Preparation of New Nitrogen-Bridged Heterocycles. 43.[1] Synthesis and Reaction of 5a*H*-Pyrido[1,2-*d*][1,3,4]thiadiazepine Derivatives

Akikazu Kakehi,*[,†] Suketaka Ito,[†] Fumihito Ishida,[†] and Yoshinori Tominaga[‡]

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan, and Faculty of Pharmaceutical Science, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852, Japan

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Reactions of some 1-pyridinio- and 1-(4-methylpyridinio)(arenethiocarbonyl)amidates with dimethyl acetylenedicarboxylate in chloroform afforded neither the expected dimethyl 2-aryl-5a*H*-pyrido-[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates nor their intramolecular Diels−Alder adducts, but gave novel rearranged products, dimethyl 4-aryl-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates in low to moderate yields. On the other hand, similar reactions of 1-(3-methylpyridinio)- and 1-(2-methylquinolinio)(arenethiocarbonyl)amidates with the same reagent provided 1:1 primary adducts, dimethyl 2-aryl-6-methyl-5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates and dimethyl 2-aryl-5a-methyl-5a*H*-[1,3,4]thiadiazepino[4,5-*a*]quinoline-4,5-dicarboxylates, respectively.

Previously, we reported on smooth formation of 10a*H*-pyrido[1,2-*d*][1,4]thiazepine derivatives and/or their intramolecular Diels−Alder adducts in the reactions of various 1-pyridinio[(alkylthio)thiocarbonyl]methylides with dimethyl acetylenedicarboxylate (DMAD).[2] In the continuation of our work for exploring new reactivities of pyridinium *N*-ylides, we were interested in the extension of this reaction to 1-pyridinio(substituted thiocarbonyl)-amidates, because such types of heterocycles cannot be obtained by other methods and because some potential pharmaceutical activities can be expected for them. However, all of our preliminary attempts to obtain any significant products such as 5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepines **B** and the intramolecular Diels−Alder adducts, 4-thia-1,2-diazatetracyclo[5.4.0.0.^{5,11}0^{6,8}]undeca-2,9-dienes **C**, from the reactions of some 1-pyridinio-[(methylthio)thiocarbonyl]amidates[3] and DMAD were unsuccessful (see Figure 1). As a reason for our inaccessibility to these products described above, we presumed an extremely high reactivity of the isocyanate dithioacetal moiety in the zwitterionic intermediate **A** and/or pyrido[1,2-*d*][1,3,4]thiadiazepines **B** toward moisture and nucleophiles. So, we next examined the use of 1-pyridinio(aryl-substituted thiocarbonyl)amidates whose reactivity at the thioimidate moiety has been lowered by the stabilizing effect of the aromatic substituent and found that their reactions with DMAD gave unexpected products, dimethyl 4-aryl-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]-undeca-3,8,10-triene-6,11-dicarboxylates,[4] together with some title compounds. In this paper we wish to report on the isolation and the novel rearrangement of 5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine derivatives.

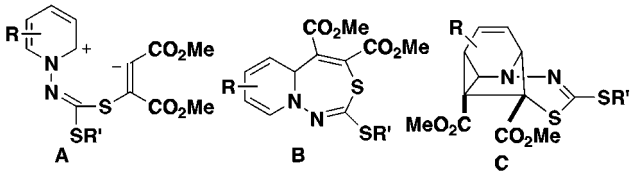

Figure 1.

Results and Discussion

Preparation of 1-Pyridinio(arenethiocarbonyl)-amidates. These 1-pyridinio(arenethiocarbonyl)amidates (**3a**−**u**) were prepared in 34−93% yields through the reactions of 1-aminopyridinium iodides (**1a**−**c**) or 1-amino-2-methylquinolinium *p*-toluenesulfonate (**1d**) with methyl dithiobenzoates (**2a**), methyl *p*-toluenedithiocarboxylate (**2b**), methyl *p*-methoxybenzenedithiocarboxylate (**2c**), methyl *o*-methoxybenzenedithiocarboxylate (**2d**), methyl *p*-chlorobenzenedithiocarboxylate (**2e**), methyl 2-thiophenedithiocarboxylate (**2f**), or methyl *p*-(dimethylamino)benzenedithiocarboxylate (**2g**) in the

† Shinshu University.
‡ Nagasaki University.
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(1) For part 42 of this series, see Kakehi, A.; Ito, S.; Hashimoto, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1769.

(2) (a) Kakehi, A.; Ito, S.; Hakui, J. *Chem. Lett.* **1992**, 777. (b) Kakehi, A.; Ito, S. *Heterocycles* **1993**, *36*, 1195. (c) Kakehi, A.; Ito, S.; Hakui, J. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3475. (d) Kakehi, A.; Ito, S.; Mitani, M.;Kanaoka, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1646. (e) Kakehi, A.; Ito, S.; Fujita, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1473.

(3) (a) Kakehi, A.; Ito, S.; Watanabe, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1775. (b) Yoshida, H.; Urushibata, K.; Ogata, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1561.

(4) Kakehi, A.; Ito, S.; Ishida, F.; Tominaga, Y. *Heterocycles*, **1995**, *41*, 2657.

(5) Kakehi, A.; Ito, S.; Nagata, K.; Kinoshita, N.; Kakinuma, N. *Chem. Pharm. Bull.* **1987**, *35*, 156.

(6) For the crystal data for compound **7h**, see ref 4.

(7) (a) Okamoto, T.; Hirobe, M.; Yabe, E. *Chem. Pharm. Bull.* **1966**, *14*, 506. (b) Sasaki, T.; Kanematsu, K.; Kakehi, A. *J. Org. Chem.* **1972**, *36*, 2978. (c) Sasaki, T.; Kanematsu, K.; Kakehi, A.; Ito, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2089. (d) Tamura, Y.; Sumida, Y.; Miki, Y.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 406.

(8) This situation is quite opposite to the relation (see ref 2b) in the interaction between the 7-methyl group and 5-substituent in 7-methyl-10a*H*-pyrido[1,2-*d*][1,4]thiazepine derivatives.

(9) According to the MM2 calculation for these pyrido[1,2-*d*]-[1,3,4]thiadiazepine derivatives **5** and **5′**, the angular conformation **D** is more favorable than the planar one **E**. This fact may suggest a reason for the inaccessibility and ready rearrangement of 6-unsubstituted pyrido[1,2-*d*][1,3,4]thiadiazepine intermediates **5**, because subsequent rearrangement starts from this comformation **D**.

(10) Though our ring system is not normal di-π-methane ring system such as 2,5-cyclohexadien-1-one, we used this word from the similarities of the apparent electron demand and the structural transformation. For di-π-methane rearrangement, see Schaffner K. *Adv. Photochem.* **1966** *4*, 81. Kropp P. J. *Org. Photochem.* **1967**, *1*, 1.

(11) Whether this reaction proceeds successfully or not is largely dependent upon the exhaustive removal of the moisture and any nucleophiles from the reaction system.

