

## REACTION OF 1-PYRIDINIOTHIOBENZOYLAMINIDES WITH DIMETHYL ACETYLENEDICARBOXYLATE<sup>1</sup>

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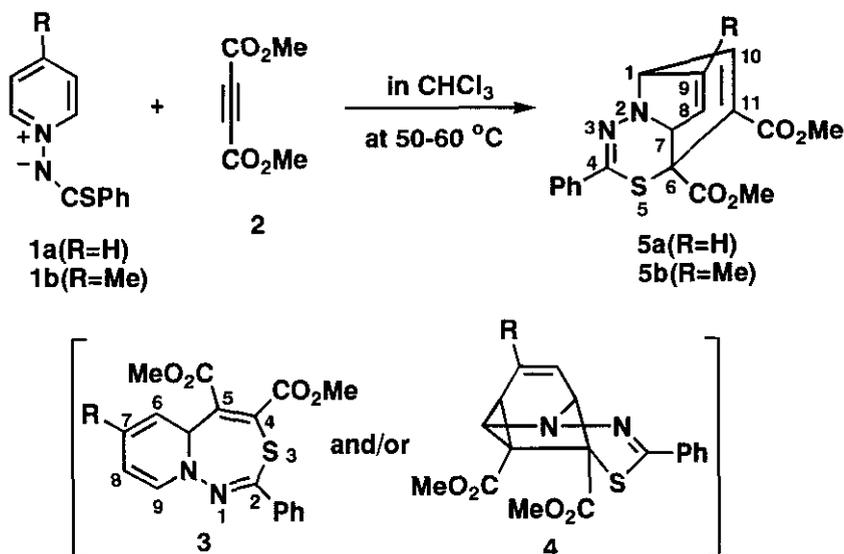
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**Abstract** -- The reactions of 1-pyridiniothiobenzoylamines with dimethyl acetylenedicarboxylate in chloroform at 50-60 °C provided dimethyl 5-thia-2,3-diazatricyclo[4.3.2.0<sup>2,7</sup>]undeca-3,8,10-triene-6,11-dicarboxylate derivatives in moderate yields. The structures of these products were assumed by their spectral and analytical data and determined finally by the X-ray analysis of one compound.

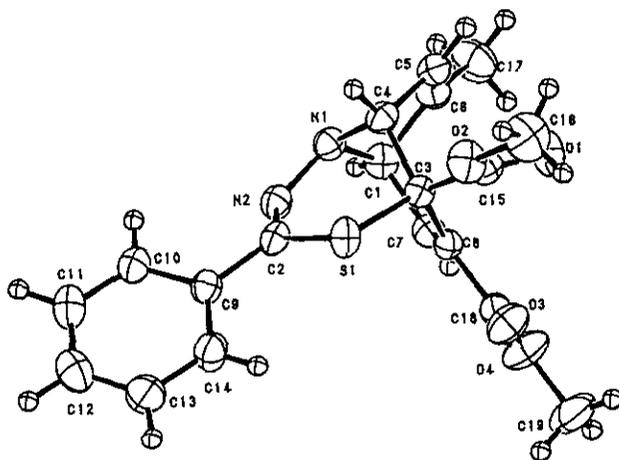
Recently, we have reported facile formations of 10a*H*-pyrido[1,2-*d*][1,4]thiazepines and their intramolecular Diels-Alder adducts from the reactions of 1-pyridinio(substituted thiocarbonyl)methylides with dimethyl acetylenedicarboxylate (DMAD).<sup>2</sup> We have also proved that this reaction is initiated by the electrophilic attack of DMAD on the sulfur atom of the thiocarbonyl group in the ylides.<sup>3</sup> In view of the readiness of these reactions and the uniqueness of the heterocycles obtained, we were next interested in extending this reaction to other pyridinium ylide, 1-pyridinio(substituted thiocarbonyl)aminide, which is already known that these aminides are subjected to an attack of some electrophiles on the same sulfur atom.<sup>4</sup> When the reaction of 1-pyridiniothiobenzoylamine (**1a**) with DMAD (**2**) was carried out in chloroform at room temperature, any significant products, such as the initially expected dimethyl 5a*H*-2-phenylpyrido[1,2-*d*][1,3,4]thiadiazepine-4,5-dicarboxylate (**3**) and/or dimethyl 4-thia-1,2-diazatetracyclo[5.4.0.0<sup>5,11</sup>.0<sup>6,8</sup>]undeca-2,9-diene-5,6-dicarboxylate (**4**), could not be

