with 75% recovery, m.p. 189.5–190°. It forms a purple solution in benzene; λ_{max} 515 mμ, log ϵ 3.20.[11]

Anal. Calcd. for C$_{29}$H$_{19}$ClO: C, 83.1; H, 4.6; Cl, 8.5. Found: C, 83.4; H, 4.4; Cl, 8.4.

4-Methoxydibenzyl Ketone (II).—p-Methoxyphenylacetyl chloride was prepared in 82% yield by treating 114 g. (0.69 mole) of p-methoxyphenylacetic acid with 100 ml. (1.4 moles) of pure thionyl chloride for two hours at room temperature, one hour at 40–50°, and one hour on the steam-

(11) After this work had been completed, S. B. Coan, D. E. Trucker and E. I. Becker [This Journal, 75, 900 (1953)] reported the preparation of several monosubstituted dibenzyl ketones by a different route than that used here. The details of their syntheses and the properties of the ketones were not given.

(12) J. Cason, Chem. Revs., 40, 15 (1947).

(13) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, This Journal, 67, 1786 (1945).

(14) C. S. Rondestvedt, Jr., ibid., 73, 4509 (1951).

(15) J. Lévy and Mme. Dvoleitzka-Gombinska, Bull. soc. chim. France, [4] 49, 1765 (1931).

(16) H. Gilman and J. F Nelson [Rec. trav. chim. 55, 518 (1936)] report a yield of 18% of methyl benzyl ketone from benzylcadmium reagent and acetyl chloride. The low yield is an exception to the generally high ones obtained in this ketone synthesis. No other example of the use of this reagent has been found.

(17) W. Dilthey and F. Quint, J. prakt. Chem., [2] 128, 139 (1930).

(18) All melting points and boiling points are corrected.

(19) Microanalyses by Schwarzkopf Microanalytical Laboratory, Middle Village 79, New York.

(20) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 471.

bath. It also was prepared[21] in 73% yield by treating a chloroform solution of the acid with an equimolar amount of phosphorus pentachloride on the steam-bath. By either route the acid chloride boiled at 121–122° at 5 mm.; reported b.p. 143° at 10 mm.[21]

A solution of 59.5 g. (0.32 mole) of p-methoxyphenylacetyl chloride in 150 ml. of absolute ether was added over a ten minute period to benzylcadmium reagent prepared from 0.8 mole of benzyl chloride as described above and the mixture was allowed to react at 0° for six hours. The mixture was worked up as above except for an extra bicarbonate wash to remove all acid. The crude product (55 g., 71%) was a viscous pale yellow oil, n^{24}D 1.568, d^{20}_4 1.10, which crystallized readily on cooling. Recrystallization from hexane (1100 ml.) gave 42.0 g. of long white needles, m.p. 47–48°. An additional 4 g., m.p. 47–48°, was obtained from the mother liquors. The total yield of pure ketone was 60%.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7; CH_3O, 12.9. Found: C, 80.0; H, 6.9; CH_3O, 12.8.

Condensation of 4-Methoxydibenzyl Ketone with Benzil. The "Tetracyclone" (IX, X = OCH_3).—This was prepared as in the preceding case in 72% yield. The "black" crystals melted about 10° lower than the m.p. reported for the same substance, 189–190°, prepared by Dilthey and co-workers by a different route.[22] A small portion was chromatographed on Florisil and gave violet-black crystals of the correct m.p. Eighty milligrams of the crude product was retreated with alcoholic potassium hydroxide for half an hour. The product (68 mg.) was recrystallized from 1.5 ml. of 1:2 benzene–absolute ethanol yielding 64 mg. of material, m.p. 190–191°. The "tetracyclone" forms a purple solution in benzene; λ_{max} 532 mμ, log ϵ 3.28.[11]

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.9; H, 5.4; CH_3O, 7.5. Found: C, 86.7; H, 5.5; CH_3O, 7.3.

