FURTHER EVIDENCE FOR THE DIENONE-IMINE INTERMEDIATE IN THE FISCHER INDOLE SYNTHESIS

AN UNCATALYZED FISCHER REACTION UNDER MILD CONDITIONS[1]

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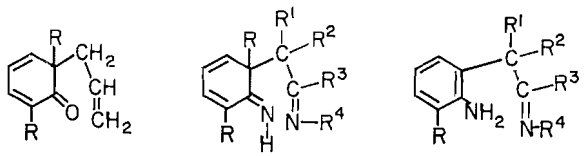
ABSTRACT

Evidence has been presented for the transient formation of a dienone-imine intermediate in the Fischer indole synthesis analogous to the dienone intermediate found in the Claisen rearrangement. The isolation of methylamine hydrochloride, 8-chloro-1,2,3,4-tetrahydrocarbazole, and 5-amino-6-chloro-9-methyl-1,2,3,4-tetrahydrocarbazole from the room temperature, uncatalyzed condensation between cyclohexanone and N′-methyl-2,6-dichlorophenylhydrazine under enamine synthesis conditions can be rationalized only on the assumption of the occurrence of a dienone-imine intermediate. An example of a facile, uncatalyzed Fischer cyclization at room temperature has been described.

INTRODUCTION

Carlin and Fisher (1) have pointed out the close analogy between the mechanism of the Claisen rearrangement (2, 3) and the Robinson mechanism (4) for the Fischer indole synthesis.* A discussion of the Fischer indole synthesis with particular reference to the mechanistic aspect has appeared recently (5). Although the dienone intermediate (I, R = CH_3) has been isolated as the Diels–Alder adduct (6) and has actually been prepared and shown to be a true intermediate in the Claisen rearrangement (7, 8), isolation of the analogous dienone-imine (II, R = CH_3) from the Fischer reaction has not yet been achieved.



I II III

There are, however, several instances in which a compound of structure III (R = H) has actually been obtained from the Fischer cyclization. Such a compound (III) could quite logically arise from a dienone-imine precursor (II, R = R^4 = H) in which aromatization occurred very rapidly and unavoidably by a tautomeric shift of the hydrogen atom. The isolation of the sparingly soluble hydrochloride of the compound α-amino-β-(*o*-aminophenyl)-γ-butyrolactone (IV) from the cyclization of α-keto-γ-butyrolactone phenylhydrazone (9, 10) and of 3-acetylamino-2-(*o*-aminophenyl)-butene-2 (V) from the treatment of 2-(N,N′-diacetyl-β-phenylhydrazino)-butene-2 (VIII) with hot aqueous potassium hydroxide (11) are specific cases which illustrate this point.

[1]*Taken from the thesis of F. P. Robinson submitted to the Faculty of Graduate Studies of the University of Alberta in partial fulfillment of the requirements for the degree of Doctor of Philosophy.*

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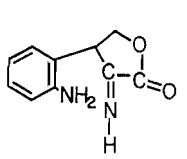
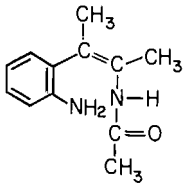
**A. A. Arbuzov and Y. P. Kitaev, J. Gen. Chem. U.S.S.R. 27, 2388 (1957), have stated that both the Claisen rearrangement and the Fischer indole synthesis are specific cases of the general intramolecular rearrangement in a polarized 1,6-conjugated system.*



