REACTION OF 1-PYRIDINIOTHIOBENZOYLAMINIDES WITH DIMETHYL ACETYLENEDICARBOXYLATE[1]

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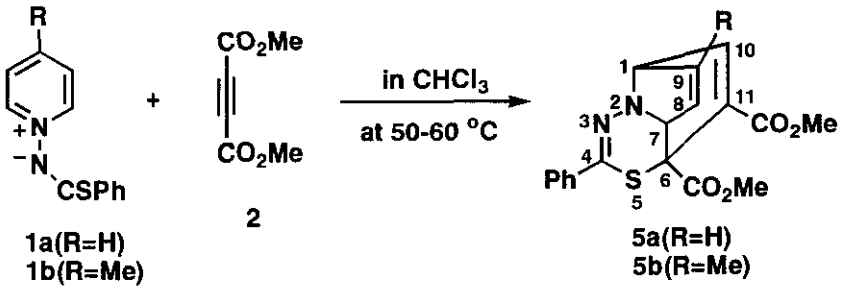
Abstract -- The reactions of 1-pyridiniothiobenzoylaminides with dimethyl acetylenedicarboxylate in chloroform at 50-60 °C provided dimethyl 5-thia-2,3-diazatricyclo[4.3.2.0^{2,7}]undeca-3,8,10-triene-6,11-dicarboxylate derivatives in moderate yields. The structures of these products were assumed by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

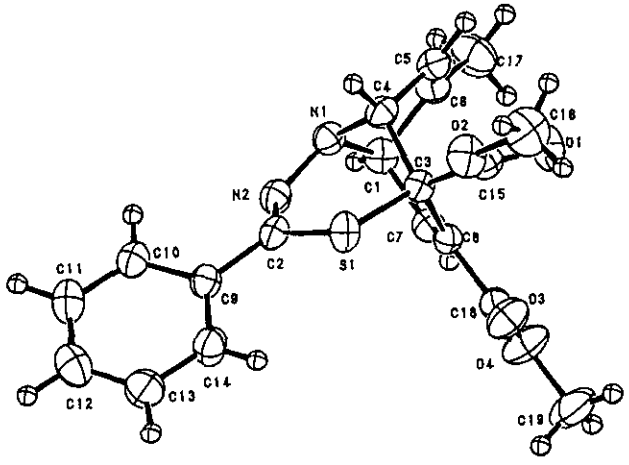
Recently, we have reported facile formations of 10a*H*-pyrido[1,2-*d*][1,4]thiazepines and their intramolecular Diels-Alder adducts from the reactions of 1-pyridinio(substituted thiocarbonyl)methylides with dimethyl acetylenedicarboxylate (DMAD).[2] We have also proved that this reaction is initiated 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-pyridiniothiobenzoylaminide (**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, 2xCO_2Me), 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, 2xCO_2Me), 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).

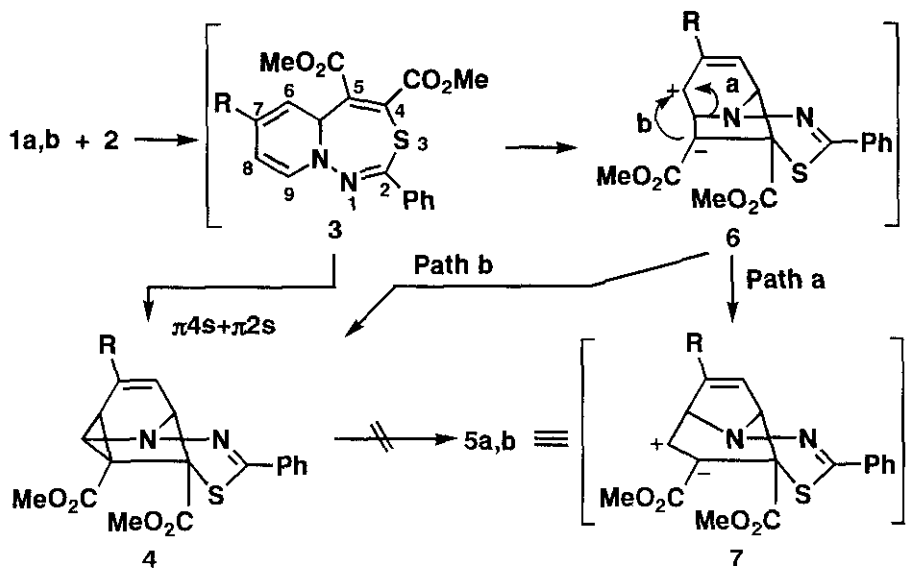


Although the elemental analyses showed clearly that products (**5a**,**b**) are 1 : 1 adducts between (1-pyridinio)thiobenzoylaminides (**1a**,**b**) and DMAD (**2**),[4] their ir and ^1H nmr spectra were quite different from the expected those for the primary adducts (**3**) and their intramolecular 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(sp^3)-C(sp^2)-C(sp^2)-C(sp^3)(-N*-)-C(sp^2)-, 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 alternative[5] 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 ±0.3% for C, H, and N) for **5a,b** were obtained.
5. The retro-di-π-methane rearrangement (vinylcyclopropane → 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 MoKα radiation and 4420 independent reflections were used for solving the structure by TEXSAN program (TEXSAN TEXRAY, Structure Analysis Package, Molecular Structure Corporation). Crystal data: $C_{19}H_{18}N_2O_4S$, FW=370.42, monoclinic, space group $P2_1/a$, a=21.718 (2) Å, b=8.581 (4) Å, c=9.680 (2) Å, β=90.87 (1) °, V=1803.7 Å^3, Z=4, D_{Calc}=1.364 g/cm^3, R=0.043, Rw=0.049.

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