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SOME EXTENSIONS OF THE VON BRAUN (BrCN) REACTION ON ORGANIC BASES

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In continuation of studies on some extensions of the von Braun (BrCN) reaction on organic bases, work on some aliphatic, aromatic, heterocyclic and four medicinally important bases has led to various amido, methyl amino, methoxy imino methyl, ethoxy imino methyl, guanido and substituted guanido derivatives, which were characterized through spectral studies.

Key words: Extensions of von Braun reaction. Von Braun reaction on simpler amines. Von Braun reaction on alkaloidal bases.

INTRODUCTION

The von Braun BrCN reaction primarily serves to convert tertiary into secondary amine while it has also been of considerable value to studies in the correlation of structure and activity in the field of alkaloids with particular reference to the nature of various radicals introduced at the secondary basic nitrogen resulting from the reaction [1-5]. In 1980 Siddiqui *et al.* [6] for the first time carried out extended studies of the reaction on a number of bases which resulted in a series of derivatives differing in their pharmacophoric groupings. As a result of these studies, they obtained acidamide and diamine from the cyanamides of conessine, *isoconessine* and simpler aliphatic and aromatic amines. Furthermore, they obtained the carbino-lamine derivative on careful treatment of the diamines with nitrous acid. The cyanamides of the steroidal bases, conessine and *isoconessine*, also gave the guanido derivatives on reaction with concentrated ammonia.

S. Siddiqui and Nighat Afza [7] later on extended these studies to tetrahydroharmine and the cyano derivative thereby formed, yielded *N*-amido tetrahydroharmine on mild hydrolysis. In 1981 Siddiqui *et al.* [8] carried out the same reaction on the sandwicine series of alkaloids, as a result of which some more important nitrogenous derivatives were obtained. During the same year, further extensions carried out by the same authors [9] on Ephedra alkaloids and simpler bases resulted in the syntheses of substituted oxazolidines and a whole series of nitrogen analogues of ephedrine, desoxy ephedrine and simpler amines. They also discussed the general applicability and limitations of this reaction. Siddiqui *et al.* [10] further reported the syntheses of some new derivatives of dis-butylamine and di-2-butylamine, such as cyano, urea and *N*-iminoethylether. However, in contrast to earlier results,

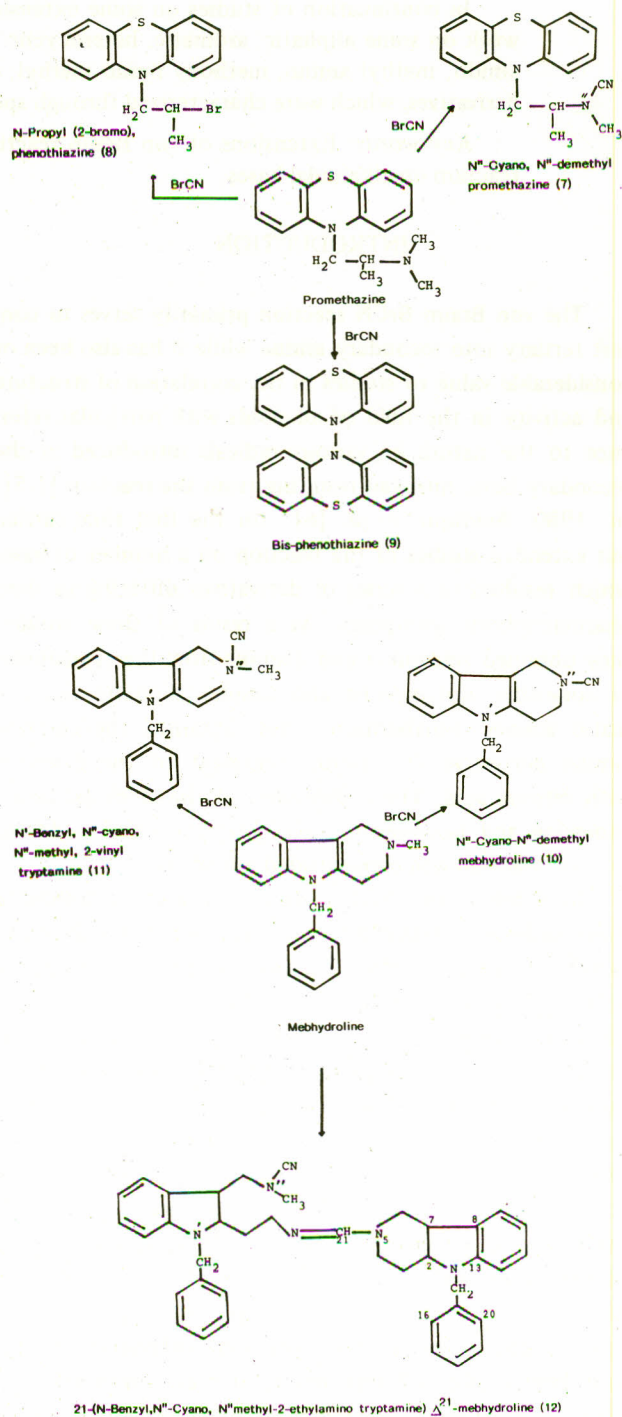
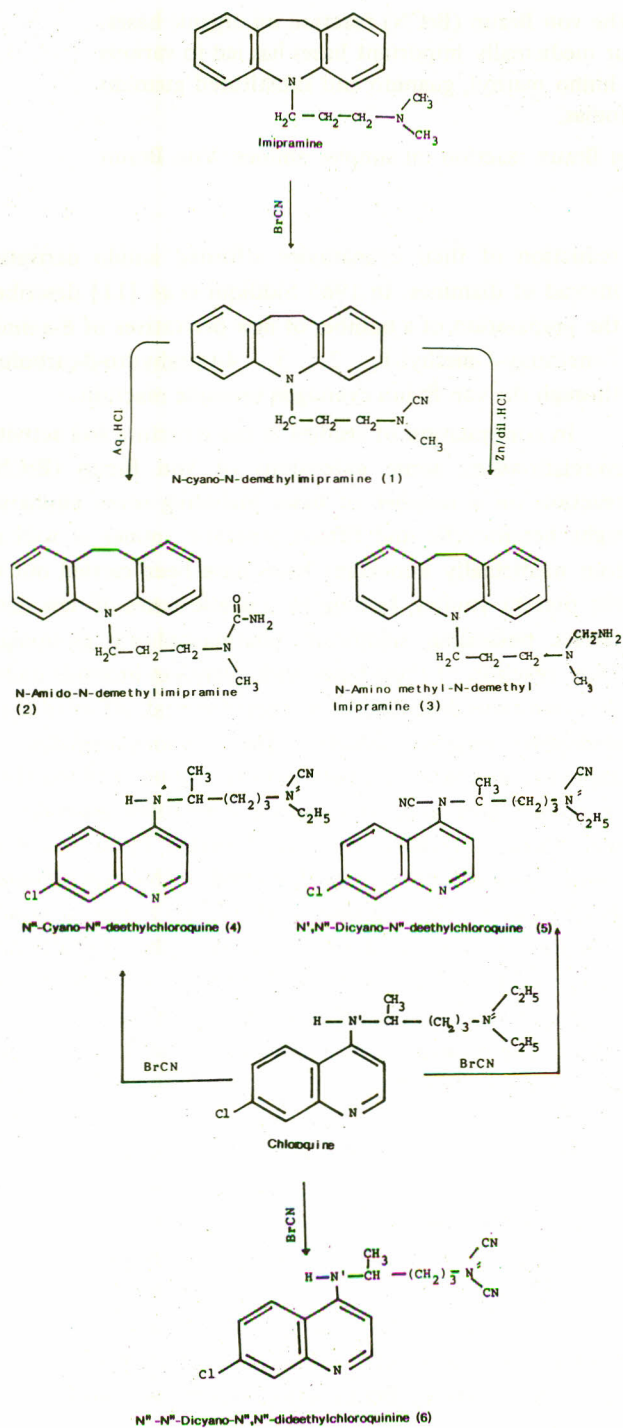
reduction of their cyanamides afforded amido derivatives instead of diamines. In 1985 Siddiqui *et al.* [11] described the preparation of a number of new derivatives of 8-amino-7-methoxy-1-methyl-1, 2, 3, 4-tetrahydro- β -carboline through the von Braun cyanogen bromide reaction.

In continuation of studies in the structure and activity co-relationship, some extensions of von Braun (BrCN) reaction on a number of bases including seven aliphatic, eight heterocyclic and fifteen aromatic amines as well as four medicinally important bases have been carried out in the present studies, leading to a whole series of new derivatives possessing significant pharmacophoric groupings. Thus, reaction of these bases with cyanogen bromide under the conditions described in the experimental, afforded their respective monocyanamides. The monocyanamides of aliphatic, aromatic and heterocyclic amines, yielded their respective urea and carboxamide derivatives generally in high yields (71-100%) on careful partial hydrolysis with dilute hydrochloric acid as described in the experimental. Furthermore, on reaction with Zn/HCl the aromatic cyanamides gave the diamines whereas the aliphatic and heterocyclic monocyanamides afforded their respective amido and carboxamide derivatives instead of the diamines. The aromatic cyanamides also yielded their respective guanido derivatives on treatment with concentrated ammonia. This reaction, however could not be applied to dimethyl aniline, naphthylamine and the aliphatic and heterocyclic cyanamides. also failed to yield any uniform product under the experimental conditions followed in other cases. On the other hand, the condensation of aromatic amines with their respective cyanamides yielded the substituted guanido derivatives in theoretical yields. Further, the aromatic monocyanamides afforded their respective methoxy iminomethyl and ethoxy iminomethyl derivatives on reduction with methanolic and ethanolic

hydrochloric acid respectively, in the presence of a little zinc dust as a catalyst.

During the course of present studies four medicinally important bases, namely, imipramine (psychomotor stimulant), chloroquine (antimalarial), promethazine and mebhydroline (antiallergic) were also subjected to the von Braun (BrCN) reaction. Imipramine yielded three derivatives

named as *N*-cyano-*N*-demethylimipramine (1), *N*-amido-*N*-demethylimipramine (2) and *N*-amino methyl-*N*-demethylimipramine (3), whereas chloroquine gave three cyano derivatives, *N*'-cyano-*N*'-deethylchloroquine (4), *N*', *N*'-dicyano-*N*'-deethylchloroquine (5) and *N*'', *N*''-dicyano-*N*'', *N*''-dideethylchloroquine (6). The von Braun BrCN reaction on promethazine afforded three new derivatives,



namely, N''-cyano-N''-demethyl promethazine (7), N-propyl (2-bromo) phenothiazine (8) and bis-phenothiazine [9], whereas the same reaction on mebhdroline led to the formation of three cyano derivatives, namely, N''-cyano-N''-demethyl mebhdroline (10) N'-benzyl, N''-cyano-N''-methyl, 2 vinyltryptamine (11) and 21 (N'-Benzyl, N''-cyano, N''-methyl, 2-ethylamino tryptamine) Δ^{21} mebhdroline (12). These derivatives have not been reported earlier through any other route. The cyanamides except imipramine when subjected to partial hydrolysis and reduction under the reaction conditions employed in other cases failed to yield any uniform constituent.

EXPERIMENTAL

All melting and boiling points were recorded in glass capillary tubes and are uncorrected. IR spectra were recorded on Unicam SP.200G and JASCO IRA-1 Infrared Spectrophotometers. UV spectra were recorded on Shimadzu UV-240 Spectrophotometer. Electron ionization mass spectra (EI) were recorded on Finnigan MAT-112 and Finnigan MAT-312 double focusing mass spectrometers connected to the PDP 11/34 computer system. NMR spectra were recorded on Bruker WP-100-SY FT-NMR spectrometers with TMS as internal reference. The purity of the samples was checked on TLC (silica gel).

Allphatic Bases

N-Cyanoheptylamine $C_6H_{13}-NH-CN$. Heptylamine (5 g) was dissolved in 200 ml ether and to it was added an ethereal solution of freshly prepared BrCN 5.1 g (1.2 mole) with constant stirring and cooling at 0°. The stirring was continued for 45 min. when white crystalline hydrobromide of the base separated out. It was filtered and washed well with ether. The ethereal solution was shaken out with 5% acetic acid to remove any unreacted base, washed with water with the addition of a little dilute ammonia to neutral pH, dried and freed of the solvent under reduced pressure yielding a brownish liquid residue (3.2 g, yield 100%) which gave a single spot on TLC. It is soluble in common organic solvents, EIMS m/z (rel. int. %); 126.1144 (M^+ calcd. for $C_7H_{14}N_2$, 126.1156) (34), 111 (4), 97 (100) and 83 (6). IR ν_{max} (cm^{-1}); 2230 ($C \equiv N$ group).

More or less similar reaction conditions were employed for the preparation of other cyano derivatives and their purity was checked by TLC (silica gel, GF 254, 0.2 mm).

Hexylurea $C_6H_{13}-NH-CO-NH_2$. 1 g of N-cyanoheptylamine was suspended in 10 ml of 15% aqueous hydrochloric

acid and stirred on boiling water bath for 1 hr. It was cooled to room temperature, basified with ammonia, and extracted out with ethyl acetate. On removal of the solvent from the ethyl acetate phase after drying over anhydrous sodium sulphate, the urea derivative was obtained as a crystalline solid which on recrystallization from methanol formed irregular plates, mp 108-109° (yield theoretical). It is soluble in chloroform, methanol and insoluble in ether and pet. ether and analyzed for $C_7H_{16}N_2O$ (obsd. C = 58.64, H = 10.08, N = 19.29, O = 11.19%; calcd. for $C_7H_{16}N_2O$ C = 58.33, H = 11.11, N = 19.44, O = 11.12%). EIMS m/z (rel. int. %); 144.1241 (M^+ , calcd. for $C_7H_{16}N_2O$, 144.1261) (100), 129 (10), 115 (64), 101 (39), 87 (20), 73 (46) and 55 (4). IR ν_{max} (cm^{-1}); 3350, 3450 (amide N-H stretching), 1640 (amide C = O stretching) and 1580 (amide N-H bending).

N-Acetyl, N'-hexylurea obtained on the reaction of the urea with Ac_2O /pyridine (overnight at room temperature), formed elongated plates on recrystallization from methanol, mp 63-64°. It was analyzed for $C_9H_{18}N_2O_2$ (obsd. C = 58.11, H = 9.55, N = 15.09, O = 17.25%; calcd. for $C_9H_{18}N_2O_2$ C = 58.06, H = 9.67, N = 15.05, O = 17.22%). EIMS m/z M^+ , 186. IR ν_{max} (cm^{-1}); 3500. (amide N-H), 1635, 1680 (acetyl and urea carbonyl stretchings). 1H -NMR δ : 9.47 (1H, s, CONH), 8.43 (1H, s, H_2C-NH), 3.35 (2H, t, $CH_2 - NH$), 2.25 (3H, s, $COCH_3$) and 2.09 - 0.73 (11 H, CH_3 , $CH_2 \times 4$).

Hydrolysis of the other cyanamides and acetylation of the urea derivatives were achieved under the experimental conditions recorded above.

N-Cyanoheptylamine $C_7H_{15}-NH-CN$. It was obtained as a viscous liquid in theoretical yield. EIMS m/z (rel. int. %); 140.1302 (M^+ , calcd. for $C_8H_{16}N_2$, 140.1313) (48), 125 (22) 111 (35), 97 (100) and 83 (84); IR ν_{max} (cm^{-1}); 2210.

Hyptylurea $C_7H_{15}-NH-CO-NH_2$. It formed irregular plates on recrystallization from methanol and melted at 113-114° (yield, 98%). It analyzed for $C_8H_{18}N_2O$ (obsd. C = 60.23, H = 11.42, N = 18.28, O = 9.53%; calcd. for $C_8H_{18}N_2O$ C = 60.75, H = 11.39, N = 17.72, O = 10.14%). EIMS m/z (rel. int. %); 158.1417 (M^+ , calcd. for $C_8H_{18}N_2O$, 158.1419) (26), 143 (3), 129 (9), 115 (9), 101 (22), 87 (19), 73 (100), 69 (6) and 55 (18). IR ν_{max} (cm^{-1}); 3380, 3500, 1630 and 1580.

N-Acetyl, N'-heptylurea formed rectangular plates on recrystallization with methanol-water (9.5:0.5), mp 75-77° (yield theoretical). It analyzed for $C_{10}H_{20}N_2O_2$ (obsd.

C = 60.15, H = 10.36, N = 14.23, O = 15.26%; calcd. for $C_{10}H_{20}N_2O_2$ C = 60.00, H = 10.00, N = 14.00, O = 16.00%. EIMS m/z M^+ , 200. IR ν_{max} (cm^{-1}): 3410, 1665 and 1710. 1H -NMR δ : 10.35 (1H, s, CO-NH), 8.45 (1H, s, CH_2-NH), 3.25 (2H, t, CH_2-NH), 2.10 (3H, s, $COCH_3$) and 2.07–0.82 (13H, CH_3 , CH_2 x 5).

