

LETTERS  
TO THE EDITOR

Preparation of Diaminomethanes  
under Microwave Irradiation

D. P. Khrustalev, G. T. Khamzina, S. D. Fazylov, and A. M. Gazaliev

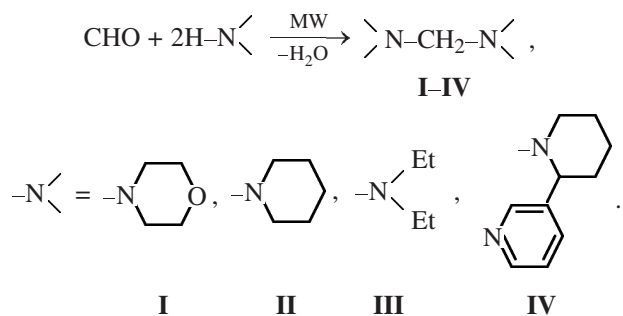
Institute of Organic Synthesis and Coal Chemistry of the Kazakhstan Republic,  
ul. Alikhanova 1, Karaganda, 100000 Kazakhstan  
e-mail: khrustalev@mail.kz

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Effect of microwave irradiation on organic reactions is being extensively studied in view of the enhancing demand for resource-saving technologies, [1–3]. The advantages of microwave irradiation over traditional activation sources include the absence of heat carrier, uniform heating of the reaction mixture, absence of heat-transfer inertia, possibility of solvent-free conditions, and shorter reaction time.

We have explored the synthesis of diaminomethanes under microwave irradiation, according to the following scheme:



Yields, %: 65 (I), 69.4 (II), 62.4 (III), 70 (IV).

It was found that under these conditions diaminomethanes I–IV are formed within 3–4 min without solvent. The overall synthetic procedure involves microwave activation (350 W) of a mixture of 0.01 mol of Paraform and 0.02 mol of a secondary amine. The reaction products were isolated by vacuum distillation.

Diaminomethanes I–III are colorless strongly basic liquids soluble in water and organic solvents.

Their structure and purity were established by means of IR and NMR spectroscopy and TLC. Physicochemical constants of compounds I–III agree with published data [4]. Compound IV is a white crystalline substance, mp 94°C. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), ppm: 1.2–1.7 m (12H, piperidine), 2.4 s (2H, CH<sub>2</sub>), 2.85 d (2H, NCH, piperidine), 3.59 d (4H, NCH<sub>2</sub>, piperidine), 7.38–8.46 m (8H, pyridine CH). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 336 [*M*]<sup>+</sup>, 175 (100), 162 (6), 146 (4), 132 (36), 118 (10), 105 (13), 98 (3), 92 (23), 84 (18), 78 (7), 65 (11), 51 (8), 44 (85).

The IR spectra were registered in thin layer between KBr plates in the range 400–4000 cm<sup>-1</sup> on a UR-20 spectrometer. The <sup>1</sup>H NMR spectra were taken on a Bruker DRX-500 (500.13 MHz) instrument. TLC was carried out on Silufol UV-254 plates, eluent propan-2-ol–benzene–ammonia (10:5:2), development in iodine vapor. The mass spectrum was obtained on an MX-1321 mass spectrometer, direct sample admission, ionizing electron energy 70 eV.

REFERENCES

1. Tselinskii, I.V., Astrat'ev, A.A., and Brykov, A.S., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 10, p. 1699.
2. Grigor'ev, A.D., Dmitrieva, N.M., El'tsov, A.V., Ivanov, A.S., Panarina, A.E., and Sokolova, N.B., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 6, p. 1042.
3. Hashemi, M.M., Rahimi, A., Karimi-Jaberi, Z., and Ahmadbeni, Y., *Acta Chim. Slov.*, 2005, vol. 52, p. 86.
4. Vlasova, L.M., *Cand. Sci. (Chem.) Dissertation*, Karaganda, 1997.