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A NOVEL ENTRY INTO THE BENZO[*b*]TIOPHENE SERIES

THE REACTION OF 5,5-DIPHENYL-4-IMIDAZOLIDINETHIONES AND 2,2-DIPHENYLGLYCINETHIOAMIDES WITH ALUMINIUM TRICHLORIDE

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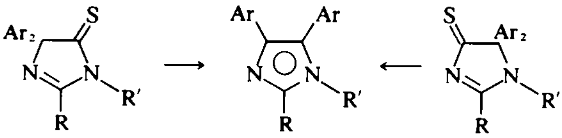
Abstract—5,5-Diphenyl-4-imidazolidinethiones (**5**) are converted by $AlCl_3$ into 2-amino-3-phenylbenzo[*b*]thiophene **8** and/or Schiff's bases **7** derived from the latter. 2,2-Diarylglycinethioamides furnish only type **8** products. On the basis of a crossing experiment, a mechanism is suggested for the above rearrangements.

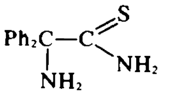
4,4 - Diaryl - 2 - imidazoline - 5 - thiones (**1**)[1] as well as 5,5 - diaryl - 2 - imidazoline - 4 - thiones (**3**)[2] are converted by $AlCl_3$ in aromatic solvents into 4,5-diarylimidazoles (**2**). In order to establish whether the C(2) atom has to be sp^2 hybridized for the above rearrangement to take place, the related 5,5 - diphenyl - 4 - imidazolidinethiones (**5**), obtained by reacting 2,2-diphenylglycinethioamide (**4**)[2] with oxo compounds, were treated with $AlCl_3$. No rearranged imidazole derivatives **6** were obtained in either case. Instead, depending on the nature of R″ and of the conditions of the work-up, Schiff's bases **7** derived from 2-amino-3-phenylbenzo[*b*]thiophene **8**, or the amine **8**, or mixtures of these two types of products were obtained in moderate to good yields (see Table 2). The non-crystalline amine **8** was isolated either as the hydrochloride or as a diacetyl derivative which has been assigned the isoimide structure **11** (see below). The aldehyde condensation products **5a–d** tend to yield type **7** products while the ketone condensation products **5f** and **g** furnished only **8**. Similarly, only **8**·HCl could be isolated in the **e** series, presumably because the reagent effected partial O-demethylation leading to the formation of tarry products. No crystalline product was obtained on $AlCl_3$ treatment of 2 - (4 - chlorophenyl) - 5 - (1 - naphthyl) - 5 - phenyl - 4 - imidazolidinethione (**10d**).

The formation of compounds **7** and **8** apparently takes place under elimination of N(1) of the starting compounds **5**, but does not require migration of a phenyl group. The presence of an sp^2 hybridized C(2) atom appears, thus, to be a necessary condition of the aryl migration with concomitant elimination of sulfur.

Since, during formation of **8**, the C(2) atom of the starting compounds **5** is lost, we were next interested in



1 **2** **3**



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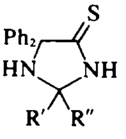

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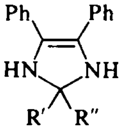

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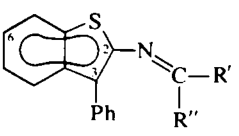

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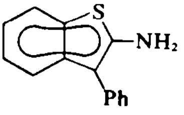

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5–7

	R′	R″
a	Ph	H
b	$2\text{-}HOC_6H_4$	H
c	$4\text{-}MeC_6H_4$	H
d	$4\text{-}ClC_6H_4$	H
e	$4\text{-}MeOC_6H_4$	H
f	Me	Me
g	$-(CH_2)_5-$	

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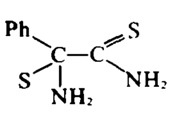

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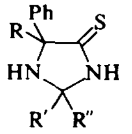
a: R = *p*-MeC$_6$H$_4$
b: R = 1-naphthyl
c: R = H
d: R = Me