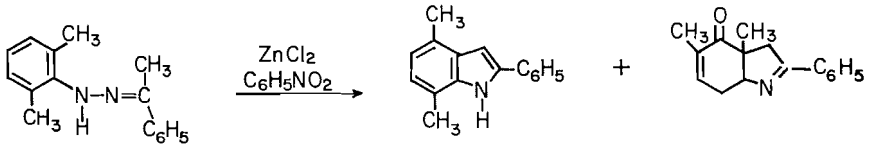
IV



V

There have been reported, also, a number of products obtained from the reaction of phenylhydrazones under Fischer cyclizing conditions which are readily explained only on the basis of a dienone-imine intermediate (II). Examples of these are the isolation of 5,7-dihaloindoles resulting from the halogen migration and interchange during the reaction of 2,6-dihalophenylhydrazones in the presence of zinc halides (1, 12, 13), and of both 2-phenyl-3*a*, 5-dimethyl-3*a*,4,7,7*a*-tetrahydro[3H]pseudoindolone-4 (VI) and the methyl migration product 4,7-dimethyl-3-phenylindole (VII) from the reaction of acetophenone 2,6-dimethylphenylhydrazone in the presence of zinc chloride (14) (equation *a*).

(a)



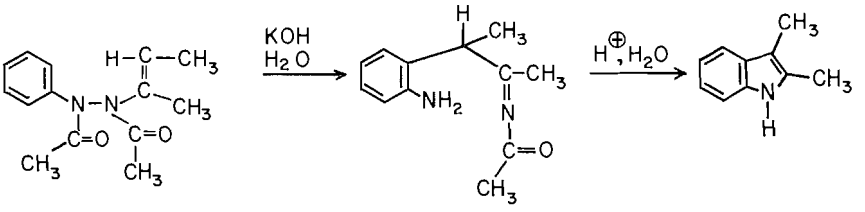
VII VI

An attempt was made by Carlin *et al.* (15) to trap the dienone-imine "intermediate" in the zinc chloride catalyzed reaction of ethyl pyruvate 2,6-dimethylphenylhydrazone as the Diels–Alder adduct with maleic anhydride as had been done by Conroy and Firestone for the Claisen rearrangement of allyl 2,6-dimethylphenyl ether (6). However, no product was obtained indicative of such an adduct, a result considered to be due to the much more rapid conversion of the dienone-imine intermediate into the indole (15). To our knowledge, no other attempt to secure the dienone-imine intermediate has been reported.

This paper describes the isolation from the Fischer indole synthesis of certain products, the formation of which can be rationalized only on the basis of a dienone-imine intermediate.

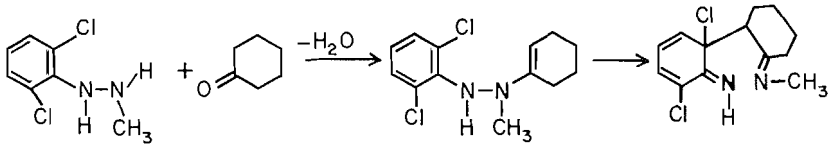
RESULTS AND DISCUSSION

The isolation from the acid-catalyzed reaction between methyl ethyl ketone phenylhydrazone and acetic anhydride (11) of 2-(N,N′-diacetyl-β-phenylhydrazino)-butene-2, (VIII), which is the diacetylated enamine considered to be the first stage of the Robinson mechanism for the Fischer indole synthesis (4), has suggested the preparation of enamines as starting materials for indole formation. Since such an enamine is one step along in the accepted scheme for Fischer indole synthesis, subsequent conversion of this enamine to an indole might be relatively easily accomplished. Suvorov (11) has shown that acid catalysis is not necessary, although probably helpful, for the second stage of the Fischer indole synthesis; that of conversion of the enamine (VIII) to (IX), the compound analogous to the product of ortho benzidine rearrangement. He found that (IX) was

(b) 

VIII IX

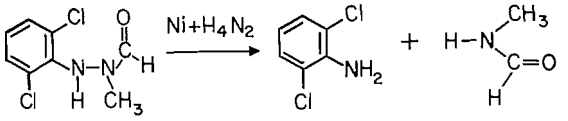
obtained by heating the intermediate diacetyl compound (VIII) in refluxing aqueous sodium hydroxide (equation *b*). Thus, if a suitable enamine were prepared, it might be readily converted to the indole merely by exposure to moderate heat. If, in addition, the 2 and 6 positions of the phenyl group are blocked by substituents which would prevent rapid aromatization (II → III, R = H), it might thus be possible to form, and either retain or trap, the dienone-imine under mild conditions (equation *c*). For the present

(c) 

X XI

work, the 2,6-dichlorophenylhydrazine rather than the 2,6-dimethylphenylhydrazine was chosen in view of the latter's well-known instability in air (14). To ensure enamine formation, this hydrazine was converted to the N′-methyl derivative (X).

