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An Improved Method for the Preparation of 2-Aryl-, 2-Hetaryl- and 2-Styrylbenzothiazoles

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ABSTRACT

An improved method for the preparation of 2-aryl-, 2-hetaryl- and 2-styryl-benzothiazoles by interaction of aryl aldehydes, heterocyclic aldehydes and cinnamaldehydes with 2-aminothiophenol in dimethyl sulphoxide with simultaneous removal of the volatile reaction products is described. The method offers a simple experimental procedure, higher yields and shorter reaction times.

INTRODUCTION

2-Aryl-, 2-hetaryl- and 2-styrylbenzothiazoles have wide practical applications and can, for example, be used as thermostabilizers for polymers,[1] as acaricides,[2] as diazotype materials,[3] in electrophotography,[4] as compounds having chelating properties in analytical chemistry,[5] as fluorescent brightening agents,[6] as intermediates for the preparation of stilbene derivatives[7] and dyes[8] and as UV stabilizers for polymer materials.[9,10]

In this paper the authors report an improved method for the preparation of this important class of compounds.

RESULTS AND DISCUSSION

Hoffmann[11] reported the reaction of benzaldehydes and 2-aminothiophenols to give 2-phenylbenzothiazoles and the reaction can be carried out

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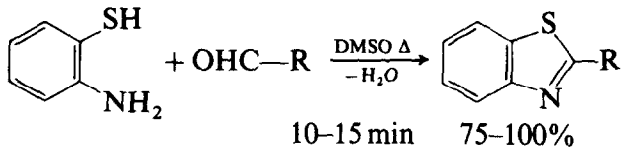
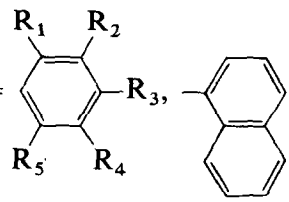
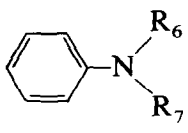
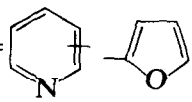
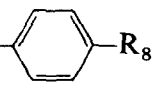


10–15 min 75–100%

R is aryl, hetaryl or styryl **1a–1h, 2a–2j, 3a–3d, 4a, 4b**

1a–1h R =  ; **2a–2j**: R = 

3a–3d: R =  ; **4a, 4b**: R = CH=CH— 

1a: $R_1 = R_2 = R_3 = R_4 = R_5 = H$; **1b** $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = CH_3$; **1c**: $R_1 = R_2 = R_3 = R_4 = H$, $R_5 = OH$; **1d**: $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = OH$; **1e**: $R_1 = R_2 = R_5 = H$, R_3 and $R_4 = OCH_2O$; **1f**: $R_1 = R_2 = R_3 = R_5 = H$, R_4 = 2-benzothiazolyl; **1g**: 1-naphthyl; **1h**: 9-anthryl; **2a**: $R_6 = H$, $R_7 = COCH_3$; **2b**: $R_6 = R_7 = CH_3$; **2c**: $R_6 = R_7 = C_2H_5$; **2d**: $R_6 = C_2H_5$, $R_7 = CH_2C_6H_5$; **2e**: $R_6 = C_2H_5$, $R_7 = C_2H_4CN$; **2f**: $R_6 = C_2H_5$, $R_7 = C_2H_4CONH_2$; **2g**: R_6 and $R_7 = (CH_2)_4$; **2h**: R_6 and $R_7 = (CH_2)_5$; **2i**: R_6 and $R_7 = C_2H_4OC_2H_4$; **2j**: R_6 and $R_7 = C_2H_4N(CH_3)C_2H_4$; **3a**: 2-furyl; **3b**: 2-pyridyl; **3c**: 3-pyridyl; **3d**: 4-pyridyl; **4a**: $R_8 = H$; **4b**: $R_8 = N(CH_3)_2$.

Scheme 1

in various media such as ethanol,[12–14] dimethylformamide,[15] dimethylacetamide[16] and acetic acid[17] as well as in the absence of a solvent.[18] It is known that the intermediate Schiff bases formed from 2-aminothiophenol and benzaldehydes cyclize spontaneously to the respective dihydrobenzothiazoles. The latter are readily oxidized to the respective benzothiazoles.[12,13] The reaction of bisulphite derivatives of aldehydes with 2-aminothiophenol[16] or the oxidation of Schiff bases prepared from aromatic aldehydes and 2-aminothiophenols[19] can also be used. The yields obtained are very dependent on the nature of aldehydes and reaction media used and in the case of the synthesis of sterically hindered products yields are low.[18] All the above methods require a reaction duration of 30 min to 24 h and yields are generally low or satisfactory.

It was established that when the interaction of arylaldehydes, heterocyclic

TABLE 1
Yields, Melting Points and Analytical Characersitics of **1a–1h, 2a–2j, 3a–3d, 4a** and **4b**