N-Cyanononylamine $C_9H_{19}-NH-CN$. A viscous liquid was obtained in theoretical yield. EIMS m/z (rel. int. %): 168. 1614 (M^+ , calcd. for $C_{10}H_{20}N_2$, 168, 1626) (8), 153 (10), 139 (24), 125 (35), 111 (44), 97 (87) and 55 (100). IR ν_{max} (cm^{-1}): 2220.

Nonylurea $C_9H_{19}-NH-CO-NH_2$. On recrystallization from methanol-water (0.5 : 0.5) it formed irregular plates mp 97-98 $^\circ$ (yield, theoretical). It analyzed for $C_{10}H_{22}N_2O$ (obsd. C = 64.32, H = 11.91, N = 15.42, O = 8.35%; calcd. for $C_{10}H_{22}N_2O$ C = 64.51, H = 11.82, N = 15.05, O = 8.60%). EIMS m/z (rel.int. %): 186.1729 (M^+ , calcd. for $C_{10}H_{22}N_2O$, 186.1732) (44), 171 (5), 157 (15), 143 (20), 115 (35), 87 (35), 73 (100), 69 (18) and 55 (35). IR ν_{max} (cm^{-1}): 3500, 3410, 1670 and 1590.

N-Acetyl, N'-nonylurea formed prismatic rods from methanol and melted at 60-61 $^\circ$. It analyzed for $C_{12}H_{24}N_2O_2$ (obsd. C = 63.13, H = 10.53, N = 12.21, O = 14.13%; calcd. for $C_{12}H_{24}N_2O_2$ C = 63.16, H = 10.52, N = 12.28, O = 14.04%), EIMS m/z M^+ , 228. IR ν_{max} (cm^{-1}): 3400, 1710 and 1665. 1H -NMR δ : 9.89 (1H, s, CONH), 8.45, (1H, 2, CH_2-NH), 3.25 (2H, t, CH_2-NH), 2.10 (3H, s, $COCH_3$). 2.09–0.85 (17H, CH_3 , CH_2 x 7).

N-Cyanododecylamine $C_{12}H_{25}-NH-CN$. The cyanamide was obtained as a viscous liquid in 100% yield. It showed single spot on TLC and is soluble in common organic solvents. EIMS m/z (rel.int.%): 210.2031 (M^+ , calcd. for $C_{13}H_{26}N_2$ 210, 2095) (10), 195 (11), 181 (26), 167 (9), 125 (36), 111 (50), 97 (74), 83 (35) and 55 (100). IR ν_{max} (cm^{-1}): 2210.

Dodecylurea $C_{12}H_{25}-NH-CO-NH_2$. The crystalline dodecylurea thus obtained (yield 96%), formed irregular plates (mp 103-104 $^\circ$) on recrystallization from methanol. It analyzed for $C_{13}H_{28}N_2O$ (obsd. C = 67.98, H = 12.45, N = 12.73, O = 6.84%; calcd. for $C_{13}H_{28}N_2O$ C = 68.42, H = 12.28, N = 12.28 O = 7.02%). EIMS m/z (rel.int. %): 228.2298 (M^+ , calcd. for $C_{13}H_{28}N_2O$ 228.2291) (36), 211 (2), 191 (5), 171 (9), 115 (20), 87 (20), 69 (100), and 61 (28), IR ν_{max} (cm^{-1}): 3400, 3320, 1660 and 1590. Similar experimental conditions were employed for the hydrolysis of other cyanamides.

N-Acetyl-N'-dodecylurea: It was obtained in 98% yield, formed prismatic rods on recrystallization from

methanol and melted at 69.70 $^\circ$. It analyzed for $C_{15}H_{30}N_2O_2$ (obsd. C = 66.62, H = 11.13, N = 10.38, O = 11.87%; calcd. for $C_{15}H_{30}N_2O_2$ C = 66.66, H = 11.11, N = 10.37, O = 11.86%). EIMS m/z M^+ , 270. IR ν_{max} (cm^{-1}): 3400, 1705 and 1660. 1H -NMR δ ($CDCl_3$) δ : 9.50 (1H, s, CONH), 8.40 (1H, s, CH_2-NH), 3.25 (2H, t, CH_2-NH), 2.10 (3H, 2, $COCH_3$), 2.09-0.79 (23H, CH_3 , CH_2 x 10).

N-Cyano-hexadecylamine $C_{16}H_{33}-NH-CN$ Chromatographically pure viscous liquid of the cyanamide was obtained in theoretical yield. EIMS m/z (rel. int. %): 226:2710 (M^+ , calcd. for $C_{17}H_{34}N_2$ 226.2721) (12), 251 (18), 195 (14), 167 (27), 97 (82) and 57 (100). IR ν_{max} (cm^{-1}): 2210.

Hexadecylurea $C_{16}H_{33}-NH-CO-NH_2$. On recrystallization from ethyl alcohol it formed irregular plates, mp 102-103 $^\circ$ (yield 98%) and analyzed for $C_{17}H_{36}N_2O$ (obsd. C = 71.92, H = 12.73, N = 10.41, O = 4.94 %; calcd. for $C_{17}H_{36}N_2O$ C = 71.83, H = 12.67, N = 9.86, O = 5.64 %). EIMS m/z (rel. int. %): 284.2820 (M^+ , calcd. for $C_{17}H_{36}N_2O$ 284.2827) (26), 267 (2), 241 (8), 185 (8), 157 (10), 129 (16), 115 (24), 73 (100) and 55 (23), IR ν_{max} (cm^{-1}): 3500, 3390, 1670 and 1600.

N-Acetyl-N'-hexadecylurea: It formed irregular plates on recrystallization from methanol-water (9.5 : 0.5), mp 78-79 $^\circ$ (yield 90%) and analyzed for $C_{19}H_{38}N_2O_2$ (obsd. C = 69.84, H = 11.69, N = 8.60, O = 9.87; calcd. for $C_{19}H_{38}N_2O_2$ C = 69.94, H = 11.65, N = 8.59, O = 9.82%). EIMS m/z M^+ , 326. IR ν_{max} (cm^{-1}): 3400, 1710 and 1660. 1H -NMR ($CDCl_3$) δ : 9.50 (1H, s, CONH), 8.40 (1H, s, CH_2-NH), 3.33 (2H, t, CH_2-NH), 2.10 (3H, s, $COCH_3$), e.g $COCH_3$ 2.09–0.85 (31H, m, CH_2 x 14).

N-Cyanocyclohexylamine $C_6H_{11}-NH-CN$. It was obtained as a viscous liquid in theoretical yield and gave a single spot on TLC. EIMS m/z (rel.int.%): 124.1031 (M^+ , calcd. for $C_7H_{12}N_2$ 124, 1000) (16), 95 (2), 83 (78), 67 (18) and 56 (100). IR ν_{max} (cm^{-1}): 2220.

Cyclohexylurea $C_6H_{11}-NH-CO-NH_2$. On recrystallization from methanol it formed rectangular plates, mp 195-196 $^\circ$ (yield 90%). It analyzed for $C_7H_{14}N_2O$ (obsd. C = 59.27, H = 9.74, N = 20.19, O = 10.80%; calcd. for $C_7H_{14}N_2O$ C = 59.15, H = 9.86, N = 19.72, O = 11.27%). EIMS m/z (rel. int. %): 142.1110 (M^+ , calcd. for $C_7H_{14}N_2O$ 142.1106) (22), 127 (2), 110 (14), 99 (34), 70 (32), 61 (100) and 56 (91). IR ν_{max} (cm^{-1}): 3500, 3410, 1660 and 1590.

N-Acetyl-N'-cyclohexylurea: On recrystallization from methanol it formed elongated rods, mp 90-92 $^\circ$ (yield

89%). It analyzed for $C_9H_{16}N_2O_2$ (obsd. C = 58.68, H = 8.67, N = 15.31, O = 17.34%; calcd. for $C_9H_{16}N_2O_2$ C = 58.69, H = 8.69, N = 15.21, O = 17.41%). EIMS m/z M^+ , 184. IR ν_{max} (cm^{-1}): 3405, 1710 and 1660. 1H -NMR ($CDCl_3$) θ : 9.70 (1H, s, CONH), 8.40 (1H, s, CH-NH), 2.10 (3H, s, $COCH_3$) and 3.85-3.25 (1H, m, CHNH).

N-cyano isopropyl cyclohexylamine $C_6H_{11}-N(C_3H_7)$ (CN). A viscous liquid of the cyanamide was obtained in theoretical yield, showed a single spot on TLC. EIMS m/z (rel. int.%): 166.1475 (M^+ , calcd. for $C_{10}H_{18}N_2$ 166.1469) (100), 151 (81), 123 (42), 95 (6) and 69 (21). IR ν_{max} (cm^{-1}): 2200.

N-Isopropyl cyclohexylurea $C_6H_{11}-N(C_3H_7)CO-NH_2$. After partial hydrolysis of *N*-isopropyl cyclohexyl cyanamide with 30% aqueous HCl, a crystalline urea derivative was obtained in 90% yield. It formed sharp needles on recrystallization from ethanol, mp 152-153° and analyzed for $C_{10}H_{20}N_2O$ (obsd. C = 64.98, H = 10.62, N = 15.11, O = 9.29%; calcd. for $C_{10}H_{20}N_2O$ C = 65.22, H = 10.86, N = 15.22, O = 8.70%). EIMS m/z (rel.int. %): 184.1564 (M^+ , calcd. for $C_{10}H_{20}N_2O$ 184.1575) (22), 169 (20), 155 (4), 141 (51), 113 (4), 98 (100), 87 (68) and 58 (54), IR ν_{max} (cm^{-1}): 3500, 3320, 1650 and 1580.

N-Acetyl-*N*'-isopropyl cyclohexylurea: It formed irregular plates on recrystallization from methanol, mp 174-176° (yield 93%) and analyzed for $C_{12}H_{22}N_2O_2$ (obsd. C = 63.81, H = 9.61, N = 12.38, O = 14.20%, calcd. for $C_{12}H_{22}N_2O_2$ C = 63.72, H = 9.73, N = 12.39, O = 14.16%). EIMS m/z M^+ , 226. IR ν_{max} (cm^{-1}): 3380, 1720 and 1640.

Aromatic Bases

N-Cyanoaniline $C_6H_5-NH-CN$. An ethereal solution of aniline (10g) was treated with an ethereal solution of freshly prepared cyanogen bromide (1.2 mole) with constant stirring at 10° and worked up in the usual way. As a result cyanoaniline was obtained as a viscous liquid in theoretical yield, bp 87-88° EIMS m/z (rel.int.%): 118.0532 (M^+ , calcd. for $C_7H_6N_2$ 118.0531) (100), 91 (72), 77 (30), 65 (20) and 51 (22), IR ν_{max} (cm^{-1}): 2180.

Phenylurea $C_6H_5-NH-CO-NH_2$. Partial hydrolysis of *N*-cyanoaniline (0.5g) was carried out with 20% aqueous HCl following the procedure described for cyclohexylcyanamide. The crystalline urea derivative formed irregular plates (mp 147-148°), on recrystallization from methanol (yield 100%). It analyzed for $C_7H_8N_2O$ (obsd. C = 62.20, H = 6.07, N = 21.10, O = 10.63%; calcd. for $C_7H_8N_2O$ C = 61.76, H = 5.88, N = 20.58, O = 11.78%). EIMS m/z (rel.int.%): 136.0635 (M^+ , calcd. for $C_7H_8N_2O$ 136.0636)

(22), 119 (10), 93 (100), 77 (10) and 66 (40). IR ν_{max} (cm^{-1}): 3510, 3410, 1690 and 1590.

N-Acetyl-*N*'-phenylurea: It formed needles on recrystallization from methanol, mp 167-168° (yield 90%) and analyzed for $C_9H_{10}N_2O_2$ (obsd. C = 61.03, H = 5.71, N = 15.63, O = 17.63%; calcd. for $C_9H_{10}N_2O_2$ C = 60.67, H = 5.62, N = 15.73, O = 17.98%). EIMS m/z 178.0741 (M^+ , calcd. for $C_9H_{10}N_2O_2$ 178.0742). IR ν_{max} (cm^{-1}): 3410, 1710 and 1665.

Anilino-imino-methoxymethane $C_6H_5-NH-C-NH(OCH_3)$. *N*-cyanoaniline (0.5g) was dissolved in 10% methanolic HCl and heated on water bath with the addition of a little quantity of zinc dust for 10 min. Unreacted zinc was filtered off and the clear solution was ammoniated with prior addition of ammonium chloride to prevent the precipitation of zinc hydroxide. It was shaken out with ethyl acetate which on usual work up afforded a crystalline residue which on recrystallization from ethyl acetate-methanol (1:1) formed elongated rods in 85% yield, mp 68-69°. It analyzed for $C_8H_{10}N_2O$ (obsd. C = 63.81, H = 6.97, N = 18.59, O = 10.63%; calcd. for $C_8H_{10}N_2O$ C = 64.00, H = 6.67, N = 18.67, O = 10.66%). EIMS m/z (rel.int.%): 150.0789 (M^+ , calcd. for $C_8H_{10}N_2O$ 150.0793) (10), 118 (100), 91 (80), 77 (32), 65 (22) and 51 (24). IR ν_{max} (cm^{-1}): 3400 (N-H stretching), 1590 (N-H bending), 1580 (C = N stretching) and 1100 (C = O stretching).

Anilino imino ethoxymethane $C_6H_5-NH-C=NH(OC_2H_5)$. Reaction of *N*-cyanoaniline (0.5g) with 10% ethanolic hydrochloric acid dust, on subsequent workup afforded anilino imino ethoxymethane derivative as a crystalline solid which on recrystallization from methanol-ethyl acetate (1:1) formed prismatic rods, mp 73.74° (yield 90%). It analyzed for $C_9H_{12}N_2O$ (obsd. C = 65.90, H = 7.28, N = 16.96, O = 9.86; calcd. for $C_9H_{12}N_2O$ C = 65.85, H = 7.32, N = 17.07, O = 9.76%) EIMS m/z (rel.int.%): 164.0941 (M^+ , calcd. for $C_9H_{12}N_2O$ 164.0949) (29), 136 (12), 120 (20), 106 (22), 93 (100), 77 (22), 66 (24), and 51 (12). IR ν_{max} (cm^{-1}): 3400, 1580, 1570 and 1100.

N-Amino methylaniline $C_6H_5-NH-CH_2-NH_2$. *N*-cyanoaniline (0.5g) was heated with zinc and dust and hydrochloric acid (15% aqueous) on water bath for 30 min. The unreacted zinc was filtered off and the filtrate was basified with prior addition of ammonium chloride and extracted out with ethyl acetate. On removal of the solvent after usual work up a viscous yellowish brown liquid was obtained in 60% yield, bp 76-77°. EIMS m/z (rel.int.%): 122.0840 (calcd. for $C_7H_{10}N_2$ 122.0844) (42), 106 (16), 93 (100), 77 (18) and 66 (58). IR ν_{max} (cm^{-1}): 3500, 3440 and 1535.

N-Phenylguanidine $C_6H_5-NH-C=NH(NH_2)$. *N*-cyanoaniline (0.5g) was treated with cold concentrated ammonia (2 ml) for a few min. The resulting guanido derivative thereby obtained was filtered, washed with water and dried over a porous plate. On recrystallization from ethyl acetate, it formed elongated rods, mp 89-90° (yield 47%) and analyzed for $C_7H_9N_3$ (obsd. C = 61.81, H = 7.01, N = 31.18%; calcd. for C = 62.22, H = 6.67, N = 31.11%). EIMS m/z (rel.int.%): 135.0798 (M^+ , calcd. for $C_7H_9N_3$ 135.0796) (100), 118 (10), 93 (90) and 66 (58). IR ν_{max} (cm^{-1}): 3300, 3200, 1660 and 1640.

N,N-Diphenylguanidine $(C_6H_5-NH)_2C=NH$ *N*-cyanoaniline (0.5g) was heated with aniline (0.4g) at 50° for 5 min under anhydrous conditions. The reaction mixture was washed with petroleum ether-ether (1:1) to remove any unreacted substances. The resulting crystalline product formed prismatic rods on recrystallization from benzene, mp 105-106° (yield 80%). It analyzed for $C_{13}H_{13}N_3$ (obsd. C = 73.93, H = 6.16, N = 19.91% calcd. for $C_{13}H_{13}N_3$ C = 73.93, H = 6.16, N = 19.91%). EIMS m/z (rel. Int. %): 211.1114 (M^+ , calcd. for $C_{13}H_{13}N_3$ 211.1109) (12), 118 (20), 93 (100), 77 (28) and 66 (18), IR ν_{max} (cm^{-1}): 3310, 3210, 1670 and 1650.

Similar reaction conditions were employed for the preparation of other cyano, urea, imino methoxymethane, imino ethoxymethane, amino methyl, guanido and substituted guanido derivatives of toluidine, dimethylaniline, anisidine, phenetidine and naphthylamine.

