ISSN 0974-4169 (Print)
0974-4150 (Online)

www.ajrconline.org

RESEARCH ARTICLE

An effective one pot synthesis of 3, 4-dihydro-8-nitro-2H-1, 2, 4-triazino[3,4-*b*] benzothiazole-3,4-dione and its derivatives

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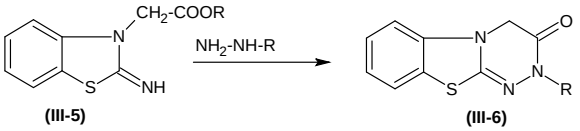
ABSTRACT:
A mixture of 6-nitro-2-hydrazino benzothiazole (I) on heated with diethyl oxalate (II) in presence of pyridine gives 3,4-dihydro-8-nitro-2H-1,2,4-triazino[3,4-*b*] benzothiazole-3,4-dione (III). Which on further reaction with different heteryl amines such as morpholine, pyrrolidine and piperidine afforded Mannich bases (IV a-c).

KEYWORDS: 6-nitro-2-hydrazino benzothiazole, pyridine, diethyl oxalate, dimethyl formamide.

INTRODUCTION:

Allen and Van Allan reported[1] the preparation of 2H-3,4-dihydro-1,2,4-triazino[3,4-*b*] benzothiazole-3-one (III-4) by the reduction of 3-carbethoxymethyl-2-nitrosoimino benzothiazoline with zinc and acetic acid. Hydrogenation of using palladium charcoal catalyst[1] gave a mixture, which was shown by its infrared spectra to be hydrazone ester contaminated with a small amount of (III-4). Paolini[2] also reported preparation of 2-alkyl-1, 2, 4-triazino[3,4-*b*] benzothiazol-3-ones (III-6) by the reaction of 3-[(hydroxycarbonyl) methyl]-2-iminobenzothiazoline (III-5-a) or its ethyl ester (III-5-b) with alkyl hydrazines.

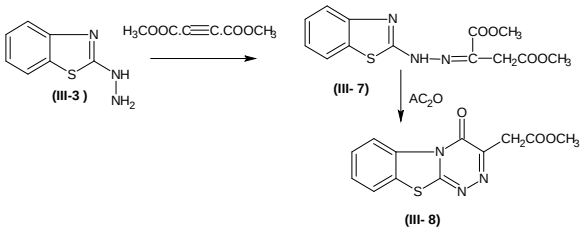


(III-5) (III-6)

(III-5)-a = R = H

(III-5)-b = R = C_2H_5

Le Count and Greer prepared[3] methyl 2-[4-oxo-1, 2, 4-triazino (3, 4-*b*) benzothiazol-3-yl] acetate (III-8) by the reaction of 2-hydrazinobenzothiazole with dimethyl acetylene dicarboxylate which gave an intermediate (III-7) It was cyclized to yield (III-8)

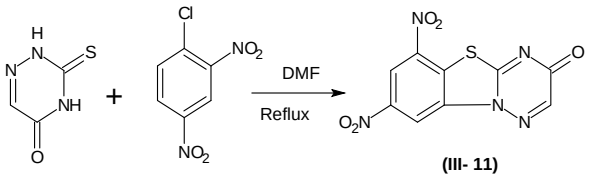


(III-3) (III- 7) (III- 8)

Ram Vishnu[4] reported one pot synthesis of dinitro-1,2,4-triazino [3, 2-*b*] benzothiazole-2-one (III-11) by the reaction of 2, 3-dihydro-3-thioxo-1,2,4-triazino-5-(4H)-one (III-9) with 1-chloro-2,4-dinitrobenzene (III-

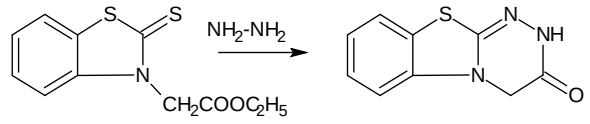
Received on 23.03.2017 Modified on 30.03.2017
Accepted on 12.04.2017
Asian J. Research Chem. 2017; 10(2):217-220.
DOI: 10.5958/0974-4150.2017.00036.0

10) in the presence of formyldimethylamine at reflux temperature.



