4. A quantitative relationship for the change of reaction velocity with temperature, has been derived from the data for gelatin.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

THE MOLECULAR REARRANGEMENT OF SOME NEW UNSYMMETRICAL HYDRAZINES

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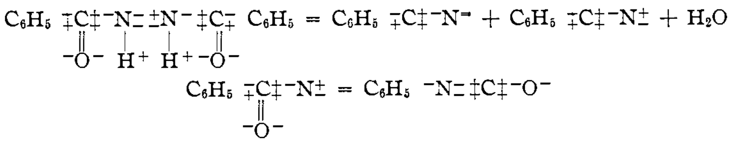
In view of the close similarity between hydroxylamine and hydrazine, particularly in their organic compounds, the probability of rearrangements of hydrazine derivatives analogous to the well-known Lossen rearrangement of hydroxamic acids was predicted by Stieglitz.[1] Subsequent work justified this prediction and several rearrangements of organic hydrazine derivatives have been reported from his Laboratory.[2] It has been shown that the cause of these rearrangements may best be ascribed to the fact that one of the nitrogen atoms of the hydrazine lacks its complete complement of electrons[3] and hence serves as a center of instability. A suitable impulse starts the rearrangement, resulting in this nitrogen atom obtaining its full quota of electrons, probably through the formation of a univalent nitrogen compound in which, as a result of the electron shift, a radical "R" migrates from carbon to the nitrogen atom. Thus, with *sym.*-dibenzoyl hydrazine it[4] was found that the impulse necessary to start the rearrangement was sudden high temperature. When subjected to this treatment the compound was completely decomposed, forming in part very stable five-membered ring compounds and in part undergoing the expected rearrangement. The molecules were here sundered between the nitrogen atoms, one part appearing as the nitrile while the other appeared as *aniline* and *carbon dioxide* (hydrolysis products of phenyl isocyanate), a phenyl group having migrated from carbon to nitrogen. The reaction may be written



$$C_6H_5\ \underset{{}^-O^-}{\underset{\|}{\mp C\ddagger}}{}^-\underset{H^+}{\underset{|}{N}}\mp\pm\underset{H^+}{\underset{|}{N}}{}^-\underset{{}^-O^-}{\underset{\|}{\ddagger C\mp}}\ C_6H_5 = C_6H_5\ \mp C\ddagger{}^-N^= + C_6H_5\ \mp C\ddagger{}^-N\pm + H_2O$$

$$C_6H_5\ \underset{{}^-O^-}{\underset{\|}{\mp C\ddagger}}{}^-N\pm = C_6H_5\ {}^-N\mp\ddagger C\ddagger{}^-O^-$$

$$C_6H_5NCO + H_2O = C_6H_5NH_2 + CO_2$$

or in terms of recent methods of expressing valence,

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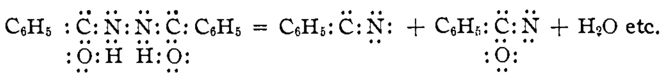
[1] Stieglitz and Senior, THIS JOURNAL, **38**, 2727 (1916).

[2] Stieglitz and Brown, *ibid.*, **44**, 1270 (1922). J. F. Smith, E. C. Gilbert, E. S. West, etc., Doctor's *Dissertations*, University of Chicago, **1922, 1922, 1923.**

[3] Stieglitz, THIS JOURNAL, **44**, 1293 (1922).

[4] Gilbert, Abstract of Theses, *University of Chicago Sci. ser.*, **1**, 177–182 (1923).



$$C_6H_5:\underset{:\ddot{O}:H}{\ddot{C}:\ddot{N}}:\underset{H:\ddot{O}:}{\ddot{N}:\ddot{C}}:C_6H_5 = C_6H_5:\ddot{C}:\ddot{N}: + C_6H_5:\underset{:\ddot{O}:}{\ddot{C}:\ddot{N}} + H_2O \text{ etc.}$$

It has been pointed out by Stieglitz[2,3] that the former method of expressing this and similar reactions has the advantage that it shows definitely that certain atoms are in an unstable condition (in this case the $^-N^{\pm}$) and offer potentially a starting point for a rearrangement. It was, in fact, the similarity of the $^-N^{\pm}$ in hydrazine to the $O^{\pm}$ in hydroxylamine and hydroxamic acids which led Stieglitz to predict the rearrangements subsequently found.[1] The "non-polar" method of graphical representation may, of course, be modified by placing the electron dots nearer to certain atoms than others, thus indicating a degree of "polarity."