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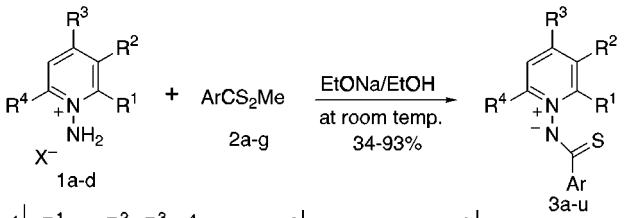
Scheme 1



1	R^1	R^2	R^3	R^4	X
a	H	H	H	H	I
b	H	H	Me	H	I
c	H	Me	H	H	I
d	-(CH=CH)$_2$-		H	Me	TsO

2	Ar
a	Ph
b	*p*-MeC_6H_4
c	*p*-$MeOC_6H_4$
d	*o*-$MeOC_6H_4$

2	Ar
e	*p*-ClC_6H_5
f	2-thienyl
g	*p*-$Me_2NC_6H_4$

3	R^1	R^2	R^3	R^4	Ar
a	H	H	H	H	Ph
b	H	H	H	H	*p*-MeC_6H_4
c	H	H	H	H	*p*-$MeOC_6H_4$
d	H	H	H	H	*o*-$MeOC_6H_4$
e	H	H	H	H	*p*-ClC_6H_4
f	H	H	H	H	2-thienyl
g	H	H	H	H	*p*-$Me_2NC_6H_4$
h	H	H	Me	H	Ph
i	H	H	Me	H	*p*-MeC_6H_4
j	H	H	Me	H	*p*-$MeOC_6H_4$
k	H	H	Me	H	*o*-$MeOC_6H_4$

3	R^1	R^2	R^3	R^4	Ar
l	H	H	Me	H	*p*-ClC_6H_4
m	H	H	Me	H	2-thienyl
n	H	H	Me	H	*p*-$Me_2NC_6H_4$
o	H	Me	H	H	Ph
p	H	Me	H	H	*p*-MeC_6H_4
q	H	Me	H	H	*p*-$MeOC_6H_4$
r	H	Me	H	H	*p*-ClC_6H_4
s	H	Me	H	H	2-thienyl
t	-(CH=CH)$_2$-		H	Me	Ph
u	-(CH=CH)$_2$-		H	Me	2-thienyl

presence of alkali, according to our previous procedure (Scheme 1).[5]

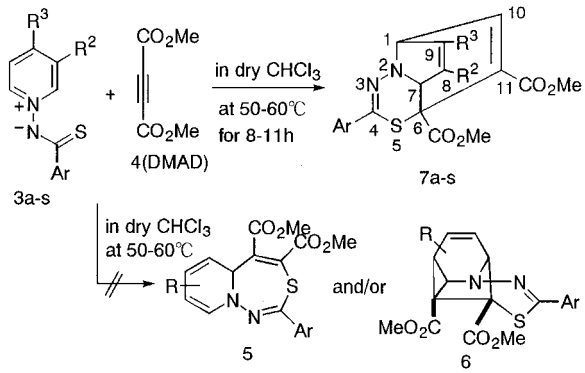
These amidates **3a**−**u** were obtained as pale yellow prisms having a characteristic sulfur odor, and their IR spectra showed an absorption band attributable to the carbon−sulfur double bond at near 1150 cm^{-1}.

Reactions of 1-Pyridinio(arenethiocarbonyl)-amidates with DMAD. As described above, all of our attempts were unsuccessful to obtain any other significant products than small amounts of dimethyl fumarate and hexamethyl benzenehexacarboxylate through the reactions of some 1-pyridinio[(methylthio)thiocarbonyl]-amidates[3] and DMAD. So, the reactions of aryl-substituted pyridinium *N*-ylides (**3a**−**u**) with the same reagent were next investigated in expectation of the stabilization of reaction intermediates and title compounds.

When a chloroform solution of 1-pyridinio(thiobenzoyl)-amidate (**3a**) and DMAD (**4**) was heated at 50−60 °C in a water bath for 8−11 h and subjected to a chromatographic separation, a product **7a** was obtained in 30% yield as colorless prisms. Similar treatments of amidates **3b**−**s** and **4** gave the corresponding adducts **7b**,**c**,**e**−**s** in low to moderate yields (1−35%) except **7d** (Scheme 2). On the other hand, the reactions of some amidates **3** with **4** at room or low temperature (0 °C) were also examined, but they gave only intractable tarry materials from which no significant products could be isolated.

Elemental analyses for products **7a**−**c**,**e**−**s** were in good accord with the compositions proposed for 1:1 adducts between 1-pyridinio(arenethiocarbonyl)amidates (**3a**−**c**,**e**−**s**) and DMAD (**4**). However, their IR and ^{1}H NMR spectral data were different largely from those for both the expected 5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepines (**5**) and the intramolecular Diels−Alder adducts, 4-thia-1,2-diazatetracyclo[5.4.0.0.^{5,11}0^{6,8}]undeca-2,9-dienes (**6**). For example, the IR spectra of **7a**−**c**,**e**−**s** exhibited a saturated and an α,β-unsaturated ester carbonyl absorption band at 1730∼1744 and 1703∼1718 cm^{-1}, respectively, and these values were clearly different from those for the two α,β-unsaturated ester carbonyl groups in **5** and the two saturated ones in **6**. Furthermore, the chemical shifts of the skeletal protons derived from the pyridine moiety of amidates **3** in the ^{1}H NMR spectra of **7a**−**c**,**e**−**s** indicated that the arrangement of the skeletal carbons attaching the corresponding protons is sp^3-sp^2-sp^2-sp^3-sp^2, which also is inconsistent with both the sp^3-sp^2-sp^2-sp^2-sp^2 in **5** and the sp^3-sp^2-sp^2-sp^3-sp^3 in **6**. In particular, the appearance of the terminal proton (10-H) as a doublet in a largely lowered region (δ 7.47−7.61) suggested a proximity to an ester group with a strong anisotropy effect. These spectral data and the mechanistic consideration (see Mechanisms) strongly supported the possibility of the ring contraction of the pyridine to the pyrrole ring during this reaction. Eventually, a single-crystal X-ray analysis on compound **7h**[6] gave the solution; the rearranged structures, dimethyl 4-aryl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates, were finally confirmed for **7a**−**c**,**e**−**s**.

