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.

NEW YORK 27, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

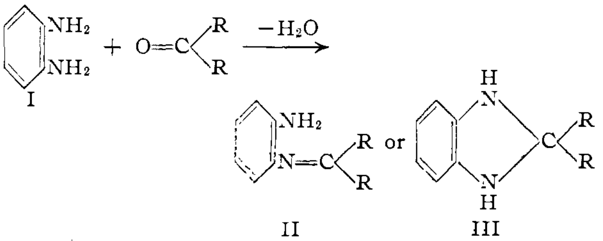
The Reaction of *o*-Phenylenediamines with Carbonyl Compounds. IV. The Primary Product from Benzophenone and Dibenzyl Ketone[1]

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

RECEIVED OCTOBER 17, 1953

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,

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(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 V. B. Meyer, THIS JOURNAL, **76**, 1883 (1954).

(4) R. C. Elderfield and J. R. McCarthy, *ibid.*, **73**, 975 (1951).

(5) O. Hinsberg and P. Koller, *Ber.*, **29**, 1497 (1896).

(6) G. B. Crippa and S. Maffei, *Gazz. chim. ital.*, **71**, 194 (1941).

(7) A. Ladenburg and L. Rügheimer, *Ber.*, **12**, 951 (1879).

(8) H. J. Barber and W. R. Wragg, *J. Chem. Soc.*, 610 (1946).

(9) R. C. Elderfield, F. J. Kreysa, J. H. Dunn and D. D. Humphreys, THIS JOURNAL, **70**, 40 (1948).

(10) C. Gastaldi and F. Cherichi, *Gazz. chim. ital.*, **43**, I, 299 (1913).

(11) K. Brand and E. Weil, *Ber.*, **56**, 105 (1923).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, pp. 53, 131.

(13) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 373, 374, 644–646, cites numerous examples of ring-chain tautomerism in which the cyclic form is the more stable including several cases of readily formed "strained" rings.

since, before any change brought about by chemical agents can be interpreted significantly, it must be shown that the rate of tautomerization is negligibly slow under the conditions obtaining.

The ultraviolet spectra of the intermediates derived from I and benzophenone, 4-nitrobenzophenone and 4-methoxybenzophenone leave no doubt that they are Schiff bases (benzhydrylidene-*o*-phenylenediamines). They are colored compounds and absorb well into the visible region, facts which are incompatible with any other structure.[14] The absorption characteristics of these compounds together with the parent benzophenones and several *o*-phenylenediamines are tabulated in Table I. Neither the benzophenones nor the *o*-phenylenediamines absorb in the visible.

In the infrared, these intermediates all absorb strongly at 6.2 μ and the band at this wave length may probably be attributed to the carbon-nitrogen double bond.[15] The weaker band normally assigned to the phenyl groups is still present as a shoulder near 6.3 μ. The nitro and methoxy compounds show the bands characteristic of these groups at 7.45 and 8.5 μ, respectively.

The stability of the Schiff base structure of the benzophenone intermediates is probably largely due to the extended conjugation which is present in these substances.

The situation in the case of the dibenzyl ketone intermediate is far more complex. The ultraviolet absorption spectrum of this compound in 95% ethanol is remarkably similar to the spectrum of 2-benzylbenzimidazole (V) (Fig. 1). That this is not due to rapid elimination of toluene from the intermediate is evidenced by the fact that it may be recrystallized from ethanol. The spectrum does not change significantly when the alcoholic solution is allowed to stand for two days.

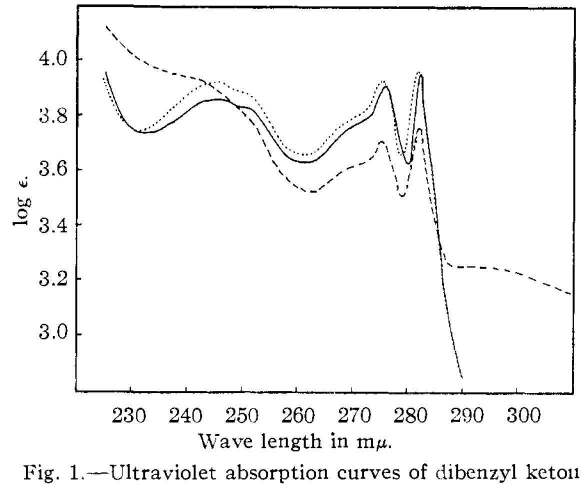
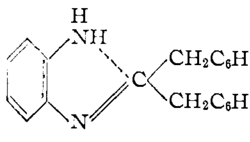
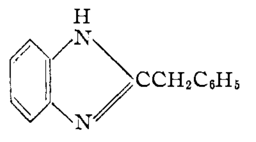


Fig. 1.—Ultraviolet absorption curves of dibenzyl ketone intermediate in 95% ethanol: ———, freshly prepared solution; - - - -, freshly prepared solution of intermediate heated at 155°; . . . ., solution of heated intermediate after standing for two days.