N-Cyano-2-methylaniline (2- CH_3) $C_6H_4-NH-CN$. The cyano derivative was obtained as a viscous liquid in 95% yield, bp 69-70°. EIMS m/z (rel.int.%): 132.0687 (M^+ , calcd. for $C_8H_8N_2$ 132.0687) (100), 106 (22), 104 (64), 91 (22), 77 (24) and 65 and (18). IR ν_{max} (cm^{-1}): 2200.

2-Methyl phenylurea (2- CH_3) $C_6H_4-NH-CO-NH_2$ It formed irregular plates on recrystallization from ethyl-alcohol, mp 190-191° (yield 100%) and analyzed for $C_8H_{10}N_2O$ (obsd. C = 64.21, H = 6.91, N = 19.02, O = 9.86%; calcd. for $C_8H_{10}N_2O$ C = 64.00, H = 6.67, N = 18.67, O = 10.66%): 150.0793 (M^+ , calcd. for $C_8H_{10}N_2O$ 150.0793) (40), 133 (8), 107 (100), 91 (10), 77 (22) and 57 (22). IR ν_{max} (cm^{-1}): 3520, 3415, 1720 and 1650.

N-Acetyl-*N*'-methyl phenylurea: On recrystallization from methanol it formed elongated rods, mp 168-169° (yield 80%) and analyzed for $C_{10}H_{12}N_2O_2$ (obsd. C = 62.04, H = 6.03, N = 14.82, O = 17.11%, calcd. for $C_{10}H_{12}N_2O_2$ C = 62.50, H = 6.25, N = 14.58, O = 16.67%) EIMS m/z (rel.int.%): 192.0890 (M^+ , calcd. for $C_{10}H_{12}N_2O_2$ 192.0898) (40), 149 (38), 106 (100), 91 (10), 77 (26), 65 (10) and 51 (12). IR ν_{max} (cm^{-1}): 3400, 1720 and 1660.

2-Methyl anilino imino methoxymethane (2- CH_3)

$C_6H_4-NH-C=NH(OCH_3)$ It formed elongated rods on recrystallization from ethyl acetate-methanol (1:1), mp 88-89° (yield 90%) and analyzed for $C_9H_{12}N_2O$ (obsd. C = 64.99, H = 7.36, N = 18.01, O = 9.64%; calcd. for $C_9H_{12}N_2O$ C = 65.85, H = 7.32, N = 17.07, O = 9.76%). EIMS m/z (rel. int.%): 164;0941 (M^+ , calcd. for $C_9H_{12}N_2O$ 164.0949) (36), 132 (28), 106 (100), 91 (12), 77 (28) and 51 (12). IR ν_{max} (cm^{-1}): 3410, 1590, 1580 and 1010.

2-Methyl anilino imino ethoxymethane (2- CH_3) $C_6H_4-NH-C=NH(OC_2H_5)$ On recrystallization from ethyl acetate-methanol (1:1), it formed rectangular plates, mp 67-68° (yield 85%) and analyzed for $C_{10}H_{14}N_2O$ (Obsd. C = 67.01, H = 7.01, N = 16.17, O = 9.8%; calcd. for $C_{10}H_{14}N_2O_1$, C = 67.42, H = 7.87, N = 15.73, O = 8.98%). EIMS m/z (rel. int.%): 178.1109 (M^+ , calcd. for $C_{10}H_{14}N_2O$ 178.1106) (20), 150 (10), 132 (18), 106 (100), 77 (28) and 51 (10). IR ν_{max} (cm^{-1}): 3400, 1590, 1475 and 1110.

N-Amino methyl-2-toluidine (2- CH_3) $C_6H_4-NH-CH_2-NH_2$. The cyanamide was obtained as a viscous liquid in 47% yield, bp 63-64°. EIMS m/z (rel.int.%): 136.1009 (M^+ , calcd. for $C_8H_{12}N_2$ 135.1000) (28), 106 (100), 91 (50) and 51 (10). IR ν_{max} (cm^{-1}): 3500, 3450 and 1585.

2-Methyl phenylguanidine (2- CH_3) $C_6H_4-NH-C=NH(NH_2)$ It formed needles on recrystallization from benzene, mp 83-84° (yield 44%) and analyzed for $C_8H_{11}N_3$ (obsd. C = 63.94, H = 8.01, N = 28.05%; calcd. for $C_8H_{11}N_3$ C = 64.43, H = 7.38, N = 28.19%). EIMS m/z (rel.int.%): 149.0948 (M^+ , calcd. for $C_8H_{11}N_3$ 149.0953) (12), 133 (14), 132 (12), 107 (100), 83 (88), 77 (20) and 75 (22). IR ν_{max} (cm^{-1}): 3300, 3200, 1660 and 1630.

N,N'-Di-2-methyl phenylguanidine [(2- CH_3) C_6H_4-NH] $_2$ C=NH. It was obtained as a crystalline solid which on recrystallization from benzene formed irregular plates, mp 84-85° (yield 68%) and analyzed for $C_{15}H_{17}N_3$ (obsd. C = 76.21, H = 6.90, N = 16.89%; calcd. for $C_{15}H_{17}N_3$ C = 75.31, H = 7.11, N = 17.58%) EIMS m/z (rel.int.%): 239.1426 (M^+ , calcd. for $C_{15}H_{17}N_3$ 239.1422) (30), 224 (10), 133 (20), 107 (100), and 91 (16), IR ν_{max} (cm^{-1}): 3320, 3215, 1670 and 1645.

N-Cyano-3-methylaniline (3- CH_3) $C_6H_4-NH-CN$ The cyano derivative was obtained as a viscous liquid in 93% yield, bp 91-92°. EIMS m/z (rel.int.%): 132.0681 (M^+ , calcd. for $C_8H_8N_2$ 132.0687) (10), 106 (48), 91 (48), 83 (50) and 61 (100). IR ν_{max} (cm^{-1}): 2210.

3-Methyl phenylurea (3- CH_3) $C_6H_4-NH-CO-NH_2$. It was obtained as a crystalline solid which on recrystallization from methanol formed needles, mp 142-143° (yield theoretical) and analyzed for $C_8H_{10}N_2O$ (obsd. C = 64.21, H = 6.91, N = 19.02, O = 9.86%; calcd. for $C_8H_{10}N_2O$

C = 64.00, H = 6.67, N = 18.67, O = 10.66%). EIMS m/z (rel. int.%): 150.0789 (M^+ , calcd. for $C_8H_{10}N_2O$ 150.0793) (18), 132 (5), 106 (100), 77 (22) and 51 (14). IR ν_{max} (cm^{-1}): 3400, 3320, 1660 and 1590.

N-Acetyl-*N*'-3-methyl phenylurea: It was obtained as a crystalline solid which on recrystallization from methanol, formed cubical plates, mp 173-174 $^{\circ}$ (yield 96%) and analyzed for $C_{10}H_{12}N_2O_2$ (obsd. C = 62.04, H = 6.03, N = 15.03, O = 16.90%; calcd. for $C_{10}H_{12}N_2O_2$ C = 62.50, H = 6.25, N = 14.58, O = 16.67%). EIMS m/z (rel.int.%): 192.0893 (M^+ , calcd. for $C_{10}H_{12}N_2O_2$ 192.0898) (10), 150 (38), 106 (100), 91 (10), 83 (84) and 51 (14). IR ν_{max} (cm^{-1}): 3400, 1720 and 1660.

3-Methyl anilino imino methoxymethane (*3*- CH_3) $C_6H_4-NH-C=NH$ (OCH_3). On recrystallization from ethyl acetate-methanol (1:1), it formed elongated rods, mp 91-92 $^{\circ}$ (yield 93%) and analyzed for $C_9H_{12}N_2O$ (obsd. C = 64.99, H = 7.36, N = 18.01, O = 9.64%; calcd. for $C_9H_{12}N_2O$ C = 65.85, H = 7.32, N = 17.07, O = 9.76%). EIMS m/z (rel.int.%): 164.0951 (M^+ , calcd. for $C_9H_{12}N_2O$ 164.0949) (26), 132 (18), 106 (100), 91 (12), 77 (22) and 51 (12), IR ν_{max} (cm^{-1}): 3400, 1640, 1590 and 1180.

3-Methyl anilino imino ethoxymethane (*3*- CH_3) $C_6H_4-NH-C=NH$ (OC_2H_5). It formed irregular plates on recrystallization from ethyl acetate-methanol (1:1), mp 83-84 $^{\circ}$ (yield 95%) and analyzed for $C_{10}H_{14}N_2O$ (obsd. C = 67.01, H = 7.01, N = 16.17, O = 9.81% calcd. for $C_{10}H_{14}N_2O$ C = 67.42, H = 7.87, N = 15.73, O = 8.98%). EIMS m/z (rel.int.%): 178.1102 (M^+ , calcd. for $C_{10}H_{14}N_2O$ 178.1106) (42), 132 (22), 107 (100), 91 (18), 77 (30), 65 (14), and 51 (12). IR ν_{max} (cm^{-1}): 3400, 1640, 1590 and 1180.

N-Amino methyl-3-toluidine (*3*- CH_3) $C_6H_4-NH-CH_2-NH_2$ It was obtained as a viscous liquid in 51% yield, bp 63-64 $^{\circ}$ EIMS m/z (rel.int.%): 136.1011 (M^+ , calcd. for $C_8H_{12}N_2$ 136.1000) (20), 106 (100), 91 (32), 77 (44) and 51 (26). IR ν_{max} (cm^{-1}): 3510, 3450 and 1590.

3-Methyl phenylguanidine (*3*- CH_3) $C_6H_4-NH-C=NH$ (NH_2). It was obtained as a crystalline solid which on recrystallization from benzene, formed cubical plates, mp 73-74 $^{\circ}$ (yield 48%) and analyzed for $C_8H_{11}N_3$ (obsd. C = 63.94, H = 8.01, N = 28.05%; calcd. for $C_8H_{11}N_3$ C = 64.43, H = 7.38, N = 28.19%). EIMS m/z (rel.int.%): 149.0949 (M^+ , calcd. for $C_8H_{11}N_3$ 149.0953) (40), 132 (10), 106 (10), 91 (18), 83 (100), 77 (12), and 57 (14), IR ν_{max} (cm^{-1}): 3310, 3240, 1680 and 1650.

N,N'-Di-3-methyl phenylguanidine [*3*- CH_3) C_6H_4-NH] $_2$ C=NH. It formed prismatic rods on recrystallization from benzene. mp 90-91 $^{\circ}$ (yield 97%) and analyzed for

$C_{15}H_{17}N_3$ (obsd. C = 76.21, H = 6.90, N = 16.89%; calcd. for $C_{15}H_{17}N_3$ C = 75.31, H = 7.11, N = 17.58%). EIMS m/z (rel.int.%): 239.1420 (M^+ , calcd. for $C_{15}H_{17}N_3$ 239.1422) (12), 224 (5), 134 (12), 132 (12), 106 (100), 77 (28) and 51 (14). IR ν_{max} (cm^{-1}): 3320, 3220, 1660 and 1640.

N-Cyano-4-methylaniline (*4*- CH_3) $C_6H_4-NH-CN$. The liquid cyanamide (yield theoretical) thereby obtained failed to crystallize (bp 71-72 $^{\circ}$) and showed a single spot on TLC. EIMS m/z (rel.int.%): 132.9690 (M^+ , calcd. for $C_8H_8N_2$, 132.0687) (100), 104 (80), 91 (18), 77 (38), 65 (18) and 51 (24). IR ν_{max} (cm^{-1}): 2160.

4-Methyl phenylurea (*4*- CH_3) $C_6H_4-NH-CO-NH_2$ *N*-cyano-*p*-toluidine (0.5g) was suspended in 20% aqueous hydrochloric acid and heated at 70 $^{\circ}$ for 2 hr. The reaction mixture was cooled, basified with ammonia and the resulting white precipitate was filtered, washed with water and dried. It formed sharp needles on recrystallization from methanol (yield, 91%), mp 182-183 $^{\circ}$ and analyzed for $C_8H_{10}N_2O$ (obsd. C = 64.31, H = 6.71, N = 18.38, O = 10.70%; calcd. for $C_8H_{10}N_2O$ C = 64.00, H = 6.66, N = 18.66, O = 10.68%). EIMS m/z (rel.int. %): 150.0788 (M^+ , calcd. for $C_8H_{10}N_2O$, 150.0792) (28), 133 (12), 107 (100%), 83 (82), 65 (12) and 51 (12). IR ν_{max} (cm^{-1}): 3400, 3320, 1660 and 1590.

The acetyl derivative of *p*-tolylurea crystallized out from methanol as short needles (yield, 88%) and melted at 200-201 $^{\circ}$. It analyzed for $C_{10}H_{12}N_2O_2$ (obsd. C = 61.51, H = 6.30, N = 15.51, O = 16.68%; calcd. for $C_{10}H_{12}N_2O_2$ C = 62.50, H = 6.25, N = 14.58, O = 16.67%). EIMS m/z (rel.int. %): 192.0879 (M^+ , calcd. for $C_{10}H_{12}N_2O_2$, 192.0898) (10), 149 (32), 106 (100), 83 (84), 65 (8) and 51 (12). IR ν_{max} (cm^{-1}): 3430, 1710 and 1670.

N-Amino methyl-4-toluidine (*4*- CH_3) $C_6H_4-NH-CH_2-NH_2$ A viscous diamino derivative was obtained, yield 38% (by 106-107 $^{\circ}$) and showed a single spot on TLC. EIMS m/z (rel.int.%): 136.1010 (M^+ , calcd. for $C_8H_{12}N_2$, 136.1000) (28), 118 (18), 106 (100), 9 (32), 77 (40) and 51 (24). IR ν_{max} (cm^{-1}): 3495, 3450 and 1595.

4-Tolyl imino methoxymethane (*4*- CH_3) $C_6H_4-NH-C=NH$ (OCH_3). The *p*-tolylcyanamide (0.5g) was heated with methanolic hydrochloric acid (20 ml) in the presence of very little quantity of zinc dust, at 70 $^{\circ}$ for 10 min. The residual zinc was filtered off and the filtrate diluted with 100 ml of water, basified with ammonia and shaken out with ethyl acetate. The crystalline residue which obtained on usual work up of the ethyl acetate layer, formed elongated rods, mp 87-88 $^{\circ}$ on recrystallization from ethyl acetate-methanol (1:1) in 91% yield and analyzed for $C_9H_{12}N_2O$ (obsd. C = 67.31, H = 7.94, N = 15.68, O = 9.07%; calcd. $C_9H_{12}N_2O$ C = 67.41, H = 7.86, N = 15.74, O = 8.99%). EIMS m/z (rel.int.%): 164.0953 (M^+ , calcd.

for $C_9H_{12}N_2O$, 164.0949) (30), 132 (30), 106 (100), 91 (18), 63 (32), 65 (18) and 51 (16). IR ν_{max} (cm^{-1}): 3390, 1650, 1590 and 1110.

4-Tolyl imino ethoxymethane (4-CH₃) C₆N₄-NH-C=NH (OC₂H₅). The procedure described above was employed by replacing the methanolic hydrochloric acid with ethanolic hydrochloric acid, *p*-tolyl imino ethoxymethane thus obtained formed irregular plates on recrystallization from ethyl acetate-methanol (1:1) (yield, 96%) mp 68-69°. It analyzed for $C_{10}H_{14}N_2O$ (obsd. C = 67.40, H = 7.81, N = 15.88, O = 8.91%; calcd. for $C_{10}H_{14}N_2O$ C = 67.41, H = 7.86, N = 15.74, O = 8.99%). EIMS m/z (rel.int.%): 178.1101 (M^+ , calcd. for $C_{10}H_{14}N_2O$ 178.1106) (30), 132 (20), 106 (100), 91 (14), 77 (26), 65 (12) and 51 (12). IR ν_{max} (cm^{-1}): 3400, 1655, 1590 and 1120.

4-Methyl phenylguanidine (4-CH₃) C₆H₄-NHC=NH (NH₂). The cyanamide (0.5g) was taken in cold concentrated ammonium hydroxide (2 ml) and rubbed for a few min. When the viscous liquidish cyano derivative changed into white crystalline residue which was filtered, washed with water and dried. On recrystallization from benzene it formed cubical plates (yield, 43%), mp 81-82° and analyzed for $C_8H_{11}N_3$ (obsd. C = 64.41, H = 7.03, N = 28.56%; calcd. for $C_8H_{11}N_3$ C = 64.43, H = 7.38, N = 28.20%). EIMS m/z (rel.int.%): 149.0940 (M^+ , calcd. for $C_8H_{11}N_3$, 149.0953) (34), 132 (5), 118 (14), 105 (10), 91 (18), 83 (100), 77 (12) and 57 (12). IR ν_{max} (cm^{-1}): 3300, 3210, 1660 and 1635.