Theoretical Part

The present work was undertaken to determine whether experiment would show dissimilarity between the nitrogen atoms in organic hydrazine derivatives in the sense that either is predominantly the one around which rearrangement takes place. The rearrangement of three unsymmetrical disubstituted hydrazines was studied. In each compound one substituent was the benzoyl group, and the other, *p*-toluyl, *p*-chlorobenzoyl and *p*-nitrobenzoyl, respectively. Upon rearrangement the benzoyl group might be the one which forms the univalent nitrogen compound, whence a phenyl group would migrate from carbon to nitrogen, or the substituted phenyl group might form the univalent nitrogen compound or, more likely, both might do so. If analysis of the products should show, for instance, with α-benzoyl-β-*p*-chlorobenzoylhydrazine, the presence of aniline and *p*-chloro-aniline in equimolar proportions, this would indicate complete non-polarity of the two nitrogen atoms, or equal sharing of the electron pair between them. On the other hand, either product might predominate unmistakably. This could be interpreted as showing that, as a statistical average, the electron pair uniting the nitrogen atoms of rearranging molecules is really closer to one than to the other.

This reasoning would lose value if the substituted phenyl group migrates more or less easily than the phenyl group itself. Jones and Hurd[5] in studying hydroxamic acids have found that the apparent ease of migration depends upon the ability of the migrating group to exist as a free radical. However, Stieglitz and his collaborators[1,6,7] found in the rearrangement of three compounds containing the phenyl and the *p*-chlorophenyl radicals that, given equal opportunity (both being attached to the same univalent nitrogen compound), these two radicals seem to migrate with equal ease. Further to minimize this complication the *p*-toluyl derivative was used

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[5] Jones and Hurd, This Journal, **43**, 2422 (1921).

[6] Stieglitz and Leech, *ibid.*, **36**, 272 (1914).

[7] Stieglitz and Vosburgh, *ibid.*, **38**, 2081 (1916).

in one investigation, since the methyl group should have a minimal effect on the ability of the phenyl group to exist as a free radical.

On the other hand, if the theory of Pauling[8] and Lucas[9] is correct concerning the effect of the "*para* bond," it would seem advisable to use *meta* derivatives in which there would be less chance of the effect of the substituent being carried through the carboxyl carbon to the nitrogen. It is hoped that this can be accomplished as a part of the problem.

Results

All three compounds were found to rearrange in the manner to be predicted by the theory of Stieglitz but in no case were the two possible rearrangement products obtained in even approximately equimolar proportions. With α-benzoyl-β-*p*-chlorobenzoylhydrazine, the proportions found were one molecule of aniline to approximately three of *p*-chloro-aniline. With α-benzoyl-β-*p*-toluylhydrazine the proportions were just the reverse. Three molecules of aniline were found for each molecule of *p*-toluidine present. The third substance, α-benzoyl-β-*p*-nitrobenzoylhydrazine, showed the presence of aniline with only a trace of impurity, but recent work indicates[10] that *p*-nitro-aniline decomposes at temperatures required in this work so its absence from the products is not a safe indication that none was formed.

The results from the first two compounds are interesting in the fact that the order of lability here observed is the exact opposite of that noted by Montagne[11] in rearrangements of α-glycols. As mentioned above, however, the work of Stieglitz and others indicates that in rearrangements involving univalent nitrogen derivatives where the phenyl and *p*-chlorophenyl groups have equal opportunity they migrate with equal readiness.

These facts might be taken to indicate that in the compounds investigated by us the unequal and quite constant proportions may be attributed to a definite tendency of one nitrogen atom to be relatively unstable electronically, rather than to a difference in the ease with which the radicals migrate. Just why the nitrogen atom adjacent to the *p*-toluyl radical is relatively stable (as evidenced by the fact that the opposite phenyl radical predominates in the rearrangement products) while the nitrogen atom adjacent to the *p*-chlorobenzoyl radical is stable by the same criterion, the present work does not show. It might be noted in this connection, however, that benzoic acid is intermediate in strength between *p*-chlorobenzoic acid and *p*-toluic acid, and aniline is intermediate in strength as a base between *p*-chloro-aniline and *p*-toluidine.[12]

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[8] Pauling, This Journal, **48,** 1132 (1926).

[9] Lucas, *ibid.*, **48,** 1827 (1926).

[10] Berliner and May, *ibid.*, **47,** 2350 (1925).

[11] Montagne, *Chem. Weekblad,* **17,** 378, 414 (1920).

[12] Scudder, "Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., **1914.**

An investigation of the rearrangement when the two possible rearrangement products would be isomers might be of value but a number of compounds must be studied before any generalization is drawn. The isolation and quantitative determination of the products is a rather time-consuming procedure, hence these are reported at the present time. The writer is deeply indebted to Professor Stieglitz for his kindness in opening this field to him.