An attractive conjecture for this striking similarity in absorption curves postulates that the intermediate is, indeed, the Schiff base, which is structurally similar to the benzimidazole except that in the latter the amino nitrogen is bonded to the azomethine carbon atom (IV–V).



IV



V

However, the infrared spectrum of the intermediate in carbon tetrachloride solution (Fig. 2) does not show the band near 6.1 μ which would be expected if the compound contained a carbon-nitrogen double bond. After the solution has stood at room temperature for two days and then was filtered from a small amount of V which had formed, its spectrum showed a weak band at 6.1 μ.[16]

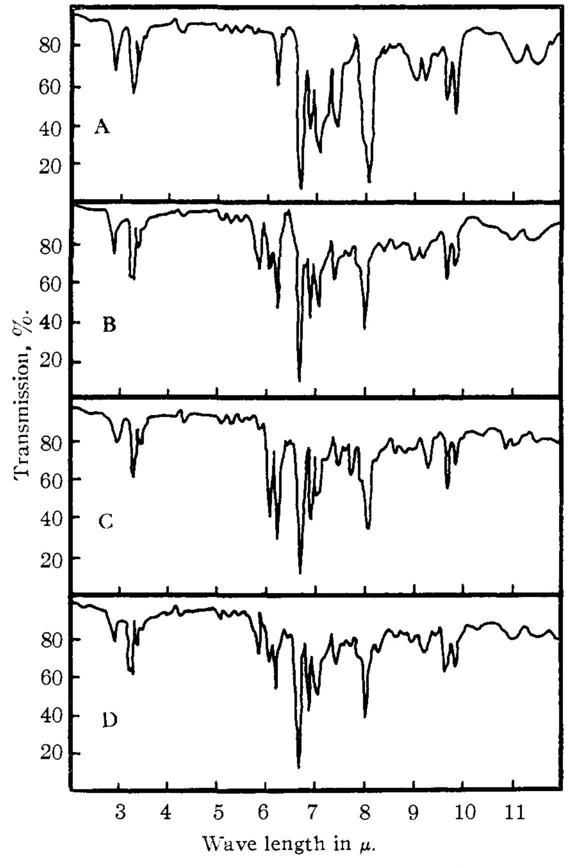


Fig. 2.—Infrared spectra of dibenzyl ketone intermediate in 10% carbon tetrachloride solution: A, freshly prepared solution; B, solution after standing two days; C, freshly prepared solution of heated intermediate; D, solution of heated intermediate after standing two days.

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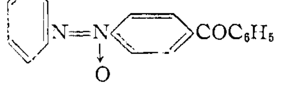
[14] The azoxybenzene formulation for the compound derived from *p*-nitrobenzophenone must be rejected because the substance is readily cleaved to its components by cold, dilute mineral acid, toward which azoxybenzenes are stable.



[15] 2-Pentylideneaniline shows a strong band at 6.1 μ ascribable to the carbon-nitrogen double bond.

[16] The band is not due to the slight amount of the sparingly soluble 2-benzylbenzimidazole remaining in solution, since the latter does not absorb at this wave length. A new weak band at 5.85 μ is probably due to a small amount of dibenzyl ketone, which could result by hydrolysis of the intermediate by traces of water in the solvent.

On the other hand, if the intermediate is heated for a few minutes at 155°, cooled, dissolved in carbon tetrachloride and filtered from V, the spectrum shows a moderately strong band at 6.1 μ. After this solution has been allowed to stand at room temperature for two days, its spectrum reverts to one similar to that of the unheated intermediate after standing.