(III- 9) **(III- 10)** **(III- 11)**

Amico John and coworkers[5] prepared 2H-1, 2, 4-triazino (3, 4-*b*) benzothiazole-3-(4H)-one (III-13) by condensing 3-(carbethoxy methyl) benzothiazo- line-2-thione (III-12) with hydrazine hydrate.



(III-12) **(III-13)**

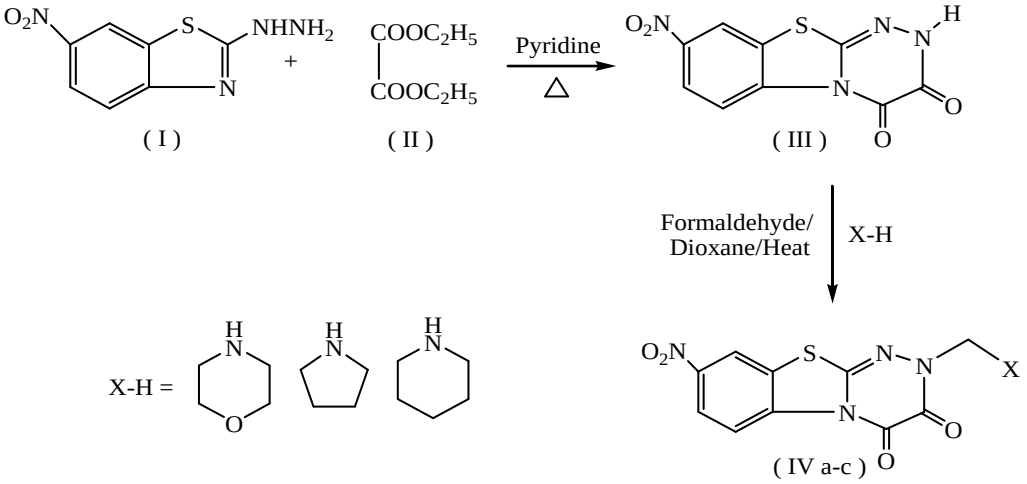
Stranskyz *et al* [6] suggested 1, 2, 4-triazine-3, 5-diones or pyrido [3, 4-*e*]-1, 2, 4-triazine diones as indicators for the determination of acid impurities in acetonitrile. The use of various 1, 2, 4-triazines derivatives as additives to photographic layers, developer both as photoconductors and in direct writing emulsions are reported as patents[7-9]. A large number of uses have been suggested for 1, , 4-triazines, reduced 1,2,4-triazines and condensed 1, 2, 4-triazines in literature. The preparations and uses of 4-amino-6-substituted-1, 2, 4-triazines as herbicides are well revealed in the patents[10-13]. From this series, 4-amino-6-tert-butyl-3-(methyl mercapto)-1, 2, 4-triazin-5-one has emerged as a well known and widely used herbicide. Another group of biochemically active 1,2,4-triazine derivatives are the 5-nitro-2-furyl substituted-1,2,4-triazines, especially 3-amino-6-[2-(5-nitro-2-furyl) vinyl]-1,2,4-triazines. These compounds are useful as antibacterial and showed [14-16] tuberculostatic activities. 1,2,4-Triazines with 2-pyridyl substituent's in the 3 and / or-5-positions form stable complexes with metal ions such as Fe^{+2}, CO^{+2}, Ni^{+2}, Zn^{+2} and Cu^{+2}. Owing to the stability of these complexes, the use of these 1,2,4-triazine derivatives was suggested for the determination of mentioned ions, especially for Fe^{+2} ions and the use of these substances as corrosion inhibitors[17-18]. The use of pyrimido (4',5':5,6)-1,2,4-triazine(4,3-*b*) imidazoles or derivatives of 1,2,4-benzotriazine-7-carboxylic acid-1-oxide as dyes is claimed by different groups [19-21].

EXPERIMENTAL SECTION:

All melting points were determined in open capillary tube and were uncorrected. IR spectra were recorded with potassium bromide pellets technique, ^{1}H NMR spectra were recorded on Avance 300 MHz Spectrometer in DMSO using TMS as internal standard. Mass spectra were recorded on a FT VG-7070 H Mass Spectrometer using EI technique at 70ev. All the reactions were monitored by thin layer chromatography.

