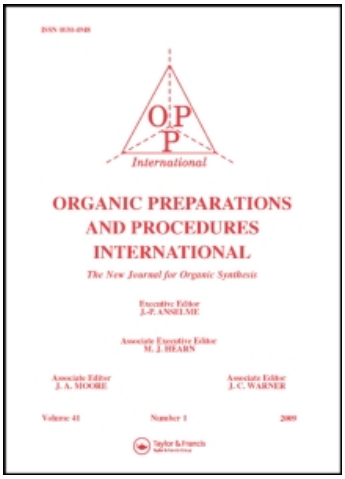

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SYNTHESIS OF SOME BENZOTHIAZOLOBENZOTRIAZEPINES

M. V. Deshmukh[a]; D. S. Deshpande[a]
[a] Department of Chemistry, Science College, Nanded, India

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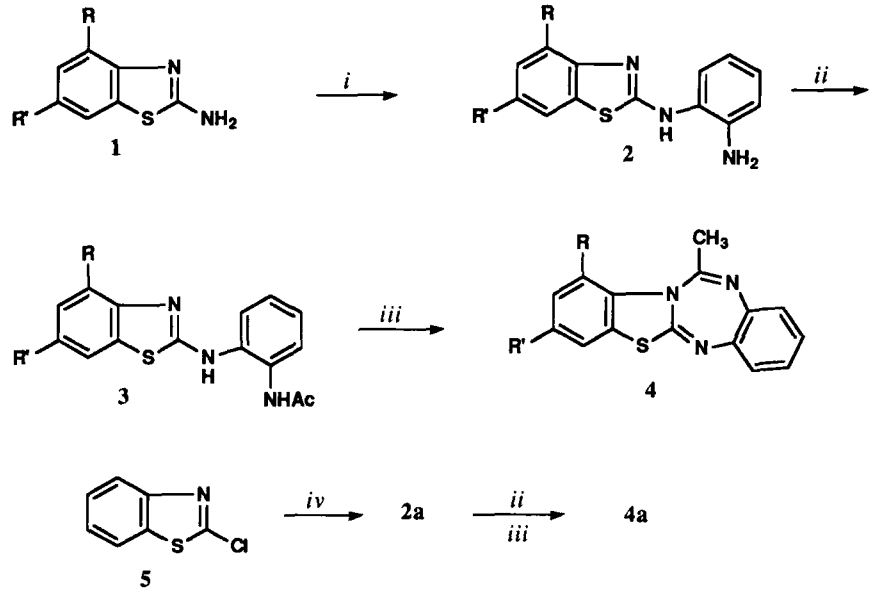
SYNTHESIS OF SOME BENZOTHIAZOLOBENZOTRIAZEPINES

Submitted by M. V. Deshmukh and D. S. Deshpande*
(05/11/92)

Department of Chemistry, Science College
Nanded 431 602, INDIA

In continuation of our earlier work on 3-substituted[1,2,4]triazepino[3,4-b]benzothiazolone[1] from 2-hydrazinobenzothiazole and ethyl acetoacetate, we now report the synthesis of benzothiazolo[2,3-b][1,3,5]benzotriazepines. Reaction of 2-aminobenzothiazole (1) with *o*-chloroaniline in the presence of pyridine, potassium carbonate and cupric oxide under the conditions of Ullmann reaction gave **2** in fair yields. These N-phenylaminobenzothiazoles were acetylated to give



a) R = R' = H b) R = H, R' = CH_3 c) R = R' = CH_3 d) R = H, R' = OEt e) R = H, R' = NO_2

i) *o*-Chloroaniline, CuO, K_2CO_3; *ii*) Ac_2O; *iii*) $POCl_3$; *iv*) *o*-Phenylenediamine

2-(*o*-acylaminophenylamino)benzothiazoles (**3**) which underwent smooth cyclization (as indicated by the absence of NH in the IR) in presence of phosphorus oxychloride to give the 12-methylbenzothiazolo[2,3-b][1,3,5]benzotriazepines (**4**). Their NMR exhibited a multiplet at δ 8.50-9.00 (ArH) and δ 2.5 (3H CH_3). An alternate approach involves the reaction of 2-chlorobenzothiazole (**5**) with *o*-phenylenediamine to give **2a**. The reported potential biological activity of simple triazepine[2] encouraged us to synthesize several other derivatives from 2-amino-6-methyl-, 2-amino-4,6-dimethyl-, 2-amino-6-nitro- and 2-amino-6-ethoxy-benzothiazoles.[3,4,5,6]

EXPERIMENTAL SECTION

Mass spectra were obtained on a VG micromass 7070 H instrument. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker instrument at 100 MHz using TMS as internal standard. IR spectra were measured with a Perkin Elmer model 710B recording spectrophotometer and reported values are given in cm^{-1}. Elemental analysis were obtained from Perkin Elmer AD-22 Autobalance. The melting points are uncorrected.

2-(*o*-Aminophenylamino)benzothiazoles (2). Typical Procedure.- A mixture of 2-aminobenzothiazole (1.5 g, 0.01 mole), *o*-chloroaniline (1.28 g, 0.01 mole), anhydrous potassium carbonate (5 g) and cupric oxide (1.5 g) in pyridine (30 mL) was heated to reflux in an oil bath for 24 hrs. The contents were cooled and the mixture was filtered. The filtrate upon acidification with 5N hydrochloric acid gave a solid which was extracted into ether. The solvent was evaporated to give 1.26 g, (52%) of black colored solid **2a**, mp. 260° (EtOH).