N,N'-Di(4-Methyl phenylguanidine [(4-CH₃) C₆H₄-NH]₂ C=NH. *p*-tolyl-cyanamide (0.5g) was treated with its parent base at 50° for 5 min in a round-bottom flask fitted with CaCl₂ tube (anhydrous conditions). The resulting semi-solid mass, was washed with ether-pet.ether (1:1), taken in ethyl acetate-methanol (1:1) and kept in cold when the guanido derivative came out as crystalline solid in 90% yield, mp 86-87°. It analyzed for $C_{15}H_{17}N_3$ (obsd. C = 75.12, H = 7.01, N = 17.78%; calcd. for $C_{15}H_{17}N_3$ C = 75.31, H = 7.11, N = 17.58%). EIMS m/z (rel.int.%): 239.1419 (M^+ , calcd. for $C_{15}H_{17}N_3$, 239.1422) (12), 224 (5), 132 (10), 106 (100), 91 (16), 77 (26), 63 (16) and 51 (14). IR ν_{max} (cm^{-1}): 3310, 3220, 1660 and 1640.

N-Cyano-2, 3-dimethylaniline [2,3(CH₃)₂] C₆H₃-NH-CN. It was obtained as a viscous liquid in theoretical yield. bp 49-50°. EIMS m/z (rel.int.%): 146.0893 (M^+ , calcd. for $C_9H_{10}N_2$ 146.0844) (68), 131 (38), 121 (100), 106 (60), 91 (38), 83 (90), 77 (72) and 51 (32). IR ν_{max} (cm^{-1}): 2200.

2,3-Dimethyl phenylurea [2,3(CH₃)₂] C₆H₃-NH-CO-NH₂. On recrystallization from methanol-water (9 : 0.1), it formed needles, mp 191192° (yield 93%) and

analyzed for $C_9H_{12}N_2O$ (obsd. C = 65.80, H = 7.36, N = 17.13, O = 9.71%; calcd. for $C_9H_{12}N_2O$ C = 65.85, H = 7.32, N = 17.07, O = 9.76%). EIMS m/z (rel.int.%): 164.0951 (M^+ , calcd. for $C_9H_{12}N_2O$ 164.0949) (10), 146 (82), 121 (100), 106 (88), 91 (40), 77 (52) and 51 (27). IR ν_{max} (cm^{-1}): 3410, 3340, 1600 and 1580.

N-Acetyl-N-2, 3-dimethyl phenylurea: It formed irregular plates on recrystallization from ethanol, mp 188-189° (yield 85%) and analyzed for $C_{11}H_{14}N_2O_2$ (obsd. C = 64.08, H = 6.85, N = 13.85, O = 15.51%; calcd. for $C_{11}H_{14}N_2O_2$ C = 64.08, H = 6.80, N = 13.59, O = 15.53%). EIMS m/z (rel.int.%): 206.1048 (M^+ , calcd. for $C_{11}H_{14}N_2O_2$ 206.1055) (20), 163 (40), 106 (100), 91 (40), 83 (70) and 51 (36), IR ν_{max} (cm^{-1}): 3400, 1750 and 1620.

2,3-Dimethyl anilino imino methoxymethane [2,3(CH₃)₂] C₆H₃-NH-C=NH (OCH₃). It was obtained as a crystalline solid which on recrystallization from ethyl acetate-methanol (1:1), formed needles, mp 107-108° (yield 89%) and analyzed for $C_{10}H_{14}N_2O$ (obsd. C = 67.40, H = 8.01, N = 15.58, O = 9.01%; calcd. for $C_{10}H_{14}N_2O$ C = 67.42, H = 7.87, N = 15.73, O = 8.98%). EIMS m/z (rel.int.%): 178.1101 (M^+ , calcd. for $C_{10}H_{14}N_2O$ 178.1106) (69), 163 (12), 146 (48), 120 (100), 106 (80), 91 (38), 77 (42) and 51 (20). IR ν_{max} (cm^{-1}): 3380, 1645, 1590 and 1120.

2,3-Dimethyl anilino imino ethoxymethane [2,3(CH₃)₂] C₆H₃-NH-C=NH (OC₂H₅). On recrystallization from ethyl acetate-methanol (1:1), it formed elongated rods, mp 96-98° (yield 90%) and analyzed for $C_{11}H_{16}N_2O$ (obsd. C = 68.70, H = 8.31, N = 14.68, O = 8.31%; calcd. for $C_{11}H_{16}N_2O$ C = 68.75, H = 8.33, N = 14.58, O = 8.34%). EIMS m/z (rel.int.%): 192.1263 (M^+ , calcd. for $C_{11}H_{16}N_2O$ 192.1262) (14), 164 (5), 134 (12), 121 (100), 106 (80), 91 (20) and 51 (12). IR ν_{max} (cm^{-1}): 3380, 1645, 1580 and 1110.

N-Imino methyl -2,3-dimethylaniline [2,3(CH₃)₂] C₆H₃-NH-CH=NH. It was obtained as a viscous liquid in 53% yield, bp 54-55° EIMS m/z (rel.int.%): 148.1013 (M^+ , calcd. for $C_9H_{12}N_2$ 148.1000) (28) 132 (30), 121 (100), 106 (70), 91 (20), 77 (36) and 51 (14), IR ν_{max} (cm^{-1}): 3505, 3405 and 1580.

N,N'-Bis-2,3-dimethyl phenylguanidine [2,3(CH₃)₂] C₆H₃-NH]₂ C=NH. It was obtained as a crystalline solid which on recrystallization from benzene formed elongated rods. mp 81-82° (yield 87%) and analyzed for $C_{17}H_{21}N_3$ (obsd. C = 76.18, H = 7.81, N = 16.01%; calcd. for $C_{17}H_{21}N_3$ C = 76.40, H = 7.87, N = 15.73%). EIMS m/z (rel.int.%): 267.1733 (M^+ , calcd. for $C_{17}H_{21}N_3$ 267.1735) (22), 252 (8), 147 (10), 121 (100), 106 (22), 77 (14) and 51 (40). IR ν_{max} (cm^{-1}): 3410, 1635, 1580 and 1120.

N-Cyano-2,5-dimethylaniline [2,5(CH₃)₂] C₆H₃-NH-CN. It was obtained as a viscous liquid (yield, 100%), showed a single spot on TLC, bp 67-68°. EIMS m/z (rel.int.%); 146,0839 (M⁺, calcd. for C₉H₁₀N₂, 146.0844) (100) 131 (58), 120 (40), 106 (42), 91 (34), 77 (42) and 51 (22). IR ν_{max} (cm⁻¹): 2160.

2,5-Dimethyl phenylurea [2,5 (CH₃)₂] C₆H₃-NH-CO-NH₂ It formed elongated rods on recrystallization from methanol (yield, 99%) and melted at 195-196° and analyzed for C₉H₁₂N₂O (obsd. C = 65.80, H = 7.36, N = 17.13 O = 9.71%; calcd. for C₉H₁₂N₂O C = 65.85, H = 7.32, N = 17.07, O = 0.76%). EIMS m/z (rel.int.%); 164,0956 (M⁺, calcd. for C₉H₁₂N₂O, 164.0949) (10), 146 (42), 120 (100), 106 (84), 91 (32), 77 (42) and 51 (20). IR ν_{max} (cm⁻¹): 3435, 3310, 1615 and 1570.

N-Acetyl, *N*'-2,5-dimethyl phenylurea was obtained as crystalline solid which on recrystallization from methanol formed irregular plates (yield, 95%), mp 181-182°. It analyzed for C₁₁H₁₄N₂O₂ (obsd. C = 64.08, H = 6.85, N = 13.56, O = 15.51%; calcd. for C₁₁H₁₄N₂O₂ C = 64.08, H = 6.80, N = 13.59, O = 15.53%). EIMS m/z (rel.int.%); 206.1059 (M⁺, calcd. for C₁₁H₁₄N₂O₂ 206.1055) (16), 163 (22), 146 (12), 120 (100), 106 (80), 91 (48) 77 (40) and 51 (22). IR ν_{max} (cm⁻¹): 3420, 1705 and 1590.

N-Imino methyl-2,5-dimethylaniline [2,5(CH₃)₂] C₆H₃-NH-CH=NH. It was obtained as a viscous liquid (yield, 43%), bp 70-71°. EIMS m/z (rel.int.%); 148,0997 (M⁺, calcd. for C₉H₁₄N₂, 148.1000) (40), 120 (100), 106 (70), 91 (26), 77 (72), 51 (18). IR ν_{max} (cm⁻¹): 3500, 3400 and 1590.

2,5-Dimethyl anilino imino methoxymethane [2,5 (CH₃)₂] C₆H₃-NH-C=NH (OCH₃). It was obtained on reaction of the cyanamide with 10% methanolic HCl and formed needles (yield, 85%) on recrystallization from ethyl acetate-methanol (1:1), mp 101-102° and analyzed for C₁₀H₁₄N₂O (obsd. C = 67.40, H = 8.01, N = 15.58, O = 9.01%; calcd. for C₁₀H₁₄N₂O C = 67.41, H = 7.86, N = 15.73, O = 9.00%). EIMS m/z (rel.int.%); 178.1110 (M⁺, calcd. for C₁₀H₁₄N₂O, 178.1106) (30), 147 (50), 120 (100), 106 (42), 91 (48), 77 (42) and 51 (10), IR ν_{max} (cm⁻¹): 3390, 1650, 1585 and 1110.

2,5-Dimethyl anilino imino ethoxymethane [2,5 (CH₃)₂] C₆H₃-NH-C=NH (OC₂H₅). Reactions of the cyanamide with 10% ethanolic HCl yielded the imino-ethoxy derivative which formed elongated rods from ethyl acetate - methanol (1:1) in 89% yield, mp 83-84° and analyzed for C₁₁H₁₆N₂O (obsd. C = 68.70, H = 8.31, N = 14.68, O = 8.31%; calcd. for C₁₁H₁₆N₂O C = 68.75, H = 8.33, N = 14.58, O = 8.34%). EIMS m/z (rel.int.%); 192.1258 (M⁺, calcd. for C₁₁H₁₆N₂O, 192.1262) (28), 164 (10), 148 (40), 120 (100), 106 (70), 91 (30), 77 (42)

and 51 (18). IR ν_{max} (cm⁻¹): 3390, 1645, 1585 and 1110.

N,N Bis (2,5-Dimethyl phenyl) guanidine [2,5(CH₃)₂] C₆H₃-NH] ₂-C=NH. The cyanamide on reaction with the parent base yielded the guanido derivative which recrystallized from benzene in rectangular plates (yield, 90%), mp 111-112° and analyzed for C₁₇H₂₁N₃ Obsd. C = 76.81, H = 7.81, N = 16.01%; calcd. for C₁₇H₂₁N₃ C = 76.40, H = 7.87, N = 15.73%). EIMS m/z (rel.int.%); 267.1730 (M⁺, calcd. for C₁₇H₂₁N₃, 267.1735) (16), 252 (8), 146 (100), 120 (80), 106 (26), 91 (28), 77 (38) and 51 (20). IR ν_{max} (cm⁻¹): 3310, 3220, 1660 and 1635.

N-Cyano-2,6-dimethylaniline [2,6 (CH₃)₂] C₆H₃-NH-CN. It was obtained as a viscous liquid (yield theoretical), bp, 40-41°, EIMS m/z (rel.int.%): 146.0839 (M⁺, calcd. for C₉H₁₀N₂, 146.0944) (78), 131 (40), 120 (100), 106 (84), 91 (38), 77 (48) and 51 (26). IR ν_{max} (cm⁻¹): 2210.

2,6-Dimethyl phenylurea [2,6 (CH₃)₂] C₆H₃-NH-CO-NH₂ It formed rectangular plates on recrystallization from methanol which melted at 170-171° (yield, 100%) and analyzed for C₉H₁₂N₂O (obsd. C = 65.84, H = 7.32, N = 17.13, O = 9.71%; calcd. for C₉H₁₂N₂O, C = 65.85, H = 7.32, N = 17.07, O = 9.76%). EIMS m/z (rel.int.%); 164,0960 (M⁺, calcd. for C₉H₁₂N₂O, 164,0949) (30), 146 (12), 120 (100), 106 (88), 91 (18), 77 (30) and 51 (12). IR ν_{max} (cm⁻¹): 3405, 3320, 1670 and 1580.

N-Acetyl, *N*' 2,6-methyl phenylurea formed irregular plates on recrystallization from ethanol which melted at 181-182° (yield, 90%). It analyzed for C₁₁H₁₄N₂O₂ (obsd. C = 64.08, H = 6.85, N = 13.51, O = 15.56%; calcd. for C₁₁H₁₄N₂O₂ C = 64.08, H = 6.80, N = 13.59, O = 15.53%). EIMS m/z (rel.int.%); 206.1041 (M⁺, calcd. for C₁₁H₁₄N₂O₂, 206.1055) (40), 163 (12), 146 (8), 120 (100), 106 (80), 91 (20), 77 (32) and 51 (24). IR ν_{max} (cm⁻¹): 3470, 1730 and 1600.

N-Imino methyl-2,6-dimethylaniline [2,6 (CH₃)₂] C₆H₃-NH-CH=NH. It was obtained as a viscous liquid (yield, 57%), bp 73-74° EIMS m/z (rel.int.%); 148.1012 (M⁺, calcd. for C₉H₁₂N₂, 148.1000) (10), 133 (16), 120 (100), 106 (40), 91 (12), 77 (24) and 51 (80). IR ν_{max} (cm⁻¹): 3560, 3485 and 1595.

2,6-Dimethyl anilino imino methoxymethane [2,6 (CH₃)₂] C₆H₃-NH-C=NH (OCH₃). On recrystallization from a mixture of ethyl acetate-methanol (1:1) it formed prismatic rods in 80% yield, mp 57-58° and analyzed for C₁₀H₁₄N₂O (obsd. C = 67.42, H = 7.85, N = 15.70, O = 9.03%; calcd. for C₁₀H₁₄N₂O C = 67.41, H = 7.86, N = 15.73, O = 9.00%). EIMS m/z (rel.int.%); 178.1100 (M⁺, calcd. for C₁₀H₁₄N₂O, 178,1106) (40), 163 (80), 146 (28), 120 (100), 106 (80), 91 (30), 77 (32) and 51 (14).

IR ν_{\max} (cm^{-1}): 3395, 1650, 1590 and 1115.

2,6-Dimethyl anilino imino ethoxymethane [2,6-(CH_3)₂] $\text{C}_6\text{H}_3\text{-NH-C=NH}(\text{OC}_2\text{H}_5)$. It crystallized from a mixture of ethyl acetate-methanol (1:1) in needles melting at 118-119 $^\circ$ (yield, 88%) and analyzed for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}$ (obsd. C = 68.75, H = 8.33, N = 14.58, O = 8.36%; calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}$ C = 68.75, H = 8.33, N = 14.58, O = 8.34%). EIMS m/z (rel.int.%): 192.1249 (M^+ , calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}$, 192.1262) (22), 177 (6), 146 (12), 120 (100), 106 (64), 91 (20) 77 (20) and 51 (61). IR ν_{\max} (cm^{-1}): 3390, 1650, 1580 and 1115.

N,N'-Bis (2,6-dimethylphenyl) guanidine [2,6(CH_3)₂ $\text{C}_6\text{H}_3\text{-NH}$]₂- CH=NH . It was obtained as a crystalline solid which on recrystallization from methanol formed irregular plates (yield, 91%), mp 98-99 $^\circ$ and analyzed for $\text{C}_{17}\text{H}_{21}\text{N}_3$ C = 76.41, H = 7.86, N = 15.63%; calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_3$ C = 76.40, H = 7.87, N = 15.73%). EIMS m/z (rel.int.%): 267.1740 (M^+ , calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_3$, 267.1735) (22), 252 (8), 146 (10), 120 (100), 106 (18), 77 (14) and 51 (6). IR ν_{\max} (cm^{-1}): 3300, 3210. 1650 and 1625.

N-Cyano-2-methoxyaniline (2-OCH₃) $\text{C}_6\text{H}_4\text{-NH-CN}$. The cyano derivative was obtained as a viscous liquid in theoretical yield, bp 89-90 $^\circ$. EIMS m/z (rel.int.%): 148.0627 (M^+ , calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}$ 148.0633) (100), 118 (20), 105 (20), 91 (28), 83 (32), 77 (12), 63 (12) and 51 (26). IR ν_{\max} (cm^{-1}): 2200.

2-Methoxy phenylurea (2-OCH₃) $\text{C}_6\text{-H}_4\text{-NH-CO-NH}_2$. On recrystallization from ethanol it formed irregular plates, mp 162-163 $^\circ$ (yield 93%) and analyzed for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ (obsd. C = 58.82, H = 6.07, N = 16.79, O = 18.32%; calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ C = 57.83, H = 6.02, N = 16.87, O = 19.28%). EIMS m/z (rel.int.%): 166.9740 (M^+ , calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ 166.0742) (52), 123 (78), 108 (100), 80 (72) and 57 (18). IR ν_{\max} (cm^{-1}): 3410, 3380, 1695 and 1590.