These results indicate that the intermediate is not a Schiff base in the crystalline form, that it is partially converted to the Schiff base on heating, that its equilibrium mixture in carbon tetrachloride solution contains only a small amount of the Schiff base form, and that it equilibrates rapidly in 95% ethanol to a mixture containing the Schiff base predominantly. That a rapid equilibration in 95% ethanol does, indeed, take place was demonstrated directly.[17]

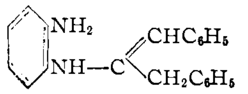
TABLE I

ABSORPTION CHARACTERISTICS OF BENZOPHENONES, OF *o*-PHENYLENEDIAMINES, AND OF THEIR CONDENSATION PRODUCTS IN 95% ETHANOL

Compound	Wave length in $m\mu$ and (log ϵ)		
	Maxima	Minima	Inflections
Benzhydrylidene-*o*-phenylenediamine	245(4.28) 376(3.44)	230(4.21) 324(3.18)	
4-Nitrobenzhydrylidene-*o*-phenylenediamine	265(4.29) 410(3.39)	233(4.22) 365(3.34)	237(4.23) 245(4.24)
4-Methoxybenzhydrylidene-*o*-phenylenediamine	252(4.21) 280(4.22) 369(3.53)	240(4.20) 266(4.20) 329(3.56)	
Benzophenone	254(4.25) 333(2.20)	227(3.66) 315(2.11)	
4-Nitrobenzophenone	266(4.30)	232(3.83)	338(2.74)
4-Methoxybenzophenone	224(4.07) 252(3.96) 290(4.21)	218(4.05) 241(3.90) 261(3.93)	
o-Phenylenediamine	238(3.80) 294(3.48)	229(3.76) 266(2.82)	
N-Methyl-*o*-phenylenediamine	248(3.89) 298(3.56)	233(3.75) 273(3.09)	
N,N-Dimethyl-*o*-phenylenediamine	293(3.45)	270(3.07)	240(3.81)
N,N'-Dimethyl-*o*-phenylenediamine	253(3.94) 297(3.62)	235(3.71) 276(3.34)	

A sample of the intermediate was dissolved in a small amount of carbon tetrachloride, the solution was diluted rapidly with 25 volumes of ethanol and the ultraviolet spectrum was examined immediately. The peaks of the maxima at 245, 276 and 282 $m\mu$ developed rapidly from the low values of the optical densities at the start and essentially constant values were attained after about 20 minutes.

Thus, if the above interpretations are adequate, and if only *two* tautomeric forms (benzimidazoline and Schiff base) are involved, then the heated intermediate should exhibit the same ultraviolet spectrum in 95% ethanol as the unheated substance, since heating would merely cause some Schiff base formation prior to dissolving the sample in ethanol. This was not, however, found to be the case. Heating the intermediate at 155° for 30 minutes did significantly alter its spectrum (Fig. 1), although after allowing the alcoholic solution to stand for two days the spectrum reverted to that of the unheated material. This can only mean that a third tautomer, the eneamine form (VI), is involved in these transformations.



VI

In the case of this particular eneamine, the ethylenic double bond is conjugated not only with the imino group, but also with a benzene ring which may explain its apparent stability relative to the other tautomers.

In conclusion, it seems clear that the intermediate derived from dibenzyl ketone and I presents a peculiarly adaptable case for the study of these systems. The application of these findings to the question of the over-all mechanism of the elimination reaction discussed in the preceding paper[3] and to the structures of the intermediates derived from other types of ketones awaits the outcome of work currently underway. It should be emphasized, as detailed in the experimental part, that in comparison with the strictly aliphatic ketones, the dibenzyl ketones lead to very reactive intermediates as far as the elimination reaction is concerned.

Experimental[18-20]

Benzhydrylidene-*o*-phenylenediamine. Procedure A.—A mixture of 18.2 g. (0.1 mole) of benzophenone, 10.8 g. (0.1 mole) of I and 20 ml. of pseudocumene was heated at 195° for 12 hours in the apparatus described in the preceding paper[3] during which 1.10 g. (60%) of water collected in the separator. The orange-red reaction mixture (44 g.) remained homogeneous on cooling. A solution of a 1.05 g. aliquot in 2 ml. of ethanol and 10 ml. of 5% hydrochloric acid was allowed to stand several hours at room temperature. Extraction of the solution with ether gave 0.41 g. of benzophenone, m.p. 47.5–48.5°, corresponding to 95% of the starting ketone. From the acid solution 0.14 g. of I corresponding to 53% of the starting diamine, m.p. 99–102°, was recovered. There was no evidence of the presence of any 2-phenylbenzimidazole.[21]

A portion of the reaction mixture, 32 g., partially crystallized on standing for six days. Filtration in a Skau tube[22] gave 10.4 g. of yellow crystals, m.p. 78–88°. Recrystallization from methanol (18 ml.) gave 6.2 g. (31%) of yellow crystals, m.p. 93–95.5°, undepressed when mixed with the same substance prepared by procedure B.