p-Methoxybenzylmagnesium Chloride.[23]—In a three-liter, three-necked flask equipped with a Hershberg stirrer, reflux condenser and addition funnel were placed 243 g. (10 g. atoms) of magnesium turnings and 1100 ml. of dry ether. Without stirring, 10 g. of p-methoxybenzyl chloride[24] and 0.25 g. of iodine were added and the reaction started almost immediately. The mixture was warmed, and, after refluxing gently for ten minutes without stirring, 68.5 g. (total of 0.5 mole) of the chloride in 470 ml. of absolute ether was added over 30 minutes with vigorous stirring. After stirring and refluxing for an additional 20 minutes the solution was cooled and allowed to settle. Acidimetric titration of an aliquot of the clear, nearly colorless solution showed that 0.45 mole (90%) of the Grignard reagent was present. Carbonation of a portion of the solution gave 81% of p-methoxyphenylacetic acid.

An attempt to prepare the cadmium reagent from the Grignard reagent with anhydrous cadmium chloride at 0° resulted in precipitation of metallic cadmium and formation of a large amount of 4,4′-dimethoxydibenzyl, m.p. 127–128°; reported m.p. 126–127°.[25]

2-(p-Chlorobenzyl)-benzimidazole (VI).—A mixture of 1.71 g. (0.01 mole) of p-chlorophenylacetic acid, 1.14 g. (0.0105 mole) of I and 0.060 g. (0.0003 mole) of o-phenylenediamine dihydrochloride was heated under nitrogen for one hour at 200°. After cooling the residue was triturated with aqueous ammonia and recrystallized from a mixture of 15 ml. of methanol and 3 ml. of water. Further recrystallization from 10:1 benzene–absolute ethanol gave white, cottony needles, m.p. 192–193°. The yield was 75% after working the mother liquors.

Anal. Calcd. for $C_{14}H_{11}ClN_2$: C, 69.3; H, 4.6; Cl, 14.6; N, 11.5. Found: C, 69.5; H, 4.7; Cl, 14.4; N, 11.8.

(21) J. C. Cain, J. L. Simonsen and C. Smith, *J. Chem. Soc.*, **103**, 1035 (1913).

(22) W. Dilthey, O. Trösken, K. Plum and W. Schommer, *J. prakt. Chem.*, [2] **141**, 331 (1934).

(23) The method here presented for the preparation of this Grignard reagent utilizes suggestions made by H. Gilman and E. A. Zoellner [*Bull. soc. chim. France*, [4] **49**, 7 (1931)] who obtained a yield of 54% from p-methoxybenzyl bromide. It dispenses with the need for magnesium powder employed in the improved procedure of M. G. Van Campen, D. F. Meisner and S. M. Parmerter [THIS JOURNAL, **70**, 2297 (1948)] without diminishing the yield.

(24) J. Lee, A. Ziering, L. Berger and S. D. Heineman, *Jubilee Vol. Emil Barell*, 264 (1946); [*C. A.*, **41**, 6252 (1947)].

(25) E. Späth, *Monatsh.*, **34**, 1965 (1913).

2-(p-Methoxybenzyl)-benzimidazole (V).—This was prepared in 56% yield from p-methoxyphenylacetic acid by the same method used for the chloro compound. After recrystallization from 60% methanol the substance melted at 165–165.5°.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.6; H, 5.9; N, 11.8; CH_3O, 13.0. Found: C, 76.0; H, 6.1; N, 11.4; CH_3O, 13.0.

Reaction of o-Phenylenediamine with Benzophenone and Dibenzyl Ketones.—In these experiments the intermediates first formed were not isolated. Isolation of the intermediates is described in the following paper.

The reactions were generally carried out in a 100-ml. flask provided with an automatic liquid separator as described earlier[3] except that the gas collection train was unnecessary and the atmosphere was oxygen-free nitrogen.