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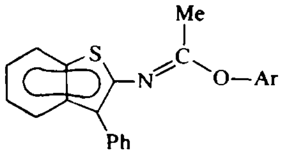
a: R = R″ = H, R′ = Ph
b: R = H, R′ = R″ = Me
c: R = R′ = R″ = Me
d: R = 1-naphthyl,
R′ = *p*-ClC$_6$H$_4$, R″ = H



11

whether the presence of C(2) is necessary for the formation of **8** at all. Accordingly, compound **4** was treated with AlCl$_3$, and **8** was obtained in moderate yield. A similar reaction took place with 2-phenyl-2-(*p*-tolyl)-glycinethioamide (**9a**); according to the MS of the product (Experimental), cyclization occurred mainly towards the tolyl, rather than towards the phenyl group. Only tars resulted on AlCl$_3$ treatment of 2-(1-naphthyl)-2-phenyl-glycinethioamide (**9b**).

Similarly, no crystalline products were obtained when the 4-imidazolidinethiones **10a–b**[5] and **c**[6], and the corresponding thioamides **9c**[2] and **9d**[2] were treated with AlCl$_3$.

The probable mechanism of the reaction **4**→**8** is shown in Scheme 1a. Surprisingly, prior to decomposition of the AlCl$_3$ complexes, **8** (or its AlCl$_3$ complex) is the main component also of the reaction mixture resulting on AlCl$_3$ treatment of **5a** because, if decomposition of the complexes is carried out in the presence of excess N,N′-(*p*-methylbenzylidene) bis(*p*-methylbenzylideneamine), almost pure **7c**, contaminated with only traces of **7a** is obtained.† A possible rationale is presented in Scheme 1b.

The amine **8** readily reacts with benzaldehyde or N,N′-benzylidenebis(benzylideneamine) even in the absence of AlCl$_3$ to yield **7a**. Prolonged refluxing with cyclohexanone furnished bis(3-phenyl-2-benzo[*b*]thienyl)amine rather than the N-cyclohexylidene derivative of **8**. Acetylation and benzoylation with acetic anhydride and benzoyl chloride, respectively, in the presence of pyridine at room temperature furnished the N-acetyl and N-benzoyl derivatives, respectively, while refluxing with acetic anhydride gave a diacetyl derivative which, according to the IR spectrum (one C=O band), is probably the isoimide **11** rather than the isomeric N,N-diacetyl-**8**.

EXPERIMENTAL

Synthesis of glycinonitriles

(a) To an ethanolic (50 ml) soln of phenyl-(*p*-toyl)methanimine[3] (19.5 g; 0.1 mole) and KCN (7.2 g; 0.11 mole) a mixture of AcOH (6.5 ml; 11 mole) and EtOH (10 ml) was added by drops under stirring and ice-cooling. The mixture was stirred for another hr to yield 20.7 g (93%) of the colourless crystals of *2-phenyl-2-(p-tolyl)glycinonitrile*, m.p. 100–101° from MeOH. (Found: C, 81.07; H, 6.18; N, 12.37. Calc. for C$_{15}$H$_{14}$N$_2$ (222.29): C, 81.05; H, 6.34; N, 12.60%).

(b) *2-(1-Naphthyl)-2-phenylglycinonitrile*, m.p. 129° (dec; from benzene), was similarly obtained in 67% yield, starting with (1-naphthyl)-phenylmethanimine.[3] (Found: C, 83.71; H, 5.41; N, 10.78. Calc. for C$_{18}$H$_{14}$N$_2$ (258.32): C, 83.69; H, 5.46; H, 10.84%).

(c) *N-Benzyl-2,2-diphenylglycinonitrile*, m.p. 107–108° (from gasoline), was similarly obtained in 95% yield, starting with N-benzyldiphenylmethanimine,[4] but the product has to be isolated by pouring the mixture into water. (Found: C, 84.52; H, 6.26; N, 9.32. Calc. for C$_{21}$H$_{18}$N$_2$ (298.39): C, 84.53; H, 6.08; N, 9.39%).