N-Acetyl-N' 2-methoxy phenylurea: It formed elongated rods on recrystallization from ethanol, mp 194-195 $^\circ$ (yield 85%) and analyzed for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ (obsd. C = 57.68, H = 5.76, N = 13.39, O = 23.17%; calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ C = 57.69, H = 5.77, N = 13.46, O = 23.08%). EIMS m/z (rel.int.%): 208.0851 (M^+ , calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ 208.0848) (10), 165, (12), 136 (26), 123 (100), 108 (78), 92 (10) and 51 (80). IR ν_{\max} (cm^{-1}): 3400, 1700 and 1620.

2-Methoxy anilino imino methoxymethane (2-OCH₃) $\text{C}_6\text{H}_4\text{NH-C=NH}(\text{OCH}_3)$. It was obtained as crystalline solid which on recrystallization from ethyl acetate-methanol (1:1), formed irregular plates, mp 67-68 $^\circ$ (yield 83%) and analyzed for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ (obsd. C = 60.01, H = 6.68, N = 15.54, O = 17.77%; calcd. for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ C =

60.00, H = 6.67, N = 15.56, O = 17.77%). EIMS m/z (rel.int.%): 180.0893 (M^+ , calcd. for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ 180, 0898) (100), 165 (12), 149 (70), 132 (28), 108 (32), 93 (40), and 51 (28). IR ν_{\max} (cm^{-1}): 3420, 1690, 1590 and 1120.

2-Methoxy anilino imino ethoxymethane (2-OCH₃) $\text{C}_6\text{H}_4\text{-NH-C=NH}(\text{OC}_2\text{H}_5)$. It formed rectangular plates on recrystallization from ethyl acetate methanol (1:1), mp 83-84 $^\circ$ (yield 90%). It analyzed for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ (obsd. C = 61.75, H = 6.98, N = 14.29, O = 16.98%; calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ C = 61.86, H = 7.22, N = 14.43, O = 16.49%). EIMS m/z (rel.int.%): 194.1049 (M^+ , calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ 194.1055) (28), 179 (20), 163 (24), 108 (100), 83 (60), 65 (26) and 52 (21). IR ν_{\max} (cm^{-1}): 3410, 1660, 1590 and 1120.

N-Amino methyl-2-anisidine (2-OCH₃) $\text{C}_6\text{H}_4\text{-NH-CH}_2\text{-NH}_2$. It was obtained as a viscous liquid in 43% yield, bp 82-83 $^\circ$ EIMS m/z (rel.int.%): 152.0956 (M^+ , calcd. for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$ 152.0949) (8), 137 (12), 123 (100), 109 (98), 92 (6), 80 (66), 65 (20) and 52 (24). IR ν_{\max} (cm^{-1}): 3498, 3400 and 1588.

2-Methoxy phenylguanidine (2-OCH₃) $\text{C}_6\text{H}_4\text{-NH-C=NH}(\text{NH}_2)$. It was obtained as a crystalline solid which on recrystallization from benzene formed irregular plates, mp 160-161 $^\circ$ (yield 49%) and analyzed for $\text{C}_8\text{H}_{11}\text{N}_3\text{O}$ (obsd. C = 57.85, H = 6.65, N = 25.46, O = 10.04%; calcd. for $\text{C}_8\text{H}_{11}\text{N}_3\text{O}$ C = 58.18, H = 6.67, N = 25.45, O = 9.70%). EIMS m/z (rel.int.%): 165.0911 (M^+ , calcd. for $\text{C}_8\text{H}_{11}\text{N}_3\text{O}$ 165.0902) (10), 148 (100), 133 (68), 120 (40), 105 (58), 78 (30), 63 (12) and 52 (26). IR ν_{\max} (cm^{-1}): 3300, 3220, 1660 and 1630.

N,N'-Di-2-methoxy phenylguanidine [(2-OCH₃) $\text{C}_6\text{H}_4\text{-NH}$]₂ C=NH . It formed needles on recrystallization from benzene, mp 91-92 $^\circ$ (yield 87%) and analyzed for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2$ (obsd. C = 66.34, H = 6.29, N = 15.49, O = 11.88%; calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2$ C = 66.42, H = 6.27, N = 15.50, O = 11.81%). EIMS m/z (rel.int.%): 271.1326 (M^+ , calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2$ 271.1321) (16), 148 (40), 123 (100), 94 (42), 80 (22) and 52 (15). IR ν_{\max} (cm^{-1}): 3320, 3240, 1660 and 1610.

N-Cyano-3-methoxy aniline (3-OCH₃) $\text{C}_6\text{H}_4\text{-NH-CN}$. The cyano derivative was obtained as a viscous liquid in theoretical yield, bp 86-87 $^\circ$. EIMS m/z (rel.int.%): 148.0630 (M^+ , calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}$ 148.0633) (100), 118 (30), 105 (18), 91 (26), 83 (24), 77 (14), 63 (12) and 53 (10). IR ν_{\max} (cm^{-1}): 2220.

3-Methoxy phenylurea (3-OCH₃) $\text{C}_6\text{H}_4\text{-NH-CO-NH}_2$. It was obtained as a crystalline solid which on recrystallization from methanol formed needles mp 134-135 $^\circ$ (yield 90%) and analyzed for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ (obsd. C = 58.72, H =

6.04, N = 16.92, O = 18.32%, calcd. for $C_8H_{10}N_2O_2$ C = 57.83, H = 6.02, N = 16.87, O = 19.28%. EIMS m/z (rel. int.%): 166.0741 (M^+ , calcd. for $C_8H_{10}N_2O_2$ 166.0742) (72), 123 (100), 94 (72), 80 (28), 20) and 57 (12). IR ν_{max} (cm^{-1}): 3400, 3200, 1640 and 1580.

N-Acetyl-*N'*-3-methoxy phenylurea: It formed irregular plates on recrystallization from ethanol, mp 193-194^o (yield 86%) and analyzed for $C_{10}H_{12}N_2O_3$ (obsd. C = 57.68, H = 5.78, N = 13.73, O = 23.17%; calcd. for $C_{10}H_{12}N_2O_3$ C = 57.69, H = 5.77, N = 13.46, O = 23.08%). EIMS m/z (rel.int.%): 208.0841 (M^+ , calcd. for $C_{10}H_{12}N_2O_3$ 208.0848) (10), 165 (12), 151 (40), 123 (100), 108 (78), 80 (20), 65 (10) and 51 (80). IR ν_{max} (cm^{-1}): 3400, 1710 and 1665.

3-Methoxy anilino imino methoxymethane (*3*-OCH₃) $C_6H_4-NH-C=NH$ (OCH₃). On recrystallization from ethyl acetate-methanol (1:1), it formed cubical plates, mp 68-69^o (yield 90%) and analyzed for $C_9H_{12}N_2O_2$ (obsd. C = 60.01, H = 6.66, N = 15.54, O = 17.79%; calcd. for $C_9H_{12}N_2O_2$ C = 60.00, H = 6.67, N = 15.56, O = 17.77%). EIMS m/z (rel.int.%): 180.0890 (M^+ , calcd. for $C_9H_{12}N_2O_2$ 180.0890) (100), 149 (28), 122 (52), 107 (20), 94 (22), 64 (18) and 52 (12). IR ν_{max} (cm^{-1}): 3400, 1660, 1580 and 1140.

3-Methoxy anilino imino ethoxymethane (*3*-OCH₃) $C_6H_4-NH-C=NH$ (OC₂H₅) (t formed irregular plates on recrystallization from ethyl acetate-methanol (1:1), mp 83-84^o (yield 93%) and analyzed for $C_{10}H_{14}N_2O_2$ (obsd. C = 61.86, H = 7.21, N = 14.42, O = 16.51%; calcd. for $C_{10}H_{14}N_2O_2$ C = 61.86, H = 7.22, N = 14.43, O = 16.49%). EIMS m/z (rel.int.%): 194.1048 (M^+ , calcd. for $C_{10}H_{14}N_2O_2$ 194.1055) (26), 180 (24), 163 (26), 123 (70), 108 (100), 93 (18), 80 (52), 65 (22) and 52 (22). IR ν_{max} (cm^{-1}): 3410, 1640 1580 and 1110.

N-Amino methyl-3-anisidine (*3*-OCH₃) $C_6H_4-NH-CH_2-NH_2$. It was obtained as a viscous liquid in 34% yield, bp 63-64^o EIMS m/z (rel.int.%): 152.0956 (M^+ , calcd. for $C_8H_{12}N_2O$ 152.0949) (100), 133 (64), 105 (10), 71 (8) and 52 (10). IR ν_{max} (cm^{-1}): 3600, 3440 and 1585.

3-Methoxy phenylguanidine (*3*-OCH₃) $C_6H_4-NH-C(=NH)(NH_2)$. It formed prismatic rods on recrystallization from benzene, mp 96-97^o (yield 57%) and analyzed for $C_8H_{11}N_3O$ (obsd. C = 57.84, H = 6.66, N = 25.45, O = 10.05%; calcd. For $C_8H_{11}N_3O$ C = 58.18, H = 6.67, N = 25.45, O = 9.70%). EIMS m/z (rel.int.%): 165.0911 (M^+ , calcd. for $C_8H_{11}N_3O$ 165.0902) (80), 123 (12), 107 (70), 91 (100), 71 (90), 57 (42) and 52 (18), IR ν_{max} (cm^{-1}): 3350, 3210, 1665 and 1625.

N,N-Di-*3*-Methoxy phenylguanidine [(*3*-OCH₃) $C_6H_4-NH/2$ C=NH]. On recrystallization from benzene it formed

cubical plates, mp 81-82^o (yield 90%). It analyzed for $C_{15}H_{17}N_3O_2$ (obsd. C = 66.43, H = 6.26, N = 15.51, O = 11.80%; calcd. for $C_{15}H_{17}N_3O_2$ C=66.42, H=6.27, N = 15.50, O =11.81%). EIMS m/z (rel.int.%): 271.1319 (M^+ , calcd. for $C_{15}H_{17}N_3O_2$ 271.1321) (24), 255 (5), 148 (20), 123 (100), 94 (36), 77 (20), 64 (10) and 52 (8), IR ν_{max} (cm^{-1}): 3440, 3220, 1660 and 1600.

N-Cyano-4-methoxyaniline (*4*-OCH₃) $C_6H_4-NH-CN$. It was obtained as a viscous liquid (yield theoretical) bp 58-59^o. EIMS m/z (rel.int.%); 148.0631 (M^+ , calcd. for $C_8H_8N_2O$, 148.0633) (24), 133 (12), 123 (48), 108 (52), 83 (100), 65 (8) and 53 (12). IR ν_{max} (cm^{-1}): 2230.

4-Methoxy phenylurea (*4*-OCH₃) $C_6H_4-NH-CONH_2$. The amido derivative formed irregular plates on recrystallization from methanol (yield, 90%), mp 160-161^o and analyzed for $C_8H_{10}N_2O_2$ (obsd. C = 57.82, H = 6.03, N = 16.87, O = 19.28%; calcd. for $C_8H_{10}N_2O_2$ C = 57.83, H = 6.02, N = 16.86, O = 19.29%). EIMS m/z (rel.int.%); 166.0731 (M^+ , calcd. for $C_8H_{10}N_2O_2$, 166.0742) (34), 123 (60), 108 (100), 80 (28), 65 (10) and 53 (10). IR ν_{max} (cm^{-1}): 3500, 3410, 1670 and 1590.

N-Acetyl, *N'*-4-methoxyphenylurea recrystallized from methanol into fine plates, mp 189-190^o (yield, 83%). It analyzed for $C_{10}H_{12}N_2O_3$ (obsd. C = 57.68, H = 5.78, N = 13.45, O = 23.09%; calcd. for $C_{10}H_{12}N_2O_3$ C = 57.69, H = 5.77, N = 13.46, O = 23.08%). EIMS m/z (rel.int.%); 208.0841 (M^+ , calcd. for $C_{10}H_{12}N_2O_3$, 208.0848) (14), 192 (8), 165 (54), 123 (100), 108 (90), 95 (80), 80 (10), 65 (6) and 53 (10). IR ν_{max} (cm^{-1}): 3400, 1710 and 1665.

N-Amino methyl-4-anisidine (*4*-OCH₃) $C_6H_4-NH-CH_2-NH_2$. It was obtained as a viscous liquid in 53% yield, bp 61-62^o. EIMS m/z (rel.int.%); 152.0940 (M^+ , calcd. for $C_8H_{12}N_2O$, 152.0949) (10), 137 (10), 123 (88), 108 (100), 80 (54), 65 (16) and 53 (20). IR ν_{max} (cm^{-1}): 3495, 3450 and 1585.

4-Methoxy anilino imino methoxymethane (*4*-OCH₃) $C_6H_4-NH-C=NH$ (OCH₃). It formed elongated rods from ethyl acetate-methanol (1:1) which melted at 74-75^o (yield, and analyzed for $C_9H_{12}N_2O_2$ (obsd. C = 60.01, H = 6.66, N = 15.56, O = 17.77%; calcd. for $C_9H_{12}N_2O_2$ C = 60.00, H = 6.67, N = 15.55, O = 17.78%). EIMS m/z (rel.int. %); 180.0879 (M^+ , calcd. for $C_9H_{12}N_2O_2$, 180.0898) (100), 165 (12), 149 (50), 123 (34), 108 (82), 93 (28), 80 (62), 65 (22) and 53 (18). IR ν_{max} (cm^{-1}): 3410, 1660 1590 and 1115.

4-Methoxy anilino imino ethoxymethane (*4*-OCH₃) $C_6H_4-NH-C=NH$ (OC₂H₅). It was obtained as a crystalline solid and formed irregular plates on recrystallization from ethyl acetate-methanol (1:1), mp 88-89^o (yield, 91%) and analyzed for $C_{10}H_{14}N_2O_2$ (obsd. C = 61.84, H = 7.23, N = 14.44, O = 16.49%; calcd. for $C_{10}H_{14}N_2O_2$ C = 61.85,

H = 7.22, N = 14.43, O = 16.50%). EIMS m/z (rel.int.%): 194.1055 (M^+ , calcd. for $C_{10}H_{14}N_2O_2$, 194.1046) (24), 179 (20), 163 (22), 123 (70), 108 (100), 93 (14), 80 (50), 65 (22) and 52 (22). IR ν_{max} (cm^{-1}): 3405, 1660, 1580 and 1110.

4-Methoxy phenylguanidine (4-OCH₃) C₆H₄-NH-C=NH (NH₂). It crystallized from benzene as fine needles, mp 130-131° (yield, 40%) and analyzed for $C_8H_{11}N_3O$ (obsd. C = 58.17, H = 6.68, N = 25.43, O = 9.72%; calcd. for $C_8H_{11}N_3O$ C = 58.18, H = 6.67, N = 25.45, O = 9.70%). EIMS m/z (rel.int.%): 165.0912 (M^+ , calcd. for $C_8H_{11}N_3O$, 165.0902) (10), 148 (100), 133 (70), 105 (80), 91 (6) and 57 (8). IR ν_{max} (cm^{-1}): 3300, 3210, 1670 and 1630.

N-N Di(4-Methoxy) phenylguanidine [(4-OCH₃) C₆H₄-NH]₂-C=NH. It formed irregular plates on recrystallization from benzene, mp 103-104° (yield, 98%) and analyzed for $C_{15}H_{17}N_3O_2$ (obsd. C = 66.41, H = 6.28, N = 15.51, O = 11.80%; calcd. for $C_{15}H_{17}N_3O_2$ C = 66.42, H = 6.27, N = 15.50, O = 11.81%). EIMS m/z (rel.int.%): 271.1319 (M^+ , calcd. for $C_{15}H_{17}N_3O_2$, 271.1321) (10), 148 (93), 123 (100), 106 (6), 94 (52), 66 (18) and 52 (18). IR ν_{max} (cm^{-1}): 3320, 3230, 1665 and 1640.

N-Cyano-2-ethoxyaniline (2-OC₂H₅) C₆H₄-NH-CN. It was obtained as a viscous liquid in theoretical yield, bp 104-105°. EIMS m/z (rel.int.%): 162.0789 (M^+ , calcd. for $C_9H_{11}N_2O$ 162.0793) (42), 134 (100), 105 (10), 79 (12) and 52 (10). IR ν_{max} (cm^{-1}): 2200.

2-Ethoxy phenylurea (2-OC₂H₅) C₆H₄-NH-CO-NH₂. It formed elongated rods on recrystallization from methanol ethanol (1:1), mp 135-136° (yield 90%) and analyzed for $C_9H_{12}N_2O_2$ (obsd. C = 60.30, H = 6.64, N = 15.59, O = 17.57%; calcd. for $C_9H_{12}N_2O_2$ C = 60.00, H = 6.67, N = 15.56, O = 17.77%). EIMS m/z (rel.int.%): 180.0899 (M^+ , calcd. for $C_9H_{12}N_2O_2$ 180.0898) (10), 165 (52), 137 (38), 122 (38), 109 (100), 80 (48), 65 (20), and 53 (32). IR ν_{max} (cm^{-1}): 3490, 3380, 1660 and 1570.