Scheme 2

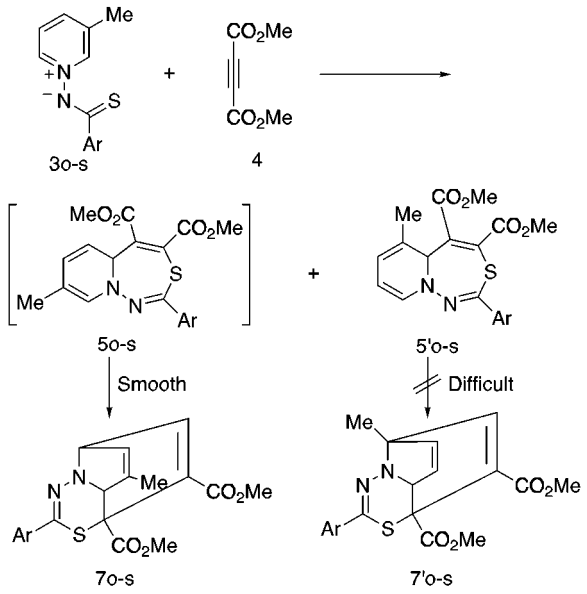


7	R^2	R^3	Ar	Yield (%)
a	H	H	Ph	30
b	H	H	*p*-MeC_6H_4	15
c	H	H	*p*-$MeOC_6H_4$	26
d	H	H	*o*-$MeOC_6H_4$	0
e	H	H	*p*-ClC_6H_4	3
f	H	H	2-thienyl	28
g	H	H	*p*-$Me_2NC_6H_4$	13
h	H	Me	Ph	30
i	H	Me	*p*-MeC_6H_4	18
j	H	Me	*p*-$MeOC_6H_4$	22

7	R^2	R^3	Ar	Yield (%)
k	H	Me	*o*-$MeOC_6H_4$	1
l	H	Me	*p*-ClC_6H_4	8
m	H	Me	2-thienyl	35
n	H	Me	*p*-$Me_2NC_6H_4$	27
o	Me	H	Ph	13
p	Me	H	*p*-MeC_6H_4	16
q	Me	H	*p*-$MeOC_6H_4$	27
r	Me	H	*p*-ClC_6H_4	11
s	Me	H	2-thienyl	16

Preparation of 5a*H*-Pyrido[1,2-*d*][1,3,4]thiadiazepines and 5a*H*-[1,3,4]Thiadiazepino[4,5-*a*]quinolines. The formation of dimethyl 4-aryl-8-methyl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (**7o**−**s**) and the absence of one more possible product, 1-methyl isomers such as **7′o**−**s**, in the reactions of the unsymmetrically substituted 1-pyridinioamidates (**3o**−**s**) with DMAD (**4**) seemed very strange to us. Mechanistically, the rearranged products **7o**−**s** and **7′o**−**s** are derived from 8-methyl-5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepines (**5o**−**s**) and their 6-methyl isomers (**5′o**−**s**), respectively, as shown in Scheme 3. Since it is well-known that thermal cycloaddition and cyclization of unsymmetrical 3-substituted pyridinium *N*-ylides afford the ring-closure isomers at the 2-position as major products and those at the 6-position as minor ones,[7] the observed exclusive formation of **5o**−**s** in these reactions requires a new mechanistic consideration. We thought

Scheme 3



that these reactions must first have given a mixture of the corresponding bicyclic adducts **5o**−**s** and **5′o**−**s**, whereas only the former must have rearranged smoothly to products **7o**−**s**, which were actually isolated. On the other hand, the transformation of the other isomers **5′o**−**s** to the corresponding compounds **7′o**−**s** with a bridgehead methyl group must be difficult because of their severe intramolecular steric interaction between the 5-methoxycarbonyl and the 6-methyl group. According to an examination of the Dreiding models for compound **5′o**, the steric interactions between the 6-methyl and the 5-methoxycarbonyl group is stronger in the angular conformation (**D**) than in the planar one (**E**) (see Figure 2).[8,9] To confirm this idea and to isolate these adducts **5′o**−**s**, we carefully reexamined the reactions of amidates **3o**−**s** and succeeded in the isolation of the aimed products **5′o**−**s** from reaction mixtures.

When a reaction solution of amidates **3o**−**s** and DMAD (**4**) was allowed to react at 50−60 °C for a shortened time (4 h), the corresponding dimethyl 2-aryl-6-methyl-5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates (**5′o**−**s**) were obtained in trace−27% yields as red prisms or needles, together with the rearranged products **7o**−**s** (6−11%). Similarly, the reactions of 1-(2-methylquinolinio)-amidates **3t**,**u** with **4** gave only the expected dimethyl 2-aryl-5a-methyl-5a*H*-1,3,4-thiadiazepino[4,5-*a*]quinoline-4,5-dicarboxylates (**8a**,**b**) in 41 and 43% yields, respectively; these results are shown in Scheme 4. The successful isolation of tricyclic compounds **8a**,**b** must be due to both the stabilization by the fused benzene ring and the resistance to the loss of the aromaticity of the benzene ring during the rearrangement.

The structures of these thiadiazepine derivatives **5′o**−**s** and **8a**,**b** were readily determined by their physical and spectral properties. These compounds had the compositions of the 1:1 adducts between amidates **3o**−**u** and DMAD (**4**), and their IR spectra exhibited characteristic ester carbonyl absorption bands at 1722−1734 cm^{-1}. Furthermore, the ^1H NMR spectra of **5′o**−**s** and **8a**,**b** showed reasonable chemical shifts and signal patterns for our proposed structures except for the considerably lowered chemical shifts of the 5a-protons (δ 7.45−7.53) in **5′o**−**s** and the 5a-methyl protons (δ 1.74 and 1.76) in **8a**,**b**. The abnormally lowered shifts for the bridgehead

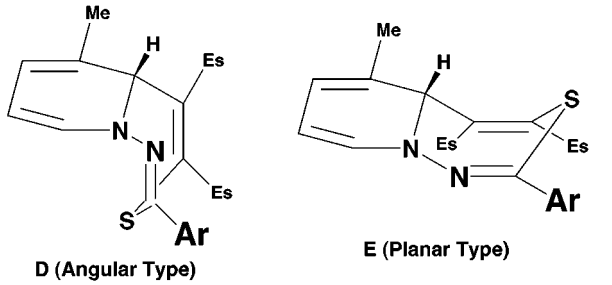
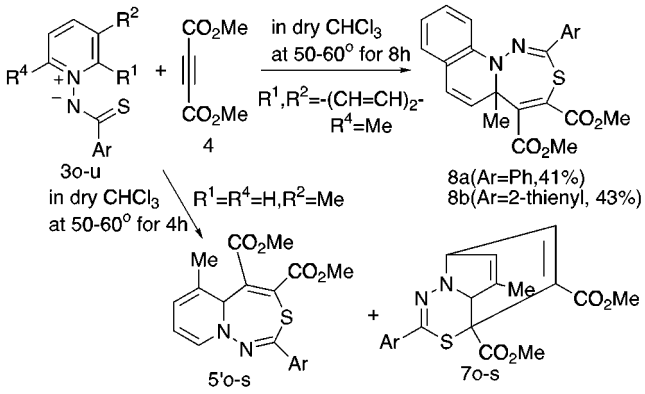


Figure 2.