General Procedure:

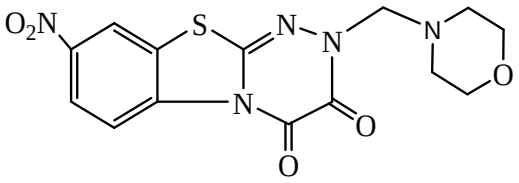
A mixture of 6-nitro-2-hydrazino benzothiazole (I) on refluxed for 1-2 hours with diethyl oxalate (II) in presence of pyridine to yield 3,4-dihydro-8-nitro-2H-1,2,4-triazino[3,4-*b*] benzothiazole-3,4-dione (III). Which on further reaction with formaldehyde independently with morpholine, pyrrolidine and piperidine gives corresponding Mannich bases (IV a-c)?



(I) (II) (III) (IV a-c)

1) Preparation of 3,4-dihydro-2-N-methyl morpholino-8-nitro-2H-1,2,4-triazino[3,4-*b*][1,3] benzothiazole-3,4-dione (IV-a).

A mixture of 3,4-dihydro-8-nitro-2H-1,2,4-triazino[3,4-*b*]benzothiazole-3,4-dione (III) [0.001mole], dioxane (5ml), formaldehyde (1 ml) and morpholine [0.002mole] mixture was refluxed on water bath at 60^0C for one hour and mixture was kept for overnight. The product was recrystallized from ethanol to give 0.20 gm of (IV-a)



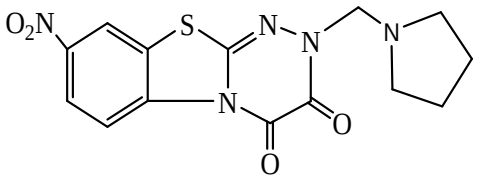
(IV a)

CHARACERIZATION :

IR: (KBr / cm^{-1}): 2920 (C-H) , 1660 (C=O) ,1652 (C=N). 1560 and 1350 (-NO_2) cm^1. ^{1}H-NMR: (300 MHz, $CDCl_3$): δ 2.4 (t, 4H, -NCH_2) δ 3.7 (t, 4H, -OCH_2), δ 4.1 (s 2H, -N-CH_2-N), δ 7.7 (d, 1H, Ar-H), δ 7.9 (d, 1H, Ar-H), δ 8.1 (s, 1H, Ar-H), EI-MS: (m/z:RA%): 364 (M+1), Elemental analysis : $C_{14}H_{13}N_5O_5S$, Calculated: (%) C 46.28, H 3.61, N 19.27, O 22.02, S 8.82 Found (%) : C 46.22, H 3.55, N 19.25, O 22.00, S 8.75

2) Preparation of 3,4-dihydro-2-N-methyl pyrrolidino-8-nitro-2H-1,2,4-triazino[3,4-*b*][1,3] benzothiazole-3,4-dione (IV-b).

A mixture of 3,4-dihydro-8-nitro-2H-1,2,4-triazino[3,4-*b*]benzothiazole-3,4-dione (III) [0.001mole], dioxane (5ml), formaldehyde (1ml) and pyrrolidine [0.002mole] mixture was refluxed on water bath at 60^0C for one hour and mixture was kept for overnight. The product was recrystallized from ethanol to give 0.22 gm of (IV-b)



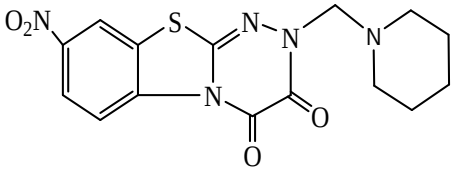
(IV-b)

CHARACERIZATION :

IR: (KBr / cm^{-1}): 2911 (C-H) , 1655 (C=O) ,1645 (C=N). 1562 and 1355 (-NO_2) cm^1. EI-MS: (m/z:RA%) :350 (M+1), Elemental analysis: $C_{14}H_{13}N_5O_4S$, Calculated: (%) C 48.41, H 3.77, N 20.16, O 18.42, S 8.23 Found (%) : C 48.34, H 3.71, N 20.10, O 18.37, S 8.20

3) Preparation of 3,4-dihydro-2-N-methyl piperidino-8-nitro-2H-1,2,4-triazino[3,4-*b*][1,3] benzothiazole-3,4-dione (IV-c).