N-Acetyl-N-2-ethoxy phenylurea: On recrystallization from ethanol it formed irregular plates, mp 212-213° (yield 85%). It analyzed for $C_{11}H_{14}N_2O_3$ (obsd. C = 59.40, H = 6.37, N = 12.59, O = 21.64%; calcd. for $C_{11}H_{14}N_2O_3$ C = 59.46, H = 6.31, N = 12.61, O = 21.62%). EIMS m/z (rel.int.%): 222.10009 (M^+ , calcd. for $C_{11}H_{14}N_2O_3$ 222.1004) (20), 179 (30), 165 (58), 137 (42), 122 (68), 109 (100), 80 (50), 65 (28) and 53 (30). IR ν_{max} (cm^{-1}): 3380, 1700 and 1610.

2-Ethoxy anilino imino methoxymethane (2-OC₂H₅) C₆H₄-NH-C=NH (OCH₃). It was obtained as a crystalline solid which on recrystallization from ethyl acetate-methanol (1:1), formed prismatic rods, mp 103-104° (yield 93%) and analyzed for $C_{10}H_{14}N_2O_2$ (obsd. C = 61.79, H = 7.22, N = 14.43, O = 16.49%; calcd. for $C_{10}H_{14}N_2O_2$

C = 61.79, H = 7.22, N = 14.43, O = 16.49%). EIMS m/z (rel.int.%): 194.1046 (M^+ , calcd. for $C_{10}H_{14}N_2O_2$ 194.1055) (72), 165 (70), 151 (12), 122 (16), 108 (100), 83 (58) (46) and 52 (12). (R ν_{max} (cm^{-1}): 3390, 1610, 1959 and 1120.

2-Ethoxy anilino imino ethoxymethane (2-OC₂H₅) C₆H₄-NH-C=NH (OC₂H₅). On recrystallization from ethyl acetate, it formed rectangular plates, mp 144-145° (yield 78%). It analyzed for $C_{11}H_{16}N_2O_2$ (obsd. C = 63.40, H = 7.74, N = 13.40, O = 15.46; calcd. for $C_{11}H_{16}N_2O_2$ C = 63.46, H = 7.69, N = 13.46, O = 15.39%). EIMS m/z (rel.int.%): 208.1210 (M^+ , calcd. for $C_{11}H_{16}N_2O_2$ 208.1212) (30), 180 (10), 164 (30), 134 (78), 108 (100), 80 (26), 65 (14), and 52 (22). IR ν_{max} (cm^{-1}): 3400, 1660, 1595 and 1115.

N-Amino methyl-2-phenetidine (2-OC₂H₅) C₆H₄-NH-CH₂-NH₂. It was obtained as a viscous liquid in 36% yield, bp 63-64°. EIMS m/z (rel.int.%): 166.1110 (M^+ , calcd. for $C_9H_{14}N_2O$ 166.1106) (28), 151 (14), 135 (98), 108 (100), 94 (18), 80 (50), 65 (22) and 53 (34), IR ν_{max} (cm^{-1}): 3500, 3450 and 1590.

2-Ethoxy phenylguanidine (2-OC₂H₅) C₆H₄-NH-C=NH (NH₂). It formed needles on recrystallization from benzene, mp 87-88° (yield 46%) and analyzed for $C_9H_{13}N_3O$ (obsd. C = 60.32, H = 6.98, N = 24.03, O = 8.67%; calcd. for $C_9H_{13}N_3O$ C = 60.33, H = 7.26, N = 23.46, O = 8.95%). EIMS m/z (rel.int.%): 179.1048 (M^+ , calcd. for $C_9H_{13}N_3O$ 179.1058) (5), 162 (40), 134 (100), 108 (48), 94 (12), 79 (18), 65 (12) and 52 (18). IR ν_{max} (cm^{-1}): 3325, 3210, 1660 and 1640.

N,N-Di-2-ethoxy phenylguanidine [(2-OC₂H₅) C₆H₄-NH]₂ C=NH. It was obtained as a crystalline solid which on recrystallization from benzene formed needles, mp 153-154° (yield 82%) and analyzed for $C_{17}H_{21}N_3O_2$ (obsd. C = 68.20, H = 7.11, N = 14.01, O = 10.68%; calcd. for $C_{17}H_{21}N_3O_2$ C = 68.23, H = 7.02, N = 14.05, O = 10.70%). EIMS m/z (rel.int.%): 299.1629 (M^+ , calcd. for $C_{17}H_{21}N_3O_2$ 299.1633) (10), 282 (5), 162 (50), 134 (100), 108 (34), 79 (10) and 52 (12). IR ν_{max} (cm^{-1}): 3320, 3220, 1650 and 1635.

N-Cyano-3-ethoxyaniline (3-OC₂H₅) C₆H₄-NH-CN. It was obtained as a viscous liquid, bp 97-98° (yield theoretical). EIMS m/z (rel.int. %): 162.0792 (calcd. for $C_9H_{10}N_2O$, 162.0793) (40), 134 (100), 108 (20), 94 (10), 79 (14) and 52 (12). IR ν_{max} (cm^{-1}): 2210.

3-Ethoxy phenylurea (3-OC₂H₅) C₆H₄-NH-CO-NH₂. On recrystallization from methanol it formed elongated rods mp 112-113° (yield, 84%) and analyzed for $C_9H_{12}N_2O_2$ (obsd. C = 60.01, H = 6.66, N = 15.54, O = 17.79%; calcd. for $C_9H_{12}N_2O_2$ C = 60.00, H = 6.67, N = 15.55, O =

17.78%). EIMS m/z (rel.int.%); 180.0891 (M^+ , calcd. for $C_9H_{12}N_2O_2$, 180.0898) (50), 163 (12), 137 (4), 134 (30), 108 (100), 80 (26) and 53 (20). IR ν_{max} (cm^{-1}): 3495, 3338, 1660 and 1570.

N-Acetyl, N-3-ethoxy phenylurea formed irregular plates on recrystallization from ethanol, mp 162-163 $^{\circ}$ (yield, 92%) and analyzed for $C_{11}H_{14}N_2O_3$ (obsd. C = 59.47, H = 6.20, N = 12.70, O = 21.63%; calcd. for $C_{11}H_{14}N_2O_3$ C = 59.46, H = 6.31, N = 12.61, O = 21.62%). EIMS m/z (rel.int.%); 222.1011 (M^+ , calcd. for $C_{11}H_{14}N_2O_3$, 222.1004) (10), 179 (30), 163 (6), 137 (40), 134 (22), 108 (100), 80 (30) and 53 (20). IR ν_{max} (cm^{-1}): 3500, 1680 and 1635.

N-Amino methyl-3-ethoxyaniline ($3-OC_2H_5$) $C_6H_4-NH-CH_2-NH_2$. It was obtained as a viscous liquid which failed to crystallize and showed a single spot on TLC, bp 83-84 $^{\circ}$ (yield, 47%). EIMS m/z (rel.int.%); 166.111 (M^+ , calcd. for $C_9H_{14}N_2O$ 166.1106) (42), 137 (60), 108 (100), 94 (6), 80 (40) and 52 (26). IR ν_{max} (cm^{-1}): 3500, 3450 and 1580.

2-Ethoxy anilino imino methoxymethane ($3-OC_2H_5$) $C_6H_4-NH-C=NH(OCH_3)$. It was obtained as a crystalline solid which on recrystallization from ethyl acetate - methanol formed square plates, mp 132-133 $^{\circ}$ (yield, 98%) and analyzed for $C_{10}H_{14}N_2O_2$ (obsd. C = 61.84, H = 7.23, N = 14.41, O = 16.52%, calcd. for $C_{10}H_{14}N_2O_2$ C = 61.85, H = 7.22, N = 14.43, O = 16.50%). EIMS m/z (rel.int.%); 194.1059 (M^+ , calcd. for $C_{10}H_{14}N_2O_2$, 194.1055) (28), 165 (62), 134 (18), 108 (100), 94 (6), 80 (18) and 52 (14). IR ν_{max} (cm^{-1}): 3350, 1660, 1595 and 1115.

3-Ethoxy anilino imino ethoxymethane ($3-OC_2H_5$) $C_6H_4-NH-C=NH(OC_2H_5)$. It formed irregular plates on recrystallization from ethyl acetate-methanol (1:1), mp 144-145 $^{\circ}$ (yield, 76%) and analyzed for $C_{11}H_{16}N_2O_2$ (obsd. C = 63.40, H = 7.74, N = 13.47, O = 15.76%; calcd. for $C_{11}H_{16}N_2O_2$ C = 63.46, H = 7.69, N = 13.46, O = 15.38%). EIMS m/z (rel.int.%); 208.1207 (M^+ , calcd. for $C_{11}H_{16}N_2O_2$, 208.1211) (22), 193 (80), 180 (80), 165 (12), 137 (24), 122 (28), 108 (100), 94 (6), 80 (22), 65 (16) and 53 (18). IR ν_{max} (cm^{-1}): 3410, 1660, 1595 and 1115.

3-Ethoxy phenylguanidine ($3-OC_2H_5$) $C_6H_4-NH-C=NH(NH_2)$. On recrystallization from benzene it formed flowers of needles, mp 91-92 $^{\circ}$ (yield, 59%) and analyzed for $C_9H_{13}N_3O$ (obsd. C = 60.44, H = 7.15, N = 23.47, O = 8.94%; calcd. for $C_9H_{13}N_3O$ C = 60.33, H = 7.26, N = 23.46, O = 8.95%). EIMS m/z (rel.int.%); 179.1052 (M^+ , calcd. for $C_9H_{13}N_3O$, 179.1058) (20), 162 (8), 137 (40), 108 (100), 97 (20), 80 (34), 71 (32) and 52 (28).

IR ν_{max} (cm^{-1}): 3300, 3200, 1660 and 1640.

N,N-Di (3-ethoxy) phenylguanidine [$(3-OC_2H_5)$ C_6H_4NH] $_2$ $C=NH$. It was obtained as a crystalline solid which on recrystallization from benzene gave elongated rods, mp 161-162 $^{\circ}$ (yield, 90%), and analyzed for $C_{17}H_{21}N_3O_2$ *obsd. C = 68.25, H = 7.00, N = 14.06, O = 10.69%; calcd. for $C_{17}H_{21}N_3O_2$ C = 68.23, H = 7.02, N = 14.05, C = 10.70%). EIMS m/z (rel.int.%); 229.1629 (M^+ , calcd. for $C_{17}H_{21}N_3O_2$ and 52 (16). IR ν_{max} (cm^{-1}): 3320, 3210, 1655 and 1640.

N-Cyano-4-ethoxyaniline ($4-OC_2H_5$) $C_6H_4-NH-CN$. The cyanamide was obtained as a viscous liquid in theoretical yield, bp 81-82 $^{\circ}$ EIMS m/z (rel.int.%); 162.0786 (M^+ , calcd. for $C_9H_{10}N_2O$, 162.0793) (38), 134 (100), 107 (6), 83 (14), 63 (6), and 52 (10). IR ν_{max} (cm^{-1}): 2200.

4-Ethoxy phenylurea ($4-OC_2H_5$) $C_6H_4-NH-CO-NH_2$. On recrystallization from methanol it formed irregular plates, mp 174-175 $^{\circ}$ (yield, 83%) and analyzed for $C_9H_{12}N_2O_2$ (obsd. C = 60.01, H = 6.69, N = 15.50, O = 17.68%; calcd. for $C_9H_{12}N_2O_2$ C = 60.00, H = 6.67, N = 15.55, O = 17.68%). EIMS m/z (rel.int.%); 180.0874 (M^+ , calcd. for $C_9H_{12}N_2O_2$, 180.0898) (38), 162 (8), 137 (32), 108 (100), 97 (8), 80 (36), 71 (72), and 57 (50). IR ν_{max} (cm^{-1}): 3390, 1670 and 1600.

N-Acetyl, N-4-ethoxy phenylurea recrystallized from methanol-water (9.9:0.1) as elongated rods, mp 220-221 $^{\circ}$ (yield, 76%). It analyzed for $C_{11}H_{14}N_2O_3$ (obsd. C = 59.47, H = 6.29, N = 12.63, O = 21.62%; calcd. for $C_{11}H_{14}N_2O_3$ C = 59.46, H = 6.31, N = 12.61, O = 21.62%). EIMS m/z (rel.int.%); 222.1014 (M^+ , calcd. for $C_{11}H_{14}N_2O_3$, 222.1004) (10), 179 (12), 162 (8), 137 (30), 108 (100), 97 (14), 80 (40), 71 (90), and 57 (52): IR ν_{max} (cm^{-1}): 3400, 1705 and 1660.

N-Amino methyl-4-ethoxy phenylamine ($4-OC_2H_5$) $C_6H_4-NH-CH_2-NH_2$. It was obtained as a viscous liquid mp 67-68 $^{\circ}$. EIMS m/z (rel.int.%); 166.1011 (M^+ , calcd. for $C_9H_{14}N_2O$, 166.1106) (38), 151 (26), 137 (58), 122 (68), 108 (100), 94 (8), 80 (40), 65 (20) and 53 (22). IR ν_{max} (cm^{-1}): 3498, 3400 and 1580.

4-Ethoxy anilino imino methoxy methane ($4-OC_2H_5$) $C_6H_4-NH-C=NH(OCH_3)$. On recrystallization from a mixture of ethyl acetate-methanol (1:1) it formed elongated rods, mp 107-108 $^{\circ}$ (yield, 70%) and analyzed for $C_{10}H_{14}N_2O_2$ (obsd. C = 61.84, H = 7.23, N = 14.41, O = 16.25%; calcd. for $C_{10}H_{14}N_2O_2$ C = 61.85, H = 7.22, N = 14.43, O = 16.50%). EIMS m/z (rel.int.%); 194.1046 (M^+ , calcd. for $C_{10}H_{14}N_2O_2$, 194.1055) (70), 165 (64), 134 (12), 122 (20), 108 (100), 94 (6), 80 (14), 65 (10), and 53 (16). IR ν_{max} (cm^{-1}): 3360, 1660, 1595 and 1115.

3-Ethoxy anilino imino ethoxymethane (4-OC₂H₅) C₆H₄-NH-C=NH (OC₂H₅). It formed prismatic rods from ethyl acetate-methanol (1:1) mp 114-115^o (yield, 83%) and analyzed for C₁₁H₁₆N₂O₂ (obsd. C = 63.45, H = 7.71, N = 13.47, O = 15.37%. calcd. for C₁₁H₁₆N₂O₂ C = 63.46, H = 7.70, N = 13.46, O = 15.38%). EIMS m/z (rel.int.%): 208.1218 (M⁺, calcd. for C₁₁H₁₆N₂O₂, 208.1212) (32), 193 (28), 180 (12), 165 (30), 151 (20), 137 (28), 120 (16), 108 (100), 93 (6), 80 (22), 65 (12) and 53 (16). IR ν_{\max} (cm⁻¹): 3410, 1655, 1595 and 1115.

4-Ethoxy phenylguanidine (4-OC₂H₅) C₆H₄-NH-C=NH (NH₂). The guanido derivative formed needles from ethyl acetate-methanol (yield, 48%), mp 87-88^o and analyzed for C₉H₁₃N₃O (obsd. C = 60.35, H = 7.25, N = 23.45, O = 8.95%; calcd. for C₉H₁₃N₃O C = 60.33, H = 7.26, N = 23.46, O = 8.95%). EIMS m/z (rel.int.%): 179.1052 (M⁺, calcd. for C₉H₁₃N₃O, 179.1058) (30), 162 (80), 151 (6), 137 (30), 120 (22), 108 (100), 94 (16), 80 (34), 65 (10), and 53 (26). IR ν_{\max} (cm⁻¹): 3305, 3295, 1665 and 1640.

N,N-Di (4-ethoxy-phenylguanidine [(4-OC₂H₅) C₆H₄-NH]₂-C=NH. It formed rectangular plates on recrystallization from benzene, mp 149-150^o (yield, 90%) and analyzed for C₁₇H₂₁N₃O₂ (obsd. C = 68.24, H = 7.01, N = 14.06, O = 10.69%; calcd. for C₁₇H₂₁N₃O₂ C = 68.23, H = 7.02, N = 14.05, O = 10.70%). EIMS m/z (rel.int.%): 299.1628 (M⁺, calcd. for C₁₇H₂₁N₃O₂, 299.1633) (10), 162 (90), 134 (100), 108 (28), 94 (20), 79 (28), 65 (10) and 52 (18). IR ν_{\max} (cm⁻¹): 3300, 3280, 1660 and 1630.

N-Cyano-1-Naphthylamine 1-C₁₀H₇-NH-CN. The cyano derivative was obtained as a viscous liquid in theoretical yield, mp 83-84^o EIMS m/z (rel.int.%): 168.0684 (M⁺, calcd. for C₁₁H₈N₂, 168.0684) (100), 143 (64), 115 (48), 89 (8), 63 (12) and 51 (8). IR ν_{\max} (cm⁻¹): 2210.