When the above reaction was carried out for two hours with addition of 0.90 g. of *o*-phenylenediamine dihydrochloride the yield was 57%.

Procedure B.—A mixture of 5.50 g. (0.03 mole) of benzophenone, 3.60 g. (0.033 mole) of I, 0.57 g. of *p*-toluenesulfonic acid monohydrate and 50 ml. of toluene was refluxed for eight hours during which 24% of water of reaction separated. After cooling and filtering from insoluble salts the solvent was removed under reduced pressure. The residual orange oil partially crystallized on stirring with 2 ml. of cold methanol. Three recrystallizations from 3-ml. portions of methanol gave 1.75 g. (21%) of golden yellow square plates, m.p. 94.5–95.5°.

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[17] We are indebted to Dr. Fausto A. Ramirez who suggested this experiment during the senior authors' absence from Columbia University.

[18] All melting points are corrected and boiling points are uncorrected.

[19] Microanalyses by Schwarzkopf Microanalytical Laboratory, Middle Village 79, N. Y.

[20] Ultraviolet spectra were taken on a Cary Recording Spectrophotometer, Model 11. Infrared spectra were taken with a Baird Infrared Recording Spectrophotometer.

[21] For an explanation of the reported formation of 2-phenylbenzimidazole under essentially similar conditions see ref. 3.

[22] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 335.

Anal. Calcd. for $C_{19}H_{16}N_2$: C, 83.8; H, 5.9; N, 10.3. Found: C, 83.6; H, 6.1; N, 10.6, 10.3.

Procedure C.—A mixture of 84 g. (0.46 mole) of benzophenone, 52 g. (0.48 mole) of I and 4.1 g. (0.023 mole) of *o*-phenylenediamine dihydrochloride in a one-liter flask fitted with a downward condenser was heated in a Wood's metal-bath for one-half hour during which the bath temperature was raised from 140 to 220° and 2.5 g. (30%) of water distilled. The residual greenish-black pasty mass was dissolved in 150 ml. of warm methanol and the acid was neutralized with excess aqueous ammonia. After standing for several hours the methanol solution deposited 28.5 g. of greenish-yellow material, m.p. 75–95°. After recrystallization from methanol, the golden yellow plates melted at 93.5–95.5°. After working the mother liquors the total yield of pure Schiff base was 23 g. (18%).

Pyrolysis of Benzhydrylidene-*o*-phenylenediamine.—When 10.9 g. of the above Schiff base was heated at 270–280° for 43 hours 0.40 g. (13%) of pure benzene, n^{25}_{D} 1.4983, b.p. 81°, distilled. On working up the residue as described previously[3] 2.80 g. (36%) of 2-phenylbenzimidazole was isolated.

4-Nitrobenzhydrylidene-*o*-phenylenediamine.—A mixture of 5.70 g. (0.025 mole) of 4-nitrobenzophenone, m.p. 138–138.5°,[23] 2.85 g. (0.026 mole) of I and 0.23 g. of *o*-phenylenediamine dihydrochloride was heated as in procedure C above at 155–160° for five minutes and then cooled rapidly. The dark red semi-crystalline mass was digested with four 10-ml. portions of hot absolute ethanol. Each portion of ethanol was decanted from the red crystals, allowed to cool to precipitate unreacted ketone and a small amount of red crystals, then heated rapidly to boiling and again decanted leaving behind the more slowly dissolved red crystals which were returned to the main batch. After four similar treatments with 95% ethanol all the ketone was removed and 2.30 g. (29%) of crude Schiff base, m.p. 153–155°, remained. Recrystallization from 95% ethanol (200 ml.) gave 1.80 g. of bright red prisms, m.p. 154.5–156°, which were readily cleaved by cold dilute hydrochloric acid to the starting diamine and ketone.

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.9; H, 4.8; N, 13.2. Found: C, 71.9; H, 4.7; N, 12.9, 13.1.