Formylation of 2,6-dichlorophenylhydrazine (1) with formamide in acetic acid (16) rather than with 50% formic acid (17) gave a good yield of N′-formyl-2,6-dichlorophenylhydrazine which, even with excess methyl sulphate, gave only the monomethyl derivative, N′-formyl-N′-methyl-2,6-dichlorophenylhydrazine (XII). Elemental analysis and a nuclear magnetic resonance spectrum agreed with this structure. Additional proof that the methyl group was on the nitrogen atom remote from the phenyl substituent was obtained by reduction of the formylated hydrazine with Raney nickel and hydrazine (18) to 2,6-dichloroaniline (equation *d*).

(d) 

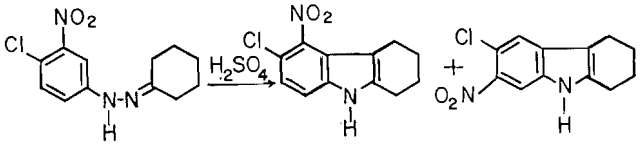
XII

When N′-methyl-2,6-dichlorophenylhydrazine was condensed with cyclohexanone under conditions advocated for enamine preparation (19), using a Dean–Stark apparatus (20) to collect the water removed azeotropically by boiling benzene, a precipitate of methylamine hydrochloride appeared. From the residual dark oil obtained after removal

of the hydrochloride and the benzene, no pure compound could be isolated. However, the formation of methylamine hydrochloride indicated that a reaction had occurred, in all likelihood forming an indole, since the β-nitrogen atom in hydrazones is eliminated as ammonia during the Fischer cyclization to indoles (21, 32). When the enamine formation was repeated, but this time, to avoid decomposition of products, with the reaction temperature maintained at about 20° by removal of the benzene and water under vacuum with a rotary evaporator, methylamine hydrochloride was again obtained (~15% yield). The residual yellow oil, left after removal of the precipitate and the solvent, when passed through a column of neutral alumina with Skellysolve B as eluant, afforded a 14% yield of a compound which proved to be identical in all respects with an authentic sample of 8-chloro-1,2,3,4-tetrahydrocarbazole (12). Further elution with a 1:1 mixture of Skellysolve B and benzene gave a compound whose elemental analysis and n.m.r. spectrum agreed with the structure 5-amino-6-chloro-9-methyl-1,2,3,4-tetrahydrocarbazole (XVI).

An authentic sample of this compound was prepared from the mixture obtained by Plant and Rosser's (22) cyclization of cyclohexanone 4-chloro-3-nitrophenylhydrazone. Of the two possible products of this reaction, 6-chloro-5-nitro-1,2,3,4-tetrahydrocarbazole and 6-chloro-7-nitro-1,2,3,4-tetrahydrocarbazole (equation *e*), one was later identified (23) as the 6-chloro-5-nitro-1,2,3,4-tetrahydrocarbazole (XIII) by its reduction with tin

(e)

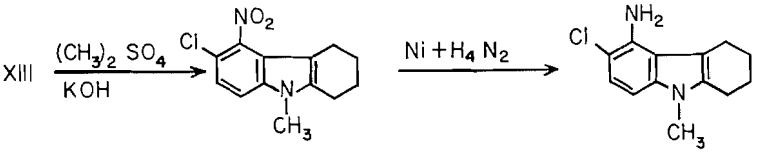


XIII XIV

and hydrochloric acid to the known 5-amino-1,2,3,4,4*a*,9*a*-hexahydrocarbazole. The other isomer, (XIV), must then be the 6-chloro-7-nitrotetrahydrocarbazole.

