Summary

1. A simplified procedure for preparing oleic acid of high purity is described.

2. The constants of three specimens of oleic acid, prepared by slight modifications of the procedure, are described.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

A Method for the Synthesis of Phenanthridine Derivatives by an Application of the Stieglitz Rearrangement

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The rearrangements of hypothetical intermediates $\begin{matrix}R_1\\R_2\\R_3\end{matrix}\!\!>\!C\!-\!N\!:$ resulting from appropriate treatment of tertiary methyl nitrogen substituted compounds of the type $\begin{matrix}R_1\\R_2\\R_3\end{matrix}\!\!>\!C\!-\!N\!<\!\begin{matrix}X\\Y\end{matrix}$ where R_1, R_2 and R_3 usually have been aromatic groups and where $-N\!<\!\begin{matrix}X\\Y\end{matrix}$ may be $-N\!<\!\begin{matrix}H\\Br\end{matrix}$,[1] $-N\!<\!\begin{matrix}Cl\\Cl\end{matrix}$,[1] $-N\!<\!\begin{matrix}H\\OH\end{matrix}$,[2] $-N(N_2)$,[3] etc.,[4] have been studied extensively by Stieglitz and co-workers.[5] When R_1 is aliphatic in nature and R_2 and R_3 are aromatic, it was noted that either R_2 or R_3 rather than R_1 migrated to the nitrogen atom and largely on the basis of this fact it has been suggested[5] that the migration of the most electronegative group attached to the carbon atom would in general be favored. The rearrangement of intermediates formed from tertiary methyl nitrogen derivatives, where two of the groups attached to the tertiary carbon atom are linked together, as for example in a 9-substituted 9-fluorylchloroamine (II), has not previously been studied. Here the situation is more complicated, since the possible influence that the five-membered ring might have on the rearrangement must be considered in addition to the electronegativities of the radicals. From the general results of recent x-ray and electron diffraction studies[6] fluorene would be expected to have the configuration shown in Fig. 1.[7] In order that the C–C distances be those shown in the figure the normal valence angle from the benzene ring must be distorted approximately 12 to 13°. Since the linkages attached to the benzene ring are known to be quite rigid the five-membered ring in fluorene, because of the considerable distortion of the normal valence angles, must be appreciably strained. Theoretically a 9-substituted fluoryl nitrogen (III) can be stabilized by undergoing two possible types of rearrangement: (1) opening of

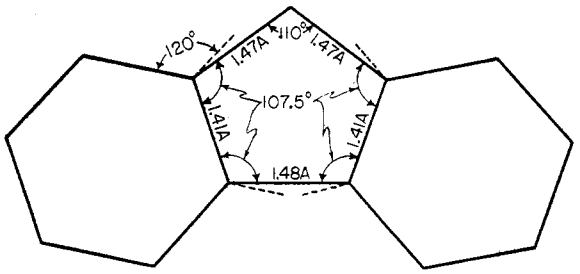
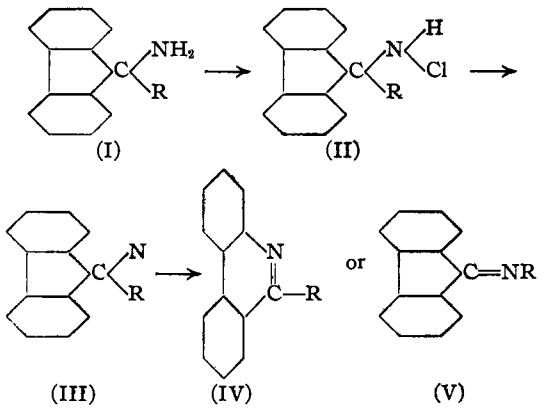


Fig. 1.—Structural formula of fluorene.



(1) Vosburgh, THIS JOURNAL, **38**, 2081 (1916).

(2) Stieglitz and Leech, *ibid.*, **36**, 272 (1914).

(3) Senior, *ibid.*, **38**, 2718 (1916).

(4) Stieglitz and Stagner, *ibid.*, **38**, 2046 (1916); Stieglitz and Senior, *ibid.*, **38**, 2727 (1916); Guthmann and Stieglitz, *J. Org. Chem.*, **1**, 31 (1936).

