J Indian Inst Sci., Mar -Apr. 1989, 69, 119–124.
© Indian Institute of Science

Reactivity of hydrazinium hydrazinecarboxylate—synthesis of 4-amino-3, 5-dimethyl-1, 2, 4-triazole[†]

J. J. VITTAL*, V. B. ANGADI** AND K. C. PATIL***,
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012.

Received on July 5, 1988; Revised on December 7, 1988.

Abstract

The reaction between hydrazinium hydrazinecarboxylate, $N_2H_5^+$ $COON_2H_3^-$ and acetonitrile at ambient conditions produces a white solid compound which was found to be 4-amino-3, 5-dimethyl-1, 2, 4-triazole by chemical analysis, IR, (^{1}H and ^{13}C) NMR spectra and mass spectral fragmentation pattern. A probable mechanism for the formation of triazole is proposed The preparative method is standardized.

Key words: Hydrazinium hydrazinecarboxylate, and 4-amino-3, 5-dimethyl-1, 2, 4-triazole.

1. Introduction

Hydrazine hydrate is known[1] to react with atmospheric carbon dioxide to form hydrazinium hydrazinecarboxylate, $N_2H_5^+$ $COON_2H_3^-$ (HHC). The reaction of this compound with transition[2,3] and rare-earth metal[4,5] salts has been studied and the mechanism of its action has been established. During the course of the present study, it has been found accidentally that HHC reacts with acetonitrile to form 4-amino-3, 5-dimethyl-1, 2, 4-triazole as one of the products. This compound and its derivatives are useful in agriculture and medicine[6-13]. The details of the reaction and probable reaction mechanism are discussed in this paper.

2. Experimental

Reagent-grade hydrazine hydrate ($N_2H_4 \cdot H_2O$, 99–100%) and acetonitrile were obtained from BDH and were used as received.

[†] This paper is dedicated to (late) Prof. C. C. Patel.

*Presently with the Department of Chemistry, University of Western Ontario, London, Ont. N6A 3K7, Canada.

**Department of Organic Chemistry.

***For correspondence.

The C, H and N analyses were obtained by microanalytical methods. IR spectrum was recorded on a Carl-Zeiss UR-10 automatic double-beam spectrometer in KBr pellet. The mass spectral fragmentation pattern was obtained using an AEI MS-702 model mass spectrometer with electron bombardment source. The proton NMR spectra were recorded on a Varian T-60 spectrometer and the carbon-13 NMR spectrum was obtained on a Bruker WH-270 model machine at a probe temperature of 25°C. For both the NMR spectra TMS was used as an internal standard and D_6-DMSO or D_2O was used as a solvent. The X-ray powder diffraction pattern was obtained using a Philips X-ray diffractometer with a vertical goniometer, model PW 1050/70 using CuK_α radiation with a nickel filter.

2.1. *Preparation of hydrazinium hydrazinecarboxylate, $N_2H_5^+ \, COON_2H_3^-$ (HHC)*

This compound was obtained as a viscous liquid by passing CO_2 through a 10 mL of liquid hydrazine hydrate for about 10 min.

When a mixture of liquid HHC and acetonitrile was kept aside at room temperature, two layers appeared, the top being acetonitrile and the lower HHC. A pink colour was developed in the acetonitrile layer after about 12 h. After 2–3 weeks, the pinkish acetonitrile layer disappeared with the formation of a white crystalline compound in the HHC layer. The solid compound was characterized by elemental microanalysis, IR and (^{1}H and ^{13}C) NMR spectroscopy, mass spectrometry and X-ray powder diffraction.

3. Analytical data

3.1. *Elemental analysis*

Calcd for $C_4H_8N_4$ (mol. wt 112.15): C, 42.85; H, 7.19; N, 49.96. Found: C, 42.67; H, 7.15; N, 49.96.

3.2. *IR spectrum* (cm^{-1})

3240_s, 3145_s, 300^{0}_{w}, 2925_w, 1645_s, 1565_s, 1510_m, 1440_s, 1390_w, 1380_w, 1090_s, 990_s, 970_m, 760_s, 725_m, 660_m, 510_m and 475_m (s—strong, m—medium and w—weak).

^{1}H NMR (D_6-DMSO, 25°C): δ_H 2.2(s, $-CH_3$), 5.7 (s, $-NH_2$)

δ_H(D_2O):2.2 (s, $-CH_3$).

^{13}C NMR (D_6-DMSO.25°C): δ_C 9.58 ($-CH_3$), 151.19 (ring C).

3.3. *X-ray powder diffraction d(Å) spacings*

d, Å (intensity): 6.811(15), 6.512(10), 5.905(60), 5.011(30), 4.652(5), 4.291(7), 4.016(20), 3.755(15), 3.351(100), 3,210(12), 2.989(25), 2.922(7), 2.550(5), 2.529(5), 2.067(10).