Experimental Part

I. α-Benzoyl-β-*p*-toluylhydrazine

Preparation.—Benzoylhydrazine (2 molecular proportions) was finely powdered and suspended in dry benzene, and *p*-toluyl chloride (Eastman Kodak Company) (1 molecular proportion) in benzene was added gradually during vigorous shaking. The mixture was warmed on the water-bath until there was no odor of the chloride and the solid material was collected on a suction filter, washed with ether and dried. The product was powdered and boiled for a minute or two with water to extract the excess of benzoylhydrazine, brought on a filter and thoroughly washed with boiling water. From the filtrate nearly one molecular proportion of the benzoylhydrazine was recovered.

The crude α-benzoyl-β-toluylhydrazine was recrystallized from alcohol with the addition of water, giving a mass of exceedingly fine, white needles. The melting point measured with a short-stem thermometer recently calibrated was 220–221°. This compound is not described in the literature but its synthesis leaves little doubt as to its constitution. The hydrazines are somewhat difficult to burn by the ordinary combustion method, so an analysis was made for the carbon content by the recently published method of Wilde and Lochte,[13] the compound being burned in the oxygen bomb of a calorimeter in the presence of barium hydroxide solution. The carbonate formed was titrated with standard acid.

Anal. Subs., 0.1916: 43.05 cc. of 0.5186 *N* HCl. Calcd. for $C_6H_5CONHNHCOC_6H_4CH_3$: C, 70.87. Found: 69.83.

Rearrangement.—The method used was essentially the same as for *sym.*-dibenzoylhydrazine.[4] The compound was heated in 1g. portions in small Pyrex flasks fitted with air condensers by immersion in a metal bath at a temperature of 450° for a period of five minutes. This was a longer time and higher temperature than was used in the previous work but no charring took place. Temperatures were measured with a calibrated thermocouple.

The cooled reaction mass was extracted with 2 *N* hydrochloric acid and the extract carefully treated as in earlier work to separate the aniline and *p*-toluidine from hydrazine, ammonia and other interfering materials. The presence of *p*-toluidine was shown qualitatively by the color test with ferric chloride,[14] and that of aniline by the hypochlorite test. It was found, incidentally, that the presence of aniline did not interfere with the test for *p*-toluidine, but that hydrazine interfered greatly.

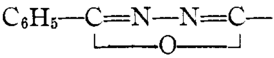
[13] Wilde and Lochte, This Journal, **47,** 440 (1925).

[14] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, **1916**, vol. 1. Biehringer and Busch, *Chem. Z.*, **26,** 1128 (1902).

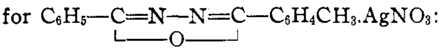
Quantitatively it was found in an average run that the bases extracted from four 1g. rearrangements required 25.3 cc. of 0.1 *N* potassium bromate for bromination (in the presence of sulfuric acid and an excess of sodium bromide). The bromination product melted at 103–105°. Tribromo-aniline melts at 119°, dibromotoluidine (1-amino-2,6-bromo-4-methylbenzene) melts at 73°. The melting points of the mixtures from different rearrangements varied only very slightly, nearly always being 103–105°.

To determine the relative amounts of the two bases present, a series of synthetic mixtures containing varied percentages of tribromo-aniline and dibromotoluidine was made up and the melting points determined. A mixture of 80% of tribromo-aniline by weight and 20% of dibromotoluidine melted at 102–105° and this showed no change when the material was mixed with the brominated products from the rearrangement. Assuming approximately equal solubility for the two bromo compounds in the solution from which they were precipitated, this indicates that about thrice as many phenyl groups migrated from carbon to nitrogen as did tolyl groups.

Identification of Additional Products.—The odor of the nitriles was very prominent as in the case of *sym.*-dibenzoylhydrazine, but no attempt was made to isolate them since there was presumably a mixture.



By analogy also a considerable amount of a compound $C_6H_5\text{—}\underbrace{C{=}N\text{—}N{=}C}_{O}\text{—}C_6H_4CH_3$ was to be expected. To avoid charring, a portion of the hydrazine was heated at 350° for one-half hour, and from this a substance was isolated and purified that melted at 114–115° and formed a complex with silver nitrate which melted with decomposition at 260°. Analysis of this complex indicated that the compound was the expected one.



Anal. Subs., 0.1540, 0.1290: Ag (residue after heating), 0.0518, 0.0343. Calcd. for $C_6H_5\text{—}\underbrace{C{=}N\text{—}N{=}C}_{O}\text{—}C_6H_4CH_3.AgNO_3$: Ag, 26.58. Found: 26.82, 26.59.

Other compounds were not isolated.

The rearrangement thus seems to proceed fundamentally in the same manner as that of the symmetrical hydrazines, since analogous side products are formed.