isolated at all. However, that of **1a** and **2** in chloroform under heating conditions (50-60 °C) gave a product (**5a**), 30%, colorless prisms, mp 175-177 °C (from chloroform-hexane),  $\nu$  (KBr) 1732 (saturated ester C=O), 1709 ( $\alpha,\beta$ -unsaturated ester C=O), and 1614  $\text{cm}^{-1}$  (C=C),  $\delta$  ( $\text{CDCl}_3$ ) 3.73 and 3.85 (each 3H, s,  $2\times\text{CO}_2\text{Me}$ ), 4.18 (1H, d,  $J=2.5$  Hz, 7-H), 4.64 (1H, dd,  $J=4.0$  and 2.5 Hz, 1-H), 6.23 (1H, dd,  $J=6.0$  and 2.5 Hz, 8-H), 6.76 (1H, q,  $J=6.0$  and 2.5 Hz, 9-H), 7.2-8.0 (5H, m, 4-Ph), and 7.50 (1H, d,  $J=4.0$  Hz, 10-H). Similarly, the reaction of [1-(4-methylpyridinio)]thiobenzoylaminide (**1b**) with **2** under the same conditions gave the corresponding compound (**5b**), 28%, colorless prisms, mp 216-218 °C (from chloroform-hexane),  $\nu$  (KBr) 1732 (saturated ester C=O), 1705 ( $\alpha,\beta$ -unsaturated ester C=O), 1645 (C=C), and 1616  $\text{cm}^{-1}$  (C=C),  $\delta$  ( $\text{CDCl}_3$ ) 1.98 (3H, d,  $J=1.0$  Hz, 9-Me), 3.71 and 3.82 (each 3H, s,  $2\times\text{CO}_2\text{Me}$ ), 4.11 (1H, d,  $J=2.5$  Hz, 7-H), 4.37 (1H, d,  $J=4.0$  Hz, 1-H), 5.75 (1H, br s, 8-H), 7.2-8.0 (5H, m, 4-Ph), and 7.54 (1H, d,  $J=4.0$  Hz, 10-H).

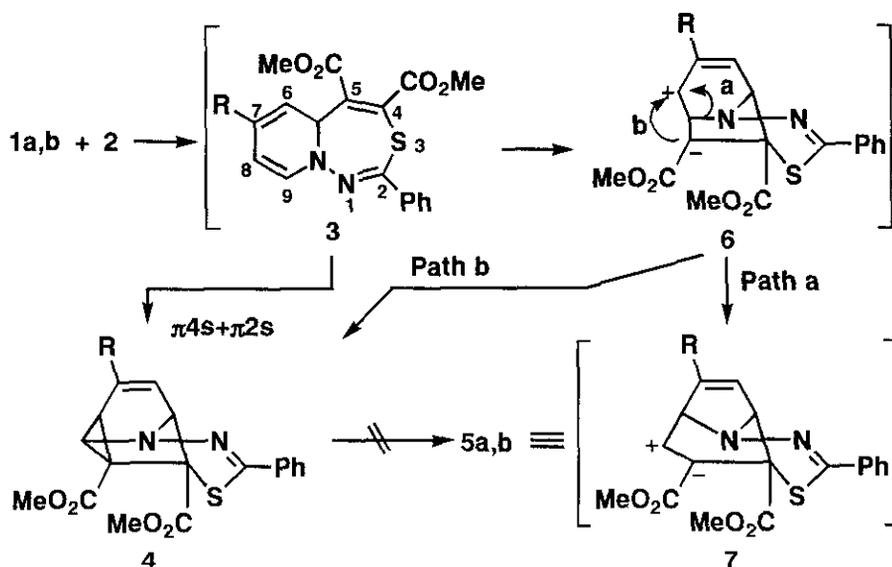


Although the elemental analyses showed clearly that products (**5a,b**) are 1 : 1 adducts between (1-pyridinio)thiobenzoylaminides (**1a,b**) and DMAD (**2**),<sup>4)</sup> their ir and  $^1\text{H}$  nmr spectra were quite different from the expected those for the primary adducts (**3**) and their intramolecular Diels-Alder adducts (**4**). For example, the presences of a saturated and an  $\alpha,\beta$ -unsaturated ester carbonyl band (1732 and 1709  $\text{cm}^{-1}$  for **5a** and 1732 and 1705  $\text{cm}^{-1}$  for **5b**) were not in accord with the expected absorption bands for both compounds (**3**) and (**4**). From the consideration of the chemical shifts and the signal patterns of the  $^1\text{H}$  nmr spectra of **5a,b**, furthermore, we could induce easily the following atomic arrangement,