(a) **With Benzophenone.**—A mixture of 18.2 g. (0.1 mole) of benzophenone and 10.8 g. (0.1 mole) of I (recrystallized from benzene, m.p. 101.5–102.5°) was heated rapidly to 170° when elimination of water began. The rate of heating was then decreased to about two degrees per minute until the temperature of the clear, orange melt reached 250°. The temperature was then held at 250–270° for 24 hours and at 270–280° for an additional 26 hours. Water and benzene collected in the separator together. A total of 1.50 g. (83%) of water, identified by refractive index, and 1.70 g. (22%) of benzene, identified by b.p., refractive index and specific gravity, was obtained. Some loss of both liquids by hold up on the walls could not be avoided. The deep purple reaction mixture (24.5 g.), which crystallized on cooling, was triturated with two 50-ml. portions of ether leaving 8.50 g. of insoluble purple powder which sintered above 265° and melted at 278–288°. One gram was recrystallized from 60 ml. of acetonitrile with carbon treatment, and identified as 2-phenylbenzimidazole, m.p. 294–296°, by mixture m.p.'s with a known sample and by ultraviolet spectra. The yield was 44%.

(b) **With Dibenzyl Ketone.**—When a mixture of 0.1 mole each of the ketone and diamine was heated evolution of water became marked at 150–160°. The temperature of the melt was held at 230–250° for 20 hours. In the separator 1.25 g. (70%) of water and 6.60 g. (72%) of toluene, identified as in the preceding case, collected. The residual melt, after trituration with absolute ether, gave 18.5 g. (89%) of 2-benzylbenzimidazole, m.p. and mixture m.p. with an authentic sample 189–190°.

(c) **With 4-Chlorodibenzyl Ketone.**—It was originally planned to analyze the mixtures of IV and V, and IV and VI by the use of phase diagrams. However, compound formation which occurred with both mixtures precluded use of this method. The composition of the mixtures was therefore determined by analyses for chlorine and methoxyl, respectively.

A mixture of 24.5 g. (0.1 mole) of the ketone and 10.8 g. (0.1 mole) of I was heated as in the dibenzyl ketone experiment. The water collected amounted to 1.45 g. (80%) and the volatile organic liquid, which on the basis of refractive index, specific gravity and odor was a mixture of roughly equal parts of toluene and p-chlorotoluene, amounted to 0.90 g. The residue in the flask (33 g.) was triturated with two 30-ml. and two 100-ml. portions of absolute ether which left 11.5 g. of pale lavender material, m.p. 149–170°. This gave analytical figures corresponding to a mixture of 34.5% of VI and 65.5% of IV (by weight).

Anal. Calcd. for the above mixture: C, 76.8; H, 5.4; Cl, 5.1; N, 12.8. Found: C, 76.9; H, 5.4; Cl, 5.0, 5.1; N, 12.5.

The final ether extract on evaporation gave 0.35 g. of crystalline residue from which 0.25 g. of material, m.p. 149–161° remained after washing with 20 ml. of ether.

Anal. Calcd. for a mixture of 57.5% of VI and 42.5% of IV (by weight): Cl, 8.4. Found: Cl, 8.4.

Since an estimated 1.0 g. of mixed benzimidazoles was removed by the ether washes, the calculated yield of VI was 4.6 g. (0.019 mole, 19%) and of IV 7.9 g. (0.038 mole, 38%).

From the first ether extract obtained above 17.6 g. of partly crystalline red material remained after removal of the solvent. From this 4.1 g. of crystalline material was filtered off. On recrystallization from benzene, 1.3 g. of I, m.p. 99–101°, was obtained. An additional 0.9 g. was recovered from the second and third ether extracts which raised the yield of recovered diamine to 20%.

Distillation of the filtrate from the crude I gave 1.0 g. of

p-chlorotoluene, b.p. 162–164°. The yields of toluene and p-chlorotoluene were thus 6 and 12%, respectively.

(d) **With 4-Methoxydibenzyl Ketone.**—The experiment using 24.0 g. (0.1 mole) of ketone and 10.8 g. (0.1 mole) of diamine paralleled the above. Water (1.40 g., 78%) and practically pure toluene (1.90 g., 20%) collected in the separator. The residue in the flask did not crystallize on cooling and was triturated with 50 ml. of absolute ether in which it partially dissolved. After stirring for several minutes a white powder separated and was filtered off as a sticky clay. After two more triturations with ether 11.5 g. of fine white powder, m.p. 142.5–147.5°, resulted. Further treatment of this with two 120-ml. portions of ether left 10.9 g. of white powder, m.p. 143.5–148°.

