of the individual hydrocarbons increases with the decrease in hydrogen, and in a similar ratio to the increase in specific viscosity. Doubtless the most valuable quality of an oil is its ability to reduce friction to the smallest value; of the hydrocarbons compared in this test, the one with least hydrogen, of the series C_nH_{2n-4} seems to show the best efficiency, as it also shows the greatest durability. Of the vegetable oils compared, the castor shows the longest life, but the sperm shows the least coefficient of friction, as it does also the lowest temperatures. The hydrocarbon C_nH_{2n-4} stands ahead of the vegetable oils in durability, and the equal of the sperm in temperatures and coefficient of friction. In the above table, temperatures are selected at the beginning of the test, at the end of two hours, and when the oil ceases to lubricate. The coefficient of friction is also calculated at these points. This method appears to be capable of giving valuable information concerning the nature of lubricating oils. Like all tests of such oils, the results are relative referring to some common standards. Evidently in practice, these standards must be based on the work required of the oil, taking into account certain data, such as speed of the journal and the load carried. The coefficient of friction as used above represents the fraction of one pound for each pound of load on the journal which is sustained by the oil in use.

With reference to the comparative value of the various series of hydrocarbons in petroleum from which lubricating oils are prepared, it must be understood that the series C_nH_{2n+2} has a low lubricating value; this was shown above in tests of specific viscosity. Lubricating oils prepared from Pennsylvania petroleum consist for the larger part of the series C_nH_{2n} and series C_nH_{2n-2}. Those from the heavier oils consist largely of the series C_nH_{2n-2} and the series C_nH_{2n-4}.

As to the structural constitution of the series of hydrocarbons in lubricating oils, at present nothing whatever is known. The series C_nH_{2n+2} is doubtless represented by the straight chain or its isomers, all with the open chain. The series poorer in hydrogen, no doubt have the cyclic ring structure of the form of condensed benzene rings in part, or condensed methylene rings, single larger rings than are at present recognized, or smaller rings with condensed side chains.

CLEVELAND, OHIO.

THE COLORED SALTS OF SCHIFF'S BASES.

II. THE HYDROCHLORIDES OF BASES FORMED BY CONDENSING *p*-AMINODIPHENYLAMINE WITH AROMATIC ALDEHYDES.

BY F. J. MOORE AND R. G. WOODBRIDGE, JR.

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In a paper recently published by one of us, in collaboration with Mr. R. D. Gale,[1] attention was called to the fact that bases of the general formula

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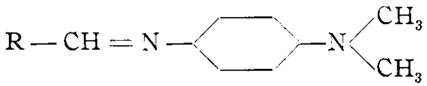
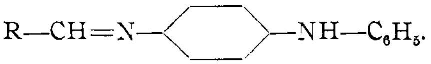
[1] THIS JOURNAL, 30, 394 (1908).



add successively two molecules of hydrochloric acid to form salts which differ markedly in color. While the bases themselves are, for the most part, of a light yellow or orange color, the salts containing one molecule of acid are dark red, while those containing two molecules are light or pale yellow, resembling the free bases in this respect.

The present investigation was undertaken in order to determine whether the behavior described was not still more general, and for this purpose, to study the color of the salts of bases formed by condensing *p*-aminodiphenylamine with aromatic aldehydes. These condensation products have the general formula



In the paper above referred to by Moore and Gale, a preliminary statement was made to the effect that these bases add one molecule of hydrochloric acid to form dark red salts, but that they do not add a second molecule of the acid. This statement requires modification. The behavior of these diphenyl compounds is, in fact, entirely analogous to that of the dimethyl compounds already described. In this case, however, the dihydrochlorides are formed with more difficulty. If one molecule of the base be treated in ethereal solution with two molecules of dry hydrochloric acid dissolved in ether, the resulting precipitate is dark colored, consisting of the monohydrochloride. If, now, the solution be kept saturated with hydrochloric acid by passing a current through it for several hours, the precipitate first formed gradually becomes lighter in color, and in some cases, practically white. When this precipitate is analyzed, it is found to contain two molecules of acid. Of the dihydrochlorides studied, all but one are sufficiently stable to retain the two molecules of hydrochloric acid when dried in a vacuum desiccator containing caustic soda. The exception is the salt of the base formed by condensing *p*-aminodiphenylamine with cinnamic aldehyde. This salt is quite light in color when first prepared, but after standing some days in the desiccator, it becomes dark, and as the analytical data clearly show, gradually loses a whole molecule of acid.

