The solvent was then distilled, and the residue was dried over sulfuric acid in a vacuum. The resulting ester was the diacetyl derivative;[15] it melted at 95.5–97°.

$$2CH_2: CO + (C_6H_5)_2CH—CO—NHOH \longrightarrow (C_6H_5)_2CH—N(COCH_3)—O—COCH_3.$$

C. Ketene and Benzhydroxamic Acid.—An excess of ketene was allowed to react with a solution of benzhydroxamic acid in ethyl acetate. The oil which remained after the solvent was removed resisted the ordinary means to induce crystallization. The oil could be hydrolyzed to benzhydroxamic acid by contact with a warm solution of sodium hydroxide. This was shown by a recurrence of the ferric chloride reaction. The oil was probably the diacetyl ester of benzhydroxamic acid, but it was not purified and analyzed.

Neither with benzhydroxamic acid nor with diphenyl-acethydroxamic acid did we attempt to isolate the mono-acetyl ester by this method. There is no doubt but that they could have been prepared simply, however, had equivalent quantities of the ketene and of the acid been employed.

In the reactions between ketene and the several hydroxamic acids, the yields in each case approached the theoretical.

Summary

The mechanism of the addition of ketene to hydroxylamine, and of ketene to hydroxamic acids is discussed. The similarity of the behavior of ketene and of phenyl-isocyanate in this respect is pointed out.

Ketene will form not only a mono-acetyl ester, but also a diacetyl ester of a mono-hydroxamic acid with great ease.

An improved apparatus for the preparation of ketene from acetone is described.

URBANA, ILLINOIS

CONTRIBUTION TO THE STRUCTURE OF BENZIDINE

BY ROGER ADAMS, J. E. BULLOCK AND W. C. WILSON

Shortly after the discovery of benzidine, unexpected reactions of this compound and its derivatives were shown to take place. In particular it was found that the two amino groups acted in many instances as they do in o-phenylenediamine; it was possible, for example, with anhydrous oxalic acid, to obtain oxalyl benzidine;[1] with phosgene, carbonyl benzidine;[2] with carbon disulfide, thiocarbobenzidine;[3] with phthalic anhydride, phthalyl-benzidine.[4] Whether these compounds consist of 1 molecule of benzidine and 1 molecule of the other reacting substance was not determined until the molecular weight of phthalyl-benzidine[5] in nitrobenzene

[15] Ref. 1, p. 2436.

[1] Borodine, *Jahresber.*, **1860**, 356.

[2] Michles and Zimmerman, *Ber.*, **14**, 2178 (1881).

[3] Strakosch, *ibid.*, **5**, 240 (1872).

[4] Koller, *ibid.*, **37**, 2882 (1904). Schaff and Vanin, *Ann.*, **258**, 363 (1890).

[5] Kaufler, *Ann.*, **351**, 156 (1907); *Ber.*, **40**, 3250 (1907).

had been shown by Kaufler to agree with that of the product obtained by the condensation of 1 molecule of benzidine with 1 molecule of phthalic anhydride with the elimination of 1 molecule of water (Formula I).