Synthesis of the glycinethioamides **9**

(a) Dry H$_2$S was introduced for 12 hr into a mixture of 2-phenyl-2-(*p*-tolyl)-glycinonitrile (11 g; 50 mmole), dry benzene (70 ml) and Et$_3$N (20 ml). The mixture was allowed to stand for 5

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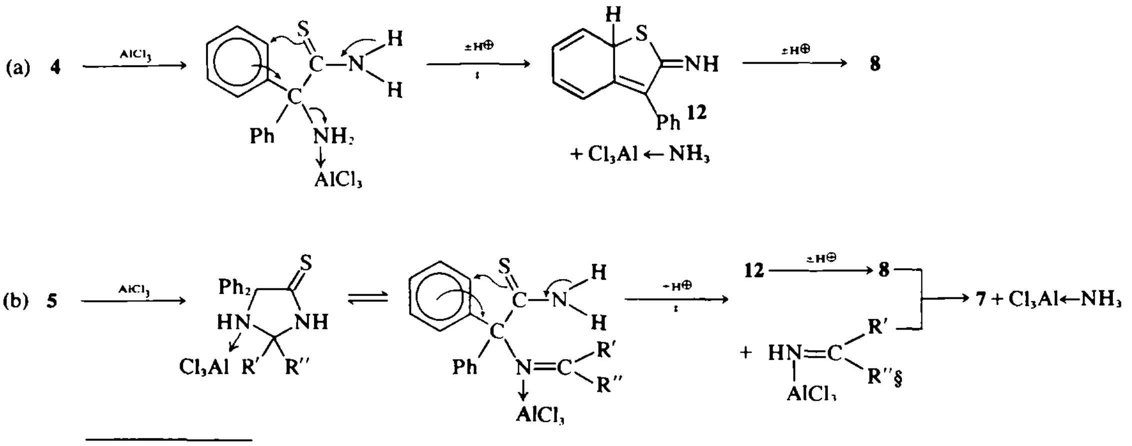
†**7a** also furnishes **7c** on treatment with excess N,N′-(*p*-methylbenzylidene)bis(*p*-methylbenzylideneamine) in the presence of AlCl$_3$, but at a much lower rate.



‡The bond formations and ruptures shown are not necessarily concerted.

§The actual compound reacting with **8** to furnish **7** may be either the complexed imine itself or a transformation product of the latter, e.g. N,N′-benzylidenebis(benzylideneamine).

Scheme 1. Tentative mechanisms of the transformations **4**→**8** and **5**→**7**.

days and evaporated to dryness. The residue was triturated with light petroleum to yield 10.7 g (84%) of the colourless crystals of **9a**, m.p. 112–113° from benzene. (Found: C, 70.04; H, 6.52; N, 10.80; S, 12.24. Calc. for $C_{15}H_{16}N_2S$ (256.37): C, 70.27; H, 6.29; N, 10.92; S, 12.24%).

(b) Compound **9b**, m.p. 203° (dec; from nitromethane), was similarly obtained in 54% yield, but the mixture was kept at 50–60° during the introduction of the H_2S. (Found: C, 73,78; H, 5.34; N, 9.47; S, 10.99. Calc. for $C_{18}H_{16}N_2S$ (292.40): C, 73.93; H, 5.51; N, 9.58; S, 10.96%).

(c) N-Benzyldiphenylmethanimime did not react under these conditions with H_2S.

4-*Imidazolidinethiones* **5** *and* **10d**

(a) Compound **4**[2] (0.1 mole) was refluxed with the appropriate oxo compounds (0.11–0.3 mole) in AcOH (20 ml) for 1 hr. The hot mixtures were filtered to yield the colourless crystals of **5** on cooling (see Table 1).