Compound (XIII) was first converted to the N-methyl derivative (XV) and then reduced with Raney nickel and hydrazine (24) to 5-amino-6-chloro-9-methyl-1,2,3,4-tetrahydrocarbazole (XVI) (equation *f*).

(f)

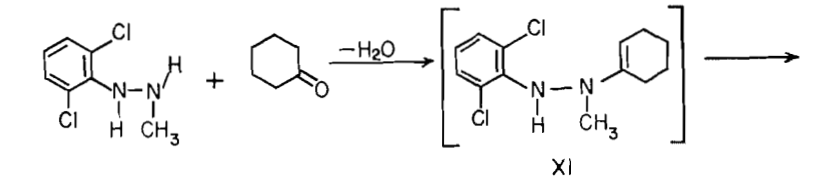


XV XVI

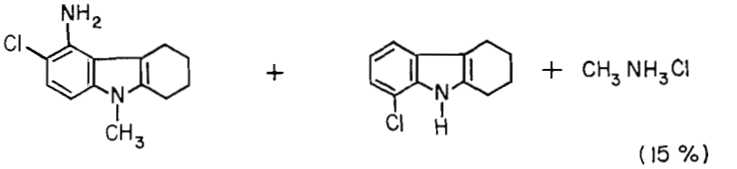
The overall reaction between cyclohexanone and N′-methyl-2,6-dichlorophenylhydrazine can be represented by equation *g*. No enamine corresponding to structure (XI) was obtained.

In our opinion the isolation of both (XVI) and (XVII) is further evidence in favor of the dienone-imine intermediate. Such an intermediate readily explains the formation of (XVI) as shown by the following scheme (equation *h*).

(g)

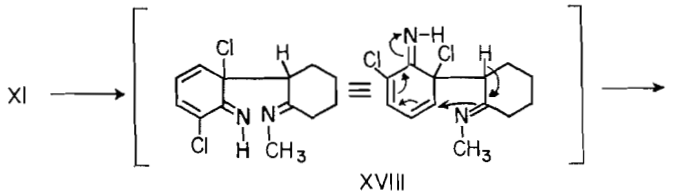


XI

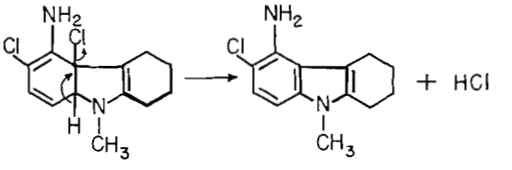


XVI (21 %) XVII (14 %) (15 %)

(h)



XVIII

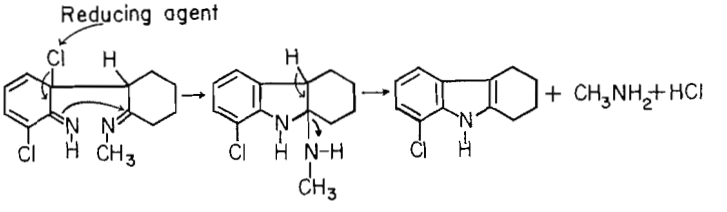


XVI

The mechanism of the formation of compound (XVI) is analogous to that proposed (14) for the formation of 2-phenyl-3*a*,5-dimethyl-3*a*,4,7,7*a*-tetrahydro[3H]pseudoindolone (VI) from the zinc chloride catalyzed cyclization of acetophenone 2,6-dimethylphenylhydrazone.

The formation of the product (XVII) can also be explained on the basis of the dienone-imine intermediate (XVIII) if one postulates that a readily oxidizable substance in the reaction mixture permits the reductive removal of the allylic halogen atom in the dienone-imine intermediate via the scheme shown in equation *i*. That the presence of oxidizable

(i)



substances does promote the reductive removal of halogen, most likely at the reactive dienone-imine stage, has been supported by the isolation of much 2-allyl-6-chlorophenol during the thermal rearrangement of allyl 2,6-dichlorophenyl ether, particularly in a solvent (e.g. decalin) which is readily oxidizable (25). The isolation of 7-chloroindoles from the stannous chloride catalyzed cyclization of 2,6-dichlorophenylhydrazones (12) can be considered as another example of this reductive removal of allylic halogen at the dienone-imine stage.

