Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 30, No. 8, August 1987

A CONVENIENT SYNTHESES OF SOME NEW SUBSTITUTED GUANIDINES

Salimuzzaman Siddiqui, S. Salman Ahmad, S. Imtiaz Haider and Tariq Mahmood

H.E.J. Research Institute of Chemistry, University of Karachi, Karachi-32

(Received April 26, 1987)

The cyanamides of piperidine, 2-methyl piperidine, 4 methyl piperidine, 2,6-dimethyl piperidine, indoline, tetrahydroisoquinoline, 2,3-dimethylaniline, 2,5-dimethylaniline, 2,6-dimethylaniline, α-naphthylamine and β-naphthylamine yielded their respective guanido derivatives on treatment with dry ammonia. Their structures have been confirmed through spectral studies.

Key words: Cyanamides; Guanido derivatives; Heterocyclic and Aromatic amines.

INTRODUCTION

In continuation of our studies directed towards the extensions of the von Braun (BrCN) reaction on alkaloidal simpler aliphatic and aromatic bases, several pharmacologically active nitrogenous compounds have been reported [1-11]. The present work has been undertaken on some aromatic and heterocyclic amines in order to provide a modified route for the preparation of guanido derivatives. During the earlier studies it was found that the cyanamides of the above mentioned bases failed to yield guanido derivatives under the reaction conditions described in the case of aromatic and steroidal bases. However in contrast to these results, treatment of the cyanamides with dry ammonia resulted in their respective guanido derivatives.

EXPERIMENTAL

Melting points were recorded in glass capillary tubes and are uncorrected. The purity of samples was checked by TLC using precoated silica gel (GF-254) plates (0.2 mm). The IR spectra were recorded in chloroform on A-302 infrared spectrometer and mass spectra on Varian MAT-112 and MAT-312 double focussing mass spectrometer connected to PDP 11/34 computer system.

Guanido piperidine. It was obtained as crystalline solid, which on recrystallization from chloroform methanol formed irregular plates, yield 31 %, mp 68-69°. It analyzed for $C_6H_{13}N_3$ (obsd. C=56.68, H=10.24, N=33.08 %, calcd. C=56.69, H=10.23, N=33.08 %). EIMS m/z (rel. int. %): 127.1108 (M^+, calcd. for $C_6H_{13}N_3$ 127.1109) (41), 111(27), 84(53), 69(100). IR ν_{max} (cm^{-1}), 3280, 3215, 1655 and 1650.

Guanido (2-methyl)piperidine. Chromatographically pure guanido derivative was obtained in 70 % yield, formed irregular plates on recrystallization from benzene, mp 61-63°. It analyzed for $C_7H_{15}N_3$ (obsd. C=59.48, H=10.80, N=29.72 %; clacd. C=59.57, H=10.64, N=29.79 %). EIMS m/z (rel. int. %): 141.1266 (M^+, calcd. for $C_7H_{15}N_3$ 141.1265) (48), 124(45), 98(56), 82(14), 69 (100). IR ν_{max} (cm^{-1}): 3280, 3210, 1650 and 1640.

Guanido (4-methyl) piperidine. It was obtained as crystalline solid, which on recrystallization from chloroform-methanol (7:3) formed sharp needles, yield 42 %, mp 71-73°. It analyzed for $C_7H_{15}N_3$ (obsd. C=59.50, H=10.86, N=29.64 %; calcd. C=59.57, H=10.64, N=29.79 %). EIMS m/z (rel. int. %): 141.1266 (M^+, clacd. for $C_7H_{15}N_3$ 141.1265)(48), 124(48), 98(58), 82(19), 69(89) and 55(100). IR ν_{max} (cm^{-1}): 3285, 3215, 1655 and 1940.

Guanido (2,6-dimethyl) piperidine. Chromatographically pure guanido derivative was obtained in 38 % yield which formed irregular plates on recrystallization from benzene, mp 91-92°. It analyzed for $C_8H_{17}N_3$ (obsd. C=61.96, H=11.06, N=26.98 %; calcd. C=61.93, H=10.97, N=27.10 %). EIMS m/z (rel.int. %): 155.1420 (M^+ calcd. for $C_8H_{17}N_3$ 155.1422) (50), 138(48), 98(60), 82(98), 69(80) and 55 (100). IR ν_{max} (cm^{-1}): 3280, 3210, 1650 and 1640.

Guanido indoline. It was obtained as a crystalline solid which on recrystallization from benzene-methanol (5:1) formed cubical plates, mp 111-112° (dec.) (yield 80 %) and analyzed for $C_9H_{11}N_3$ (obsd. C=67.16, H=6.71, N=26.13 %; calcd. C=67.08, H=6.83, N=26.09 %). EIMS m/z (rel.int. %) 161.0954 (M^+, calcd. for $C_9H_{11}N_3$ 161.0929) (62), 144(26), 118(70), 91(100) and 55(44). IR ν_{max} (cm^{-1}): 3310, 3220, 1660 and 1635.

Guanido tetrahydroisoquinoline. It was obtained as a crystalline solid which on recrystallization from ethyl acetate-methanol (1:1) formed irregular plates, mp 120-121° (yield 33 %) and analyzed for $C_{10}H_{13}N_3$ (obsd.

