A Convenient Synthesis of 3-Methylthiazolo[3,2-*a*]benzimidazoles, 3-Benzylthiazolo[3,2-*a*]benzimidazoles, and 4-Phenylthiazeno[3,2-*a*]benzimidazoles

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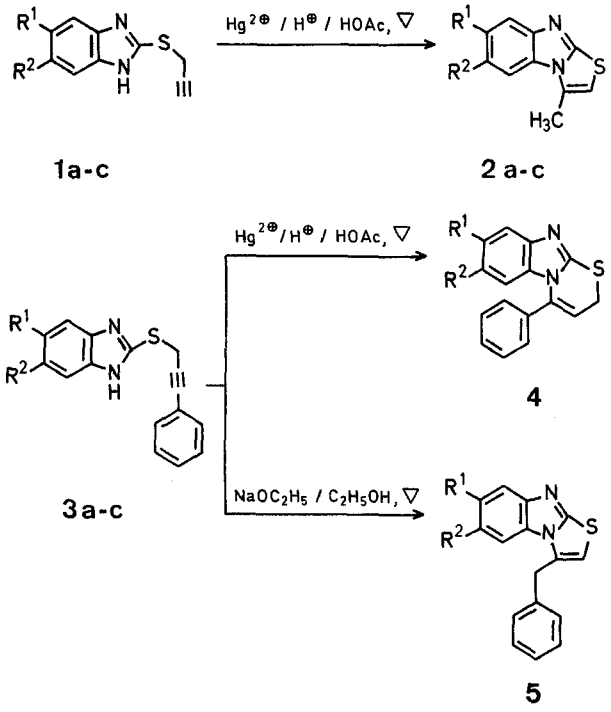
The methods reported in literature for the synthesis of 3-methylthiazolo[3,2-*a*]benzimidazoles involve either a cyclisation of 2-(2-propynylthio)-benzimidazoles under alkaline conditions[1] or of 2-(acetonylthio)-benzimidazoles in acidic medium[2]. We wish to portray in this communication, a facile and convenient mercury(II) ion catalysed reaction of 2-(2-propynylthio)-benzimidazoles (**1**) resulting in the formation of 3-methylthiazolo[3,2-*a*]benzimidazoles (**2**) and of 2-(3-phenylprop-2-ynylthio)-benzimidazoles (**3**) furnishing the hitherto unknown 4-phenyl[1,3]thiazeno[3,2-*a*]benzimidazoles (**4**). In contrast, when 2-(3-phenylprop-2-ynylthio)-benzimidazoles were subjected to alkaline conditions[1], they afforded the new 3-benzylthiazolo[3,2-*a*]benzimidazoles (**5**) in good yields.



When a mixture of 2-mercaptobenzimidazole and one equivalent of propynyl bromide was stirred at room temperature in acetone with sodium acetate and a few drops of glacial acetic acid, a selective alkylation at sulfur could be achieved leading to 2-(2-propynylthio)-benzimidazoles. Under identical conditions, instead of propynyl bromide, when 3-phenylpropynyl bromide was employed, the 2-mercaptobenzimidazoles furnished 2-(3-phenylprop-2-ynylthio)-benzimidazoles, the m.p. and the yields of which are listed in the Table.

General Procedure for the Mercury(II) Ion Catalysed Reaction: The 2-propynylthiobenzimidazole or 2-(3-phenylprop-2-ynylthio)-benzimidazole was refluxed in glacial actic acid with a catalytic amount of mercury(II) acetate in presence of a few drops of concentrated sulfuric acid for a duration of five hours. The reaction mixture was cooled to room temperature, poured on to crushed ice, and neutralised with saturated sodium hydrogen carbonate solution. The crude solid was filtered off, washed with water, dried, and recrystallised from suitable solvents (see Table). Any ketonic product (or products), emerging out of a normal hydration reaction was shown to be totally absent by the I.R. and N.M.R. spectra of the crude hydration product in all the cases.

Table. Preparation of 3-Methylthiazolo[3,2-*a*]benzimidazoles (**2**), 2-(3-Phenylprop-2-ynylthio)-benzimidazoles (**3**), 4-Phenylthiazeno[3,2-*a*]benzimidazoles (**4**), and 3-Benzylthiazolo[3,2-*a*]benzimidazoles (**5**).

Product	R^1	R^2	m.p. (solvent)	Yield (%)	Brutto formula[a]
2a	H	H	165–166°[b] (benzene)	68	$C_{10}H_8N_2S$ (188)
2b	CH_3	CH_3	206–207° (benzene)	75	$C_{12}H_{12}N_2S$ (216)
2c	H(Cl)[c]	Cl(H)	138–139° (benzene)	80	$C_{10}H\text{-}ClN_2S$ (222.5)
3a	H	H	144–145° ($CHCl_3$/hexane)	90	$C_{16}H_{12}N_2S$ (264)
3b	CH_3	CH_3	177° ($CHCl_3$/hexane)	91	$C_{18}H_{16}N_2S$ (292)
3c	H(Cl)[c]	Cl(H)	175° ($CHCl_3$/hexane)	89	$C_{16}H_{11}ClN_2S$ (298.5)
4a	H	H	148–149° ($CHCl_3$)	70	$C_{16}H_{12}N_2S$ (264)
4b	CH_3	CH_3	213–214° ($CHCl_3$)	63	$C_{18}H_{16}N_2S$ (292)
4c	H(Cl)[c]	Cl(H)	180–181° ($CHCl_3$)	61	$C_{16}H_{11}ClN_2S$ (298.5)
5a	H	H	80–81° (CH_3OH)	80	$C_{16}H_{12}N_2S$ (264)
5b	CH_3	CH_3	201–202° (CH_3OH)	82	$C_{18}H_{16}N_2S$ (292)
5c	H(Cl)[c]	Cl(H)	124–125° (CH_3OH)	85	$C_{16}H_{11}ClN_2S$ (298.5)

[a] All products gave satisfactory elemental analyses (C ± 0.3%, H ± 0.3%).

[b] Lit.[1] m.p. (ethanol): 165°.

[c] The exact position of the chlorine cannot be determined due to tautomerisation of the proton between the 2 nitrogen atoms in the starting material. T.L.C. and N.M.R. analysis revealed only one isomer.

In the Table are summarised the m.p., solvents for recrystallisation, and the yields of the various 3-methylthiazolo[3,2-*a*]benzimidazoles and 4-phenylthiazeno[3,2-*a*]benzimidazoles, respectively.

Procedure for the Synthesis of 3-Benzylthiazolo[3,2-*a*]benzimidazoles (5):

To a solution 2-(3-phenyl-prop-2-ynylthio)-benzimidazole (0.002 mol) in ethanol (15 ml) was added slowly an equivalent of sodium in alcohol (5 ml) at 0° and the mixture was refluxed over a water bath for 2 h. The solution was cooled to room temperature and poured on to crushed ice. The solid was filtered off and recrystallized from suitable solvents as outlined in the Table.

All the new compounds reported here gave satisfactory elemental analyses and their I.R., N.M.R., U.V., and mass spectral data were fully consistent with the structures assigned. M.p.'s given in the Table are not corrected.

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