Scheme 4



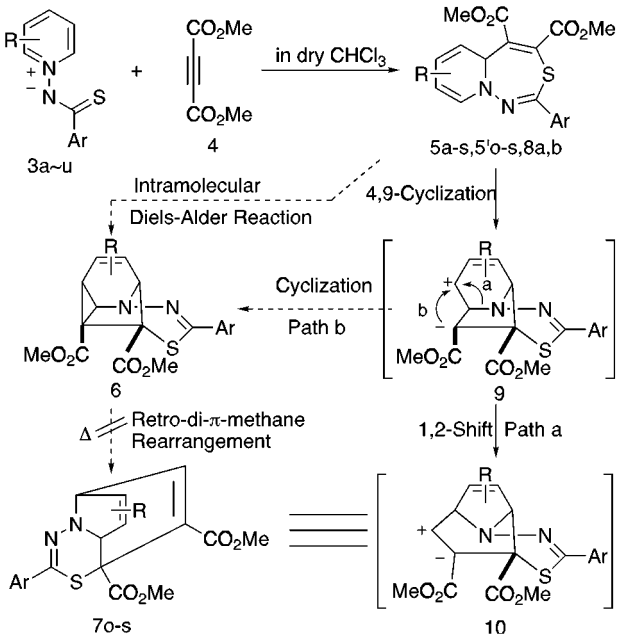
5′	Ar	Yield (%)
o	Ph	22
p	*p*-MeC_6H_4	20
q	*p*-$MeOC_6H_4$	27
r	*p*-ClC_6H_4	Trace
s	2-thienyl	22

7	Yield (%)
o	10
p	9
q	11
r	6
s	11

proton and methyl protons are possibly due to the anisotropy effects of the lone pair on the adjacent nitrogen atom and of the π orbital of the adjacent carbon−carbon double bond. X-ray analyses on the two compounds **5′o** and **8a** were also performed, and their structures were finally confirmed. Interestingly, the crystal structure of **5′o** resembled to the planar comformation (**E**) and that of **8a** the angular one (**D**). Furthermore, these crystal data also clarified that the bridgehead nitrogen atom is almost trigonal planar. This fact may explain well the abnormality of the chemical shifts for the bridgehead hydrogen and methyl protons described above.

Reaction Mechanisms. Possible mechanisms for this reaction are shown in Scheme 5. Since some primary adducts **5′o**−**s** were actually isolated, it may be considered that this rearrangement proceeds via the initial formation of the corresponding 5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepine intermediate (**5**) (path a). The subsequent ring closure between the 4- and 9-positions in the molecule **5**, leading to the construction of the 1,3,4-thiadiazine ring, followed by the 1,2-cationic shift of a nitrogen−carbon single bond in the resulting ionic intermediate **9** to the vicinal carbon atom, may produce the rearranged products **7**. Although there is an alternative route (path b) via the intervention of the intramolecular Diels−Alder type of adduct **6** from **5** and/or **9**, this is not likely because it is a thermally forbidden process (retro-di-π-methane rearrangement).[10] As already described by us,[2d] no thermolyses of 4-thia-1-azatetracyclo[5.4.0.0.^{5,11}0^{6,8}]-

Scheme 5



undeca-2,9-dienes, which are the 2-deaza analogues of **6**, afforded the corresponding tricyclic products.

The reason is unclear why the formation of dimethyl 3-aryl-4-thia-1,2-diazatetracyclo[5.4.0.0.^{5,11}0^{6,8}]undeca-2,9-diene-5,6-dicarboxylates (**6**) via the intramolecular Diels−Alder reaction of **5** and/or the combination between the ionic centers in **9** did not occur. However, the fact that the inclusion of one nitrogen atom, as seen in tetracycles **6**, increases its ring strain more than in the 2-deaza analogues may be one reason, since the nitrogen−nitrogen single bond and the nitrogen−carbon double bond are considerably shorter than the nitrogen−carbon single bond and the carbon−carbon double bond, respectively. Eventually, tetracycles such as **6**, even if formed, must rapidly decompose under the reaction conditions employed, leaving only the stabler tricycles **7** formed.

Experimental Section

Melting points are uncorrected. The ^{1}H NMR spectra were determined at 60 MHz in deuteriochloroform with TMS as an internal standard; chemical shifts are expressed in δ values.

Preparation of 1-Pyridinio(arenethiocarbonyl)amidates. These amidates were prepared from the reactions of 1-aminopyridinium salt (**1**) and methyl arenedithiocarboxylate (**2**) in the presence of an alkali according to the procedure reported previously by us.[5]

Although 1-pyridinio- (**3a**−**s**) and 1-(2-methylquinolinio-)(arenethiocarbonyl)amidates (**3t**,**u**) were smoothly synthesized by this method, the corresponding 1-quinolinio- and 2-isoquinolinio(arenethiocarbonyl)amidates could not be obtained from the reactions of 1-aminoquinolinium and 2-aminoisoquinolinium mesitylenesulfonate with **2**. Physical and spectral data for known 1-pyridinio(thiobenzoyl)amidates (**3a**,**h**) were in accord with those for authentic samples.[5]

Some data for new 1-pyridinio(arenethiocarbonyl)amidates (**3b**−**g**,**i**−**u**) are as follows:

1-Pyridinio(*p*-toluenethiocarbonyl)amidate (3b): 62% (from **1a** and **2b**), mp 169−171 °C, IR (KBr) 1176 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.42 (3H, s), 7.1−8.8 (9H, m). Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27%. Found: C, 68.36; H, 5.30; N, 12.19%.

1-Pyridinio(*p*-methoxybenzenethiocarbonyl)amidate (3c): 93% (from **1a** and **2c**), mp 139−141 °C, IR (KBr) 1171 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 3.86 (3H, s), 6.8−8.7 (9H, m). Anal. Calcd for $C_{13}H_{12}N_2OS$: C, 63.91; H, 4.95; N, 11.47%. Found: C, 64.17; H, 4.95; N, 11.21%.

1-Pyridinio(*o*-methoxybenzenethiocarbonyl)amidate (3d): 87% (from **1a** and **2d**), mp 125−127 °C, IR (KBr) 1159 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 3.86(3H, s), 7.1−8.8 (9H, m). Anal. Calcd for $C_{13}H_{12}N_2OS$: C, 63.91; H, 4.95; N, 11.47%. Found: C, 63.73; H, 5.02; N, 11.61%.

1-Pyridinio(*p*-chlorobenzenethiocarbonyl)amidate (3e): 69% (from **1a** and **2e**), mp 143−145 °C, IR (KBr) 1159 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 7.2−8.7 (9H, m). Anal. Calcd for $C_{12}H_9ClN_2S$: C, 57.95; H, 3.65; N, 11.26%. Found: C, 57.95; H, 3.55; N, 11.36%.

1-Pyridinio(2-thiophenethiocarbonyl)amidate (3f): 64% (from **1a** and **2f**), mp 158−160 °C, IR (KBr) 1151 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 7.0−9.0 (8H, m). Anal. Calcd for $C_{10}H_8N_2S_2$: C, 54.52; H, 3.66; N, 12.72%. Found: C, 54.58; H, 3.64; N, 12.84%.

1-Pyridinio(*p*-(dimethylamino)benzenethiocarbonyl)-amidate (3g): 59% (from **1a** and **2g**), mp 108−110 °C, IR (KBr) 1174 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 3.01 (6H, s), 7.6−8.7 (9H, m). Anal. Calcd for $C_{14}H_{15}N_3S$: C, 65.34; H, 5.88; N, 16.33%. Found: C, 65.06; H, 6.17; N, 16.33%.