3.4. *Mass spectrometry*

M/e (intensity): 113(4.9), 112(81.3), 111(0.3), 97(1.0), 82(0.5), 67(0.7), 66(0.8), 57(4.6), 56(3.7), 55(0.6), 54(0.7), 53(0.9), 52(0.9), 51(0.5), 44(0.3), 43(4.7), 42(100), 41(14.6), 40(9.7), 39(4.7), 38(2.1), 37(0.6), 32(5.3), 31(0.5), 30(19.9) and 29(6.8).

3.5. *Synthesis of 4-amino-3, 5-dimethyl-1, 2, 4-triazole*

A 5-mL portion of HHC was mixed with 20 mL of acetonitrile and refluxed under nitrogen using a water condenser for 4 h. The resultant solution was evaporated over a water bath to get colourless crystals of the triazole. The crystals were separated by filtration, washed with a small amount of acetone and then with acetonitrile and dried in air. Yield: 1.3 g. M.P.: 198–199°C. The compound is freely soluble in DMSO and water, slightly soluble in acetone, and insoluble in benzene, carbontetrachloride and acetonitrile.

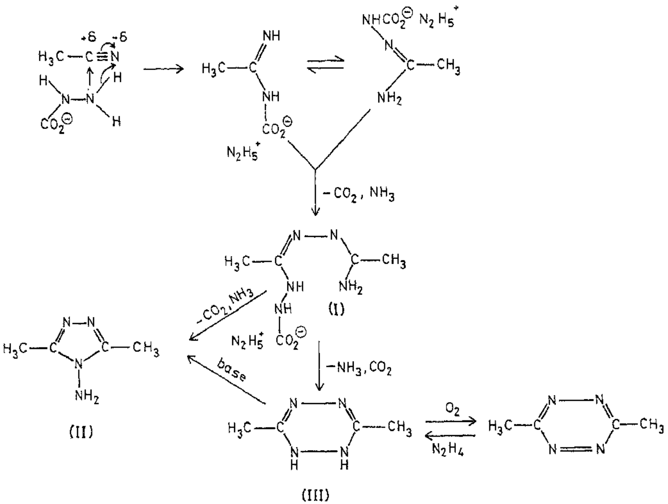
4. Results and discussion

The molecular formula of the compound obtained from the elemental analysis and the molecular weight by mass spectrometry was found to be $C_4H_8N_4$. The ^1H NMR spectrum of the white solid compound in D_6-DMSO solvent has two singlets, one at 2.2 ppm and another at 5.7 ppm with the integrated intensity ratio of 3:1, respectively. The peak occurring at 5.7 ppm disappears on shaking the solution with D_2O forming DHO resulting from exchange, suggesting that it may be assigned to NH protons. The singlet at 2.2 ppm may result from CH_3 protons. From the integrated intensity ratio and the molecular formula, it is inferred that there are two CH_3 groups and two NH protons. Further, the simple spectrum with singlet peaks suggests that the structure of the compound is symmetrical. The ^{13}C NMR spectrum of the compound in D_6-DMSO solvent shows two peaks, with the chemical shifts 9.58 and 151.20 ppm indicating two types of carbon atoms and the molecular structure to be highly symmetrical. The peak at higher field may be due to CH_3 carbons and the other at lower field may be due to carbons in the ring system.

The IR spectrum of the compound has a doublet at 3240 and 3145 cm^{-1}, which are assigned to N–H stretchings, and suggests the presence of an $-NH_2$ group in the compound[14]. The presence of the CH_3 group is evidenced from the $-CH_3$ asymmetric (at 3000 cm^{-1}) and symmetric (1390 and 1380 cm^{-1}) deformations and C–CH_3 rockings at 1090 cm^{-1}. Further, a strong band observed at 1645 cm^{-1} is assigned to $\nu_{(c=N)}$ and two types of $\nu_{(N-N)}$ are found at 970 and 990 cm^{-1} in the solid state.

All these analytical and spectral data appear to confirm the compound to be 4-amino-3, 5-dimethyl-1, 2, 4-triazole. On the basis of the structure the mass spectral fragmentation pattern has been successfully interpreted[15].

Hydrazine hydrate reacts with acetonitrile in the presence of sulfur[16,17], sulfur-containing compounds[18] or ethanol[19,20] to form 4-amino-3, 5-dimethyl-1, 2, 4-triazole.



Scheme I

The compound triazole is obtained by the reaction of HHC and acetonitrile or hydrazine hydrate and acetonitrile in CO_2 atmosphere. The probable mechanism for this reaction is given in Scheme I.

Amidrazone salts are reported[21–23] to be formed by the nucleophilic attack of hydrazine or its salts on acetonitrile as a first step. The intermediate (I) is proposed to be formed by the reaction between two amidrazone salts. This intermediate is similar to the 'enol' form of diacylhydrazide which was an intermediate proposed by Herbst and Harrison[24] in the decomposition of hydrazinium salts of aliphatic carboxilic acids. The self-condensation of the intermediate (I) will produce oxadiazole derivative under acidic condtions[23] and, therefore, is not considered here.

