

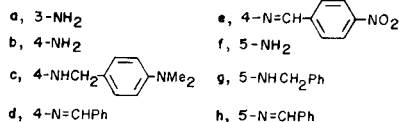
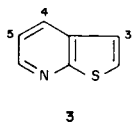
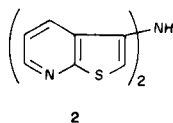
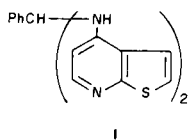
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The mass spectra of some secondary amines and aldimines in the thieno[2,3-*b*]pyridine (**3**) system are presented. α,α -Bis(4-thieno[2,3-*b*]pyridylamino)toluene (**1**) undergoes (a) electron impact-induced dissociation at 80° to give the spectrum of 4-amino-**3** (**3b**) and (b) thermal dissociation at 200° to give a composite spectrum of **3b** and its benzylidene derivative. Spectra of benzylamino and dimethylaminobenzylamino derivatives of **3** are dominated by benzyl-type fragments, while benzylideneimino derivatives show more varied fragmentation.

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In previous papers in this series [3,4] we reported the reactions of 4- and 5-aminothieno[2,3-*b*]pyridines **3b** and **3f** with benzaldehyde. While the aldimine **3h** formed readily from the 5-isomer, a 2:1 adduct **1** resulted from the 4-isomer. No 4-aldimine **3d** was isolated from benzaldehyde, despite the facts that (a) the corresponding 4-aldimine **3e** formed with *p*-nitrobenzaldehyde and (b) isomeric 4- and 5-aldimines were produced on reaction of *p*-dimethylaminobenzaldehyde with the two simple amines. The present study concerns the stability of **1** toward heat and electron impact and a comparison of mass spectral fragmentation patterns for some available aldimines and secondary aromatic amines containing the thieno[2,3-*b*]pyridine (**3**) nucleus.



Compound **1** melts at 141° without apparent decomposition. However, when mass spectra were obtained on **1** at ion source temperatures of 80°, 150° and 200° no molecular ion was observed and dissociation of **1**, according to the reaction $\mathbf{1} \rightarrow \mathbf{3b} + \mathbf{3d}$, was noted (Table I). At the lowest inlet temperature, **1** showed a spectrum virtually identical with that reported for **3b** [5], while at the higher temperatures both daughter ions **3b**⁺ (*m/e* 150) and **3d**⁺ (*m/e* 238) were apparent. No significant peaks above 238 were found. Formation of the ion **3d**⁺ was corroborated by the presence of fragmentation peaks at *m/e* 134 and 135 at 200°. Peaks at these two values were also found in the mass spectrum of the nitrobenzylideneimino compound

Table I
 Comparison of Mass Spectra for Compounds **1** and **3b**
 at Various Inlet Temperatures

Compound No.:	1	1	1	3b [a]	
Inlet Temp.:	80°	150°	200°	100°	
<i>m/e</i>	% Relative Abundance [b]				Structural Interpretation
238		7	43		3d ⁺ [c,d]
237			18		
151	10	10	10	10	
150	100	100	100	100	3b ⁺ [c,e]
135			10		3 ⁺
134			18		TP ⁺ [f]
123	12	13	13	9	(3b - HCN) ⁺ [g]
122	9	8	9	6	
106			15	6	
105			18	10	(3b - CHS) ⁺
77			15	9	
63				10	
52	6	11	12	4	
51			10	9	
45			7	9	CHS ⁺

[a] Reported in reference [5]. [b] All peaks of relative abundance $\geq 6\%$ are included. [c] Determined by high resolution. [d] Calcd. for C₁₄H₁₀N₂S: Exact mass, 238.056. Found: 238.055. [e] Calcd. for C₇H₆N₂S: Exact mass, 150.025. Found: 150.025. [f] TP⁺ represents the thienopyridyl cation. [g] All spectra show a metastable peak at *m/e* 100-102 that corresponds to the transformation 150 → 123.

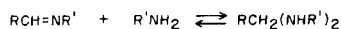
3e, where they were identified as corresponding to the thienopyridyl ion (TP⁺) and the parent ring molecular ion **3**⁺, respectively, by use of high resolution. Benzylideneimino derivative **3h** also has a significant peak at 134, while primary amine **3b** does not show either of these fragments.

Since compound **1** appears to be stable at its melting point it is concluded that the fragmentation pathway in the mass spectrometer at 80° is represented by the sequence of steps $\mathbf{1} \rightarrow \mathbf{1}^+ \rightarrow \mathbf{3b}^+ + \mathbf{3d}$, *i.e.* that dissociation of **1** is triggered by electron impact. At 150°, and especially at 200°, however, thermal decomposition of **1** into **3b** and **3d** occurs (at least to a significant extent) in the inlet

chamber prior to electron impact. Thus, the spectrum at 200° may be considered to be a composite of the spectra of preformed **3b** and **3d**. It is apparent that in all of these cases **3b** is more readily susceptible to ionization than is **3d**.