(5) For a review, which also includes unpublished results, see Porter, "Molecular Rearrangements," Chemical Catalog Co., Inc., New York, 1928, pp. 30–33.

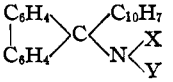
(6) Robertson, *Chem. Rev.*, **16**, 417 (1935); Hendricks, *ibid.*, **7**, 341 (1930).

(7) Stuart "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934, p. 76, has interpreted the results obtained in an x-ray examination of fluorene by Hengstenberg and Mark, *Z. Krist.*, **70**, 283 (1929), as favoring a planar configuration of the molecule. Since this manuscript was written, additional articles on the configuration of fluorene have appeared. Cook and Iball, *Chemistry and Industry*, **55**, 467 (1936), on the basis of crystallographic data consider it to be a non-planar molecule, whereas dipole moment measurements by Hughes, LeFevre and LeFevre, *ibid.*, **55**, 545 and 561 (1936), suggest that fluorene is a flat molecule.

the ring with subsequent reformation to give a phenanthridine derivative (IV) or (2) migration of R to form an imide (V). As will be shown below even when R is more electronegative than the phenylene radical the rearrangement involves primarily the formation of (IV). Thus it follows that the strained condition of the five-membered ring is an important factor, if not the most important one, in directing the course of the rearrangement.

In order that the electronegativities of R in (I) be widely different, both 9-aryl- and 9-alkyl-9-fluorylamines were investigated. Examples chosen as being representative of the two types were the 9-phenyl- (VI), 9-(α-naphthyl) (VII) and 9-methyl-9-fluorylamines (VIII). Although the first two were prepared smoothly by treating the corresponding 9-chloro compounds with ammonia, considerable trouble was encountered in preparing the 9-methyl derivative. A solution of ammonia in toluene gave with 9-bromo-9-methylfluorene, a mixture of amines, consisting of (VIII), an isomer, probably 9-fluorylmethylamine, and a secondary amine, as well as an appreciable amount of polymerized biphenyleneethylene.[8] The difficulty in this case is to be attributed to the relatively labile hydrogen of the neighboring methyl group. It is of interest that a number of these amine hydrochlorides are soluble in benzene and chloroform and that practically all have an anesthetic action on the tongue.[9]

Interaction of hypochlorous acid with alcoholic solutions of (VI), (VII) and (VIII) gave the corresponding chloroamines. The hydrogen and chlorine atoms attached to the nitrogen were most conveniently removed by treating the chloroamine in anhydrous pyridine with sodium methylate at room temperature. Of some significance in possibly offering a clue as to the nature of the intermediate formed in the reaction may be the color changes exhibited by the reaction mixture. During the degradation of 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine a red color developed in the solution and persisted for a short time; however, in the case of the 9-methyl analog the color remained over a period of twelve hours. The rearrangement products formed from 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine are 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-phenanthridine, respectively. In every case the yield was excellent. The structures of 9-methyl- and 9-phenylphenanthridine were established by comparison of these compounds with authentic specimens prepared from acetyl- and benzoyl-*o*-xenylamine according to the method of Morgan and Walls.[10] If the formation of the rearranged compound had been controlled only by a shift of the most electronegative group attached to the tertiary carbon atom, the predicted[11] products from 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine would have been 9-methylphenanthridine, 9-phenyliminofluorene (V where R = C_6H_5) and 9-(α-naphthyl)-iminofluorene (V where R = $C_{10}H_9$). Actually, imino compounds, which could have been easily detected even if formed in minor amounts, were found to be absent.

In order to find if other compounds of the type  could be converted into derivatives of phenanthridine an investigation of the thermal decomposition of 9-(α-naphthyl)-9-fluorylazide was carried out. 9-(α-Naphthyl)-9-fluorylhydrazine (IX) was prepared by the interaction of 9-(α-naphthyl)-9-chlorofluorene with hydrazine. The reaction was not smooth and owing to its lability the hydrazine derivative was difficult to obtain in the pure state. Nitrous acid with (IX) gave the azide. This when heated to 190–200° evolved nitrogen and formed 9-(α-naphthyl)-phenanthridine in good yield. Because of the difficulty encountered in dealing with (IX), the phenanthridine derivatives are much more conveniently prepared by way of the chloroamines.