I   II
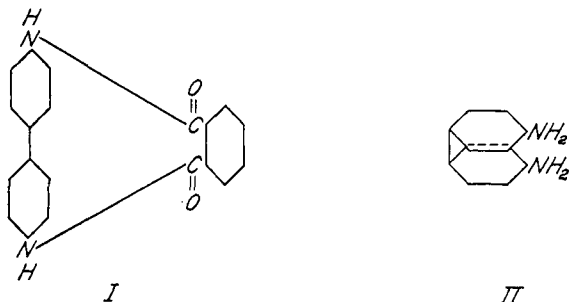
Kaufler concluded that, as the 2 amino groups in benzidine reacted so readily with a single carbon or adjacent carbons as an o-phenylene diamine, the 2 amino groups must be nearer together than was indicated by the ordinary formula of benzidine. As further evidence for this conclusion, he offered the fact that after benzidine is tetrazotized, the second diazo group couples with various substances with much more difficulty than the first diazo group, indicating the steric hindrance effect of one group upon the other. Steric hindrance, however, would hardly be expected if benzidine had the structure as ordinarily represented. Kaufler concluded that benzidine must have a formula with the two rings superimposed upon each other (Formula II). Such a formula also explains satisfactorily the formation of isomeric dinitro benzidines studied by Cain[6] and his assistants and the dinitro-diphenic acids of Kenner and Stubbings.[7] In a recent extremely interesting paper, excellent experimental evidence for the Kaufler formula has been recorded. Christie and Kenner[8] have tested in the laboratory the prediction of H. King[9] that if Kaufler's formula was correct, one of each of the pairs of isomeric benzidine derivatives studied by Cain should be capable of resolution to optically-active forms. They found that one of the 6,6'-dinitro-diphenic acids and one of the 4,6,4',6'-tetranitro-diphenic acids were resolvable.

This communication describes still another type of ring compound derived from benzidine and certain of its derivatives. It has been found that they condense as readily with various m- and p-di-substituted benzene compounds as they do with o-di-substituted products. Benzidine reacts with isophthalaldehyde (Formula III), terephthalaldehyde (Formula IV,)

[6] Cain, J. Chem. Soc., 101, 2298 (1912); 103, 586, 2074 (1913); 105, 1437 (1914). See also Turner, ibid., 107, 1495 (1915); 111, 1 (1917); 117, 1140 (1920).

[7] Kenner and Stubbings, ibid., 119, 593 (1921).

[8] Christie and Kenner, ibid., 121, 614 (1922).

[9] King, Proc. Chem. Soc., 30, 249 (1914).

and resodiacetophenone to give products analyzing for 1 molecule of benzidine and 1 molecule of the dialdehyde or diketone with the elimination of 2 molecules of water.
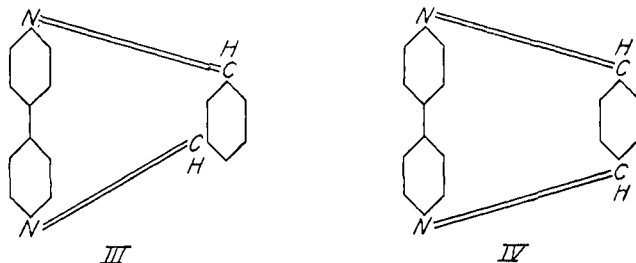
It is thus seen that the two amino groups in benzidine are condensed with the 2 aldehyde groups separated by 3 or 4 carbon atoms of the benzene nucleus. In benzidine, therefore, the amino groups cannot be placed as they are in o-phenylenediamine when entering into the above condensations. These results lead to the conclusion that the benzene rings in diphenyl and its derivatives are perhaps in motion within the molecule with the limiting positions the ordinary formula of benzidine and Kaufler's formula.
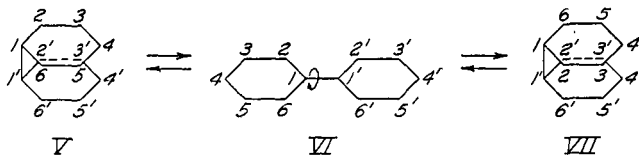
The assumption is then made that free rotation between the 2 benzene nuclei is possible only when no strain exists between them (Formula VI). The position and nature of the substituent groups in diphenyl would undoubtedly influence the motion of the benzene rings. Thus, some groups such as the amino, tend to cause the ring to approach each other closely as in the Kaufler structure (V or VII), thus leading to characteristic reactions of the 2 amino groups in benzidine, whereas many other groups do not influence the rings to approach as closely or perhaps not at all, and hence, no reactions occur such as would take place provided the substituting groups were adjacent. It is known that 3,3'-diphenyl-dicarboxylic acid[10] does not form an anhydride, that 4,4'-dibromo diphenyl[11] does not condense with sodium, that 4,4'-dinitro diphenyl[11] does not give intramolecular azo or azoxy compounds when treated with sodium amalgam and that diphenic acid and benzidine-m,m'-disulfonic acid cannot be resolved into optically-active forms.[12]

[10] Ullmann, *Ann.*, **332**, 73 (1903).