(b) A mixture of **9b** (2.9 g; 10 mmole), *p*-chlorobenzaldehyde (1.8 g; 13 mmole) and AcOH (20 ml) was refluxed for 1 hr and allowed to cool. Water (60 ml) was added. The resulting product was filtered off, thoroughly washed with water and taken up in toluene (100 ml). The water was removed by distillation in an apparatus equipped with a water separator. The soln was evaporated to dryness to yield 3.80 g (92%) of **10d**, m.p. 220–221° from nitromethane. (Found: Cl, 8.53; 8.53; N, 6.75; S, 7.92. Calc. for $C_{25}H_{19}ClN_2S$ (414.96): Cl, 8.54; N, 6.75; S, 7.73%).

(c) NMR spectra ($CDCl_3$, reference: TMS, δ scale). **5a**: 9.6, bs, 1H, 3-H; 8.0, m, 2H, two *o*-H's of the two 5-Ph groups; 7.5–7.3, m, 13H, other ArH's; 5.6, s, 1H, 2-H; 2.65, bs, 1H, 1-H. **5c**: 9.7, bs, 1H, 3-H; 8.0, m, two *o*-H's of the two 5-Ph groups; 7.5–7.2, m, 12H, other ArH's; 5.55, s, 1H, 2-H; 2.8, bs, 1H, 1-H; 2.35, s, 3H, *p*-Me. **5d**: 9.6, bs, 1H, 3-H; 7.95, m, 2H, two *o*-H's of the 5-Ph groups; 7.55–7.3, m, 12H, other ArH's; 5.65, s, 1H, 2-H; 2.7, bs, 1H, 1-H. **5e**: 9.5, bs, 1H, 3-H; 8.0, m, 2H, two *o*-H's of the two 5-Ph groups; 7.47 and 6.97, both d, $J_{AB} = 9.5$ Hz, 2H, each, AA'BB' spectrum of the 2-(4-$MeOC_6H_4$) group; 7.5–7.3, m, 8H, other ArH's; 5.6, s, 1H, 2-H; 3.85, s, 3H, *p*-MeO; 2.75, bs, 1H, 1-H.

Reactions of the 4-imidazolinethiones **5a–g** *with* $AlCl_3$

A mixture of the 4-imidazolinethiones (10 mmole), anhyd $AlCl_3$ (50 mmole) and dry toluene (70 ml) was refluxed for 2 hr† and, after cooling, poured into ice-water (100 ml). The resulting mixture was stirred until decomposition of the $AlCl_3$ complexes was complete. The aqueous layer was separated and washed with benzene (two portions, 50 ml, each). The combined organic solns were dried ($MgSO_4$) and evaporated to dryness. The residue was dissolved in ether (50 ml). Ether, saturated with HCl (100 ml) was added to precipitate **8**·HCl which was filtered off and washed with ether. The combined filtrate and washings were evaporated to dryness and triturated with EtOH to yield the Schiff's bases **7a–d**. Only tarry material was obtained at this point in the **e** series, and no Schiff bases were formed in the **f** and **g** series. For the yields, etc. see Table 2.

NMR spectra ($CDCl_3$, reference: TMS, δ scale). **7b**: 12.3, s, 1H, OH; 8.6, s, 1H, N=CH; 7.8–6.9, m, 13H, ArH's. **7c**: 8.65, s, 1H, N=CH; 7.85 and 7.3, both d, $J_{AB} = 9.5$ Hz, 2H, each, AA'BB' spectrum of *p*-tolyl group; partially merged with the m, 9H, at 8.0–7.35 of the other ArH's; 2.4, s, 3H, Me. **7d**: 8.45, s, 1H, N=CH; 7.85–7.15, m, 13H, ArH's.