1-Naphthylurea 1-C₁₀H₇-NH-CO-NH₂. On recrystallization from methanol it formed elongated rods, mp 220-221^o (yield, 90%). It analyzed for C₁₁H₁₀N₂O (obsd. C = 70.90, H = 5.31, N = 15.36, O = 8.43%; calcd. for C₁₁H₁₀N₂O C = 70.96, H = 5.38, N = 15.05, O = 8.61%). EIMS m/z (rel.int.%): 186.0791 (M⁺, calcd. for C₁₁H₁₀N₂O 186.0793) (28), 143 (100), 115 (48), 89 (10), 71 (6), 63 (10), and 52 (5). IR ν_{\max} (cm⁻¹): 3500, 3410, 1660 and 1590.

N-Acetyl-N-1-naphthylurea: It formed irregular plates on recrystallization from methanol, mp 214-215^o (yield 95%) and analyzed for C₁₃N₁₂N₂O₂ (obsd. C = 68.71, H = 5.20, N = 12.23, O = 13.86%; calcd. for C₁₃H₁₂N₂O₂ C = 68.42, H = 5.26, N = 12.28, O = 14.04%). EIMS m/z (rel.int.%): 228.0891 (M⁺, calcd. for C₁₃H₁₂N₂O₂ 228.0890) (10), 185 (26), 143 (100), 134 (20), 115 (40), 89

(80), 63 (60), and 51 (5). IR ν_{\max} (cm⁻¹): 3405, 1710, and 1660.

1-Naphthyl amino, imino methoxymethane (1-C₁₀H₇-NH-C=NH (OCH₃). It was obtained as a crystalline solid which on recrystallization from ethyl acetate-methanol (1:1) formed elongated rods, mp 87-88^o (yield 91%) and analyzed for C₁₂H₁₂N₂O (obsd. C = 72.01, H = 6.07, N = 14.13, O = 7.79%; calcd. for C₁₂H₁₂N₂O C = 72.00, H = 6.00, N = 14.00, O = 8.00%). EIMS m/z (rel.int.%): 200.0942 (M⁺, calcd. for C₁₂H₁₂N₂O 200.0949) (20), 169 (16), 143 (54), 115 (100), 88 (10), 63 (80), and 51 (16). IR ν_{\max} (cm⁻¹): 3400, 1660, 1590 and 1100.

1-Naphthyl amino, imino ethoxymethane 1-C₁₀H₇-NH-C=NH (OC₂H₅). It formed irregular plates on recrystallization from ethyl acetate-methanol (1:1), mp 103-104^o (yield 87%) and analyzed for C₁₃H₁₄N₂O (obsd. C = 71.98, H = 6.49, N = 13.96, O = 7.57%; calcd. for C₁₃H₁₄N₂O C = 72.90, H = 6.54, N = 13.08, O = 7.48%). EIMS m/z (rel.int.%): 214.1101 (M⁺, calcd. for C₁₃H₁₄N₂O 214.1106) (10), 186 (8), 169 (8), 143 (100), 115 (52), 89 (71 (10), 63 (8), and 51 (5). IR ν_{\max} (cm⁻¹): 3390, 1645, 1595 and 1090.

N-Imino methyl-1-naphthylamine 1-C₁₀H₇-NH-CH=NH. It was obtained as a viscous liquid in 49% yield, bp 74-75^o EIMS m/z (rel.int.%): 170.0839 (M⁺, calcd. for C₁₁H₁₀N₂, 170.0894) (10), 143 (100), 89 (72 (10), 63 (14) and 51 (80). IR ν_{\max} (cm⁻¹): 3300, 3200, 1665 and 1640.

N-N'-Dinaphthylguanidine (1-C₁₀H₇-NH)₂C=NH. On recrystallization from benzene it formed needles, mp 111-112^o (yield 93%). It analyzed for C₂₁H₁₇N₃ (obsd. C = 81.06, H = 5.40, N = 13.54%; calcd. for C₂₁H₁₇N₃ C = 81.03, H = 5.47, N = 13.50%). EIMS m/z (rel.int.%): 311.1429 (M⁺, calcd. for C₂₁H₁₇N₃ 311.1422) (12), 168 (10), 143 (100), 115 (28), 82 (18), 63 (80), and 51 (5). IR ν_{\max} (cm⁻¹): 3300, 3290, 1660 and 1630.

N-Cyano-2-naphthylamine 2-C₁₀H₇-NH-CN. The cyano derivative was obtained as a viscous liquid in theoretical yield, bp 89-90^o. EIMS m/z (rel.int.%): 168.0679 (M⁺, calcd. for C₁₁H₈N₂, 168.0687) (54), 143 (100), 115 (70), 82 (78), 74 (22) and 59 (36). IR ν_{\max} (cm⁻¹): 2200.

2-Naphthylurea 2-C₁₀H₇-NH-CO-NH₂. It formed fine needles from methanol (yield, 96%), mp 219-220^o and analyzed for C₁₁H₁₀N₂O (obsd. C = 70.95, H = 5.39, N = 15.04, O = 8.62%; calcd. for C₁₁H₁₀N₂O C = 70.96, H = 5.38, N = 15.05, O = 8.61%). EIMS m/z (rel.int.%): 186.0792 (calcd. for C₁₁H₁₀N₂O, 186.0793) (10), 165 (12), 143 (48), 122 (52), 108 (100), 94 (14), 80 (44), 74 (26), 65 (22), and 53 (30). IR ν_{\max} (cm⁻¹): 3500, 3320, 1660 and 1600.

N-Acetyl, N-2-naphthylurea recrystallized from methanol in irregular plates, mp 202-203^o (yield, 80%) and analyzed for C₁₃H₁₂N₂O₂ (obsd. C = 68.41, H = 5.27, N = 12.29, O = 14.03%; calcd. for C₁₃H₁₂N₂O₂ C = 68.42, H = 5.26, N = 12.28, O = 14.04%). EIMS m/z (rel.int. %); 228.0891 (M⁺, calcd. for C₁₃H₁₂N₂O₂, 228.0898) (10), 185 (20), 143 (100), 115 (38), 79 (14), 60 (16) and 52 (12). IR ν_{mac} (cm⁻¹): 3380, 1720 and 1640.

N-Imino methyl-2-naphthylamine C₁₀H₇-NH-HC=NH. The cyanamide was obtained as a viscous liquid, mp 72-73^o (yield, 43%). EIMS m/z (rel.int.%); 170.0839 (M⁺, calcd. for C₁₁H₁₀N₂, 170.0844) (10), 144 (100), 115 (58), 89 (10), 72 (12), 63 (10) and 51

2-Naphthyl amino imino methoxymethane 2-C₁₀H₇-NH-C=NH (OCH₃). It formed rectangular plates from ethyl acetate-methanol (1:1), mp 114-115^o (yield, 94%) and analyzed for C₁₂H₁₂N₂O (obsd. C = 72.00, H = 6.06, N = 14.14, O = 8.79%; calcd. for C₁₂H₁₂N₂O C = 72.00, H = 6.00, N = 14.00, O = 8.00%). EIMS m/z (rel.int.%); 200.0952 (M⁺, calcd. for C₁₂H₁₂N₂O, 200.0949) (40), 184 (6), 169 (12), 143 (100), 115 (58), 89 (10), 72 (10), 63 (10) and 51 (8). IR ν_{max} (cm⁻¹): 3400, 1650, 1575, and 1100.

2-Naphthyl amino imino ethoxymethane 2-C₁₀H₇-NH-C=NH (OC₂G₅). On recrystallization from methanol it formed irregular plates, mp 60-61^o (yield, 89%) and analyzed for C₁₃H₁₄N₂O (obsd. C = 72.91, H = 6.53, N = 13.07, O = 7.49%; calcd. for C₁₃H₁₄N₂O C = 72.90, H = 6.54, N = 13.08, O = 7.48%). EIMS m/z (rel.int.%); 214.1101 (M⁺, calcd. for C₁₃H₁₄N₂O, 214.1106) (12), 186 (8), 143 (100), 115 (12), 89 (6), 72 (8), 63 (6), and 51 (8). IR ν_{max} (cm⁻¹): 3400, 1640, 1575 and 1100.

N,N'-Di-2-naphthylguanidine 2(C₁₀H₇-NH)₂-C=NH. It was obtained as a crystalline solid which on recrystallization from benzene formed elongated rods, mp 69-70^o (yield, 85%) and analyzed for C₂₁H₁₇N₃ (obsd. C = 81.06, H = 5.48, N = 13.46%; calcd. for C₂₁H₁₇N₃ C = 81.03, H = 5.47, N = 13.50%). EIMS m/z (rel.int.%); 311.1420 (M⁺, calcd. for C₂₁H₁₇N₃, 311.1422) (18), 169 (6), 143 (100), 127 (10), 115 (14), 80 (12) and 51 (80). IR ν_{max} (cm⁻¹): 3300, 3280,.

Heterocyclic Amines

Cyano derivatives were prepared following the procedure described in the case of aliphatic bases.

N-Cyanopiperidine C₅H₁₀N-CN. It was obtained as a viscous liquid in theoretical yield. EIMS m/z (rel.int.%); 110.0832 (M⁺, calcd. for C₆H₁₀N₂, 110.0845) (90), 95 (8), 82 (12), 69 (90) and 55 (100). IR ν_{max} (cm⁻¹): 2180. UV λ_{max} (nm): 209.

Piperidine-N-carboxamide C₅H₁₀N-CO-NH₂. On heating a solution of N-cyanopiperidine (1 g) in 10 ml of 10% aqueous HCl for 2.4 hr at 70^o and keeping the reaction mixture overnight at room temperature a colourless crystalline product separated out, which was filtered, washed with water and dried. On recrystallization from methanol it formed irregular plates, mp 105-106^o (yield, 73%). It is soluble in methanol, acetone and chloroform and insoluble in ether and pet.ether. It analyzed for C₆H₁₂N₂O (obsd. C = 56.10, H = 9.44, N = 21.39, O = 13.07%; calcd. for C₆H₁₂N₂O C = 56.25, H = 9.37, N = 21.87, O = 12.51%). EIMS m/z (rel.int.%); 128.0948 (M⁺, calcd. for C₆H₁₂N₂O, 128.0937) (100), 113 (26), 99 (18), 84 (80), 70 (38), and 56 (62). IR ν_{max} (cm⁻¹): 3500 and 3320 (N-H stretching), 1650 (amide C=O stretching) and 1590 amide N-H bending) UV λ_{max} (n.m): 209.

Acetyl, *N*-piperidine-*N*-carboxamide, obtained on reaction of the carboxamide with Ac₂O/pyridine (overnight, room temperature), formed prismatic rods on recrystallization from methanol and melted at 151-152^o. It analyzed for C₈H₁₄N₂O₂ (obsd. C = 55.98, H = 8.29, N = 16.85, O = 18.86%; calcd. for C₈H₁₄N₂O₂ C = 56.47, H = 8.23, N = 16.47, O = 18.83%). EIMS m/z (M⁺, 170). IR ν_{max} (cm⁻¹): 3400 (amide N-H), 1660 and 1640 (acetyl and urea carbonyl stretching) UV λ_{max} (nm); 209.

N-Cyano-2-methylpiperidine (2-CH₃) C₅H₉N-CN. The cyanamide derivative was obtained as a viscous liquid in 90% yield. EIMS m/z (rel.int.%); (M⁺, calcd. for C₇H₁₂N₂, 124.1000), 109 (100), 95 (10), 67 (18) and 56 (38). IR ν_{max} (cm⁻¹): 2200. UV λ_{max} (nm): 209.

2-Methylpiperidine-N-carboxamide (2-CH₃) C₅H₉N-CO-NH₂. Following the hydrolysis conditions noted above the carboxamide derivative was obtained as a crystalline solid (yield, 71%) which formed needles, mp, 81-82^o. It analyzed for C₇H₁₄N₂O (obsd. C = 58.80 H = 9.69, N = 20.19, O = 11.32%; calcd. for C₇H₁₄N₂O C = 59.15, H = 9.86, N = 19.72, O = 11.27%). EIMS m/z (rel.int.%); 142.1108 (M⁺, calcd. for C₇H₁₄N₂O, 142.1131) (12), 127 (44), 83 (100), 69 (12) and 56 (30). IR ν_{max} (cm⁻¹): 3320, 1640 and 1580. UV λ_{max} (nm): 209.

Acetyl, 2-methylpiperidine-*N*-carboxamide formed cylindrical rods on recrystallization from methanol, mp, 127-128^o. It analyzed for C₉H₁₆N₂O₂ (obsd. C = 58.45, H = 8.89, N = 15.41, O = 17.26%; calcd. for C₉H₁₆N₂O₂ C = 58.69, H = 8.69, N = 15.20, O = 17.40%). EIMS m/z (M⁺, 184). IR ν_{max} (cm⁻¹): 3410, 1710 and 1665. UV λ_{max} (nm): 209.

N-Cyano-4-methylpiperidine: (4-CH₃) C₅H₉N-CN. It was obtained as a viscous liquid in 96% yield and gave a single spot on TLC. EIMS m/z (rel.int.%); 124.1032 (M⁺,

calcd. for $C_7H_{12}N_2$, 124.1031) (50), 97 (80), 82 (20), 69 (22) and 56 (100). IR ν_{\max} (cm^{-1}): 2200. UV λ_{\max} (nm): 209.

4-Methylpiperidine-N-Carboxamide $(4-CH_3)C_5H_9N-CO-NH_2$. The carboxamide derivative obtained, following the reaction conditions described above, formed cylindrical rods on recrystallization from alcohol, mp 84-85 $^{\circ}$ (yield, 92%). It analyzed for $C_7H_{14}N_2O$ (obsd. C = 59.10, H = 9.74, N = 19.89, O = 11.27%; calcd. for $C_7H_{14}N_2O$ C = 59.15, H = 9.86, N = 19.72, O = 11.27%). EIMS m/z (rel. int.%); 142.1170 (M^+ , calcd. for $C_{17}H_{14}N_2O$, 142.1106) (72), 127 (100), 114 (10), 98 (36), 84 (82) and 56 (91). IR ν_{\max} (cm^{-1}): 3520, 3400, 1560 and 1640 UV λ_{\max} (nm) 209.

Acetyl, 4-methylpiperidine-N-carboxamide formed prismatic rods on recrystallization from methanol, mp 104-105 $^{\circ}$. It analyzed for $C_9H_{16}N_2O_2$ (obsd. C = 58.41, H = 8.59, N = 15.64, O = 17.36%; calcd. for $C_9H_{16}N_2O_2$ C = 58.69, H = 8.69, N = 15.20, O = 17.40%). EIMS m/z M^+ , 184. IR ν_{\max} (cm^{-1}): 3400, 1720 and 1660. UV λ_{\max} (nm): 209.

N-Cyano-2,6-dimethylpiperidine $[2,6(CH_3)_2]C_5H_8-CN$. Chromatographically pure liquid of cyano derivative was obtained in theoretical yield. EIMS m/z (rel.int.%); 138. 1135 (M^+ , calcd. for $C_8H_{14}N_2$, 138.1156) (42), 123 (16), 81 (33) and 69 (44). IR ν_{\max} (cm^{-1}): 2200. UV λ_{\max} (nm): 207, 272 and 310.

2,6-Dimethylpiperidine-N-carboxamide $[2-6(CH_3)_2]C_5H_8-N-CO-NH_2$. N-cyano-2,6-dimethylpiperidine (1g) was heated with 20 ml 30% aqueous HCl at 70 $^{\circ}C$ for 2.5 hr. After usual workup a crystalline residue was obtained in 71% yield which on recrystallization from methanol formed elongated rods, mp 110-111 $^{\circ}$. It analyzed for $C_8H_{16}N_2O$ (obsd. C = 61.23, H = 10.11, N = 18.21, O = 10.45%; calcd. for $C_8H_{16}N_2O$ C = 61.54, H = 10.25, N = 17.95, O = 10.45%). EIMS m/z (rel.int.%); 156.1251 (M^+ , calcd. for $C_8H_{16}N_2O$, 156.1262) (10) 142 (32), 127 (57), 98 (100), 84 (74), 69 (62) and 56 (66). IR ν_{\max} (cm^{-1}): 3480, 1640 and 1580. UV λ_{\max} (nm): 209, 272 and 310.

Acetyl-2,6-dimethylpiperidine-N-carboxamide formed prismatic rods on recrystallization from methanol, mp 163-164 $^{\circ}$. It analyzed for $C_{10}H_{18}N_2O_2$ (obsd. C = 59.93, H = 9.44, N = 14.25, O = 16.38; calcd. for $C_{10}H_{18}N_2O_2$ C = 60.60, H = 9.09, N = 14.14, O = 16.17%). EIMS m/z M^+ 198. IR ν_{\max} (cm^{-1}): 3400, 1710 and 1665. UV λ_{\max} (nm); 209, 272 and 310.

4-Cyano morpholine C_4H_8ON-CN . The cyano derivative showing a single spot on TLC was obtained as a liquid residue in 92% yield. EIMS m/z (rel.int.%); 112.0624 (M^+ , calcd. for $C_5H_8N_2O$, 112.0636) (72), 97 (10), 85 (22),

71 (38) and 55 (100). IR ν_{\max} (cm^{-1}): 2220. UV λ_{\max} (nm); 211.