[11] Turner, *J. Chem. Soc.*, **107**, 1495 (1915).

[12] Private communication from Oliver Kamm, of Parke, Davis and Co., Detroit, Michigan.

If the existence of 2 *o,o'*-dinitro-benzidines which are apparently perfectly stable under ordinary conditions is to be explained by this same theory (Formulas V and VII), it is necessary to assume great stability for the isomers in positions with one ring over another. If such structures are correct, it should be possible to produce a cyclic azo or azoxy compound from one but not from the other, and both should be interconvertible. This has not yet been determined experimentally. Evidence that such transformation does take place in the dinitro-diphenic acid derivatives has been found.[7,8]

With the ordinary conception of benzene nuclei, Kaufler's formula for diphenyl assumes a tremendous strain within the molecule. On the other hand, Baeyer's strain theory is hardly adequate to explain satisfactorily the known facts in regard to ring formation. Many 3-membered rings[13] and others containing from 10 to 20 or more atoms,[14] have been as readily produced as 5- or 6-membered rings. It seems likely, at least in many instances, that ring-closing is a periodic function of the length of the chain.[15]

The compounds from benzidine and the *m*- and *p*-dialdehydes and ketones are characterized by their extreme insolubility and high melting or decomposition point, not one of the substances being soluble to any extent in the ordinary organic solvents such as anisole, benzyl alcohol, nitrobenzene, etc., and not one melting or decomposing under 275°. It was, therefore, impossible to obtain them in crystalline form. When they were analyzed, it was noticed that when a high enough temperature was reached, the substances decomposed suddenly and sometimes almost with explosive violence.

Unfortunately, the insolubility of the benzidine condensation product just described makes it impossible to determine the molecular weight. It might be argued, therefore, that the compounds may perhaps consist of 2 molecules of benzidine and 2 molecules of dialdehyde or diketone with the elimination of 4 molecules of water. Under these conditions, the formula for the terephthalaldehyde-benzidine compound would be represented by Formula VIII.
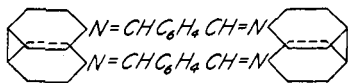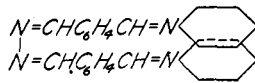
[13] Kohler, THIS JOURNAL, **41**, 1697 (1919), in which references to previous articles in the same field are given.

[14] (a) Autenrieth and Beuttel, *Ber.*, **42**, 4346, 4357 (1909). (b) Gabriel, *ibid.*, **38**, 2392, 2404 (1905). (c) Ruggli, *Ann.*, **392**, 92 (1912); (d) **399**, 174 (1913). Meyer, *ibid.*, **347**, 43 (1906).

[15] Mohr, *J. prakt. Chem.*, [2] **98**, 349 (1918). See also Scholtz, *Ber.*, **24**, 2407 (1891); **31**, 1702 (1898). Phookan and Krafft, *ibid.*, **25**, 2252 (1892). Michael, *J. prakt. Chem.*, [2] **49**, 28 (1894). v. Braun, *Ber.*, **38**, 3085 (1905). Ref. 14d, p. 175.

The stable position of the benzene rings directly over each other could still be assumed. Formula VIII, however, seems unlikely, first because of the analogy of these compounds to the monomolecular condensation products of benzidine previously studied, and second because of the fact that the compounds are readily obtained in a pure state as shown by the complete analyses of several different samples of each substance. If the compounds have double formulas it is very unlikely that the reactions would run completely and smoothly enough to prevent the contamination of the product with one or more complex intermediate substances which would also undoubtedly be insoluble in the reaction solvent.

