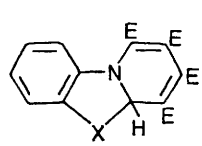
Structures of 2:1 Molar Adducts from Dimethyl Acetylenedicarboxylate with Thiazoles and Related Heterocycles

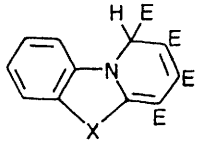
By PATRICK J. ABBOTT, R. MORRIN ACHESON,* ULLI EISNER, DAVID J. WATKIN,† and J. ROBERT CARRUTHERS†
(*Department of Biochemistry and †The Chemical Crystallography Laboratory, South Parks Road, Oxford* OX1 3QS)

Summary Thiazoles and related heterocycles with dimethyl acetylenedicarboxylate combine directly to give 1:2 molar adducts [*e.g.* (**12**)], and also two types of isomeric products which can be formed from the initial adducts by a [1,5] sigmatropic hydrogen shift [*e.g.* (**4**)] or by molecular rearrangement [*e.g.* (**11**)]; the structures were established by ^{13}C n.m.r. spectroscopy and for the pyridothiazoles (**11**) and (**12**) also confirmed by *X*-ray crystallography.

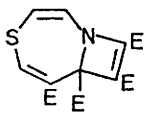
THE recent publication of Ogura *et al.*[1] on the reaction of dimethyl acetylenedicarboxylate with benzothiazole in methanol prompts us to report our findings with the same reaction but using a different work-up procedure (evaporation and warming the residue). This yielded a new 2:1 molar yellow fluorescent adduct (34% yield, m.p. 249—249·5°) together with small amounts of the previously reported[2] isomeric adduct (m.p. 234°). Unlike the latter compound, which has a single olefinic proton at τ 1·50 the new compound had a single proton at τ 3·77, similar to that of the corresponding benzoxazole[2] (τ 3·82) and 'yellow' *N*-methylbenzimidazole[3] (τ 3·74) adducts. The ^{13}C n.m.r. spectra of the last three adducts all showed high-field absorption (δ *ca.* 57) close to that of C-4 in tetramethyl 7,9-dimethyl-4*H*-quinolizine-1,2,3,4-tetracarboxylate (δ 65·5). In our earlier work the benzoxazole adduct had been formulated as (**1**)[2] and the 'yellow' *N*-methylbenzimidazole adduct as (**6**).[3] The new results indicate that the last two adducts and the new benzthiazole adduct are analogous. Structures (**1**)—(**3**) are hardly tenable, since for these the resonances due to the bridgehead hydrogen



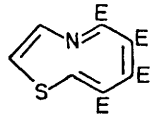
(1) X=O
(2) X=S
(3) X=NMe



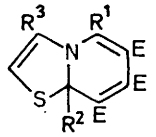
(4) X=O
(5) X=S
(6) X=NMe



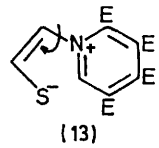
(7)



(8)



	R^1	R^2	R^3
(9)	E	H	H
(10)	H	E	H
(11)	Me	E	H
(12)	E	Me	Me



(13)

E = CO_2Me

and carbon atoms might be expected to change on altering the adjacent heteroatom. Structures (**4**), (**5**), and (**6**), respectively, are in accordance with the observed properties. They are presumably formed from the primary adducts (**1**)—(**3**) by a [1,5] sigmatropic hydrogen shift which can take place extremely easily.[4]

Reid *et al.*[5] noted that the n.m.r. spectra of the 1 : 2 molar adducts from thiazole (m.p. 150°), and its 2- (m.p. 163—164°) and 4-methyl derivatives (m.p. 226°) with dimethyl acetylenedicarboxylate, showed the hydrogen atom or methyl group corresponding to position 2 of the original thiazole at resonance positions suggesting attachment to sp^2 carbon atoms. They therefore assigned structures such as (**7**) or possibly (**8**) to these adducts, but were unable to decide between them. The resemblance of the u.v. spectra of these adducts to those of tetramethyl 9a*H*-quinolizine-1,2,3,4-tetracarboxylates had led us to prefer structures such as (**9**);[2] similarly, the corresponding benzothiazole[2] (m.p. 234°) and 'red' *N*-methylbenzimidazole[3] adducts (m.p. 173—174°) were formulated as (**2**) and (**3**), respectively, even though the chemical shifts (τ 1·5—1·9) of the bridgehead protons were not in good agreement with such structures. The ^{13}C n.m.r. spectra of the above adducts from the thiazoles and benzothiazole show the presence of an sp^3 carbon (δ *ca.* 75), similar to C-2 in 1,2-dimethylbenzothiazoline (δ 69·9), which eliminates structures such as (**8**). Moreover, the sp^3 carbon in the adduct from thiazole itself was tertiary, thus also eliminating (**9**), and, by analogy, the related structures (**2**) and (**3**). The data, however, are consistent with structures such as (**10**), which has now been established in the case of the 2-methylthiazole adduct (**11**) by *X*-ray crystallography. The formation of (**10**) from the isomeric (**9**), which is the expected primary reaction product, could take place by a [1,5] sigmatropic shift or *via* the intermediate vinyl sulphide (**13**), analogous to the stable phenanthridine 5-vinyloxides.[6] The n.m.r. spectra of the 4- and 5-mono- and 2,5-di-methylthiazole, the benzothiazole[2] (m.p. 234°) and 'red' *N*-methylbenzimidazole[3] (m.p. 173—174°) adducts show that they have analogous structures and must therefore have undergone a similar rearrangement.

2,4-Dimethylthiazole forms an adduct (m.p. 149—149·5°) with the acetylenic ester which has been assigned structure (**12**) on the basis of its ^1H n.m.r. spectrum.[5] The ^{13}C spectrum bears out this formulation (sp^3 carbon at δ 76·9) and the structure has now been confirmed by *X*-ray crystallography.

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