The failure as yet to obtain the desired enamine (XI) might be due to the presence of the N′-methyl group which could facilitate cleavage of the N—N bond with subsequent formation of the dienone-imine (XVIII) which then rapidly decomposes. It is known that α-N-methylphenylhydrazones are very readily converted to 1-methylindoles (26, 27).

To our knowledge, this is the first example of a room temperature, non-catalyzed Fischer indole synthesis. The mild conditions required and the much cleaner reaction obtained might now permit isolation of products which under the usual more stringent conditions end up as tars. The surprising ease of the conversion of the enamine (XI) to the dienone-imine and then to indole products supports Suvorov's suggestion that this step need not be acid-catalyzed (11). It might now be possible to obtain, under these modified conditions, an intermediate analogous to compound II (R = CH_3).

We are continuing work on these interesting aspects of the reaction.

EXPERIMENTAL

Preparation of Phenylhydrazines

N′-Formyl-2,6-dichlorophenylhydrazine

Formylation of 2,6-dichlorophenylhydrazine was carried out by the following modification of the method described by Baker *et al.* (16). The use of 50% formic acid (17) proved to be less satisfactory in our experiments.

To a solution of 33.6 g (0.19 mole) of 2,6-dichlorophenylhydrazine (1) in 150 ml of glacial acetic acid was added 7.6 ml (0.19 mole) of formamide in a dropwise fashion. The resulting solution was stirred at room temperature for 1 h during which time the solution thickened because of the formation of a colorless precipitate. The thick slurry was then diluted with 150 ml of water and the solid collected. Crystallization from ethanol gave 29.6 g (76%) of pure product melting at 160–161°. Calc. for $C_7H_6N_2Cl_2O$: C, 40.99; H, 2.95; N, 13.66; Cl, 34.58. Found: C, 41.09; H, 3.10; N, 13.84; Cl, 34.72.

N′-Methyl-N′-formyl-2,6-dichlorophenylhydrazine

Methylation was accomplished by the following modification of a published procedure (17).

To a solution of 41 g (0.20 mole) of N′-formyl-2,6-dichlorophenylhydrazine in 200 ml of dimethylsulphoxide both 21.4 ml (0.22 mole) of dimethylsulphate and a solution of 8.8 g (0.22 mole) of sodium hydroxide in 20 ml of water were added simultaneously and dropwise. The reaction mixture was stirred for 2 h and then diluted with 150 ml of water. The oil which separated solidified on cooling. This oily solid was collected and crystallized from Skellysolve B, yielding 27.6 g (63%) of N′-formyl-N′-methyl-2,6-dichlorophenylhydrazine, m.p. 73–75°. Calc. for $C_8H_8N_2Cl_2O$: C, 43.86, H, 3.68, N, 12.79; Cl, 32.37. Found: C, 43.57; H, 3.64; N, 12.17; Cl, 32.54. That the methyl group was attached to the N′-nitrogen atom was shown by Raney nickel – hydrazine reduction (18) of the compound and isolation of the known 2,6-dichloroaniline. The other product, N-methylformanide was not isolated. The n.m.r. spectrum of N′-formyl-N′-methyl-2,6-dichlorophenylhydrazine showed a sharp signal for the methyl group at 7.1 τ and also agreed with the structure assigned.

N-Methyl-2,6-dichlorophenylhydrazine Hydrochloride

The following procedure is a modification of that described by Neber *et al.* (17).