A mixture of 3,4-dihydro-8-nitro-2H-1,2,4-triazino[3,4-*b*]benzothiazole-3,4-dione (III) [0.001mole], dioxane (5ml), formaldehyde (1 ml) and piperidine [0.002mole] mixture was refluxed on water bath at 60^0C for one hour and mixture was kept for overnight. The product was recrystallized from ethanol to give 0.21 gm of (IV-c)



(IV-c)

CHARACERIZATION :

IR: (KBr / cm^{-1}): 2905 (C-H) , 1651 (C=O) ,1643 (C=N). 1557 and 1348 (-NO_2) cm^1. EI-MS: (m/z:RA%): 362 (M+1), Elemental analysis: $C_{15}H_{15}N_5O_4S$, Calculated: (%) C 49.85, H 4.18, N 19.38, O 17.71, S 8.87, Found (%) : C 49.81, H 4.13, N 19.34, O 17.65, S 8.82

RESULTS AND DISCUSSION:

One pot reactions constitute an especially attractive recent synthetic strategy since they provide easy and rapid access to large number of organic compounds with diverse substitution pattern. In present work, we report one pot synthesis of novel fused heterocyclic compound, 3,4-dihydro-2-N-methyl morpholino-8-nitro-2H-1,2,4-triazino[3,4-*b*][1,3] benzothiazole-3,4-dione and its 2-substituted derivatives.

ACKNOWLEDGEMENTS:

The authors are thankful to the Principal, Yeshwant Mahavidyalaya, Nanded for providing laboratory facilities and the Director, Indian Institute of Chemical Technology, Hyderabad for providing spectra.

REFERENCES:

1. Allen, C. F. H. and Van Allan, J. A., J. Org. Chem.1948, 13, 603.
2. Paolini, J., J. Org. Chem., 1968, 33, 888.
3. Le Count, D. J. and Greer, A. T., J. Chem. Soc., Perkin, 1974, 1, 297.
4. Ram Vishnu J., Leibigs Ann. Chem., 1988 11, 1089-90: Chem. Abstr, 1989,110, 8172t.
5. Amico John, D. J., Bollinger, F. G. and Dahl William, 1988, 35, 71: Chem. Abstr. 1989 109, 170391g.
6. Stransky Z., Cap. L. and Slouka, J., Colleot Czech. Chem. Commun., 1973, 38, 2712.
7. Kalle, A. G., Ger, Pet. 1, (Feb. 16, 1961), 099, 846; Chem. Abstr., 1963, 58, 11382h.
8. Gevaert Photo production N. V. Belg. Pat. (Dec. 16, 1954), 531, 277: Chem. Abstr. 1959, 53, 13853e.
9. Bielow, J. H., U. S. Pat. (Mar.28, 1972), 3, 652, 287, Chem. Abstr. 1972, 77, 27403k.
10. Garside S. C., Hartely D., Lunts L. H. C. and Oxford A. W., Ger. Offen. 2, 255, 172; Chem. Abstr, 1973, 79, 53376q.
11. Dickose K., Draber W, Timmler H, Eue L. and Schmidt R. R, 121008u (1974).
12. Draber W., Timmler H., Dickose K., Schmidt R. R., 2, 224, 161; Chem. Abstr, 1974, 80, 48042u.
13. Dickose, K., Draber, W. and Eue, L. Ger. Offen, (Sept. 7 1972); 2, 107, 757; Chem. Abstr. 1972, 77, 164767 w.
14. Ako M., Kuroda, K. and Miyaki, M., Blochem. Pharmacol. 1971, 20, 3091; Chem. Abstr. 1972, 76, 68035a.
15. McCalla, D. R. and Reuvers, J. Protozool, (1970), 12, 129; Chem. Abstr. 1970, 72, 118743i.
16. McCalla D. R., J. Protozool. 1965, 12, 34; Chem. Abstr. 1965, 62, 121199b.
17. Culberton, B. M., U. S. Pat. (July 20, 1971), 3, 594, 349; Chem. Abstr, 1971 75, 15304q.
18. Chriswell, C. D., Anal. Chem, 1974, 46, 992.
19. Kaupp, G. and Voltz, J., Ger. Offen. (Feb. 26, 1970), 1, 941, 542; Chem. Abstr 1970, 73, 36578r.
20. Geigy I. R. and Demande A. G., Fr., (July 13, 1972), 2, 11, 641; Chem. Abstr 1973, 78, 99050m.
21. Sandoz Ltd., Fr. Pat. (Dec. 16, 1966), 1, 462, 672, Chem. Abstr, 1968, 68, 106069y.