Compounds **2b-e** were obtained using the same procedure (see Table)

2-(*o*-Aminophenylamino)benzothiazole (2a) from 2-Chlorobenzothiazole.- A mixture of 2-chlorobenzothiazole (3.39 g,0.02 mole), *o*-phenylenediamine (3.24 g, 0.03 mole), anhydrous potassium carbonate (4.5 g), cupric oxide (1.5 g) in pyridine (25 mL) was heated on oil bath for 30 hrs. The contents were cooled and the product was isolated as described above to give 2.12 g, (44%) of **2a**, mp. 260°.

2-(*o*-Acylaminophenylamino)benzothiazole (3a-e). Typical Procedure.- To a solution of 2-aminophenylaminobenzothiazole (1.2 g, 0.005 mole) in acetic acid (0.80 mL), acetic anhydride (1.5 mL) was added and the mixture was heated to reflux for 10 minutes. The contents were poured over crushed ice and the precipitated product was extracted into benzene. The solution was washed with water and dried over anhydrous magnesium sulfate and the solvent was evaporated to give desired product (Table).

Cyclization of 2-(*o*-Acylaminophenylamino)benzothiazoles to Substituted 12-Methylbenzothiazolo[2,3-b][1,3,5]benzotriazepines (4a-e).- A mixture of **3** (1 g), dry benzene (15 mL) and phosphorus oxychloride (3 mL) was heated in a water bath for 6 hrs. The solvent was removd under reduced pressure. The resulting residue was treated with ice-cold water (50 mL) and then basified with ammonium hydroxide (20 mL). The crude product thus obtained was purified by column chromatography over silica gel using benzene-ethyl acetate (9:1) as eluent to give **4** (Table).

TABLE 1. Analytical and Spectral Data of Compounds **2, 3** and **4**[a]

Compd	mp. (°C)	Yield (%)	IR (cm^{-1})	MS	^1H NMR (δ ppm)	Elemental Analysis (Found) C	H	N
2a	260	52	3300	241	5.2(NH, NH_2)	67.43 (67.26)	4.56 (4.23)	17.42 (17.32)
2b[b]	140	40	3100	255	5.2 (NH,NH_2) 1.9 (3H CH_3)	65.88 (65.67)	5.09 (5.19)	16.47 (16.38)
2c[b]	200	36	3200 NH	267	—	66.91 (66.71)	5.57 (5.34)	15.61 (15.58)
2d[b]	230	54	3300	235	—	63.15 (62.88)	5.26 (5.11)	14.73 (14.55)
2e[b]	120	91	3100	286	5-5.3	54 54 (54.26)	3.49 (3.37)	19.58 (19.26)
3a[c]	116	57	3400-3200	283	9.5 (CONH, exch.D_2O)	63.60 (63.40)	4.59 (4.38)	14.88 (14.62)
3b[c]	160	61	1650	297	—	64.64 (64.42)	5.05 (4.96)	14.14 (13.95)
3c[c]	130	85	1620	311	9.1, 1.8 (3H CH_3)	65.59 (65.48)	5.46 (5.32)	13.50 (13.42)
3d[c]	200	78	1660	307	9.0, 3.8 (3H -OEt) 4.0 (2H -OEt)	62.35 (62.35)	5.19 (4.97)	12.84 (12.71)
3e[c]	182	44	1680	328	9.4	54.86 (53.78)	4.65 (4.41)	17.06 (16.94)
4a[d]	122	41	1250	265	2.3 (3H CH_3, triazepine) 8.5 (ArH)	67.91 (67.67)	4.65 (4.51)	15.80 (15.68)
4b[d]	180	80	1260	279	2.4 (3H CH_3), 1.3 (3H CH_3)Bz, 7.8 (ArH)	68.81 (68.72)	4.65 (4.48)	15.05 (14.88)
4c[d]	175	88	-	293	2.2 (3H CH_3)	69.60 (69.48)	5.10 (4.92)	14.33 (14.16)
4d[d]	225	89	1280	309	2.5 (3H CH_3) 3.9 (3H -OEt) 4.1 (2H -OEt), 7.1 (ArH)	66.01 (65.84)	4.85 (4.72)	14.59 (14.52)
4e[e]	230	74	1268	310	2.8 (3H CH_3), 8.5 (ArH)	58.05 (57.98)	3.22 (3.01)	18.06 (17.99)

a) All products were crystallized from ethanol. b) Black c) Reddish brown d) Pale brown e)Black colored.

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A NEW ROUTE FOR THE SYNTHESIS OF Z-11-HEXADECEN-1-OL, A SEX PHEROMONE OF *CHILO INFUSCATELLUS* (SNELL)

Submitted by (06/17/92) S. Narasimhan* and K. Ganeshwarprasad

Centre for Agrochemical Research, SPIC Science Foundation 110, Mount Road, Madras - 600 032, INDIA

Chilo infuscatellus Snell (Crambidae; Lepidoptera), the early shoot borer of sugar cane, affects the shoots during germination stages prior to internode formation resulting in the drying up of the entire clump and hence decrease in yield and quality.[1] There have been a few reports on the utility of pheromone technology to control this insect.[2,3] However, the composition of the pheromone components recommended varied from a mixture of Z-11- hexadecen-1-ol and Z-11-hexadecenal to Z-11-hexadecen-1-ol alone as an attractant. These reports could lead to the use of varying compositions in the lures which would be less effective and inferior to the virgin females. In order to establish the effective composition, pure components were needed. We report here a new route for the synthesis of Z-11-hexadecen-1-ol in high purity(>98%):