It is true of all the dihydrochlorides that their color becomes much darker on standing, even in dry air, and some of them become quite deep red again· We are at some loss to account for this. It may be due to the fact that there are two dihydrochlorides, one red and the other yellow. Another explanation would be that some acid had been lost, resulting in the formation of sufficient monohydrochloride to account for the color observed. Inspection of the analytical data presented below will show that any such loss is too small to clearly show itself in the analyses. This, however, is not conclusive, as we know, for example, that a very extensive blackening of silver chloride has very little influence upon its composition, and thus, in this case also, the presence of a small amount of the salt containing only one molecule of acid might account for the phenomenon. The behavior of the cinnamic aldehyde compound above referred to, would certainly point, by analogy, to a loss of acid as the cause of the change in color. If two kinds of salts are present, whatever their nature, it may prove possible, by means of solvents, to isolate one or both of them, and some experiments in this direction are in progress.

Experimental Part.

The *p*-aminodiphenylamine used in this investigation was prepared from diphenylamine by treatment with nitrous acid, forming the nitrosamine. The latter was then subjected to the Fischer-Hepp rearrangement, forming the *para* nitroso compound, and this was finally reduced with ammonium sulphide. So prepared, the substance forms almost colorless needles of a pearly luster melting at 75°.

Benzylidene p-aminodiphenylamine.—This compound was first prepared by Heucke[1] by the action of *p*-aminodiphenylamine upon benzaldehyde. The base is of a pale yellow color.

The monohydrochloride is blood-red. Calculated for $C_{19}H_{16}N_2,HCl$; Cl, 11.43; found, 13.48.

The saturated salt, prepared by subjecting the ethereal solution to the action of hydrochloric acid gas for some hours, is nearly white when first precipitated. When kept in a desiccator over caustic soda it turns reddish. The analysis speaks, however, for the presence of two molecules of acid in the salt. Calculated for $C_{19}H_{18}N_2,2HCl$: Cl, 20.53; found, 19.95 and 19.90.

Salicylidene p-aminodiphenylamine.—This compound was also prepared by Heucke. The base is light yellow.

The red hydrochloride has the following composition: Calculated for $C_{19}H_{16}ON_2,HCl$: Cl, 10.91; found, 11.21.

The dihydrochloride is light yellow. Calculated for $C_{19}H_{16}ON_2,2HCl$: Cl, 19.63; found, 20.59.

Piperonylidene p-aminodiphenylamine.—The base is of a light yellow color and melts at 116°.

Red hydrochloride. Calculated for $C_{20}H_{16}O_2N_2,HCl$: Cl, 10.07; found, 10.24.

The saturated salt is light yellow. Calculated for $C_{20}H_{16}O_2N_2.2HCl$: Cl, 18.22; found, 18.49.

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[1] *Ann.*, **255**, 189 (1889).

Anisylidene p-aminodiphenylamine.—This substance crystallizes from alcohol in silver-gray scales of a pearly luster which melt at 105°. Its composition was confirmed by a nitrogen determination. Calculated for $C_{20}H_{18}ON_2$: N, 9.30; found, 9.48.

The monohydrochloride is red, but of a lighter shade than most of the others hitherto examined. Calculated for $C_{21}H_{16}ON_2,HCl$: Cl, 10.47; found, 12.42.

The dihydrochloride as we obtained it, was of a pale pink color. Calculated for $C_{20}H_{18}ON_2,2HCl$: Cl, 18.90; found, 19.57 and 19.75. Although these results are a little high, we should hardly be justified in ascribing this to a tendency to add three molecules of acid as does anisylidene *p*-aminodimethylaniline.

Cinnamylidene p-aminodiphenylamine.—This compound was prepared by condensing *p*-aminodiphenylamine with cinnamic aldehyde. The base crystallizes from alcohol in brilliant yellow scales and melts at 145°. Its composition was checked by a nitrogen determination. Calculated for $C_{20}H_{18}N_2$: N, 9.42; found, 9.37.

When an ethereal solution of this base is treated with dry hydrochloric acid, the resulting precipitate is extremely dark in color, almost black. Calculated for $C_{20}H_{18}N_2,HCl$: Cl, 10.59; found, 10.55.

An excess of hydrochloric acid finally yields a product of much lighter color, which, when first filtered off, is pale pink. This substance, however, when dried in a vacuum desiccator over sulphuric acid and caustic soda, rapidly turns dark. A sample of this product, after standing in the desiccator for two days, still retained a perceptible odor of hydrochloric acid and contained 16.14 per cent. of chlorine. A dihydrochloride should contain 19.10 per cent. The same material, after standing for five days, was nearly black, and no odor of hydrochloric acid was noticeable. This material contained 11.06 per cent. of chlorine, which is only slightly in excess of that required for a monohydrochloride, as indicated above.

Summary.

When *p*-aminodiphenylamine is condensed with aromatic aldehydes, the resulting bases show the same curious color phenomena in the formation of their salts which are exhibited by the analogous compounds of *p*-aminodimethylaniline; that is, they unite with one molecule of acid to form dark colored salts and with two molecules to form light colored ones. The salts containing two molecules of acid are less easily formed than in the cases hitherto studied, and, in a single instance, the second molecule of acid is readily lost.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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