Compound	*Present work*		*Previous work*		*Analysis*		
					Calc. (%)/found (%)		
	Yield (%)	*M.p. (°C)*	*Yield (%)*	*M.p. (°C)*	*C*	*H*	*N*
1a	100	113–114	79	113–114[19]	—	—	—
1b	92	85	82	84–85[22]	—	—	—
1c	96	127–128	58	125–127·5[23]	—	—	—
1d	96	227–228	47	227–229[9,24]	—	—	—
1e	100	127–128	62·5	125[14]	—	—	—
1f[a]	95	183–185		—	69·7 69·5	3·5 3·2	8·1 8·2
1g	94	126	39	127[18]	—	—	—
1h	95	221–223	31	212–213·5[18]	81·0 81·3	4·2 4·5	4·5 4·5
2a	100	237–238	—	226–228[3]	—	—	—
2b	95	176–178	70	174–175[25]	70·8 70·8	5·5 5·2	11·0 10·7
2c	92	125–126	—	125[17]	—	—	—
2d	85	131–133	—	120–122[17]	76·7 76·8	5·85 6·0	8·1 7·9
2e[a]	75	102–103	—	—	70·8 70·5	5·6 6·0	13·65 13·65
2f[a]	97	115–117		—	66·4 66·3	5·9 6·0	12·9 12·7
2g[a]	95	241–243		—	72·8 72·55	5·75 5·2	10·0 9·6
2h[a]	98	175–176		—	73·5 74·1	6·1 5·9	9·5 9·5
2i	100	277–278	—	273[3]	68·9 69·3	5·4 5·8	9·45 9·46
2j[a]	100	211–212		—	69·9 69·8	6·2 6·3	13·6 13·6
3a	97	103	36	105[14]	—	—	—
3b	91	136–137	—	137–138[26]	67·9 68·1	3·8 4·05	13·20 13·1
3c	96	137–138	53	127[27]	—	—	—
3d	94	135–136	50	133–134[15]	67·9 68·4	3·8 4·05	13·20 13·1
4a	90	112–113	—	112[28]	—	—	—
4b	95	206–208	—	206–208[29]	—	—	—

[a] Compounds **1f, 2e, 2f, 2g, 2h** and **2j** are new. They were recrystallized from ethanol (**2e, 2f**), dimethyl sulphoxide:ethanol (1:1) (**1f, 2g, 2j**) or methoxyethanol (**2h**).

aldehydes or cinnamaldehydes with 2-aminothiophenol is carried out in dimethyl sulphoxide with simultaneous removal of the volatile reaction products by distillation (until the boiling point of the solvent is reached), the 2-aryl-, 2-hetaryl- and 2-styryl-benzothiazoles respectively are obtained in good yield (Scheme 1; Table 1).

Comparison with the known methods for the preparation of benzothiazole derivatives from aromatic aldehydes and 2-aminothiophenols shows that this new method requires shorter reaction times and yields are higher by 10–60% than those described previously; yields of 95–100% are often observed. The reaction is insensitive to steric hindrance and sterically hindered products are also obtained with good yields.

It is known that dimethyl sulphoxide is an oxidant[20,21] and probably the solvent acts as such in this case too.

The simple experimental procedure, high yields and short reaction times render this reaction more effective in the preparation of this valuable class of compounds.

EXPERIMENTAL

The melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Tesla BS-487 80 MHz instrument in trifluoroacetic acid, acetone-d_6 and a mixture of DMSO-d_6 and trifluoroacetic acid with TMS as internal reference. IR spectra were recorded on a spectrophotometer Specord IR 71 in nujol and chloroform.

General procedure

A mixture of the respective arylaldehyde, heterocyclic aldehyde or cinnamaldehyde (0·05 mol), 2-aminothiophenol (0·05 mol) and dimethyl sulphoxide (30–40 ml) was heated until the temperature of the vapours reached 180–186°C (*c.* 10–15 min). After this time, about 10–15 ml of volatile products distilled off. The reaction mixture was then cooled and the precipitate was filtered and dried. In cases when a precipitate was not observed, the reaction mixture was diluted with water (15–20 ml) and the resultant solid collected and dried.

Analytical characteristics of the compounds, yields and melting points are given in Table 1.

^{1}H-NMR and IR spectra of some compounds were recorded.

^{1}*H-NMR spectra*

δ (ppm): **1f** (CF_3COOH), 7·85–9·12 (m, 11H-3ArH); **2e** (acetone-d_6), 1·20 (t, 3H-CH_3), 2·79 (t, 2H-NCH_2), 3·62 (q, 2H-$\underline{CH_2}CH_3$), 3·81 (t, 2H-CH_2CN),

6·79–8·05 (m, 8H-2ArH); **2f** (acetone-d_6), 1·16 (t, 3H-CH_3), 2·51 (t, 2H-$N\underline{CH_2}CH_2CO$), 3·47–3·82 (q, 4H-CH_2CO, $\underline{CH_2}CH_3$), 7·95–8·57 (m, 8H-2ArH); **2g** (CF_3COOH), 2·57 (t, 4H-CH_2NCH_2), 4·19 (t, 4H-CH_2CH_2), 7·95–8·57 (m, 8H-2ArH); **2h** (CF_3COOH), 1·87–2·50 (m, 6H-$CH_2CH_2CH_2$), 3·92 (t, 4H-CH_2NCH_2), 7·87–8·65 (m, 8H-2ArH); **2i** (CF_3COOH), 4·09 (t, 4H-CH_2NCH_2), 4·44 (t, 4H-CH_2OCH_2), 7·90–8·55 (m, 8H-2ArH); **2j** (DMSO-d_6 and CF_3COOH), 2·95 (s, 3H-CH_3), 3·20–4·25 [m, 8H-$N(CH_2CH_2)_2$], 7·10–8·12 (m, 8H-2ArH).

IR spectra

ν (cm^{-1}): **1f** (nujol) 715, 790; **2e** ($CHCl_3$) 1615, 2260; **2f** ($CHCl_3$) 1610, 1690, 3440, 3550; **2g** (nujol) 750, 815, 1615; **2h** (nujol) 755, 820, 1610; **2i** (nujol) 760, 815, 1610; **2j** ($CHCl_3$) 1380, 1610, 2820–2960.

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