Mass spectrum of **7d** (AEI-MS-902, 70 eV, 140°, direct insertion): *m/e* 349 (34%, i); 347 (100%, $M^{+\cdot}$); 346 (21%), 311 (1.8%), 310 (5.5%), 270 (0.45, $[M-Ph]^+$); 236 (45%, $[M-C_6H_4{}^{35}Cl]^+$); 208 (4.7%); 190 (4.2%); 173.5 (9.7%, M^{2+}); 155.5 (8.2%, 311^{2+}); 155 (7.9%, 310^{2+}).

Reactions of the imidazolidinethione **5a** *and of the benzo*[b]*thiophene* **7a** *with* $AlCl_3$ *in the presence of* N,N' - (p - *methylbenzylidene*) - *bis*(p - *methylbenzylideneamine*)

(a) A mixture of **5a** (1.65 g; 5 mmole), $AlCl_3$ (3.3 g; 25 mmole) and anhyd toluene (35 ml) was refluxed for 2 hr and allowed to cool. N,N' - (*p* - Methylbenzylidene) - bis(*p* - methylbenzylideneamine) (5.1 g; 15 mmole) was added. The mixture was allowed to stand for 10 min and poured into ice-water. The non-acidic organic material was extracted with benzene (two portions, 25 ml, each) and chromatographed over Kieselgel (60 g; solvent: benzene) to yield 1.0 g (60%) of almost pure **7c**, m.p. 115°, as shown by the intensity ratio of the Me and N=CH signals in the CCl_4 NMR spectrum.

(b) A mixture of **7a** (1.6 g; 5 mmole), $AlCl_3$ (3.3 g; 25 mmole) and anhyd toluene (35 ml) was refluxed for a few min until the $AlCl_3$ was dissolved almost completely.‡ The mixture was allowed to cool. N,N' - (*p* - Methylbenzylidene) - bis(*p* - methylbenzylideneamine) (5.1 g; 15 mmole) was added. The mixture was allowed to stand for 10 min and worked up as described above to yield 1 g of a mixture of **7a** and **7c**, m.p. 124–126° which, as derived from the intensity ratio of the Me and N=CH signals in the CCl_4 NMR spectrum, contained about 10% of **7c**.

Reactions of the thioamides **4** *and* **9a** *with* $AlCl_3$

(a) The reactions and work-ups of the mixtures were performed as described above for the analogous reactions of **5**, taking into

Table 1. Synthesis of the 4-imidazolidinethiones **5**

					Calc./found			
Product	Excess of oxo compound	Yield %	M.p., °C recryst. from	Formula Mol. wt	C%	H%	N%	S%
5a	25%	91	162–163	$C_{21}H_{18}N_2S$	76.33	5.49	8.48	9.70
			EtOAc-light petroleum	330.43	76.10	5.70	8.20	9.75
5b	10%	84	210	$C_{21}H_{18}N_2OS$	72.81	5.23	8.08	9.25
			EtOH	346.45	72.71	5.15	7.87	9.15
5c	10%	82	142–143	$C_{22}H_{20}N_2S$	76.71	5.85	8.13	9.30
			gasoline	344.48	76.40	5.84	8.14	9.07
5d§	10%	66	153–154	$C_{21}H_{17}ClN_2S$	69.13	4.69	7.67	8.78
			EtOH	364.89	68.87	5.01	7.42	8.56
5e	10%	61	148	$C_{22}H_{20}N_2OS$	73.30	5.59	7.77	9.07
			EtOAc-light petroleum	360.48	73.01	5.89	7.73	8.73
5f	200%	71	195–196	$C_{17}H_{18}N_2S$	72.30	6.42	9.92	11.36
			EtOH	282.30	72.14	6.56	9.75	10.00
5g	200%	93	224–225	$C_{20}H_{22}N_2S$	74.49	6.88	8.69	9.94
			n-BuOH	322.47	74.28	6.64	8.63	9.94

§The product separated when the reaction mixture was diluted with water.

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†Work-up of an aliquot as described below, and TLC of the benzene solution (Kieselgel F_{254}, Merck; solvent: benzene; detection: UV light or I_2 vapour) at this point demonstrated that the starting compound was completely used up.