Another similar condensation of benzidine is that with the monazine of terephthalaldehyde. The reaction takes place just as readily as with terephthalaldehyde itself. The product probably has a formula like IX.

The extremely large rings present in all these compounds are of interest. Moreover, the fact is significant that these rings are formed through the *meta* and *para* positions of benzene with apparently as great ease as if the condensations took place through the *ortho* positions.

An attempt was made to condense iso- and terephthalaldehyde with *m*- and *p*-phenylenediamine and iso- and terephthalaldehyde with ethylenediamine. In none of these cases, however, were homogeneous products obtained. Moreover, tolidine and terephthalaldehyde or isophthalaldehyde gave products which were not homogeneous.

Experimental Part

The analysis of the very insoluble and high-melting condensation products was extremely difficult because the moment the combustion started all of the material burned at once. Only after much experience was it possible to obtain reliable results.

General Method for the Condensations.—Benzidine and di-anisidine were condensed with isophthalaldehyde and terephthalaldehyde by the following procedure: A solution of a known weight of the aldehyde in alcohol was mixed with a solution of a molecular equivalent quantity of the benzidine dissolved in alcohol. Within a few minutes a solid started to separate. The reaction mixture was refluxed for 1 to 4 hours, after which time the condensations were complete. The products were filtered and purified by boiling twice with water, thrice with alcohol, and finally were dried in an oven at 115°. None of the products melted below 275° and they were all insoluble in the common organic solvents. They were readily hydrolyzed with dil. hydrochloric acid and gave a red solution upon treatment with conc. sulfuric acid.

Isophthalaldehyde and Benzidine, $(C_6H_4N=CH)_2C_6H_4$.—The product was a yellow amorphous solid.

Analyses. Subs., 0.2024: CO_2, 0.6282; H_2O, 0.0886. Subs., 0.2774: 23.9 cc. of N_2 (24°, 745 mm.). Calc. for $C_{20}H_{14}N_2$: C, 85.1; H, 5.0; N, 9.9. Found: C, 84.65; H, 4.9; N, 9.7.

Terephthalaldehyde and Benzidine, $(C_6H_4N = CH)_2C_6H_4$.—The product was a deep yellow compound.

Analyses. Subs. 0.1474: CO_2, 0.4625; H_2O, 0.0688. Subs., 0.1502: 14.2 cc. of N $_2$ (33°, 765 mm.). Calc. for $C_{40}H_{28}N_4$: C, 85.1; H, 5.0; N, 9.9. Found: C, 85.4; H, 5.2; N, 10.6.

Terephthalaldehyde and Di-anisidine, $(CH_3OC_6H_3N = CH)_2C_6H_4$.—The product was yellowish-green in color.

Analyses. Subs., 0.2466: CO_2, 0.6920; H_2O, 0.1196. Subs., 0.1634: 12.2 cc. N_2 (25°, 748 mm.). Calc. for $C_{22}H_{18}N_2O_2$: C, 77.20; H, 5.6; N, 8.18. Found: C, 76.53; H, 5.42, N, 8.18.

Resodiacetophenone and Benzidine.—This substance was made according to the directions of H. A. Torrey.[16] The product was a yellow solid.

Terephthalaldehyde Monazine, $(N = CHC_6H_4CHO(p))_2$.—A solution of 5 g. of terephthalaldehyde in about 300 cc. of alcohol was made and cooled to 20°. At this temperature hydrazine hydrate corresponding to 0.5 molecular equivalent dissolved in 10 cc. of alcohol was added all at once. A yellow color immediately developed and the solution after standing for 5 or 10 minutes solidified to a pasty yellow mass. This was very finely divided and filtered very slowly. It was dried on a porous plate and recrystallized from toluene (1 g. dissolved in 600 cc. of boiling solvent). The substance when pure formed yellow crystals melting at 232°.