The Schiff base was obtained in 24% yield by procedure B above.

4-Methoxybenzhydrylidene-*o*-phenylenediamine.—This was prepared from 5.30 g. of 4-methoxybenzophenone, m.p. 61–62.5°,[24] by procedure C above. The temperature was raised from 150 to 200° over ten minutes and held at 200° for an additional five minutes. The cooled reaction mixture was stirred with 30 ml. of chloroform, the resulting suspension was filtered from undissolved I, and the chloroform solution was washed successively with dilute sodium carbonate solution and water. Evaporation of the chloroform left an orange oil which solidified on stirring with petroleum ether. The solid (3.2 g.) was recrystallized from 7 ml. of methanol to give 3.0 g. (40%) of the Schiff base as golden yellow cubes, m.p. 96.5–97.5°.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.4; H, 6.0; N, 9.3. Found: C, 79.6, 79.4; H, 6.5, 6.4; N, 9.4, 9.4.

The Intermediate from Dibenzyl Ketone and *o*-Phenylenediamine. Procedure A.—A mixture of 21.0 g. (0.1 mole) of pure dibenzyl ketone, m.p. 34–34.5°, 10.8 g. (0.1 mole) of I and 40 ml. of benzene was heated as usual[3] for 23 hours during which 1.25 g. (70%) of water collected in the separator. Removal of the solvent from the clear yellow reaction mixture at reduced pressure left 31.5 g. of honey-like residue. On solution of this in 40 ml. of methanol crystallization began almost immediately. After refrigerating, the precipitate was collected and washed with 10 ml. of cold methanol giving 20.4 g. (68%) of pale yellow crystals. Concentration of the mother liquor under nitrogen to half its volume gave only 0.25 g. additional. The crude product was recrystallized from 40 ml. of methanol giving 11.4 g. of nearly white needles which formed a clear solution in carbon tetrachloride. The infrared spectrum was identical with that of the product obtained by procedure B below.

Removal of the solvent from the original methanol mother liquor left 8.9 g. of partly crystalline orange oil from which 1.60 g. (7.5%) of 2-benzylbenzimidazole was isolated after trituration with ether.

Procedure B.—The amounts of reactants were the same as in procedure A except that 0.38 g. of *p*-toluenesulfonic acid monohydrate was added. After two hours 1.50 g. (83%) of water had collected. On cooling 0.35 g. of *o*-phenylenediamine *p*-toluenesulfonate separated and was filtered off. Addition of 0.2 ml. of diethylamine caused no further precipitate. Removal of the solvent under nitrogen at reduced pressure left 34 g. of viscous yellow oil which was completely soluble in ether. Recrystallization from 30 ml. of methanol gave 22.2 g. (74%) of nearly white needles. This substance does not show a normal m.p. When heated in the usual manner it softens at 75–80°, melts partially at 85–92°, resolidifies and is finally completely liquid at about 160°. On immersion of the capillary into the bath preheated to 95–97° the sample melts completely and slowly resolidifies on continued heating. When pure, the intermediate forms perfectly clear, fairly concentrated solutions in carbon tetrachloride and in benzene, solvents in which 2-benzylbenzimidazole is sparingly soluble (1 ml. of benzene dissolves over 300 mg. of the intermediate but less than 2 mg. of 2-benzylbenzimidazole). It is readily cleaved to the ketone and diamine by cold dilute hydrochloric acid. The substance rapidly turns deep yellow on exposure to air with development of a benzaldehyde-like odor. When carefully dried and stored under nitrogen in the dark it is reasonably stable.

Anal. Calcd. for $C_{21}H_{20}N_2$: C, 84.0; H, 6.7; N, 9.3. Found: C, 84.3, 84.2; H, 6.6, 6.5; N, 9.3, 9.3.

From the original mother liquor 0.95 g. (4.5%) of 2-benzylbenzimidazole was isolated.

Pyrolysis of the above Intermediate.—When 10.5 g. of the intermediate was heated at an initial temperature of 150° and the temperature was raised at the rate of 2° per minute to 250° and held at 250–260° for 8.5 hours 1.25 g. (39%) of pure toluene, n^{24}_{D} 1.4952, d^{20}_{4} 0.872, was collected. After trituration of the residue with ether, 85% of 2-benzylbenzimidazole was isolated.