A solution of 43.8 g (0.20 mole) of N′-formyl-N′-methyl-2,6-dichlorophenylhydrazine, 80 ml of concentrated hydrochloric acid, and 60 ml of ethanol was refluxed for 6 h. The solution was cooled, and poured into ice water whereupon an oil separated. An ether extract of this oil was dried ($MgSO_4$) and after removal of the drying agent was treated with anhydrous hydrogen chloride gas until precipitation of the hydrochloride of N′-methyl-2,6-dichlorophenylhydrazine was complete. Crystallization from ethanol gave 30.5 g (67%) of pure N′-methyl-2,6-dichlorophenylhydrazine hydrochloride, melting at 181–182°. Calc. for $C_7H_8N_2Cl_3$: C, 36.95; H, 3.99; N, 12.31; Cl, 46.75. Found: C, 36.84; H, 3.89; N, 12.36; Cl, 46.61. The infrared spectrum

of this compound showed the following bands: 3220 cm^{-1} (NH), a broad peak centered at 2930 cm^{-1} (CH_3), 2690 cm^{-1} (NH_2^+) (28), and a peak at 1560 cm^{-1} (aromatic unsaturation). The n.m.r. spectrum in D_2O showed signals at 7.0 τ (singlet, N—CH_3), 5.3 τ (singlet for DOH), and an AB_2 pattern at 2.3 to 2.9 τ. The hydrazine could be preserved undecomposed if kept as the hydrochloride.

4-Chloro-3-nitrophenylhydrazine

The 4-chloro-3-nitroaniline (29) was converted to 4-chloro-3-nitrophenylhydrazine by the procedure of Plant and Rosser (22). However, after the solution had been left to stand overnight, the precipitated hydrazine hydrochloride was separated by filtration (rather than heated again as these authors advocated) and dissolved in 200 ml of boiling water. The resulting solution was then filtered free of insoluble material and the filtrate treated with saturated aqueous sodium acetate to precipitate the hydrazine. This product was *crystallized immediately from Skellysolve B.* If the crystallization was not done at once, decomposition resulted. Yield of 4-chloro-3-nitrophenylhydrazine was 45.3%, m.p. 108–109° (reported m.p. 109° (22)).

Preparation and Cyclization of Phenylhydrazones

Cyclohexanone o-Chlorophenylhydrazone

This compound was prepared in 91% yield according to published directions (12). This compound decomposed readily, hence had to be used soon after its preparation.

Cyclization was accomplished preferably by the boron trifluoride – etherate procedure described by Snyder and Smith (30), affording an 82% yield of 8-chloro-1,2,3,4-tetrahydrocarbazole, m.p. 55–56° (from benzene – Skellysolve B). Reported m.p. 56° (12). The product decomposed rapidly at room temperature.

Cyclohexanone 4-Chloro-3-nitrophenylhydrazone

This compound was prepared in 84% yield according to the procedure of Plant and Rosser (22) and cyclized with boron trifluoride – etherate (30). The solid obtained was repeatedly crystallized from ethanol yielding 6-chloro-7-nitro-1,2,3,4-tetrahydrocarbazole (44%) melting at 186–187°, reported m.p. 184° (22, 23). Removal of the ethanol from the filtrate gave a yellow solid which when crystallized from benzene gave 6-chloro-5-nitro-1,2,3,4-tetrahydrocarbazole (11%) having the reported melting point of 162–163° (22, 23).

6-Chloro-5-nitro-9-methyl-1,2,3,4-tetrahydrocarbazole

6-Chloro-5-nitro-1,2,3,4-tetrahydrocarbazole was converted to 6-chloro-5-nitro-9-methyl-1,2,3,4-tetrahydrocarbazole by use of methyl sulphate according to published procedure (31). Yield of pure material, 61%, m.p. 154–155° (from ethanol). Calc. for $C_{13}H_{13}N_2O_2Cl$: C, 58.98; H, 4.95; N, 10.59; Cl, 13.40. Found: C, 59.09; H, 5.19; N, 10.50; Cl, 13.21.

That the nitrogen atom at position 9 had been methylated was shown by the disappearance of the NH signal at 4.94 τ found in the n.m.r. spectrum of the starting material, and the appearance of the N—CH_3 signal at 6.65 τ in the spectrum of the product.