The compound, 4-amino-3, 5-dimethyl-1, 2, 4-triazole (II), is formed directly by the decomposition of intermediate I or through the six-membered compound (III) *i.e.*, 3, 6-dimethyl-1, 2-dihydro-1, 2, 4, 5-tetrazine, which rearranges further in basic solution to the triazole[18,21,25,26]. It has been explained[25] that the substituent with more electron-withdrawing power tends to stabilize the six-membered ring, *viz.*, 3, 6-disubstituted-1, 2-dihydro-1, 2, 4, 5-tetrazine and the more electron-releasing character of the substituted group facilitates the conversion to five-membered ring. The isolation of compound III is, therefore, improbable in the present case. However, Abdel Rehman *et al*[27] have reported the isolation of intermediate III for aryl derivatives.

Acknowledgements

The authors wish to thank Dr S. Renganathan, presently in the Oregon State University, for his help and encouragement in this project.

References

1. Audrieth, L F. and Ogg, B A. *The chemistry of hydrazine*, Wiley, 1951, pp 209–223
2. Patil, K. C., Budkuley, J. S and Pai Verneker, V. R. *J. Inorg. Nucl. Chem*, 1979, **41**, 953–955.
3. Patil, K. C., Soundararajan, R and Pai Verneker, V. R. *Proc. Indian Acad. Sci.*, 1978, **87A**, 281–284.
4. Ravindranathan, P and Patil, K C. *Proc. Indian Acad Sci. (Chem Sci.)*, 1985, **95**, 345–356.
5. Ravindranathan, P, Mahesh, G. V and Patil, K. C. *Proc. Indian Acad. Sci (Chem. Sci.)*, 1986, **97**, 117–123
6. Wade, P C, Vogt, B R and Kissick, T P. *US Patents*, 4,154,843, *Chem. Abstr.*, 1979, **91**, 57025v, and 4,076,823, *Chem Abstr.*, 1978, **88**, 190920n.
7. Wade, P C. and Vogt, B. R. *US Patent*, 4,169,148, *Chem. Abstr*, 1980, **92**, 28590r; *Eur. Patent* 3,895 and *US Patent*, 878,209, *Chem. Abstr.*, 1980, **92**, 76517u.
8. Webb, M. A and Parsons, J. H. *US Patent, Ger Offen*, 2,822,014, *Chem. Abstr*. 1979, **90**, 121607v
9. Wade, P C and Kissick, T. P *US Patent*, 4,093,728, *Chem Abstr*, 1978, **89**, 163599d.
10. Goldman, P, Ramos, S. M. and Wuest, J D. *J. Org. Chem.*, 1984, **49**, 932–935
11. Konishiroku Photo Industry Co. Ltd. *Japan Kokai*, 57,138,645, *Chem. Abstr.*, 1984, **100**, 28131a.
12. Boeckelmann, J., Gragert, R., Grossmann, N., Fanghaenel, E. and Schmook, M. *Ger(East) DD*, 232,564, *Chem. Abstr.*, 1987, **106**, 41524z.
13. Wade, P. C., Vogt, B. R, Kissick, T P, Simpkins, L. M., Palmer, D. M. and Millonig, R C. *J Med. Chem.*, 1982, **25**, 331–333.
14. Bellamy, L. J. *The infrared spectra of complex molecules*, Vol. 2, Second edn, Chapman & Hall, 1980.
15. Vittal, J J *Studies on hydrazinium salts*, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1981.
16. Kotone, A., Hoda, M., Hori, T. and Nakane, Y *Japan Kokai*, 76,16,670, *Chem. Abstr.*, 1976, **85**, 192740r; *Japan Kokai*, 2,248,257, *Chem Abstr*, 1974, **81**, 25678n and *Japan Kokai*, 7,231,982, *Chem. Abstr*, 1973, **78**, 29776d.
17. Konishi, K., Osaka, T. and Koto, H. *Japan Kokai*, 7,402,532, *Chem Abstr.*, 1974, **81**, 136194w

18. Bowie, R. A., Gardner, M. D, Neilson, D. G., Watson, K. M., Mahmood, S. and Ridd, V. *J. Chem. Soc, Perkin I*, 1972, 2395–2399

19 Müller, E. and Herrdegen, L. *J. Prakt Chem.* (2), 1921, **102**, 113–160.

20. Curtius, T., Darapsky, A. and Müller, E. *Ber Chem*, 1915, **48**, 1614–1634.

21. Neilson, D. G., Roger, R., Heatlie, J W. M. and Newlands, L. R *Chem. Rev*, 1970, **70**, 151–170.

22. Rusanov, A. L. *Russ. Chem Rev.*, 1974, **43**, 795–804

23. Polya, J. B. *Comprehensive heterocyclic chemistry*, eds A. R. Katritzky, C N Rees and K. T. Potts, Pergamon, Vol. 5, Part 4A, 1984, pp. 733–790.

24. Herbst, R M and Garrison, J. A. *J. Org Chem.*, 1953, **18**, 872–877.

25. Potts, K T. *Chem. Rev*, 1961, **61**, 87–127.

26. Wystrach, V. P. *Heterocyclic compounds*, ed. R. C. Elderfield, Vol. 8, Wiley, 1967, p. 105.

27 Abdel Rehman, M O. *Tetrahedron Lett.*, 1968, **35**, 3871–3872