The Intermediate from 4-Chlorodibenzyl Ketone and *o*-Phenylenediamine.—This was prepared by procedure B given for the dibenzyl ketone intermediate. In three hours 55% of the theoretical water had been removed. Treatment of the residue with ice-cold methanol gave 45% of yellow tinged white prisms which crystallized slowly. The m.p. was 85–87° followed by resolidification on further heating.

Anal. Calcd. for $C_{21}H_{19}ClN_2$: C, 75.3; H, 5.7; Cl, 10.6; N, 8.4. Found: C, 75.0, 75.1; H, 5.6, 5.6; Cl, 10.6, 10.8; N, 8.4, 8.3.

Pyrolysis of this compound paralleled the results obtained when the ketone and diamine were heated directly.[3]

N,N′-Dimethyl-*o*-phenylenediamine.[25]—N,N′-Di-*p*-toluenesulfon-*o*-phenylenediamide was prepared by treating I (0.2 mole) with excess *p*-toluenesulfonyl chloride in pyridine on the steam-bath. To obtain a pure product, the crude material was digested with portions of hot 95% ethanol and the digests were discarded until the crystals obtained by cooling showed nearly the same m.p. as the residue (204–207°). The latter was then recrystallized (with charcoal) from 40 volumes of 95% ethanol giving 27% of white prisms, m.p. 206.5–207.5°; reported m.p. 201–202°.[26]

The diamide was converted to its N,N′-dimethyl derivative with dimethyl sulfate in 4 *N* sodium hydroxide in the usual fashion. After recrystallization of the crude product from 20 volumes of 95% ethanol 70% of white needles, m.p. 178–179°, was obtained.

Anal. Calcd. for $C_{22}H_{24}N_2O_4S_2$: C, 59.4; H, 5.5; N, 6.3; S, 14.4. Found: C, 59.7; H, 5.3; N, 6.4; S, 14.6.

The dimethylsulfonamide also was obtained by further methylation of the monomethylsulfonamide from tosylation of N-methyl-*o*-phenylenediamine[3] as above. The monomethylsulfonamide melts at 138–139° after recrystallization from 95% ethanol.

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(23) G. Schroeter, *Ber.*, **42**, 3356 (1909).

(24) S. Chodroff and H. C. Klein, This Journal, **70**, 1647 (1948).

(25) The method given in the literature for preparing this compound [O. Fischer and E. Fussenegger, *Ber.*, **34**, 930 (1901)] which involves heating 1,3-dimethylbenzimidazolium iodide with "dilute alkali" gave, with 6 *N* sodium hydroxide, a product of doubtful purity which appeared to be a mixture of bases. The procedure here given, while not suited for large quantities, was resorted to in order to obtain a sample of unquestioned purity.

(26) F. Reverdin and P. Crepieux, *ibid.*, **35**, 314 (1902).

Anal. Calcd. for $C_{21}H_{22}N_2O_4S_2$: C, 58.6; H, 5.2; N, 6.5; S, 14.9. Found: C, 59.0; H, 5.3; N, 6.6; S, 15.0.

Hydrolysis of the dimethylsulfonamide with glacial acetic acid–concd. sulfuric acid gave a red oil which on distillation under nitrogen gave a 30% yield of N,N′-dimethyl-*o*-phenylenediamine as a colorless oil, b.p. 108.5–109° at 5 mm., $n^{25.5}_D$ 1.5914, m.p. 30.5–31°.

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.5; H, 8.9; N, 20.6. Found: C, 70.6; H, 8.7; N, 20.5.

2-Pentylideneaniline.[27]—A mixture of 9.5 g. of freshly distilled aniline and 35 g. of methyl *n*-propyl ketone was refluxed in a nitrogen atmosphere in the usual apparatus[3] for four days during which 0.6 g. (33%) of water collected. The mixture was distilled under reduced pressure. After removal of excess ketone, unreacted aniline (4.0 g., 43%) and an intermediate fraction (2.5 g., b.p. 58–83° at 5 mm.), 3.5 g. (20%) of anil, b.p. 84° at 5 mm., $n^{25.5}_D$ 1.5190, d^{20}_4 0.939, was collected. It has a fishy odor and is readily hydrolyzed by dilute mineral acid.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.9; H, 9.4; N, 8.7. Found: C, 81.6; H, 9.4; N, 9.2, 9.0.