5-Amino-6-Chloro-9-methyl-1,2,3,4-tetrahydrocarbazole

The nitro group of 6-chloro-5-nitro-9-methyl-1,2,3,4-tetrahydrocarbazole was reduced with Raney nickel and hydrazine (24). The solid amine obtained after removal of the nickel and the solvent was crystallized from ethanol and yielded pure material (79%) melting at 90–91°. Calc. for $C_{13}H_{15}N_2Cl$: C, 66.51; H, 6.44; N, 11.94; Cl, 15.11. Found: C, 66.64; H, 6.57; N, 12.18; Cl, 14.98. The n.m.r. spectrum in $CDCl_3$ showed the following signals: an aromatic AB pattern at 3.0–3.8 τ, N—H at 5.9 τ, N—CH_3 at 6.75 τ, methylene at 7.24, 7.58, and 8.30 τ.

Treatment of the amine in a small amount of benzene with a slight excess of acetic anhydride heated on the steam bath for 10 min afforded colorless crystals (from ethanol) of the N-acetyl derivative, m.p. 245°. Calc. for $C_{15}H_{17}N_2ClO$: C, 65.09; H, 6.18; N, 10.11; Cl, 12.81. Found: C, 65.24; H, 5.96; N, 10.29; Cl, 13.09.

Condensation of Cyclohexanone with N'-Methyl-2,6-dichlorophenylhydrazine

A quantity (6.84 g, 0.03 mole) of N'-methyl-2,6-dichlorophenylhydrazine hydrochloride was dissolved in water. The resulting solution was basified with dilute sodium hydroxide and the oil which separated was extracted with two 25 ml portions of ether. The combined extracts were dried ($MgSO_4$) and freed from ether with a rotary evaporator. To the residue left in the evaporator was added 50 ml of benzene followed by 2.94 g (0.03 mole) of cyclohexanone and the resulting solution slowly reduced to half its original volume in the rotary evaporator (bath temperature ~20°). A colorless precipitate was removed by filtration and when crystallized from ethanol it melted at 222–225° (0.30 g, 14.8%). This precipitate was quite water soluble. Its aqueous solution gave an instantaneous precipitate with silver nitrate. The aqueous solution of this colorless precipitate, when made alkaline with sodium hydroxide, produced an ammoniacal odor. Mixed melting point, and n.m.r. spectrum showed it to be identical with methylamine hydrochloride.

The rest of the benzene solution, after removal of the methylamine hydrochloride, was freed from benzene and gave a yellow oil. By chromatography on neutral alumina with Skellysolve B as eluant, 0.86 g (14.0%) of a pale yellow solid melting at 55–56° was obtained. This compound was shown to be identical with 8-chloro-1,2,3,4-tetrahydrocarbazole by mixed melting point and by infrared and n.m.r. spectra comparison with an

authentic sample (12). The compound was too unstable to be sent away for elemental analysis. Its infrared spectrum showed bonded N—H at 3100 cm^{-1}. The n.m.r. spectrum showed methylene signals at 7.29 τ and 8.20 τ and an N—H signal at 1.39 τ.

Further elution of the remaining material on the column with a 1:1 mixture of Skellysolve B and benzene yielded a tan, crystalline solid, m.p. 87–90°. Crystallization from alcohol gave 1.48 g (21%) of a colorless material, m.p. 90–91°. Calc. for $C_{13}H_{15}N_2Cl$: C, 66.51; H, 6.44; N, 11.94; Cl, 15.11. Found: C, 66.59; H, 6.49; N, 11.75; Cl, 15.37. The n.m.r. spectrum in $CDCl_3$ showed an aromatic AB pattern in the region 3.0 to 3.8 τ, an $-NH_2$ signal at 5.9 τ, an N—CH_3 signal at 6.75 τ, and methylene signals at 7.24, 7.58, and 8.30 τ. The above data agreed with the structure 5-amino-6-chloro-9-methyl-1,2,3,4-tetrahydrocarbazole. This compound showed properties identical with those of an authentic sample of 5-amino-6-chloro-9-methyl-1,2,3,4-tetrahydrocarbazole prepared by another route described above.

ACKNOWLEDGMENT

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