Analyses. Subs., 0.1904: CO_2, 0.5047; H_2O, 0.0759. Subs., 0.1987: 19.7 cc. of N_2 (28°, 759 mm.). Calc. for $C_{16}H_{12}O_2N_2$: C, 72.7; H, 4.5; N, 10.6. Found: C, 72.4; H, 4.4; N, 11.2.

Terephthalaldehyde Monazine and Benzidine, $(N = CHC_6H_4CH = NC_6H_4)_2$.—A solution was made of 0.5 g. of monazine in 400 cc. of boiling toluene and when the solution was complete the calculated amount for 1 mole of benzidine in toluene was added through a reflux condenser and the mixture boiled for 15 to 20 hours. At the beginning no condensation seemed to take place, but after some time an orange-colored solid began to separate and increased in bulk during the period of refluxing. The compound was insoluble in all of the common solvents and did not melt below 350°.

Analyses. Subs., 0.1509: CO_2, 0.4547; H_2O, 0.0654. Subs., 0.2000: 24.1 cc. of N_2 (22°, 757 mm.). Calc. for $C_{28}H_{20}N_4$: C, 81.6; H, 4.8; N, 13.6. Found: C, 82.0; H, 4.8; N, 13.8.

This substance was also made by the condensation of monazine in boiling xylene and gave very satisfactory results.

Terephthalaldehyde Dihydrazone, $C_6H_4(CH = NNH_2)_2$.—A solution of 2 g. of terephthalaldehyde in alcohol was treated in the cold with 3 moles of hydrazine hydrate in alcohol. The mixture was allowed to stand at room temperature for several days at the end of which time no appreciable amount of solid had separated. The solution was filtered and the filtrate evaporated until a volume of 50 cc. was left. Upon cooling, the solution a heavy yellowish-white mass of crystals separated. These were soluble in the mother liquor but upon warming in fresh alcohol only partial solution was attained and the substance obtained by cooling was a yellow powder. It was found, however, that the original crystals, upon evaporation of the filtrate, could be recrystallized from alcohol provided that a small amount of hydrazine hydrate was added. The

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16 Torrey, THIS JOURNAL, **30**, 857 (1908).

compound when pure is yellowish-white and melts at 165° with decomposition, giving a yellow compound which does not melt below 300°. It was necessary to make a rapid determination in order to secure accurate results. The compound is soluble in cold alcohol to the extent of 0.5 g. in 400 cc.

Analyses. Subs., 0.2024: CO_2, 0.4424; H_2O, 0.1128. Subs., 0.1500: 45.6 cc. of N_2 (25°, 753 mm.). Calc. for $C_8H_{10}N_4$: C, 59.2; H, 6.2; N, 34.6. Found: C, 59.5; H, 6.2; N, 34.5.

It was found that terephthalaldehyde monazine which was described above, was readily converted into terephthalaldehyde dihydrazone by dissolving the former in boiling toluene and adding an excess of hydrazine hydrate in toluene. No solid separated upon boiling the mixture, but after cooling, a mass of crystals was deposited which proved to be the dihydrazone, melting at 162°.

Summary

1. Benzidine and certain of its derivatives condense readily with terephthalaldehyde and isophthalaldehyde to form substances which presumably have the following structures.
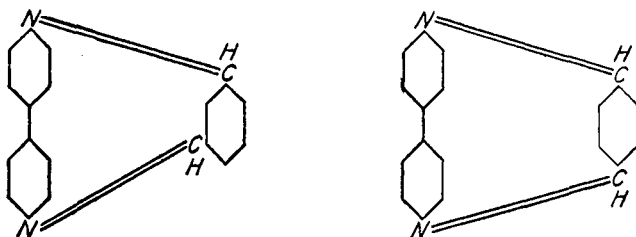
2. The structure of benzidine is discussed. From the results obtained it seems probable that the benzene rings in diphenyl derivatives are in motion with the limiting positions of the two possible Kaufler formulas and the intermediate position of the formula which is usually assigned to diphenyl.

URBANA, ILLINOIS