The compounds to which the Stieglitz rearrangement has been applied in the past yield imides as the end-products of the reaction. Since these are much more easily prepared by other methods the rearrangement was chiefly of theoretical interest. In view of the present work it appears that this rearrangement may also assume considerable practical importance as a method for converting suitable five-membered cyclic compounds to six-membered nitrogen rings.

We are grateful to Mrs. M. S. Sherman for carrying out the analyses recorded in the experimental work.

(8) Wieland, Reindel and Ferrer, *Ber.*, **55**, 3313 (1922).

(9) Nakamura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **14**, 184 (1930), reported the local anesthetic action of 9-fluorylamine hydrochloride.

(10) Morgan and Walls, *J. Chem. Soc.*, 2447 (1931).

(11) From a comparisou of the reactivities of diphenylmethyl with biphenylenemethyl derivatives or of triphenylmethyl with phenylfluoryl derivatives, the phenyl group would be expected to be more electronegative than the phenylene radical.

Experimental

9-Phenyl-9-fluorylamine, its Derivatives and its Conversion to 9-Phenylphenanthridine

9-Phenyl-9-fluorylamine.—A mixture of 10 g. of 9-phenyl-9-chlorofluorene and about 15 cc. of liquid ammonia was heated in a sealed tube at 60° for several hours.[12] An oil separated and upon evaporation of the ammonia a sirupy residue remained. Owing to its marked sluggishness in crystallizing, the amine was purified only with difficulty by numerous crystallizations from either petroleum ether or 75% ethyl alcohol. It separated as colorless prisms melting at 82°[13] and was very soluble in most organic solvents.

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.67; H, 5.88; N, 5.45. Found: C, 88.85; H, 6.15; N, 5.47.

9-Phenyl-9-fluorylamine was not hydrolyzed when heated at 100° for one hour with 20% hydrochloric acid, whereas under similar conditions triphenylmethylamine yielded an appreciable amount of the carbinol. The amine was also recovered unchanged after treatment with a solution of potassium permanganate in purified acetone in the presence of anhydrous sodium sulfate[14] for several days at room temperature. The stability of 9-phenyl-9-fluorylamine toward oxidizing agents is further shown by its recovery after refluxing for two hours an alcoholic solution to which had been added bromine and sodium ethylate.[15]

The hydrochloride was prepared by passing dry hydrogen chloride into a benzene solution of the amine; it crystallized from dilute hydrochloric acid as microscopic prisms melting at 310° with decomposition.

Anal. Calcd. for $C_{19}H_{15}N \cdot HCl$: C, 77.66; H, 5.49; N, 4.88. Found: C, 78.00; H, 5.32; N, 4.93.

The acetyl derivative was secured in the usual manner and crystallized from alcohol as microscopic prisms, m. p. 232°.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.24; H, 5.72; N, 4.68. Found: C, 83.79; H, 5.92; N, 4.65.

The monobromoamine was prepared according to the method of Vosburgh.[1] The amounts of reagents used were 2.60 g. of 9-phenyl-9-fluorylamine, 1.62 g. of bromine, and 3.22 cc. of an aqueous solution containing 0.41 g. of sodium hydroxide. The chloroform solution was concentrated and the sirupy residue dissolved in 30 cc. of warm, low-boiling ligroin. Upon cooling a pale yellow microcrystalline material separated; yield 1.60 g. After recrystallization it melted at 105° (dec.).

Anal. Calcd. for $C_{19}H_{14}NBr$: Br, 23.78. Found: Br, 24.09.[16]

The monochloroamine was prepared by using a method similar to that of Hellerman and Sanders.[17] A solution of 2.72 g. of 9-phenyl-9-fluorylamine hydrochloride in 75 cc. of 95% ethyl alcohol[18] was treated at 0° with 10 cc. of cold 0.926 *N* potassium hypochlorite. Minute colorless crystals immediately precipitated. The reaction mixture was shaken in an ice-bath for thirty minutes and cold water added to ensure complete precipitation. The colorless solid was collected, washed with cold water and dried *in vacuo* over phosphorus pentoxide; yield, practically quantitative. The monochloroamine separates from hexane as colorless prisms; m. p. 102°.