1-(4-Methylpyridinio)(*p*-toluenethiocarbonyl)amidate (3i): 72% (from **1b** and **2b**), mp 168−170 °C, IR (KBr) 1174 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.42 (3H, s), 2.64 (3H, s), 7.1−8.6 (8H, m). Anal. Calcd for $C_{14}H_{14}N_2S$: C, 69.39; H, 5.82; N, 11.56%. Found: C, 69.41; H, 5.92; N, 11.44%.

1-(4-Methylpyridinio)(*p*-methoxybenzenethiocarbonyl)amidate (3j): 92% (from **1b** and **2c**), mp 141−143 °C, IR (KBr) 1174 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.60 (3H, s), 3.87 (3H, s), 6.8−8.8 (8H, m). Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84%. Found: C, 65.13; H, 5.46; N, 10.80%.

1-(4-Methylpyridinio)(*o*-methoxybenzenethiocarbonyl)amidate (3k): 89% (from **1b** and **2d**), mp 132−134 °C, IR (KBr) 1165 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.59 (3H, s), 3.89 (3H, s), 6.8−8.8 (8H, m). Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84%. Found: C, 64.92; H, 5.44; N, 11.02%.

1-(4-Methylpyridinio)(*p*-chlorobenzenethiocarbonyl)-amidate 3l; 69% (from **1b** and **2e**), mp 160−162 °C, IR (KBr) 1167 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.62 (3H, s), 7.2−8.5 (8H, m). Anal. Calcd for $C_{13}H_{11}ClN_2S$: C, 59.42; H, 4.22; N, 10.66%. Found: C, 59.42; H, 4.22; N, 10.75%.

1-(4-Methylpyridinio)(2-thiophenethiocarbonyl)amidate (3m): 69% (from **1b** and **2f**), mp 151−153 °C, IR (KBr) 1140 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.60 (3H, s), 6.9−8.6 (7H, m). Anal. Calcd for $C_{11}H_{10}N_2S_2$: C, 56.38; H, 4.30; N, 11.95%. Found: C, 56.36; H, 4.37; N, 12.21%.

1-(4-Methylpyridinio)(*p*-(dimethylamino)benzenethiocarbonyl)amidate (3n): 87% (from **1b** and **2g**), mp 109−111 °C, IR (KBr) 1184 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.55 (3H, s), 3.00 (6H, s), 6.5−8.5 (8H, m). Anal. Calcd for $C_{15}H_{17}N_3S$: C, 66.39; H, 6.31; N, 15.48%. Found: C, 66.17; H, 6.09; N, 15.32%.

1-(3-Methylpyridinio)thiobenzoylamidate (3o): 73% (from **1c** and **2a**), mp 137139 °C, IR (KBr) 1169 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.55 (3H, s), 7.2−8.6 (9H, m). Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27%. Found: C, 68.28; H, 5.36; N, 12.32%.

1-(3-Methylpyridinio)(*p*-toluenethiocarbonyl)amidate (3p): 70% (from **1c** and **2b**), mp 132−134 °C, IR (KBr) 1176 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.41 (3H, s), 2.54 (3H, s), 7.1−8.6 (8H, m). Anal. Calcd for $C_{14}H_{14}N_2S$: C, 69.39; H, 5.82; N, 11.56%. Found: C, 69.20; H, 5.82; N, 11.75%.

1-(3-Methylpyridinio)(*p*-methoxybenzenethiocarbonyl)amidate (3q): 93% (from **1c** and **2c**), mp 150−152 °C, IR (KBr) 1163 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.49 (3H, s), 3.82 (3H, s), 6.8−8.5 (8H, m). Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84%. Found: C, 65.06; H, 5.50; N, 10.85%.

1-(3-Methylpyridinio)(*p*-chlorobenzenethiocarbonyl)-amidate (3r): 80% (from **1c** and **2e**), mp 127−129 °C, IR (KBr) 1163 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.57 (3H, s), 7.2−8.8 (8H, m). Anal. Calcd for $C_{13}H_{11}ClN_2S$: C, 59.42; H, 4.22; N, 10.66%. Found: C, 59.51; H, 4.22; N, 10.57%.

1-(4-Methylpyridinio)(2-thiophenethiocarbonyl)amidate (3s): 90% (from **1c** and **2f**), mp 144−146 °C, IR (KBr)

1143 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.55 (3H, s), 7.0−8.6 (7H, m). Anal. Calcd for $C_{11}H_{10}N_2S_2$: C, 56.38; H, 4.30; N, 11.95%. Found: C, 56.17; H, 4.26; N, 11.97%.

1-(2-Methylquinolinio)(thiobenzoyl)amidate (3t): 42% (from **1d** and **2a**), mp 189−191 °C, IR (KBr) 1167 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.91 (3H, s), 7.3−8.7 (11H, m). Anal. Calcd for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.07; N, 10.06%. Found: C, 73.36; H, 5.16; N, 9.95%.

1-(2-Methylquinolinio)(2-thiophenethiocarbonyl)amidate (3u): 34% (from **1d** and **2f**), mp 186−188 °C, IR (KBr) 1168 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.92 (3H, s), 7.0−8.7 (9H, m). Anal. Calcd for $C_{15}H_{12}N_2S_2$: C, 63.35; H, 4.25; N, 9.05%. Found: C, 63.09; H, 4.27; N, 9.75%.

Reactions of 1-Pyridinio- and 1-Quinolinio(arenethiocarbonyl)amidates with DMAD. General Method A. A solution of amidate (**3**, 1 mmol) in 40 mL of dry $CHCl_3$ was concentrated to about 20 mL in order to completely remove moisture and alcohol,[11] and then DMAD (**4**, 0.143 g, 1.2 mmol) was added. The resulting solution was heated at 50−60 °C for 8−11 h. The reaction solution was concentrated, and the residue was separated by column chromatography on alumina using ether and then $CHCl_3$. Concentration of the $CHCl_3$ fraction and recrystallization of the crude crystals form $CHCl_3$−hexane gave dimethyl 4-aryl-5-thia-2,3-diazatricyclo-[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (**7a**−**s**) as colorless prisms or dimethyl 2-aryl-5a-methyl-5a*H*-[1, 3,4]-thiadiazepino[4,5-*a*]quinoline-4,5-dicarboxylates (**8a**,**b**) as yellow prisms.

Genaral Method B. The $CHCl_3$ solution of 1-(3-methylpyridinio)amidates (**3o**−**s**, 1 mmol) and DMAD (**4**, 0.143 g, 1.2 mmol) prepared by the above procedure was heated at 50−60 °C for 4 h. Usual workups of the resulting mixtures gave the corresponding dimethyl 2-aryl-6-methyl-5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepine-4,5-dicarboxylates (**5′o**−**s**) as red prisms or needles, together with dimethyl 4-aryl-5-thia-2,3-diazatricyclo-[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (**7o**−**s**).

Although the reactions of 1-pyridinio(arenethiocarbonyl)-amidates (**3**) with **4** at rt or at 0 °C were also examined, any significant products could not be isolated.