-N\*-C(sp<sup>3</sup>)-C(sp<sup>2</sup>)-C(sp<sup>2</sup>)-C(sp<sup>3</sup>)-(-N\*-)-C(sp<sup>2</sup>)-, in this skeleton and also realize the presence of the last methine proton (10-H,  $\delta$  7.50 for **5a** and  $\delta$  7.54 for **5b**) in the above arrangement which is shifted to low magnetic field by a strong anisotropy effect of an ester carbonyl group. Apparently, this atomic arrangement suggested the transformation from original pyridine ring to 2,5-dihydropyrrole ring possessing the 2-vinyl substituent. From these spectral inspection and the possible structural alternative<sup>5</sup> for one compound (**4**) initially expected, we assumed products (**5a,b**) to be dimethyl 5-thia-2,3-diazatricyclo[4.3.2.0<sup>2,7</sup>]undeca-3,8,10-triene-6,11-dicarboxylate derivatives. These structures were finally confirmed by single crystal X-ray analysis for **5b**.<sup>6</sup> The ORTEP drawing for **5b** is shown below.



Mechanistically, the formation of products (**5a,b**) can be considered *via* the intervention of the primary adduct (**3**) and/or its intramolecular Diels-Alder adduct (**4**), since a 1,3,4-thiadiazine moiety is present in the molecules. However, the fact that a divinylmethane-vinylcyclopropane rearrangement is photochemical process and *vice versa*<sup>5</sup> excluded clearly the possibility of the formation of **5a,b** from the latter (**4**). An alternative route from the primary adduct (**3**) to final products (**5a,b**) can be considered: It is the bond formation between the 4- and the 9-positions of the pyrido[1,2-*d*][1,3,4]thiadiazepines (**3**) followed by the cationic 1,2-sigmatropic shift of a nitrogen-carbon single bond of the resulting zwitterionic intermediate (**6**) with the generation of new carbon-carbon double bond (path a). On the other hand, the bond formation between the ionic centers in the intermediate (**6**) should lead to adduct (**4**) (path b), though we could not isolate them. One of the reasons why the adduct such as **4** was not formed in these reactions may be owing to the presence of the strained cyclopropane ring in this molecule.



## REFERENCES AND NOTES

1. Preparation of New Nitrogen-Bridged Heterocycles. Part 41. For Part 40 of this series, see A. Kakehi, S. Ito, S. Hayashi, and T. Fujii, *Bull. Chem. Soc. Jpn.*, in press.
2. a) A. Kakehi, S. Ito, and J. Hakui, *Chem. Lett.*, **1992**, 777; b) A. Kakehi and S. Ito, *Heterocycles*, **1993**, **36**, 1195; c) A. Kakehi, S. Ito, and J. Hakui, *Bull. Chem. Soc. Jpn.*, **1993**, **66**, 3475; d) A. Kakehi, S. Ito, M. Mitani, and M. Kanaoka, *Bull. Chem. Soc. Jpn.*, **1994**, **67**, 1646.
3. A. Kakehi, S. Ito, and S. Fujita, *Bull. Chem. Soc. Jpn.*, **1995**, **68**, 1473.
4. Satisfactory elemental analyses (within  $\pm 0.3\%$  for C, H, and N) for **5a,b** were obtained.
5. The retro-di- $\pi$ -methane rearrangement (vinylcyclopropane  $\rightarrow$  divinylmethane) was first considered as a possible reaction route for the ring opening of the strained cyclopropane in compound (**4**). For di- $\pi$ -methane rearrangement, see the following reviews: a) H. E. Zimmerman, *Advances in Photochemistry*, **1963**, **1**, 183; b) O. L. Chapman, *ibid.*, **1963**, **1**, 323; c) K. Schaffner, *ibid.*, **3**, 81 (1966); P. J. Kropp, *Organic Photochemistry*, **1967**, **1**, 1.
6. The X-ray crystallography of **5b** was carried out on a RIGAKU AFC5S diffractometer. The diffraction data were collected with the use of  $\text{MoK}\alpha$  radiation and 4420 independent reflections were used for solving the structure by TEXSAN program (TEXSAN TEXRAY, Structure Analysis Package, Molecular Structure Corporation). Crystal data:  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ , FW=370.42, monoclinic, space group  $P2_1/a$ ,  $a=21.718$  (2) Å,  $b=8.581$  (4) Å,  $c=9.680$  (2) Å,  $\beta=90.87$  (1)°,  $V=1803.7$  Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{Calc}}=1.364$  g/cm<sup>3</sup>,  $R=0.043$ ,  $R_w=0.049$ .