Anal. Calcd. for 70.0% of IX and 30.0% of IV (by weight): C, 77.2; H, 5.9; N, 12.2; CH_3O, 9.1. Found: C, 77.4; H, 5.7; N, 12.0; CH_3O, 9.1, 9.1.

Evaporation of the final ether extract gave 0.25 g. of tan crystals from which 0.15 g. of white powder, m.p. 146–151.5°, remained after washing with 20 ml. of ether.

Anal. Calcd. for a mixture of 50% of V and 50% of IV: CH_3O, 6.6. Found: CH_3O, 6.6.

Since an estimated 0.9 g. of mixed benzimidazoles was removed in the ether extractions the calculated yield of V was 8.1 g. (0.034 mole, 34%) and of IV was 3.7 g. (0.018 mole, 18%).

Evaporation of the ether from the first three extractions left 18.5 g. of partly crystalline orange oil. This was exhaustively extracted with hexane. Removal of the hexane and distillation of the residue gave a few drops of p-methoxytoluene, b.p. 170–172°, $n^{23.8}D$ 1.5087. The other fractions were not investigated.
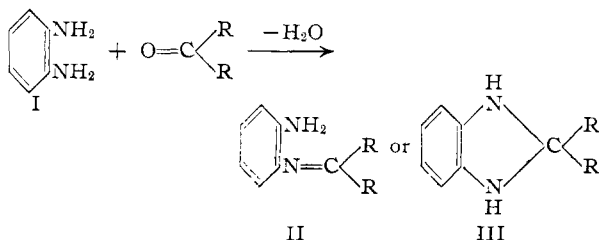
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The Reaction of o-Phenylenediamines with Carbonyl Compounds. IV. The Primary Product from Benzophenone and Dibenzyl Ketone[1]

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The structures of the substances formed in the primary reaction between o-phenylenediamine and benzophenones and dibenzyl ketone is discussed. The former compounds are Schiff bases whereas the latter is a complex mixture of tautomers.

In the preceding paper[3] the over-all reaction occurring when o-phenylenediamine (I) and benzophenone and representative dibenzyl ketones are pyrolyzed together was discussed. In this paper we wish to present some observations on the structures of the so-called "intermediates" which are formed in the initial reaction between I and the ketones and which on heating lead to 2-substituted benzimidazoles with elimination of hydrocarbons. These intermediates can be isolated in crystalline form when the condensation of I with the ketones is carried out at temperatures below that at which the intermediates lose hydrocarbon. Further, the formation of the intermediates is catalyzed by acid whereas it has been shown that the subsequent loss of hydrocarbon is not subject to such catalysis.[3,4] Pyrolysis of the intermediates discussed in the present paper leads to the same benzimidazoles as are obtained when the reactants are heated directly, which makes it highly probable that the reaction follows the same course with benzophenones and dibenzyl ketones as with the aliphatic ketones studied previously.[4]

The compound arising from the reaction of I with a ketone by loss of a molecule of water may be represented by either a Schiff base (II) or benzimidazoline (III) structure or a tautomeric system involving both II and III. Examples of both forms have been claimed in the literature[4–11] although no clear cut evidence for a simple, stable benzimidazoline for which an alternate Schiff base structure is possible has yet been presented. There is no *a priori* reason to believe that either form is intrinsically more stable than the other. Although calculations involving the compound from I and benzophenone using Pauling's values for bond energies[12] lead to similar results (the five-membered ring is favored by 3 kcal.), such calculations do not take into account differences in resonance energies due to conjugation. In addition, the often strong tendency toward ring formation may be an important factor.[13] Finally, which of the forms will actually be encountered in a particular instance may well also depend on the nature of the groups present in the ketone and on the prevailing experimental conditions as will be shown.

Spectrographic studies appear to afford the most reliable tool for obtaining evidence on this question,

(1) The material here presented is taken from a dissertation submitted by Victor B. Meyer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Columbia University.

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