Anal. Calcd. for $C_{19}H_{14}NCl$: C, 78.20; H, 4.84; N, 4.80; Cl, 12.16. Found: C, 77.68; H, 4.84; N, 4.58; Cl, 12.21.

The dichloroamine was synthesized by passing an excess of chlorine into an alcoholic solution of 9-phenyl-9-fluorylamine. It was obtained in good yield and after crystallizing from ligroin melted at 150° (dec.). This material is unusually stable and may be kept for several years without any apparent alteration.

Anal. Calcd. for $C_{19}H_{13}NCl_2$: C, 69.94; H, 4.02; N, 4.30: Cl, 21.75. Found: C, 70.09; H, 4.43; N, 4.35; Cl, 20.33.

Di-(9-phenyl-9-fluoryl)-amine was obtained as a by-product in the following experiment. Forty grams of 9-phenyl-9-chlorofluorene and a large excess of dry ammonia were heated in a steel bomb at 180° for four hours. The reaction product, after evaporation of the ammonia, was triturated with 100 cc. of alcohol[19] and the residue extracted with toluene. The hot toluene filtrate was treated with an equal volume of hot alcohol and on cooling the secondary amine separated. Several crystallizations from a solution of alcohol and toluene gave 3 g. of glistening, elongated, hexagonal plates, m. p. 230°.

Anal. Calcd. for $C_{38}H_{27}N$: C, 91.71; H, 5.47; N, 2.82. Found: C, 91.89; H, 5.62; N, 2.90.

Conversion of 9-Phenyl-9-fluorylchloroamine to 9-Phenylphenanthridine.—A solution of 2 g. of the chloroamine in 20 cc. of anhydrous pyridine[20] was treated with

(12) 9-Phenyl-9-chlorofluorene is much less reactive toward ammonia than triphenylmethyl chloride. Considerable heat was generated when the latter was treated with liquid ammonia at room temperature. Upon slow cooling beautiful crystals of triphenylmethylamine separated; from the interaction between 10 g. of triphenylmethyl chloride and 15 cc. of liquid ammonia 9.3 g. of the amine was isolated. Triphenylmethylamine was recovered unchanged after being subjected to a solution of ammonium chloride in ammonia for several days at room temperature. Evidently the equilibrium is shifted to a remarkable extent by an appreciable temperature change as Kraus and Rosen, THIS JOURNAL, **47**, 2739 (1925), reported that at the temperature of liquid ammonia: (1) triphenylmethyl chloride was ammonolyzed to the amine only to a slight extent and (2) the amine was converted to triphenylmethyl chloride by ammonium chloride.

(13) All melting points are corrected.

(14) Goldschmidt and Beuschel [*Ann.*, **447**, 197 (1926)] used similar conditions in dehydrogenating 9-fluorylamine to 9-iminofluorene.

(15) These conditions were used by Hellerman and Sanders, THIS JOURNAL, **49**, 1745 (1927), to dehydrogenate diphenylmethylamine.

(16) The compounds containing active halogen were analyzed by titrating in chloroformic solution against a standardized solution of sodium thiosulfate in the presence of hydriodic acid.

(17) Hellerman and Sanders, THIS JOURNAL, **49**, 1745 (1927), and private communications from Dr. Hellerman which have facilitated the work immensely.

(18) Water is usually used as the medium for the preparation of the monochloroamines. However, when water was used in the above halogenation, the reaction product was always contaminated with some unchanged amine. The use of alcohol, in which the amine hydrochloride was appreciably soluble, overcame this difficulty.

(19) From the alcoholic extract after suitable manipulation, 24.5 g. of pure 9-phenyl-9-fluorylamine hydrochloride was obtained.