Some data for these products (**5′o**−**s**, **7a**−**s**, and **8a**,**b**) are as follows:

Dimethyl 6-methyl-2-phenyl-5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepine-4,5-dicarboxylates (5′o): 22% (from **3o** and **4**), mp 129−131 °C, IR (KBr) 1726, 1651, 1608 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.84 (3H, s), 3.84 (3H, s), 3.87 (3H, s), 4.87 (1H, q, J = 6.0, 7.0 Hz), 5.86 (1H, br d, J = 6.0 Hz), 6.49 (1H, d, J = 7.0 Hz), 7.50 (1H, s), 7.2−8.0 (5H, m). Anal. Calcd for $C_{19}H_{18}N_2O_4S$: C, 61.61; H, 4.90; N, 7.56%. Found: C, 61.64; H, 4.88; N, 7.56%.

Dimethyl 6-methyl-2-(*p*-tolyl)-5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepine-4,5-dicarboxylates (5′p): 20% (from **3p** and **4**), mp 132−134 °C, IR (KBr) 1730, 1660, 1589 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.83 (3H, s), 2.39 (3H, s), 3.82 (3H, s), 3.86 (3H, s), 4.86 (1H, q, J = 6.0, 7.0 Hz), 5.86 (1H, br d, J = 6.0 Hz), 6.49 (1H, d, J = 7.0 Hz), 7.48 (1H, s), 7.1−7.9 (5H, m). Anal. Calcd for $C_{20}H_{20}N_2O_4S$: C, 62.48; H, 5.24; N, 7.29%. Found: C, 62.43; H, 5.18; N, 7.22%.

Dimethyl 2-(*p*-methoxyphenyl)-6-methyl-5a*H*-pyrido-[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates (5′q): 27% (from **3q** and **4**), mp 94−95 °C, IR (KBr) 1734, 1655, 1602 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.83 (3H, s), 3.81 (3H, s), 3.85 (6H, s), 4.84 (1H, q, J = 6.0, 7.0 Hz), 5.85 (1H, br d, J = 6.0 Hz), 6.48 (1H, d, J = 7.0 Hz), 7.45 (1H, s), 6.7−7.9 (5H, m). Anal. Calcd for $C_{20}H_{20}N_20_5S$: C, 59.99; H, 5.03; N, 7.00%. Found: C, 60.07; H, 5.13; N, 6.93%.

Dimethyl 2-(*p*-chlorophenyl)-6-methyl-5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylates (5′r): Trace (from **3r** and **4**), ^1H NMR ($CDCl_3$) δ 1.82 (3H, s), 3.85 (3H, s), 3.87 (3H, s), 4.86 (1H, q, J = 6.0, 7.0 Hz), 5.81 (1H, br d, J = 6.0 Hz), 6.42 (1H, d, J = 7.0 Hz), 7.56 (1H, s), 7.2−7.9 (5H, m). The preparation of pure sample for **5′r** was unsuccessful because of its low yield.

Dimethyl 6-methyl-2-(2-thienyl)-5a*H*-pyrido[1,2-*d*][1,3,4]-thiadiazepine-4,5-dicarboxylates (5′s): 22% (from **3s** and **4**), mp 146−148 °C, IR (KBr) 1722, 1653, 1564 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.83 (3H, s), 3.81 (3H, s), 3.85 (6H, s), 4.84 (1H, q, J = 6.0, 7.0 Hz), 5.85 (1H, br d, J = 6.0 Hz), 6.48 (1H, d, J = 7.0 Hz), 7.45 (1H, s), 6.7−7.9 (5H, m). Anal. Calcd for $C_{17}H_{16}N_2O_4S_2$: C, 54.24; H, 4.28; N, 7.44%. Found: C, 54.31; H, 4.25; N, 7.40%.

Dimethyl 4-phenyl-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]-undeca-3,8,10-triene-6,11-dicarboxylates (7a): 30% (from **3a** and **4**), mp 175−177 °C, IR (KBr) 1733, 1709, 1614 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.73 (3H, s), 3.85 (3H, s), 4.18 (1H, d, J = 3.0 Hz), 4.64 (1H, q, J = 3.0, 5.0 Hz), 6.23 (1H, q, J = 3.0, 6.0 Hz), 6.76 (1H, q, J = 3.0, 6.0 Hz), 7.50 (1H, d, J = 5.0 Hz), 7.2−8.0 (5H, m). Anal. Calcd for $C_{18}H_{16}N_2O_4S$: C, 60.66; H, 4.53; N, 7.86%. Found: C, 60.56; H, 4.51; N, 7.83%.

Dimethyl 4-(*p*-tolyl)-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]-undeca-3,8,10-triene-6,11-dicarboxylates (7b): 15% (from **3b** and **4**), mp 225−227 °C, IR (KBr) 1741, 1714, 1612 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.37 (3H, s), 3.75 (3H, s), 3.86 (3H, s), 4.21 (1H, d, J = 3.0 Hz), 4.66 (1H, q, J = 3.0, 5.0 Hz), 6.27 (1H, q, J = 3.0, 6.0 Hz), 6.82 (1H, q, J = 3.0, 6.0 Hz), 7.57 (1H, d, J = 5.0 Hz), 7.0−7.9 (4H, m). Anal. Calcd for $C_{19}H_{18}N_2O_4S$: C, 61.61; H, 4.90; N, 7.56%. Found: C, 61.63; H, 4.94; N, 7.50%.

Dimethyl 4-(*p*-methoxyphenyl)-5-thia-2,3-diazatricyclo-[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (7c): 30% (from **3c** and **4**), mp 185−187 °C, IR (KBr) 1738, 1712, 1605 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.72 (3H, s), 3.84 (6H, s), 4.17 (1H, d, J = 3.0 Hz), 4.62 (1H, q, J = 3.0, 5.0 Hz), 6.24 (1H, q, J = 3.0, 6.0 Hz), 6.76 (1H, q, J = 3.0, 6.0 Hz), 7.50 (1H, d, J = 5.0 Hz), 6.8−7.9 (4H, m). Anal. Calcd for $C_{19}H_{18}N_20_5S$: C, 59.06; H, 4.70; N, 7.25%. Found: C, 59.33; H, 4.76; N, 7.12%.

Dimethyl 4-(*p*-chlorophenyl)-5-thia-2,3-diazatricyclo-[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (7e): 3% (from **3e** and **4**), mp 192−194 °C, IR (KBr) 1736, 1714, 1606 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.73 (3H, s), 3.86 (3H, s), 4.16 (1H, d, J = 3.0 Hz), 4.63 (1H, q, J = 3.0, 5.0 Hz), 6.21 (1H, q, J = 3.0, 6.0 Hz), 6.77 (1H, q, J = 3.0, 6.0 Hz), 7.49 (1H, d, J = 5.0 Hz), 7.2−7.9 (4H, m). Anal. Calcd for $C_{18}H_{15}ClN_2O_4S$: C, 55.32; H, 3.87; N, 7.17%. Found: C, 55.31; H, 3.82; N, 7.13%.