As an additional check on the preceding interpretation we investigated the thermal stability of **1** above its melting point, specifically in a sealed tube maintained at 155-158° for 4 minutes. Comparison of the infrared spectra of **1**, amine **3b**, and the thermolysate (from the sealed tube) under identical conditions showed the presence of both a primary amino group (for **3b**) and a C=N group (for **3d**) in the thermolysate. In fact, subtraction of the C=N band from the spectrum of the thermolysate gives a difference spectrum which is virtually identical with that of **3b**.

The dissociation of **1**, induced either by means of heat or of electron impact, is analogous to the situation which occurs in the retro-Diels-Alder reaction [6,7]. On electron impact the Diels-Alder adduct may yield a spectrum largely or exclusively of the "dienic" component [8]. Moreover, the reaction is thermally reversible [9]. In fact, only rarely is the secondary amine adduct isolated [10].



It is not surprising that the most abundant mass spectral ion from compound **3g** is the benzyl (or tropylium) ion (m/e 91), derived from fragmentation of the substituent on the thienopyridine ring. However, measurements of exact mass were necessary in order to ascertain that peaks at 135, 134 and 118 in the spectrum of **3c** likewise arise from the substituent (ion formulas C₉H₁₃N⁺, C₉H₁₂N⁺ and C₈H₈N⁺, respectively) rather than from the thienopyridine ring. Thus, the facility for formation of the *p*-dimethylaminobenzyl ion (m/e 134) appears to be an overwhelming influence in the fragmentation of **3c**.

It should be noted that neither **3g** nor **3h** shows a mass spectral peak at 150 corresponding to the aminothienopyridine ion **3f**. Likewise, a peak at 150 (for the ion **3a**⁺ or **3b**⁺) is absent from the spectra of **2**, **3c** and **3e**. Thus, the strong 150 peak in the spectrum of **1** clearly distinguishes this compound from the other five studied here.

EXPERIMENTAL

Syntheses of compounds **1**, **2**, **3a-3c** and **3e-3h** have been reported previously [3,4,11].

Mass Spectra.

Mass spectra were determined by Drs. Susan Rottschaefer and Richard Wielesek by means of a CEC model 21-110 double focusing instrument operated at 70 eV. Data for the simple aminothienopyridines **3a**, **3b** and **3f** have been recorded [5]. Significant peaks for **1** at three different inlet temperatures are presented in Table I. In the following list of

data are given the temperature of the ion source (°C), m/e values for all peaks of relative abundance (shown in parentheses) ≥ the minimal value shown for the compound, observed metastable peaks (indicated by asterisks) plus the corresponding ion decomposition pathways, and ion formulas ascertained by high resolution (HR). TP designates a thienopyridyl group.

Bis(3-thieno[2,3-*b*]pyridyl)amine (**2**).

This compound had ms (200°): 285 (15), 284 (22), 283 (M⁺, 100), 282 (19), 281 (6), 250 (9), 180 (8), 148 (M⁺ - 3, 22), 141.5 (M⁺, 6), 134 (TP⁺, 5), 122 (6), 78 (6), 63 (8), 45 (CHS⁺, 8).

4-(4-Dimethylaminobenzylamino)thieno[2,3-*b*]pyridine (**3c**).

This compound had ms (195°): 283 (M⁺, 14), 135 (C₉H₁₃N⁺, 14) (HR), 134 (MeNC₆H₄CH₂⁺, 100) (HR), 118 (C₈H₈N⁺, 13) (HR), 91 (5).

4-(4-Nitrobenzylideneimino)thieno[2,3-*b*]pyridine (**3e**).

This compound had ms (190°): 285 (7), 284 (19), 283 (M⁺, 100), 282 (6), 237 (7), 236 (M⁺ - HNO₂, 23), 135 (3⁺, 21) (HR), 134 (TP⁺, 41) (HR), 90 (7), 76 (6), 63 (17), 50 (6), 280-282* (283 - 282).

5-Benzylaminothieno[2,3-*b*]pyridine (**3g**).

This compound had ms (140°): 241 (15), 240 (M⁺, 75), 239 (10), 163 (6), 149 (6), 134 (9), 122 (14), 92 (9), 91 (C₇H₇⁺, 100), 65 (12), 63 (6).

5-Benzylideneiminothieno[2,3-*b*]pyridine (**3h**).

This compound had ms (140°): 240 (7), 239 (19), 238 (M⁺, 100), 237 (49), 161 (6), 134 (TP⁺, 32), 119 (6), 90 (6), 63 (9).

Thermal Dissociation of **1**.

A sample of pure **1** (mp 140-141°), sealed in a capillary tube, was inserted into a metal block maintained at 155-158° for 4 minutes. The compound melted within 30 seconds and turned slightly brown. The tube was removed from the block, allowed to cool and crushed. While **1** was only slightly soluble in chloroform at room temperature, the contents of the tube (thermolysate) dissolved readily under the same conditions. Comparison of infrared absorption spectra (obtained by means of a Beckman IR-5 instrument) of saturated solutions of **1**, amine **3b**, and the thermolysate in chloroform was made. While **1** showed little absorption at any frequency, **3b** exhibited sharp bands at 3520 and 3420 cm⁻¹ (NH₂) [12a], and the spectrum of the thermolysate was virtually identical with that of **3b** except for the presence of a weak, additional band at 1650 cm⁻¹ (C=N) [12b] in the former.

REFERENCES AND NOTES

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