(20) Absolute alcohol as a solvent resulted in the formation of the amine.

an excess of dry sodium methylate.[21] Considerable heat was generated and the solution developed a light red color which persisted for several minutes and then changed to a straw yellow. After standing overnight the pyridine was distilled from the reaction mixture under diminished pressure, the residue triturated with dry ether and the resulting extract treated with dry hydrogen chloride in order to precipitate the base as the salt. The hydrochloride was exceedingly soluble in water and crystallized as straw colored needles containing water of crystallization; m. p. 95–100° and 226°.[22] 9-Phenylphenanthridine was regenerated from the salt and crystallized from petroleum ether; colorless glistening plates, m. p. 107–108°.

Anal. Calcd. for $C_{19}H_{13}N$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.53; H, 5.36; N (Dumas), 5.48.

Comparison of its properties with those of a specimen synthesized according to the method of Morgan and Walls[10] showed them to be identical; a melting point of the mixture was not depressed.

9-(α-Naphthyl)-phenanthridine

9-(α-Naphthyl)-9-fluorylamine was prepared by heating 9-(α-naphthyl)-9-chlorofluorene (36 g.)[23] with dry ammonia in a steel bomb at 80° for forty hours. The ammonia was evaporated and the amine separated from the residue by dissolving in boiling benzene. After decolorizing with charcoal and numerous recrystallizations from solutions of benzene and alcohol, the amine melted at 186°; colorless prisms; yield 13.4 g.

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.86; H, 5.58; N, 4.56. Found: C, 89.92; H, 5.66; N, 4.52.

The hydrochloride was soluble in benzene; m. p. 271° (dec.).

Anal. Calcd. for $C_{23}H_{17}N \cdot HCl$: N, 4.1. Found: N, 3.9.

The chloroamine was obtained in a practically quantitative yield and separated from a solution of benzene and hexane as beautiful colorless prisms; m. p. 133–135° (dec.).

Anal. Calcd. for $C_{23}H_{16}NCl$: C, 80.80; H, 4.72; N, 4.10; Cl, 10.38. Found: C, 81.11; H, 5.03; N, 3.91; Cl, 10.00.

9-(α-Naphthyl)-phenanthridine was prepared from 9-(α-naphthyl)-9-fluorylchloroamine (1.5 g.) in the same manner as that described for the phenyl analog. The reaction mixture in this case was not as highly colored. After removal of the volatile matter, the phenanthridine derivative was extracted with ether. It crystallized from petroleum ether in clusters of irregularly shaped colorless crystals; yield 1.1 g.; m. p. 123.5°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.45; H, 4.96; N, 4.59. Found: C, 90.37; H, 5.08; N (Dumas), 4.59.

The hydrochloride crystallized from boiling water as cream colored needles with water of crystallization melting at 120–125°; the anhydrous product melted at 224° (dec.).

Anal. Calcd. for $C_{23}H_{15}N \cdot HCl$: C, 80.80; H, 4.72; N, 4.10. Found: C, 80.97; H, 5.10; N, 3.99.

The picrate was prepared in and recrystallized from alcohol; yellow prisms; m. p. 251°.

Anal. Calcd. for $C_{29}H_{18}N_4O_7$: C, 65.15; H, 3.40. Found: C, 65.43; H, 3.58.

9-Methyl-9-fluorylamine and 9-Methylphenanthridine

Interaction of 9-Methyl-9-bromofluorene with Ammonia.—A solution of 37 g. of 9-methyl-9-bromofluorene[9] in 30 cc. of dry toluene and 30 g. of liquid ammonia was heated in a steel bomb at 75° for twenty hours. After removing the ammonia, the insoluble fraction was collected, thoroughly washed with 150 cc. of toluene, and identified as the polymeric form of biphenyleneethylene; wt. 6.9 g.; m. p. 270°.[8]

Anal. Calcd. for $(C_{14}H_{10})_x$: C, 94.34; H, 5.66. Found: C, 93.94; H, 5.84.

The filtrate and washings were combined and acidified with an alcoholic solution of hydrogen chloride. On heating, the slight precipitate that formed dissolved and the hot solution was concentrated at reduced pressure. Fractionation of the resulting residue was effected by extraction with water; further manipulation of the aqueous insoluble portion (A) is described below. The aqueous extract was concentrated to about 75 cc. and treated with an equal volume of hydrochloric acid. Upon cooling the hot solution a mixture of colorless crystalline amine hydrochlorides (9.5 g.) separated. Efforts to resolve the mixture into its components by repeated crystallization from water failed. Advantage was taken of the differential solubility of the two amine hydrochlorides in chloroform; 9-methyl-9-fluorylamine hydrochloride was quite soluble in contrast to the other amine hydrochloride which was practically insoluble. To the chloroformic extract of the mixture was added benzene; beautiful needles separated; m. p. 266° (dec.).