Dimethyl 4-(2-thienyl)-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]-undeca-3,8,10-triene-6,11-dicarboxylates (7f): 28% (from **3f** and **4**), mp 220−222 °C, IR (KBr) 1732, 1709, 1614 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.72 (3H, s), 3.85 (3H, s), 4.19 (1H, d, J = 3.0 Hz), 4.64 (1H, q, J = 3.0, 5.0 Hz), 6.21 (1H, q, J = 3.0, 6.0 Hz), 6.75 (1H, q, J = 3.0, 6.0 Hz), 6.9−7.7 (4H, m). Anal. Calcd for $C_{16}H_{14}N_2O_4S_2$: C, 53.02; H, 3.89; N, 7.73%. Found: C, 53.05; H, 3.95; N, 7.85%.

Dimethyl 4-(*p*-(dimethylamino)phenyl)-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (7g): 13% (from **3g** and **4**), mp 115−117 °C, IR (KBr) 1736, 1716, 1606 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.98 (6H, s), 3.71 (3H, s), 3.83 (3H, s), 4.16 (1H, d, J = 3.0 Hz), 4.62 (1H, q, J = 3.0, 5.0 Hz), 6.20 (1H, q, J = 3.0, 6.0 Hz), 7.47 (1H, d, J = 5.0 Hz), 6.5−7.9 (5H, m). Anal. Calcd for $C_{20}H_{21}N_3O_4S$: C, 60.13; H, 5.30; N, 10.52%. Found: C, 60.35; H, 5.21; N, 10.38%.

Dimethyl 9-methyl-4-phenyl-5-thia-2,3-diazatricyclo-[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (7h): 30% (from **3h** and **4**), mp 216−218 °C, IR (KBr) 1732, 1705, 1645, 1616 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.98 (3H, s), 3.71 (3H, s), 3.82 (3H, s), 4.11 (1H, d, J = 3.0 Hz), 4.37 (1H, d, J = 5.0 Hz), 5.75 (1H, br s), 7.55 (1H, d, J = 5.0 Hz), 7.3−8.0 (5H, m). Anal. Calcd for $C_{19}H_{18}N_2O_4S$: C, 61.61; H, 4.90; N, 7.56%. Found: C, 61.63; H, 4.98; N, 7.68%.

Dimethyl 9-methyl-4-(*p*-tolyl)-5-thia-2,3-diazatricyclo-[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (7i): 18% (from **3i** and **4**), mp 228−230 °C, IR (KBr) 1740, 1716, 1647, 1614 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.00 (3H, s), 2.39 (3H, s), 3.74 (3H, s), 3.85 (3H, s), 4.12 (1H, d, J = 3.0 Hz), 4.40 (1H, d, J = 5.0 Hz), 5.80 (1H, br s), 7.61 (1H, d, J = 5.0 Hz), 7.0−7.9 (4H, m). Anal. Calcd for $C_{20}H_{20}N_2O_4S$: C, 62.48; H, 5.24; N, 7.29%. Found: C, 62.42; H, 5.37; N, 7.20%.

Dimethyl 4-(*p*-methoxyphenyl)-9-methyl-5-thia-2,3-diazatricyclo[4.3.2.$0^{2,7}$]undeca-3,8,10-triene-6,11-dicarboxylates (7j): 22% (from **3j** and **4**), mp 250−252 °C, IR (KBr) 1732, 1711, 1649, 1605 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.99 (3H, s), 3.72 (3H, s), 3.82 (6H, s), 4.10 (1H, d, J = 3.0 Hz), 4.36 (1H, d, J = 5.0 Hz), 5.77 (1H, br s), 7.55 (1H, d, J = 5.0 Hz), 6.7−7.9

(4H, m). Anal. Calcd for $C_{20}H_{20}N_20_5S$: C, 59.99; H, 5.03; N, 7.00%. Found: C, 59.96; H, 5.08; N, 7.05%.

Dimethyl 4-(*o*-methoxyphenyl)-9-methyl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7k): 1% (from **3k** and **4**), mp 247−249 °C, IR (KBr) 1732, 1711, 1604 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.99 (3H, s), 3.74 (3H, s), 3.85 (6H, s), 4.11 (1H, d, J = 3.0 Hz), 4.38 (1H, d, J = 5.0 Hz), 5.77 (1H, br s), 7.53 (1H, d, J = 5.0 Hz), 6.8−7.9 (4H, m). Anal. Calcd for $C_{20}H_{20}N_20_5S$: C, 59.99; H, 5.03; N, 7.00%. Found: C, 60.17; H, 5.01; N, 6.84%.

Dimethyl 4-(*p*-chlorophenyl)-9-methyl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7l): 8% (from **3l** and **4**), mp 149−151 °C, IR (KBr) 1747, 1716, 1651, 1614 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.00 (3H, s), 3.75 (3H, s), 3.87 (3H, s), 4.13 (1H, d, J =3.0 Hz), 4.40 (1H, d, J = 5.0 Hz), 5.80 (1H, br s), 7.61 (1H, d, J = 5.0 Hz), 7.2−7.9 (4H, m). Anal. Calcd for $C_{19}H_{17}ClN_2O_4S$: C, 56.37; H, 4.23; N, 6.92%. Found: C, 56.54; H, 4.25; N, 6.73%.

Dimethyl 9-methyl-4-(2-thienyl)-5-thia-2,3-diazatricyclo-[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7m): 35% (from **3m** and **4**), mp 209−211 °C, IR (KBr) 1730, 1703, 1645, 1614 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.98 (3H, s), 3.73 (3H, s), 3.83 (3H, s), 4.14 (1H, d, J = 3.0 Hz), 4.38 (1H, d, J = 5.0 Hz), 5.75 (1H, br s), 6.8−7.8 (4H, m). Anal. Calcd for $C_{17}H_{16}N_2O_4S_2$: C, 54.24; H, 4.28; N, 7.44%. Found: C, 54.16; H, 4.34; N, 7.57%.

Dimethyl 4-(*p*-(Dimethylamino)phenyl)-9-methyl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7n): 27% (from **3n** and **4**), mp 219−221 °C, IR (KBr) 1736, 1716, 1606 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.98 (3H, s), 2.98 (6H, s), 3.73 (3H, s), 3.81 (3H, s), 4.10 (1H, d, J = 3.0 Hz), 4.33 (1H, d, J = 5.0 Hz), 5.76 (1H, br s), 7.53 (1H, d, J = 5.0 Hz), 6.5−7.9 (4H, m). Anal. Calcd for $C_{21}H_{23}N_3O_4S$: C, 61.00; H, 5.61; N, 10.16%. Found: C, 60.94; H, 5.55; N, 10.28%.