II. α-Benzoyl-β-*p*-chlorobenzoylhydrazine

Preparation.—A sufficient quantity (2 molecular proportions) of benzoylhydrazine for the ordinary method was not available when this compound was prepared, so the procedure was varied. Benzoylhydrazine (1 molecular proportion) was dissolved in water, and sodium hydroxide (1 molecular proportion) was added. To this, *p*-chlorobenzoyl chloride was added with shaking (1 molecular proportion in ether). The resulting mass was ground in a mortar, collected on a filter and washed with boiling water, a little alcohol and ether. Upon recrystallization from alcohol, the compound melted at 222–223° (uncorr.), using a calibrated thermometer. This compound has not been described in the literature.

Anal. Subs., 0.2184, 0.2155: AgCl, 0.1150, 0.1141. Calcd. for $C_6H_5CONHNHCOC_6H_4Cl$: Cl, 12.92. Found: 13.02, 13.10.

Rearrangement.—This compound gave results at lower temperatures and with shorter heating periods than the others. A temperature of 410° and a time of three minutes were used for heating. Longer time or higher temperatures did not increase the yield or the ratio of the products. The rearrangement products were worked up as in the previous experiment to isolate the bases present. The aniline and *p*-chloro-aniline were thus obtained in ethereal solution which was dried. To this was added a solution of dry hydrogen chloride in ether, precipitating the hydrochlorides in pure white flocs. These were gathered on a filter with suction, dried and weighed. They were then dissolved in water and the bases titrated bromometrically with 0.1 *N* potassium bromate solution. From the weight of hydrochlorides taken and the volume of bromate required, the weight of each constituent was calculated by simultaneous equations. It was assumed that a molecule of aniline required three atoms of bromine and each molecule of *p*-chloro-aniline two, as is the case when they are titrated separately.

Anal. Hydrochloride mixture, 0.040, 0.019: 0.1 *N* $KBrO_3$ required, 12.50 cc., 5.77 cc. Aniline, % by weight, 27.4, 23.4; *p*-chloro-aniline, 72.6, 76.6.

The brominated product melted at 98–103°. Tribromo-aniline melts at 119° and 2,6-bromo-4-chloro-aniline melts at 93°. No qualitative test was known for *p*-chloro-aniline so it was isolated in the pure form to prove its presence. A large amount (30 g.) of the hydrazine was heated in 0.5–1g. portions, cooled and extracted with ether. The ethereal solution was evaporated to small volume, dried with potassium carbonate and the bases were precipitated with anhydrous oxalic acid. The combined oxalates were recrystallized from hot water and the crystals separating out above 40° were rapidly filtered from the solution. These crystals gave practically no test for aniline but the filtrate gave a strong test. The *p*-chloro-aniline oxalate was thus practically all in the crystals first separating. It was decomposed with sodium hydroxide solution and the free base taken up in ether. The ether was evaporated, the residue taken up in hydrochloric acid and the extraction procedure repeated. Upon evaporation of the dried ether solution there remained an oil which solidified upon scratching with a glass rod. It melted at 65°, unpurified. When mixed with pure *p*-chloro-aniline (Eastman Kodak Company), melting at 70°, it melted at 68°. The bromination product melted at 92–93° after recrystallization and did not lower the melting point of material similarly obtained from pure *p*-chloro-aniline. This established its identity.

In this case the chlorophenyl radical seemed to migrate more readily than the phenyl.

Side products were not identified nor isolated in this instance since the rearrangements of all the hydrazines seem to give analogous products whether symmetrical or unsymmetrical.

III. α-Benzoyl-β-*p*-nitrobenzoylhydrazine

This compound was prepared from benzoylhydrazine and *p*-nitrobenzoyl chloride and its rearrangement investigated. It is a slightly yellowish material, melting sharply at 239° (uncorr.). It is less soluble in alcohol than the other compounds studied. It has not been described in the literature.

Upon rearrangement a very small amount of aniline was obtained. The brominated product melted at 112–115°. There was so much decomposition even in an atmosphere of hydrogen that work was discontinued. It has since been found that *p*-nitro-aniline is decomposed at the temperatures necessary, so definite results would have been impossible, though some rearrangement takes place as evidenced by the presence of aniline.

Summary

1. The preparation of three new unsymmetrical hydrazines is described.

2. The intramolecular rearrangement of these compounds is studied with the idea of determining whether the rearrangement may properly be ascribed to a shifting of the electron pair between the nitrogen atoms toward the one or the other, giving in effect the unstable "positive" nitrogen atom postulated in the Stieglitz theory of the rearrangement.

3. Definite and quite constant inequality in the ratio of the two possible rearrangement products indicates that such is a logical conclusion for the compounds studied, the rearrangement taking place predominantly around one nitrogen atom in each case.

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