When toluene was used to aid in the removal of water, the yield was 30%.

The infrared spectrum shows a strong band at 6.1 μ which is not present in N-(2-pentyl)-aniline. There is no peak at 3.0 μ.

The anil (1.26 g.) absorbed the calculated amount of hydrogen over platinum oxide in alcohol solution at room temperature. The reduction product agreed in properties with the substance described below.

N-(2-Pentyl)-aniline.—Nitrobenzene (12.3 g.) and methyl *n*-propyl ketone (25.8 g.) was reduced in 10 ml. of glacial acetic acid and 150 ml. of 95% ethanol over platinum oxide at room temperature and 2 atm.[28] Distillation of the crude product under nitrogen after removal of the forerun gave 9.0 g. (55%) of the amine, b.p. 104.5–106.5° at 9 mm., 242° at atmospheric pressure, $n^{25.2}_D$ 1.523.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.9; H, 10.5; N, 8.6. Found: C, 80.7; H, 10.3; N, 8.6.

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[27] This anil is one of a series of aliphatic ketone anils reported by G. H. Reddelien [U. S. Patent 2,218,587; *C. A.*, **35**, 1065 (1941)] who used an excess of aniline in contrast to the procedure given here. He reported the b.p. of methyl-*n*-propylanil as 101° at 11 mm.

[28] W. S. Emerson and C. A. Uraneck, THIS JOURNAL, **63**, 749 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Reaction of 1-Methyl-2-(*t*-butyl)-benzimidazole with Organolithium Compounds[1]

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The reaction of 1-methyl-2-(*t*-butyl)-benzimidazole with methyllithium and with phenyllithium has been studied. The former reaction took an abnormal course and the product of the second reaction was unexpectedly labile to dilute acid.

When 2,2-dialkylbenzimidazolines or 1-methyl-2,2-dialkylbenzimidazolines are heated one of the substituents at the 2-position is lost in combination with the hydrogen at the 3-position as hydrocarbon[3] and a mechanism involving loss of the 2-substituent as an anion has been suggested.[3,4]

It was hoped that observation of the behavior of the products of addition of organolithium compounds to suitable 2-substituted benzimidazoles might provide additional evidence bearing on the suggested mechanism of the elimination reaction. If the postulated mechanism be correct the organolithium adduct may be considered analogous to the salt of the benzimidazoline. Although the reaction of organolithium compounds with benzimidazoles has not been studied, comparable reactions with similar types of compounds containing the azomethine linkage are well known.[5] In view of the unexpected outcome of these studies we should like to record our experience with the reaction.

For the purpose at hand 1-methyl-2-(*t*-butyl)-benzimidazole (I) was chosen. This would not be expected to be amphoteric since a hydrogen is lacking at the 1-position; the absence of an α-hydrogen located in the 2-substituent would minimize competitive metalation reactions; finally, inasmuch as the *t*-butyl group should be eliminated more readily than other alkyl groups it would provide a direct test of whether the elimination reaction proceeds in accordance with the predicted course when, for example, methyllithium is the reagent. However, the reactions took a different course.

When an ether solution of I was added to excess methyllithium in ether at −5°, a white precipitate formed which did not dissolve on refluxing in either ether or benzene. It consisted of I and lithium iodide (from the preparation of the reagent) in a molar ratio of approximately 1:2. Since the filtrate from this solid contained 90% of the original methyllithium (by titration) it was obvious that formation of the insoluble complex removed most of the benzimidazole from solution and thereby effectively prevented it from reacting with the methyllithium.

When I was allowed to react with phenyllithium in ether again a white precipitate appeared. However, in this instance the precipitate dissolved after stirring for two hours at room temperature. After acid hydrolysis of the reaction mixture 15% each of N-methyl-*o*-phenylenediamine and trimethylacetophenone together with unreacted I was obtained. This indicated that phenyllithium had added slowly to the azomethine linkage of I but that the adduct was unstable in the presence of acid used in working up the product.

The anomalous results noted raise the questions of whether the benzimidazole azomethine linkage *per se* represents an exception to the generally observed course of reaction of other heterocycles containing a similar linkage with organolithium

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

(4) R. C. Elderfield and V. B. Meyer, *ibid.*, **76**, 1887 (1954).

(5) H. Gilman and J. A. Beel, *ibid.*, **71**, 2328 (1951), *inter alia.*