‡Only tarry products were obtained when the above mixture was refluxed for 2 hr.

Table 2. Products obtained in the reactions of the 4-imidazolidinethiones **5** with $AlCl_3$

	Schiff's base **7**							**8**·HCl				
Starting compound	Yield %	M.P. recryst. from	Formula Mol. wt	Calc./found				Yield %	M.p.§	Formula Mol. wt	Calc./found§	
				C%	H%	N%	S%				Cl%	S%
5a	64	136–137° i-PrOH	†					‡				
5b	30	154°	$C_{21}H_{15}NOS$	76.57	4.61	4.25	9.73	20				
		EtOH	329.42	76.70	4.68	4.42	9.57					
5c	57	115–116°	$C_{22}H_{17}NS$	80.69	5.23	4.28	9.79	‡	173–174°	$C_{14}H_{12}ClNS$	13.54	12.24
		EtOH	327.43	80.41	5.22	4.21	9.70		(dec.)	261.78	13.80	12.01
5d	76	147–148°	$C_{21}H_{14}ClNS$	72.51	4.05	4.02		‡				
		n-BuOH	347.87	72.57	3.96	4.21						
5e	¶							23				
5f	—							60				
5g	—							76				

†Identical (IR spectra, m. m.p.) with an authentic sample,[7] lit. m.p. 137–140°.

‡Traces, detected by TLC.

§Crude product. We were unable to recrystallize this compound.

¶Only tarry products were obtained.

account that no type **7** Schiff-bases could be formed in these cases.

54% of **8**·HCl, m.p. 170–174° (dec.) was obtained from the thioamide **4**,† and 60% of a monomethyl derivative of **8**·HCl, m.p. 178° (crude product‡), which was characterized in form its condensation product with *p*-chlorobenzaldehyde (see below), was obtained from **9a**. According to the MS of the latter (see below), the Me group in the main product of the rearrangement is attached to C(6) of the benzo[*b*]thiophene ring rather than to the *p*-position of the 3-Ph group.

(b) The reaction of **4** with $AlCl_3$ was performed as above but the crude gummy **8**, obtained on evaporation of its benzene soln, was refluxed for 2 hr with Ac_2O (2 ml/mmole of the starting thioamide). The soln was evaporated to dryness, and the residue was triturated with EtOH to yield 32% of **11**, m.p. 116–117° (from EtOH), identical (m.p., m.m.p., IR) with an authentic sample obtained as described below.

Reactions of compound **8**·HCl *and its 6-methyl derivative*

(a) The soln of **8**·HCl (1.0 g 3.8 mmole) in EtOH (10 ml) was treated with PhCHO (0.46 ml, 20% excess). The yellow crystals of **7a** (0.95 g; 80%), m.p. 134–135° (identical, according to IR and TLC, with the sample obtained by $AlCl_3$ treatment of **5a**) immediately started to separate.

(b) The soln of **8**·HCl (0.86 g; 3.3 mmole) in EtOH (10 ml) was treated with N,N'-benzylidenebis(benzylideneamine) (0.4 g; 1.3 mmole) to yield 0.9 g (87%) of **7a**, m.p. 134–136°.

