

REACTION OF 1-PYRIDINIOTHIENZOYLAMINIDES WITH DIMETHYL ACETYLENEDICARBOXYLATE¹

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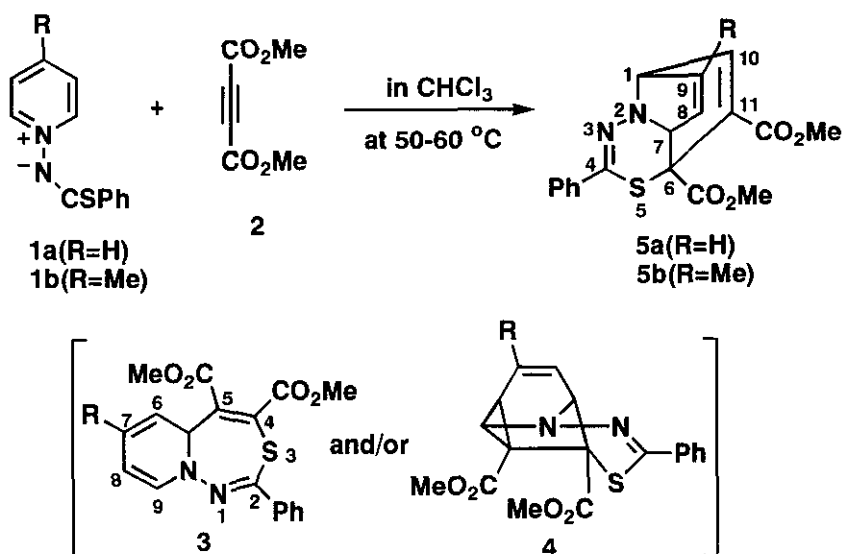
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Abstract -- The reactions of 1-pyridiniothiobenzoylamines with dimethyl acetylenedicarboxylate in chloroform at 50-60 °C provided dimethyl 5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylate derivatives in moderate yields.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

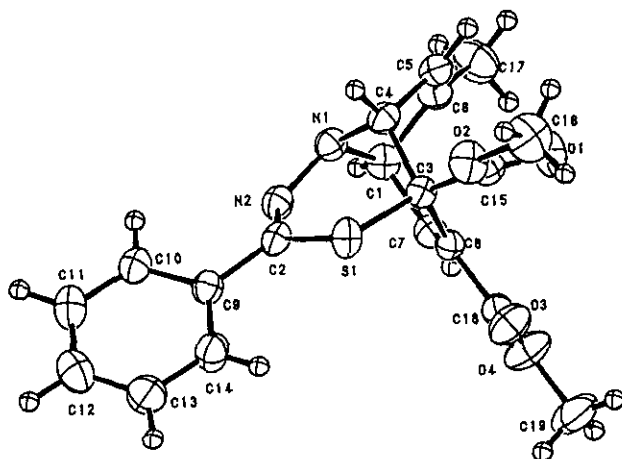
Recently, we have reported facile formations of 10a*H*-pyrido[1,2-*d*][1,4]thiazepines and their intramolecular Diels-Alder adducts from the reactions of 1-pyridinio(substituted thiocarbonyl)methylides with dimethyl acetylenedicarboxylate (DMAD).² We have also proved that this reaction is initiated by the electrophilic attack of DMAD on the sulfur atom of the thiocarbonyl group in the ylides.³ 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.⁴ 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^{5,11}.0^{6,8}]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), ν (KBr) 1732 (saturated ester C=O), 1709 (α,β -unsaturated ester C=O), and 1614 cm^{-1} (C=C), δ (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), ν (KBr) 1732 (saturated ester C=O), 1705 (α,β -unsaturated ester C=O), 1645 (C=C), and 1616 cm^{-1} (C=C), δ (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).

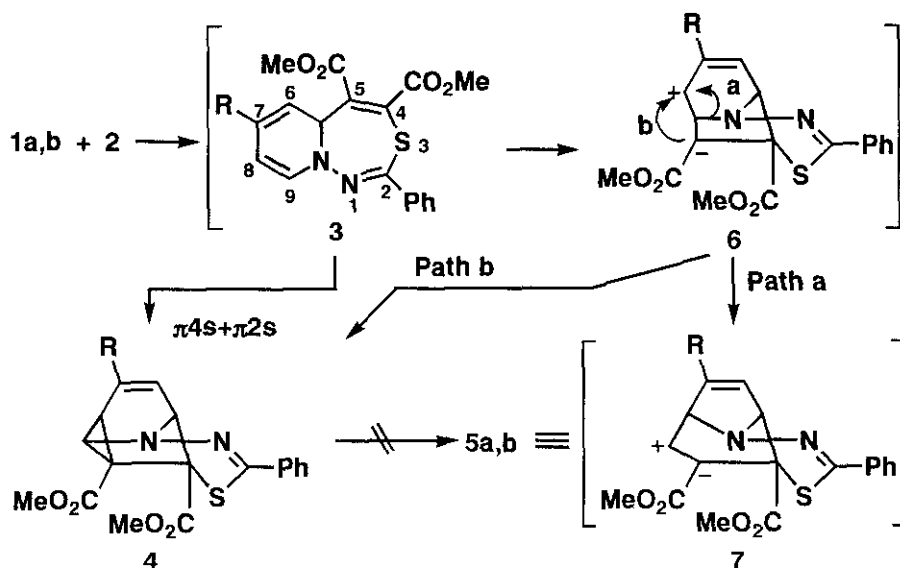


Although the elemental analyses showed clearly that products (**5a,b**) are 1 : 1 adducts between (1-pyridinio)thiobenzoylaminides (**1a,b**) and DMAD (**2**),⁴⁾ their ir and ^1H nmr spectra were quite different from the expected those for the primary adducts (**3**) and their intramolecular Diels-Alder adducts (**4**). For example, the presences of a saturated and an α,β -unsaturated ester carbonyl band (1732 and 1709 cm^{-1} for **5a** and 1732 and 1705 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 ^1H nmr spectra of **5a,b**, furthermore, we could induce easily the following atomic arrangement,

-N*-C(sp³)-C(sp²)-C(sp²)-C(sp³)-(-N*-)-C(sp²)-, in this skeleton and also realize the presence of the last methine proton (10-H, δ 7.50 for **5a** and δ 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 alternative⁵ for one compound (**4**) initially expected, we assumed products (**5a,b**) to be dimethyl 5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylate derivatives. These structures were finally confirmed by single crystal X-ray analysis for **5b**.⁶ 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*⁵ 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.



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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- π -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- π -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 MoK α radiation and 4420 independent reflections were used for solving the structure by TEXSAN program (TEXSAN TEXRAY, Structure Analysis Package, Molecular Structure Corporation). Crystal data: C₁₉H₁₈N₂O₄S, FW=370.42, monoclinic, space group *P2₁/a*, *a*=21.718 (2) Å, *b*=8.581 (4) Å, *c*=9.680 (2) Å, β =90.87 (1)°, *V*=1803.7 Å³, *Z*=4, *D*_{calc}=1.364 g/cm³, *R*=0.043, *R*_w=0.049.

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