Dimethyl 8-methyl-4-phenyl-5-thia-2,3-diazatricyclo-[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7o): 13% (method A) or 10% (method B) (from **3o** and **4**), mp 171−173 °C, IR (KBr) 1734, 1718, 1639, 1616 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.85 (3H, s), 3.74 (3H, s), 3.86 (3H, s), 4.02 (1H, s), 4.54 (1H, q, J = 3.0, 5.0 Hz), 6.39 (1H, br s), 7.55 (1H, d, J = 5.0 Hz), 7.3−8.0 (5H, m). Anal. Calcd for $C_{19}H_{18}N_2O_4S$: C, 61.61; H, 4.90; N, 7.56%. Found: C, 61.84; H, 4.94; N, 7.29%.

Dimethyl 8-methyl-4-(*p*-tolyl)-5-thia-2,3-diazatricyclo-[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7p): 16% (method A) or 9% (method B) (from **3p** and **4**), mp 239−241 °C, IR (KBr) 1734, 1716, 1639, 1612 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.87 (3H, s), 2.40 (3H,s), 3.74 (3H, s), 3.88 (3H, s), 4.02 (1H, s), 4.58 (1H, q, J = 3.0, 5.0 Hz), 6.41 (1H, br s), 7.57 (1H, d, J = 5.0 Hz), 7.1−7.9 (4H, m). Anal. Calcd for $C_{20}H_{20}N_2O_4S$: C, 62.48; H, 5.24; N, 7.29%. Found: C, 62.41; H, 5.24; N, 7.28%.

Dimethyl 4-(*p*-methoxyphenyl)-8-Methyl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7q): 27% (method A) or 11% (method B) (from **3q** and **4**), mp 215−217 °C, IR (KBr) 1744, 1717, 1641, 1605 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.84 (3H, s), 2.40 (3H,s), 3.71 (3H, s), 3.82 (6H, s), 3.98 (1H, s), 4.53 (1H, q, J = 3.0, 5.0 Hz), 6.41 (1H, br s), 7.50 (1H, d, J = 5.0 Hz), 6.7−7.9 (4H, m). Anal. Calcd for $C_{20}H_{20}N_20_5S$: C, 59.99; H, 5.03; N, 7.00%. Found: C, 60.14; H, 5.12; N, 6.84%.

Dimethyl 4-(*p*-chlorophenyl)-8-methyl-5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7r): 11% (method A) or 6% (method B) (from **3r** and **4**), mp 244−246 °C, IR (KBr) 1732, 1716, 1643, 1620 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.85 (3H, s), 3.73 (3H,s), 3.86 (3H, s), 3.99 (3H, s), 4.56 (1H, q, J = 3.0, 5.0 Hz), 6.39 (1H, br s), 7.52 (1H, d, J = 5.0 Hz), 7.2−7.9 (4H, m). Anal. Calcd for $C_{19}H_{17}ClN_2O_4S$: C, 56.37; H, 4.23; N, 6.92%. Found: C, 56.45; H, 4.32; N, 6.74%.

Dimethyl 8-methyl-4-(2-thienyl)-5-thia-2,3-diazatricyclo-[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylates (7s): 16% (method A) or 11% (method B) (from **3s** and **4**), mp 199−201 °C, IR (KBr) 1734, 1716, 1639, 1612 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.85 (3H, s), 3.71 (3H,s), 3.83 (3H, s), 4.01 (1H, s), 4.55 (1H, q, J = 3.0, 5.0 Hz), 6.37 (1H, br s), 6.9−7.7 (4H, m). Anal. Calcd for $C_{17}H_{16}N_2O_4S_2$: C, 54.24; H, 4.28; N, 7.44%. Found: C, 54.29; H, 4.24; N, 7.50%.

Dimethyl 5a-methyl-2-phenyl-5a*H*-[1,3,4]thiadiazepino-[4,5-*a*]quinoline-4,5-dicarboxylates (8a): 41% (from **3t** and **4**), mp 122−127 °C, IR (KBr) 1732, 1649, 1599 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.76 (3H, s), 3.86 (3H,s), 3.89 (3H, s), 5.99 (1H, d, J = 10.0 Hz), 6.53 (1H, d, J = 10.0 Hz), 6.5−8.6 (9H, m). Anal. Calcd for $C_{23}H_{20}N_2O_4S$: C, 65.70; H, 4.79; N, 6.66%. Found: C, 65.63; H, 4.87; N, 6.55%.

Dimethyl 5a-methyl-2-(2-thienyl)-5a*H*-[1,3,4]thiadiazepino[4,5-*a*]quinoline-4,5-dicarboxylates (8b): 43% (from **3u** and **4**), mp 115−117 °C, IR (KBr) 1732, 1643, 1597 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.74 (3H, s), 3.80 (3H,s), 3.85 (3H, s), 5.87 (1H, d, J = 10.0 Hz), 6.49 (1H, d, J = 10.0 Hz), 6.5−7.4 (5H, m), 7.59 (1H, d, J = 5.0 Hz), 7.85 (1H, d, J = 4.0 Hz). Anal. Calcd for $C_{21}H_{18}N_2O_4S_2$: C, 59.14; H, 4.25; N, 6.57%. Found: C, 59.34; H, 4.41; N, 6.31%.

Crystallography of Dimethyl 6-Methyl-2-phenyl-5a*H*-pyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylate (5′o).[12] A single crystal (0.46 × 0.78 × 1.00 mm) grown from $CHCl_3$−hexane was used for the unit-cell determinations and the data collections of a Rigaku AFC5S four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). Crystal data of **5′o**: $C_{19}H_{18}N_2O_4S$; M = 370.42; monoclinic, space group $P2_1/c$ (no. 14), Z = 4 with a = 12.210(3) Å, b = 7.551 (4) Å, c = 19.538(2) Å; b = 94.29 (1)°; V = 1796.2 (7) Å,^{3} and D_{calc} = 1.370 g/cm^3. All calculations were performed using the TEXSAN program.[13] The structure was solved by a direct method (MITHRIL).[14] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The final R- and R_w-factors after full-matrix least-squares refinements were 0.045 and 0.050 for 2883 observed reflections.

Crystallography of Dimethyl 5a-Methyl-2-phenyl-5a*H*-[1,3,4]- thiadiazepino[4,5-a]quinoline-4,5-dicarboxylate (8a).[12] A single crystal (0.04 × 0.22 × 0.64 mm) grown from $CHCl_3$−hexane was used for the unit-cell determinations and the data collections of a Rigaku AFC5S four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). Crystal data of **8a**: $C_{23}H_{20}N_2O_4S$; M = 420.48; orthorhombic, space group $Pbca$ (no. 61), Z = 8 with a = 19.18(3) Å, b = 25.827(6) Å, c = 8.694(6) Å; V = 4307(7) Å,^{3} and D_{calc} = 1.297 g/cm^3. All calculations were performed using the TEXSAN program.[13] The structure was solved by a direct method (MITHRIL).[14] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were not refined. The final R- and R_w-factors after full-matrix least-squares refinements were 0.055 and 0.063 for 866 observed reflections.

Supporting Information Available: Copies of ^{1}H NMR spectra of compounds (3 pages). This material is contained in libraries on microfiche, immediately follws this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(13) "TEXSAN TEXRAY", Structure Analysis Package," Molecular Structure Corporation, 1985.

(14) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.