(c) The warm ethanolic (20 ml) soln of 6-methyl-**8**·HCl (0.60 g; 2.3 mmole) was treated with *p*-chlorobenzaldehyde (0.42 g; 3 mmole). The yellow needles of the product (0.6 g; 65%), m.p. 162–163° (from EtOH) immediately started to separate. (Found: Cl, 9.75; N, 4.05; S, 8.64. Calc. for $C_{22}H_{16}ClNS$ (361.89): Cl, 9.88; N, 3.90; S, 8.93%). NMR ($CDCl_3$, reference: TMS, δ scale): 8.6, s, 1H, N=CH; 7.8 and 7.45, both d, $J_{AB} = 10.5$ Hz, 2H, each, AA'BB' spectrum of *p*-ClC_6H_4 group; partially merged with the m, 8H, at 7.85–7.6 of the other ArH's; 2.5, s, 3H, Me. MS(AEI-MS-902, 70 eV, direct insertion, 140°): *m/e* 363 (34%, i); 361 (100%, $M^{+\cdot}$); 360 (15%); 324 (2.7%); 284 (0.55%, $[M-Ph]^+$); 270 (0.01%, $[M-p\text{-}MeC_6H_4]^+$); 250 (26%, $[M-C_6H_4{}^{35}Cl]^+$); 180.5 (9.3%, M^{2+}). The presence of the $[M-Ph]^+$ ion in the MS (cf. with the MS of **7d** below) proves the Me group to be attached to C(6); the presence and abundance of the $[M-p\text{-}MeC_6H_4]^+$ ion, on the other hand, may indicate that, in contrast to the results of the TLC studies, the main component is contaminated with about 2% the 3-(*p*-tolyl) analog of **7d**.

(d) **8**·HCl (1.3 g; 5 mmole) was refluxed with cyclohexanone (10 ml) in an apparatus equipped with a water separator. The mixture was evaporated to dryness. The residue was dissolved in benzene and chromatographed through a silica column. The oily residue of the main fraction was triturated with light petroleum until it turned crystalline, and recrystallized from EtOAc to yield 0.1 g (10%) of bis(3 - phenyl - 2 - benzo[*b*]thienyl)amine, m.p. 190–191° dec. (Found: C, 77.29; H, 4.13; N, 3.31; S, 14.29. Calc. for $C_{28}H_{19}NS_2$ (433.59): C, 77.56; H, 4.41; N, 3.23; S, 14.79%).

(e) PhCOCl (0.57 ml; 5 mmole) was added to the soln of **8**·HCl (1.3 g; 5 mmole) in pyridine (5 ml). The mixture was allowed to stand overnight. Water (50 ml) was added, and the insoluble, partly crystalline product was triturated with a small amount of MeOH to yield 0.7 g (43%) of N-benzoyl-**8**, m.p. 149° (from MeOH), identical (m.p., IR) with the product described in literature.[7]

(f) A mixture of **8**·HCl (1.3 g; 5 mmole), pyridine (3 ml) and Ac_2O (1 ml) was allowed to stand overnight. Water (50 ml) was added to yield 1.20 g (90%) of N-acetyl-**8**, m.p. 209–210° from EtOH. (Found: C, 71.87; H, 4.77; N, 5.54; S, 11.83. Calc. for $C_{16}H_{13}NOS$ (267.35): C, 71.88; H, 4.90; N, 5.23; S, 11.90%). IR (KBr): 3270, νNH; 1660, νC=O.

(g) N-Acetyl-**8** 0.5 g; 1.8 mmole) was refluxed with Ac_2O (5 ml) for 1 hr. The mixture was evaporated to dryness *in vacuo*, and the residue which, according to TLC (Kieselgel F_{254}, Merck; solvent benzene; detection: UV light) contained but traces of the starting substance, was recrystallized from EtOH to yield 0.30 g (52%) of the isoimide **11**, m.p. 116–117°. (Found: C, 69.80; H. 4.83; N, 4.49. Calc. for $C_{18}H_{15}NO_2S$ (309.39): C, 69.88; H, 4.89; N, 4.52%). IR (KBr): 1730, νC=O and 1680, sh, νC=N, which favourably compare with the literature[8,9] data for related compounds. NMR (DMSO-d_6, reference: DMSO-d_5, δ scale): 8.3–7.4, m, 9H, ArH's; 2.2, s, 6H, two Me groups.

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†This result contrasts with an earlier statement of ours,[2] according to which compound **4** is insensitive to $AlCl_3$. However, the reactions were now performed at higher temperature (in refluxing toluene, rather than benzene).

‡Similarly to **8**·HCl, this methyl derivative resisted all attempts of recrystallization.

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