C=68.47, H=7.68, N=23.85 % calcd. C=68.57, H=7.43, N=24.00 %). EIMS m/z (rel. int. %): 175.1101 (M^+; calcd. for $C_{10}H_{13}N_3$ 175.1109) (30), 118(20), 104(100), 90(19) and 76(8). IR ν_{max} (cm^{-1}): 3310, 3220, 1665 and 1640.

Guanido (2,3-dimethyl)aniline. Chromatographically pure guanido derivative was obtained in 30 % yield and formed irregular plates on recrystallization from benzene; mp 81-82°. It analyzed for $C_9H_{13}N_3$ (obsd. C=66.08, H=8.01, N=25.91 %; calcd. C=66.26, H=7.97, N=25.77 %). EIMS m/z (rel. int. %): 163.1108 (M^+, calcd. for $C_9H_{13}N_3$ 163.1109), 146(16), 133(19), 106(100) and 77(9). IR ν_{max}(cm^{-1}): 3310, 3220, 1665 and 1645.

Guanido (2,5-dimethyl) aniline. It was obtained as a crystalline solid which on recrystallization from chloroform-methanol (1:1) formed irregular plates, mp 120-121° (yield 33 %) and analyzed for $C_9H_{13}N_3$ (obsd. C=66.31, H=7.83, N=25.86 %; calcd. C=66.26, H=7.97, N=25.77 %). EIMS m/z (rel.int. %): 163.1107 (M^+, calcd. for $C_9H_{13}N_3$ 163.1109(20), 146(19), 133(23), 106(100) and 77(15). IR ν_{max} (cm^{-1}): 3310, 3220, 1660 and 1640.

Guanido (2,6-dimethyl)aniline. Chromatographically pure guanido derivative was obtained in 29 % yield and formed sharp needles on recrystallization from benzene, mp 102-103°. It analyzed for $C_9H_{13}N_3$ (obsd. C=66.07, H=8.03, N=25.90 %; calcd. C=66.26, H=7.97, N=25.77 %). EIMS m/z (rel. int. %): 163.1108 (M^+, calcd. for $C_9H_{13}N_3$ 163.1109), 146(18), 133(20), 106(100) and 77(16). IR ν_{max} (cm^{-1}): 3310, 3220, 1660 and 1640.

Guanido (α-naphthylamine). It was obtained as a crystalline solid which on recrystallization from ethyl acetate-methanol (9:1) formed irregular plates, mp 119-120° (yield 41 %) and analyzed for $C_{11}H_{11}N_3$ (obsd. C=71.38, H=5.85, N=22.77 %; calcd. C=71.35, H=5.95, N=22.70 %). EIMS m/z (rel.int. %): 185.0950 (M^+, calcd. for $C_{11}H_{11}N_3$ 185.0952(10), 127 (100), 115(48), 89(8), 63(12) and 51(8). IR ν_{max}(cm^{-1}): 3310, 3222, 1665 and 1645.

Guanido (β-naphthylamine). Chromatographically pure guanido derivative was obtained in 23 % yield and formed sharp needles on recrystallization from benzene, mp. 106-107°. It analyzed for $C_{11}H_{11}N_3$ (obsd. C=71.3, H=5.80, N=22.90 %; calcd. C=71.35, H=5.95, N=22.70 %). EIMS m/z (rel.int. %): 185.0950 (M^+, calcd. for $C_{11}H_{11}N_3$ 185.0952(25), 127(100), 115(47), 89(9), 63(8) and 51(10) IR ν_{max}(cm^{-1}): 3310, 3220, 1660 and 1640.

REFERENCES

1. S. Siddiqui and B.S. Siddiqui Z. Naturforschung, **35B**, 1049 (1980).
2. N. Afza and S. Siddiqui, Pakistan J. Sci. Ind. Res., **22**, 290 (1979).
3. A. Malik, N. Afza, N. Sultana and S. Siddiqui, Heterocycles, **16**, 1101 (1981).
4. A. Malik, N. Afza and S. Siddiqui, Z. Naturforschung, **37B**, 512 (1982).
5. S. Siddiqui, S. Begum and B.S. Siddiqui, Z. Naturforschung, **37B**, 1481 (1982).
6. S. Siddiqui, B.S. Siddiqui and S. Begum, Pakistan J. Sci. Ind. Res., **28**, 221 (1985).
7. S. Siddiqui, S. Imtiaz Haider, S. Salman Ahmad and B.S. Siddiqui, Z. Naturforschung, **40B**, 546 (1985).
8. S. Siddiqui, S. Imtiaz Haider, S. Salman Ahmad and B.S. Siddiqui, Pakistan J. Sci. Ind. Res., **28**, 295 (1985).
9. S. Siddiqui, S. Salman Ahmad, S. Imtiaz Haider and B.S. Siddiqui, J. Chem. Soc. Pakistan, **8**, 331 (1986).
10. S. Siddiqui, S. Salman Ahmad and S. Imtiaz Haider, Z. Naturforschung, (in press).
11. S. Siddiqui, S. Salman Ahmad and S. Imtiaz Haider, Pakistan J. Sci. Ind. Res. (in press).