Anal. Calcd. for $C_{14}H_{13}N \cdot HCl$: C, 72.55; H, 6.09; N, 6.05. Found: C, 72.62; H, 6.12; N, 5.83.

This salt was decomposed in the usual manner to liberate the free base. **9-Methyl-9-fluorylamine** was recrystallized from ligroin and separated as colorless needles melting at 96°.

Anal. Calcd. for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.18. Found: C, 86.19; H, 6.80; N, 7.22.

On interacting with nitrous acid, 9-methyl-9-fluorenol was formed in good yield; m. p. and mixed m. p. 176°.

The chloroformic insoluble hydrochloride (*ca.* 1.0 g.) was crystallized from dilute hydrochloric acid; irregular

(21) 9-Phenylphenanthridine was also prepared by treating 9-phenyl-9-fluorylbromoamine in ether with freshly precipitated silver oxide [Willstätter and Müller, *Ber.*, **41**, 2580 (1908)] in the presence of preheated sodium sulfate. Under these conditions the reaction, probably because some amine is regenerated, was not as smooth as the above, since numerous recrystallizations were required to purify the phenanthridine derivative.

(22) Pictet and Hubert [*ibid.*, **29**, 1182 (1896)] reported it to melt at 95–96 and 220°.

(23) In working up 9-α-naphthyl-9-fluorenol prepared by a Grignard reaction [Wanscheidt and Moldavski, *ibid.*, **63**, 1362 (1930)] it was noticed that the unchanged fluorenone combined with the fluorenol derivative to form a relatively stable deep yellow crystalline molecular compound melting at 109–110°. This view regarding the nature of the product was confirmed by preparing it from an alcoholic solution containing equimolal amounts of fluorenone and 9-(α-naphthyl)-9-fluorenol. Schlenk and Herzenstein, *Ann.*, **372**, 27 (1910), reported the formation of a similar type of compound between fluorenone and 9-*p*-diphenyl-9-fluorenol.

shaped crystals with marked twinning in the form of crosses; m. p. 294° (dec.).

Anal. Calcd. for $C_{14}H_{13}N \cdot HCl$: C, 72.55; H, 6.09; N, 6.05. Found: C, 72.79; H, 6.24; N, 5.96.

The free base, which is considered to be **9-fluorylmethylamine,** was prepared from the salt and crystallized from ether as colorless needles melting at 99–100°; when mixed with 9-methyl-9-fluorylamine the melting point was depressed considerably. There was insufficient material for further purification and for analysis.

The aqueous insoluble fraction (A) was triturated with benzene and from this benzene extract there was recovered 0.9 g. of a colorless crystalline hydrochloride; m. p. 263–265° (dec.). Treatment of the salt with liquid ammonia gave the free base, which was recrystallized from a solution of 20% benzene and 80% alcohol; colorless prisms; m. p. 166°.

Anal. Calcd. for $C_{25}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.19; H, 6.44; N, 3.67.

This analysis agrees with that required for a disubstituted amine. Of the number of secondary amines possible, that which seems to agree best with the facts is **di-(9-methyl-9-fluoryl)-amine.** Thus the peculiar solubility of the salt in benzene suggests that in this solvent it is present in the dissociated form and that the base is therefore a weak one (as compared, for example, to di-(9-fluorylmethyl)-amine which would be expected to be much more strongly basic).[24] The above suggested structure for the secondary amine is in accord with the expectation that it would be formed from the amine present in largest amounts in the reaction mixture.