N-Cyanoindoline C_8H_8N-CN . N-cyanoindoline was obtained as a viscous liquid in theoretical yield, bp 108-109 $^{\circ}$. EIMS m/z (rel.int.%): M^+ , calcd. for $C_9H_8N_2$ 144. 0687) (100), 17 (74), 90 (26), 77 (8) and 51 (10). IR ν_{\max} (cm^{-1}): 2200 UV λ_{\max} (nm): 218, 245 and 283.

Indoline-N-carboxamide $C_8H_8N-CO-NH_2$. N-cyanoindoline (1g) was taken in 15 ml of 10% aqueous HCl and heated at 70 $^{\circ}$ for 30 min. On keeping the reaction mixture overnight at room temperature, a crystalline product separated out, which was filtered, washed with water and dried over a porous plate. On recrystallization from methanol it formed elongated rods, mp 157-158 $^{\circ}$ (yield theoretical). It analyzed for $C_9H_{10}N_2O$ (obsd. C = 66.66, H = 6.29, N = 17.54, O = 9.51%; calcd. for $C_9H_{10}N_2O$ C = 66.66, H = 6.17, N = 17.28, O = 9.89%). EIMS m/z (rel. int.%): 162.0761 (M^+ , calcd. for $C_9H_{10}N_2O$ 162.0793) (46), 118 (100), 91 (25) and 57 (10). IR ν_{\max} (cm^{-1}): 3490, 3380, 1660 and 1570. UV λ_{\max} (nm): 217, 245 and 283.

Acetylandoline-N-carboxamide: On recrystallization from methanol it formed elongated rods, mp 180-181 $^{\circ}$ (yield 70%). It analyzed for $C_{11}H_{12}N_2O_2$ (obsd. C = 64.32, H = 6.05, N = 13.83, O = 15.80%; calcd. for $C_{11}H_{12}N_2O_2$ C = 64.70, H = 5.88, N = 13.72, O = 15.70%). EIMS m/z M^+ , 204. IR ν_{\max} (cm^{-1}): 3380, 1700 and 1610. UV λ_{\max} (nm): 218, 245 and 283.

N-Cyanotetrahydroquinoline $C_9H_{10}N-CN$. The cyano derivative was obtained as a viscous liquid, mp 96-97 $^{\circ}$ (yield theoretical). EIMS m/z (rel.int.%): 158.0831 (M^+ , calcd. for $C_{10}H_{10}N_2$ 158.0843) (30), 132 (100), 118 (20), 104 (16), 77 (18) and 51 (8). IR ν_{\max} (cm^{-1}): 2210. UV λ_{\max} (nm): 207, 265 and 273.

N-Cyanotetrahydroisoquinoline $C_9H_{10}N-CN$. It was obtained as a viscous liquid in theoretical yield, bp 105-106 $^{\circ}$. EIMS m/z (rel.int.%): 158.0822 (M^+ , calcd. for $C_{10}H_{10}N_2$ 158.0843) (54), 104 (100), 82 (22), 78 (18) and 51 (8). IR ν_{\max} (cm^{-1}): 2200, UV λ_{\max} (nm): 207, 265 and 273.

Tetrahydroisoquinoline-N-carboxamide $C_9H_{10}N-CO-NH_2$. N-cyanotetrahydroisoquinoline (1g) was taken in 20 ml of 30% aqueous hydrochloric acid and heated at 70 $^{\circ}$ for 3 hr. The reaction mixture was cooled neutralized with dilute ammonia, and extracted out with ethyl acetate, and washed with water and freed of the solvent. The resulting crystalline residue formed irregular plates on recrystallization from alcohol, mp 164-165 $^{\circ}$ (yield 81%) and analyzed for $C_{10}H_{12}N_2O$ (obsd. C = 68.49, H = 6.74, N = 15.63, O = 9.14%; calcd. for $C_{10}H_{12}N_2O$ C=68.18,

H = 6.82, N = 15.91, O = 9.09%). EIMS m/z (rel.int.%): 176.0948 (M^+ , calcd. for $C_{10}H_{12}N_2O$ 176.0949) (42), 115 (20), 104 (100), 78 (28) and 51 (71). IR ν_{\max} (cm^{-1}): 3400, 3200, 1650 and 1590. UV λ_{\max} (nm): 207, 265 and 273.

Acetyltetrahydroisoquinoline-N-carboxamide: It formed irregular plates on recrystallization from methanol, mp 194-195° (yield 90%) and analyzed for $C_{12}H_{14}N_2O_2$ (obsd. C = 65.89, H = 7.01, N = 12.98, O = 14.12%; calcd. for $C_{12}H_{14}N_2O_2$ C = 66.05, H = 6.42, N = 12.84, O = 14.69%). EIMS m/z M^+ , 218. IR ν_{\max} (cm^{-1}): 3400, 1710 and 1660. UV λ_{\max} (nm): 207, 265 and 273.

Alkaloidal Bases

N-Cyano-N-demethylimipramine (1) To a solution of imipramine (5g) in dry ether (100ml), and ethereal solution of freshly prepared cyanogen bromide was added 1.2 mole) with good cooling and mechanical stirring for 15 min. The white crystalline hydrobromide of the base which separated out was filtered and the ethereal filtrate was extracted with dilute acetic acid to remove any unreacted base. The ethereal layer was neutralized with a little dilute ammonia, washed with water, dried over anhydrous Na_2SO_4 and freed of the solvent. The cyanamide thereby obtained, in theoretical yield, as a yellowish viscous liquid, bp 163°, is soluble in chloroform, ethyl acetate and ether while insoluble in petroleum ether. EIMS m/z (rel.int.%): 291.17321 (M^+ , calcd. for $C_{19}H_{21}N_3$ 291.17353) (26), 265 (4), 235 (2), 208 (100), 193 (56), 167 (12), 83 (64) and 57 (66). IR ν_{\max} (cm^{-1}): 2210. ($C\equiv N$), 3060, 1610, and 1480 (aromatic vibrations.) UV λ_{\max} (nm): 215, 255 and 280. 1H -NMR δ : 7.40-6.86 (8H, m, aromatic proton) 3.69 (2H, t, H-1), 3.31 (4H, s, H-10, H-11), 2.82 (2H, t, H-3'), 2.54 (3H, s, N-CH₃) and 1.81 (2H, m, H-2').

N-Amido-N-demethylimipramine (2). N-Cyano-N-demethylimipramine (1g) was taken in 10 ml of aqueous hydrochloric acid (10%) and mechanically stirred for about an hour at 70° till a clear solution was obtained. It was cooled, basified with ammonia and extracted out with ethyl acetate. The crystalline residue left on usual workup and removal of the solvent, formed irregular plates from methanol-water (0.5:0.5), mp 135° (yield 88%). It is soluble in chloroform and methanol, insoluble in ether, benzene and petroleum ether. It analyzed for $C_{19}H_{23}N_3O$ (obsd. C = 73.76, H = 7.41, N = 13.62, O = 5.21%; calcd. for $C_{19}H_{23}N_3O$ C = 73.79, H = 7.44, N = 13.59, O = 5.18%). EIMS m/z (rel.int.%): 309.1839 (M^+ , calcd. for $C_{19}H_{23}N_3O$ 309.1841) (18), 234 (20), 208 (100), 193 (52), 167 (12), 83 (50) and 57 (38). IR ν_{\max} (cm^{-1}): 3400, and 3520 (N-H stretch-

ing). 1640 (amide C=O stretching) and 1570 (N-H bending). UV λ_{\max} (nm): 215, 256 and 262. 1H -NMR δ : 7.44-6.91 (8H, m, aromatic protons), 4.74 (2H, s, NH₂), 3.69 (2H, t, H-1'), 3.26 (4H, s, H-10, H-11), 2.81 (2H, t, H-3'), 2.60 (3H, s, N-CH₃) and 1.79 (2H, m, H-2').

N-Amino methyl-N-Demethylimipramine (3). N-cyano-N-demethylimipramine (1g) was taken in 10% aqueous hydrochloric acid and heated with Zn dust on water bath, till it went into solution. Heating was continued for 15 min. The unreacted zinc was filtered off, the filtrate basified with ammonia after prior addition of ammonium chloride and the liberated base was extracted out with ethyl acetate. The darkish ethyl acetate solution on purification with petroleum ether and removal of the solvent afforded the diamine as a brownish liquid in 71% yield soluble in common organic solvents. The hydrochloride obtained on treatment of the diamine with ethereal hydrochloric acid formed elongated rods, mp 123°. It analyzed for $C_{19}H_{26}N_3Cl$ (obsd. C = 68.74, H = 7.80, N = 12.64, Cl = 10.82%; calcd. for $C_{19}H_{26}N_3Cl$ C = 68.78, H = 7.84, N = 12.67, Cl = 10.71%). EIMS m/z (rel.int.%): 295.2041 (M^+ , calcd. for $C_{19}H_{25}N_3$ 295.2048) (24), 234 (20), 208 (100), 193 (46), 167 (6), 83 (10) and 57 (12). IR ν_{\max} (cm^{-1}): 3420, 3390 (N-H stretching) and 1590 (N-H bending). UV λ_{\max} (nm): 215, 250 and 278. 1H -NMR δ : 7.25-6.88 (8H, m, aromatic protons), 3.32 (2H, t, NH₂) 3.81 (2H, s, N-CH₂-N), 3.70 (2H, t, H-1), 3.28 (4H, s, H-10, H-11) 2.79 (2H, t, H-3'), 2.49 (3H, s, N-CH₃) and 1.80 (2H, m, H-2').

Cyanochloroquine. To a solution of chloroquine (5g) in dry chloroform (100 ml) was gradually added freshly prepared cyanogen bromide (1.2 mole). It was stirred at 0°C for 20 min and the white hydrobromide of the unconverted chloroquine which settled down was filtered off. The filtrate worked up according to the procedure described for cyano imipramine afforded a yellowish liquid showing three spots on TLC and subjected to prep. Thick layer chromatography (silica gel, benzene-chloroform (6:4). As a result N'-cyano-N'-deethylchloroquine, (Rf = 0.8, bp 80-81°), N',N''-dicyano-N'-deethylchloroquine (Rf = 0.6, bp 101-02°) and N',N'' dicyano-N',N''-dideethylchloroquine (Rf = 0.9, bp 148-49°) were obtained as colourless liquids in 60, 18 and 7% yields, respectively.

N'-cyano-N'-deethylchloroquine (4). EIMS m/z (rel.int.%): 316.6300 (M^+ , calcd. for $C_{17}H_{21}N_4$ 316.6288) (10), 290 (5), 287 (6), 246 (14), 231 (34), 205 (64), 177 (20), 94 (100) and 57 (98). IR ν_{\max} (cm^{-1}): 2200 ($C\equiv N$) and 3400 (N-H stretching). UV λ_{\max} (nm): 215, 265 and 335.

N',N''-dicyano-N'-deethylchloroquine (5). EIMS m/z

(rel.int.%): 341.6145 (M^+ , calcd. for $C_{18}H_{20}N_5$ CI 341.6140) (6), 315 (6) 289 (7), 245 (14), 230 (38), 205 (100), 177 (20), 83 (78) and 57 (98). IR ν_{max} (cm^{-1}): 2205 ($C\equiv N$), UV λ_{max} (nm): 215, 262 and 333.

N,N-dicyano-*N,N*-dideethylchloroquine (6). EIMS m/z (rel.int.%): 313.5913 (M^+ , calcd. for $C_{16}H_{16}N_5$ CI 313.5928) (12), 246 (34), 231 (100), 205 (80), 177 (5), 83 (30) and 57 (68). IR ν_{max} (cm^{-1}): 2200 ($C\equiv N$). UV λ_{max} (nm): 215, 260 and 330.

Reaction of Promethazine with BrCN. To a solution of promethazine (1g) in chloroform (20 ml) was added freshly prepared cyanogen bromide accompanied by good cooling and mechanical stirring. On usual workup the resulting liquidish brown residue (0.05 g) showed three spots on TLC and was divided into ether soluble and insoluble fractions. The former showing only a single spot on TLC was subjected to thick layer chromatography (silica gel, chloroform-methanol (9:1) affording two components which were characterized as *N*-propyl (2-bromo) phenothiazine and bis-phenothiazine.

N-Cyano *N*-demethyl promethazine (7). It was obtained as a light brown liquid (yield, 58%). EIMS m/z (rel.int.%): 295.2293 (M^+ , calcd. for $C_{17}H_{17}N_3S$, 295.2310) (20), 212.1573 ($C_{13}H_{10}NS$, 212.1570) (100), 198.1439 ($C_{12}H_8NS$, 198.1410), (10) and 180.088 ($C_{13}H_{10}N$, 180.089) (32). IR ν_{max} (cm^{-1}): 2220 ($C\equiv N$). UV ν_{max} (nm): 215, 262 and 305.

N-propyl (2-bromo), phenothiazine (8). It formed sharp colourless needles on recrystallization from moist methanol mp 253-254 $^{\circ}$ (yield, 18%). EIMS m/z (rel.int.%): 320.1140 (M^+ , calcd. for $C_{15}H_{15}NSBr$, 320.1110) (18), 240.0799 ($C_{15}H_{14}NS$, 240.0851) (10), 212.1560 ($C_{13}H_{10}NS$, 212.1571) (100), 198.1401 ($C_{12}H_8NS$, 198.1410) (82) and 180.0829 ($C_{13}H_{10}N$, 180.089) (40). IR ν_{max} (cm^{-1}): 3100 and 1450-1590 (aromatic vibrations) UV λ_{max} (nm); 215, 260 and 307.

Bis-phenothiazine (9). On recrystallization from methano, it formed white irregular plates, mp 186-187 $^{\circ}$ (yield, 11%). EIMS m/z (rel.int.%): 396.2990 (M^+ , calcd. for $C_{24}H_{16}N_2S_2$, 396.2820) (32), 364.2137 ($C_{24}H_{16}N_2S$ 364.2140) (5), 198.1422 ($C_{12}H_8NS$, 198.1410) (100) and 166.0729 ($C_{12}H_8N$, 166.0739) (20). IR ν_{max} (cm^{-1}): 3150 and 1470-1600 (aromatic vibrations). UV λ_{max} (nm): 215, 265 and 308.

Reaction of mebhhydroline with BrCN. The reaction of mebhhydroline with BrCN was carried out following the procedure described for promethazine. The reaction pro-

duct ultimately obtained was similarly divided into ether-soluble and insoluble fractions. The former yielded, *N*-cyano-*N*-dimethyl mebhhydroline, while the ether insoluble fraction gave two compounds *N*-benzyl *N*-cyano-*N*-methyl, 2-vinyltryptamine and 21 *N*-benzyl, *N*-cyano, *N*-methyl, 2-ethyl aminotryptamine) Δ^{21} mebhhydroline through preparative thick layer chromatography (silica gel, chloroform-methanol (5.0:0.5).

N-Cyano-*N*-demethyl mebhhydroline (10). It was obtained as a yellowish brown liquid (yield, 43%). EIMS m/z (rel.int.%): 287.1623 (M^+ , calcd. for $C_{19}H_{17}N_3$, 287.1630) (34), 261.1531 ($C_{18}H_{17}N_2$, 261.1540) (12), 170.0962 ($C_{11}H_{10}N_2$, 170.0980) (10) and 91.0564 (C_7H_7 , 91.056) (100). IR ν_{max} (cm^{-1}): 2200 ($C\equiv N$). UV λ_{max} (nm): 220 and 280.

N-Benzyl, *N*-cyano-*N*-methyl 2-vinyltryptamine (11). The yellowish liquid of the cyano derivative was obtained in 19% yield. EIMS m/z (rel.int. %): 301.1782 (M^+ , calcd. for $C_{20}H_{19}N_3$, 301.1790) (20), 275.1689 ($C_{19}H_{19}N_2$, 275.1688) (5), 232.1279 ($C_{17}H_{14}N$, 232.1290) (24), 141.0576 ($C_{10}H_7N$, 141.0578) (18) and 91.0562 (C_7H_7 , 91.0560) (100). IR ν_{max} (cm^{-1}): 2240 ($C\equiv N$). UV λ_{max} (nm): 220 and 270.

21 (*N*-Benzyl *N*-cyano *N*-methyl 2-ethyl aminotryptamine) Δ^{21} mebhhydroline (12). It formed light yellow elongated rods on recrystallization from methanol, mp 160-161 $^{\circ}$ (yield, 8.5%). EIMS m/z (rel.int.%): 590.3570 (M^+ , calcd. for $C_{39}H_{38}N_6$, 590.3580) (12), 534; 4350 ($C_{37}H_{34}N_4$, 534.4351) (20), 499.3101 ($C_{32}H_{31}N_6$, 499.3102) (8), 302.1868 ($C_{20}H_{20}N_3$, 302.1877) (12). 289.7490 ($C_{19}H_{19}N_3$, 289.7492) 246.1366 ($C_{18}H_{16}N$, 246.1376) (20) and 91.0539 (C_7H_7 , 91.0536) (100). IR ν_{max} (cm^{-1}): 2210 ($C\equiv N$). UV λ_{max} (nm): 220, 215 and 275.

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