9-Methylphenanthridine.—9-Methyl-9-fluorylchloroamine was prepared from the hydrochloride (2.1 g.) of 9-methyl-9-fluorylamine. It was isolated as a sirup and gave a strong test for active halogen. Owing to its lability and to the difficulty in purifying it, the product in this crude form was subjected to the rearrangement conditions. When the pyridine solution of the chloramine was treated with sodium methylate a deep reddish-purple color developed and persisted until the reaction mixture was worked up. After twelve hours the pyridine was removed under diminished pressure, and the residue extracted with petroleum ether. The extract was concentrated and the material remaining dissolved in alcohol. Addition of hydrogen chloride precipitated the hydrochloride of 9-methylphenanthridine; yield 1.3 g., m. p. 287°. This was converted to the free base, which was purified by sublimation *in vacuo;* m. p. 83°. The melting point was not depressed when the material was mixed with a specimen prepared from acetyl-*o*-xenylamine.[10]

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.00; H, 5.74; N, 7.28. Found: C, 86.93; H, 5.76; N, 7.13.

The picrate was prepared and crystallized from a solution of nitrobenzene and alcohol as yellow prisms; m. p. 250° (dec.).[25]

(24) In this connection it is pertinent to call attention to solubility of 9-methyl-9-fluorylamine hydrochloride in chloroform, as compared to the insolubility of the supposed 9-fluorylmethylamine hydrochloride.

(25) Pictet and Hubert, *Ber.*, **29**, 1182 (1896), reported it to decompose at 233°.

Conversion of 9-(α-Naphthyl)-9-fluorylazide to 9-(α-Naphthyl)-phenanthridine

9-(α-Naphthyl)-9-fluorylhydrazine.—Much trouble was met in attempting to prepare this type of compound. In preliminary experiments it was apparent that 9-phenyl-9-fluorylhydrazine has less favorable properties than the 9-(α-naphthyl) analog and the investigation was therefore directed toward the preparation of the latter. Owing to the unstable nature of the free base, which we were unsuccessful in preparing, the work was limited to the preparation and purification of the hydrochloride. Of the numerous experiments carried out the following directions for preparing and purifying the hydrochloride gave the best results; even in this case the salt was not quite analytically pure.

To a cooled, vigorously agitated mixture of 7 cc. of 100% hydrazine hydrate (a large excess in order to minimize the formation of the hydrazo compound) and 75 cc. of acetonitrile was gradually added, over a period of several hours, 13 g. of 9-(α-naphthyl)-9-chlorofluorene. Considerable heat was generated and after standing overnight in the ice chest the two liquid layers of the reaction mixture were separated. The solvent was removed from the upper one by distillation at room temperature under diminished pressure. The resulting residue after triturating with water was practically colorless and had an amorphous appearance; m. p. 98° with dec. and previous sintering. Conversion to the hydrochloride was effected in the manner described by Wieland[26]; yield 10 g. Repeated recrystallizations from solutions of toluene and chloroform and from solutions of alcohol and ether gave colorless prisms melting at 217° (dec.).

Anal. Calcd. for $C_{23}H_{18}N_2 \cdot HCl$: C, 76.96; H, 5.34; HCl, 10.17. Found: C, 76.02; H, 5.93; HCl (by titration), 9.43.

9-(α-Naphthyl)-9-fluorylazide was prepared in the usual manner by treating a slightly acidified aqueous alcoholic solution of the above hydrazine hydrochloride with an aqueous solution of sodium nitrite. The azide separated and was recrystallized from hexane and from 75% alcohol. It crystallized as long needles. The product was desolvated by heating in the molten state under diminished pressure; even under these conditions the process was an extremely slow one; m. p. 133°.

Anal. Calcd. for $C_{23}H_{15}N_3$: C, 82.85; H, 4.54; N, 12.65. Found: C, 82.89; H, 4.72; N, 12.23.

9-(α-Naphthyl)-phenanthridine.—The azide (0.2 g.) was decomposed by heating at 194° for ten minutes. The reaction product was extracted with boiling dilute hydrochloric acid. Upon cooling the acidic extract deposited 0.15 g. of an almost colorless hydrochloride. This was recrystallized from water and after drying at 100° melted at 224° (dec.). The free base was prepared from the hydrochloride and crystallized from hexane; m. p. 124°. The melting point of a mixture of this material with 9-(α-naphthyl)-phenanthridine prepared in a previous section was not depressed.

Summary

The Stieglitz rearrangement has been utilized

(26) Wieland, *Ber.*, **42**, 3025 (1909).

to develop a new and practical method for the preparation of nitrogen ring compounds of the phenanthridine type. 9-Methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine have been converted to 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-phenanthridine. That this method is not restricted to the halogenoamines is indicated by the thermal conversion of 9-(α-naphthyl)-9-fluorylazide to 9-(α-naphthyl)-phenanthridine. The primary factor in directing the course of the rearrangement of the intermediate free radical seems to be the highly strained condition of the five-membered ring in biphenylenemethylene, rather than the electronegativities of the radicals attached to the tertiary carbon atom.

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The Adjacent Charge Rule and the Structure of Methyl Azide, Methyl Nitrate, and Fluorine Nitrate

BY LINUS PAULING AND L. O. BROCKWAY

With the recognition of the fact that in many cases the normal state of a molecule cannot be represented satisfactorily by a single valence-bond structure of the Lewis type but can be approximated by a combination of several such structures (among which it is said to resonate) there arose the problem of determining for each resonating molecule the magnitudes of the contributions of various reasonable structures. Information regarding these magnitudes is being obtained in many ways, such as from the interpretation of experimental values of interatomic distances, force constants, electric dipole moments, etc., and some progress is being made in the formulation of empirical rules expressing this information in a succinct form. Four years ago it was pointed out[1] that the observed moment of inertia of nitrous oxide corresponds to resonance between the structures $:\bar{\ddot{N}}{=}\overset{+}{N}{=}\ddot{O}:$ and $:N{\equiv}\overset{+}{N}{-}\ddot{\underset{\cdot\cdot}{O}}:$, the third reasonable structure, $:\ddot{\underset{\cdot\cdot}{\bar{N}}}{-}\overset{+}{N}{\equiv}O:$, making no appreciable contribution, whereas the closely similar molecule carbon dioxide resonates among all three analogous structures; and in explanation of this unexpected fact the suggestion was advanced that, in general, structures in which adjacent atoms have electrical charges of the same sign are much less important than other structures, the diminution in importance resulting from the increase in coulomb energy corresponding to the adjacent charges. This *adjacent charge rule* was reported also to apply to the methyl azide molecule.[2] We have now reinvestigated methyl azide by electron diffraction and have similarly studied methyl nitrate and fluorine nitrate. The configurations found for all of these substances are those predicted on the basis of the rule.

Methyl Azide.—In our earlier investigation of methyl azide[2] it was concluded that the molecules contain a linear azide group with dimensions corresponding to resonance between the structures $H_3C{-}\ddot{N}{=}\overset{+}{N}{=}\bar{\ddot{N}}:$ and $H_3C{-}\ddot{\underset{\cdot\cdot}{\bar{N}}}{-}\overset{+}{N}{\equiv}\ddot{N}:$. The photographs used in this work were very light, showing only one measurable apparent maximum and one minimum. With improved technique we have now obtained photographs of methyl azide showing five well-defined apparent maxima, the interpretation of which has led to the verification and refinement of the earlier results. The

TABLE I

METHYL AZIDE

Max.	Min.	I	s, obsd	s, calcd. for model H-120°	s, calcd. for model I-120°	C-N for model H-120°, Å.	C-N for model I-120°, Å.
1		5	6.17	6.15	6.28	1.465	1.496
2		2	8.32	8.26	8.36	1.460	1.477
	3		10.20	9.70	10.15	1.397	1.461
3		3	11.49	11.49	11.77	1.470	1.507
	4		12.75	12.47	12.70	1.437	1.464
4		1	13.81	13.68	13.66	1.455	1.454
	5		15.54	15.20	15.38	1.438	1.455
5		1	16.77	17.12	17.40	1.500	1.524
				Average C-N		= 1.453	1.480
				N-N′		= 1.246	1.229
				N′-N″		= 1.087	1.107

Averaged results: C-N = 1.47 ± 0.02 Å.
N-N′ = 1.24 ± 0.02 Å.
N′-N″ = 1.10 ± 0.02 Å.
Angle C-N-N = 120 ± 5°

(1) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 498 (1932).
(2) L. O. Brockway and L. Pauling, *ibid.*, **19**, 860 (1933).