Communications to the Editor

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ADDITION REACTION OF 1,2,3-TRIAZINE 2-IMINES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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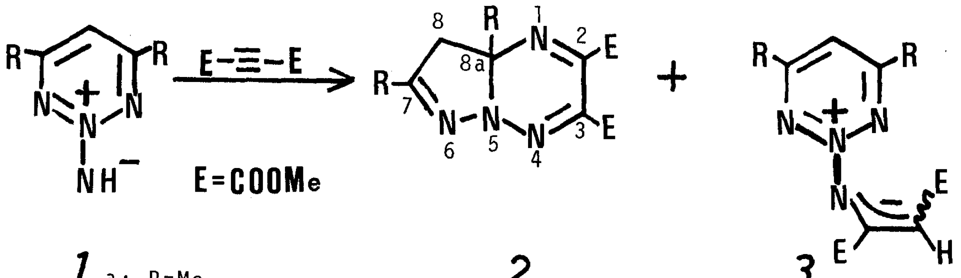
1,2,3-Triazine 2-imine reacted with dimethyl acetylenedicarboxylate to give adducts of a novel type (2,3-bis(carbomethoxy)-8,8a-dihydropyrazolo[2,3-b][1,2,4]triazines) which were considered to be formed from the primary 1,3-dipolar cycloadducts via a ring transformation.

KEYWORDS —— 1,2,3-triazine; 2-imino-1,2,3-triazinium ylide; 1,3-dipolar cycloaddition; ring transformation; Michael-addition; dimethyl acetylenedicarboxylate; N-ylide; cycloaddition; X-ray analysis

Although addition reactions of pyridine and pyridazine N-ylides with electron deficient olefins and acetylenes have been widely investigated,[1)] the reaction of N-ylides of 1,2,3-triazines has not previously been reported. We have prepared substituted 1,2,3-triazine 2-imines (1)[2)] and found that the reaction of 1 with dimethyl acetylenedicarboxylate (DAC) affords the rearranged cycloadducts (2) of a new type which is described in this paper.

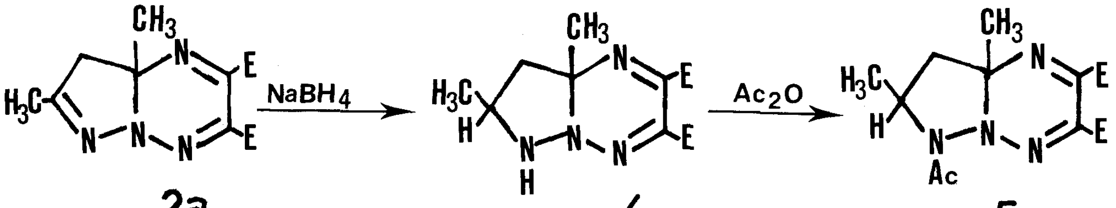


1 a: R=Me
b: R=Ph

	2 yield(%)	2 mp(°C)	3 yield(%)	3 mp(°C)
a	35	72-73	46	153-156(dec.)
b	64	201	18	178(dec.)

Chart 1

The imine (1a) was allowed to react with DAC in methylene chloride at room temperature for 0.5-2 h. The residue obtained after evaporation of the solvent was subjected to silica gel flash column chromatography (Et_2O) to give two crystalline products. The first product 2a was obtained as yellow plates (Et_2O-pentane), mp 72-73 °C. The PMR spectrum of the compound showed five signals at δ ($CDCl_3$) 1.29 (3H), 2.21 (3H), 3.16 (2H), 3.86 (3H), and 3.92 (3H), indicating the presence of four (singlet) methyl groups and one (singlet) methylene group. The IR spectrum (KBr) showed absorptions at 1744, 1705 (ester), 1609, and 1570 cm^{-1} (C=C and/or C=N). The mass spectrum of the product showed a fragmentation peak corresponding to the formula $C_5H_8N_2$ (high resolution mass spectrum) which was assignable to the  ion. When 2a was treated with sodium borohydride in methanol at room temperature for 5 min a crystalline dihydro product (4), mp 141-142 °C, was obtained. The PMR spectrum showed signals at δ (CD_3OD) 1.33 (3H, d, J=6 Hz), 1.36 (3H, s), 1.78 (1H, dd, J=12 and 10 Hz), 2.82 (1H, dd, 12 and 5 Hz), 3.77 (3H, s), 3.78 (3H, s), and 4.51 (1H, m). The signals at δ 1.78 and 2.82 suggest that 4 contains a methylene group whose geminal protons are not equivalent (J=12 Hz). The compound 4 afforded the acetamide derivative 5 (Ac_2O, room temperature, overnight, yield 86%), mp 159-160 °C.



2a 4 5

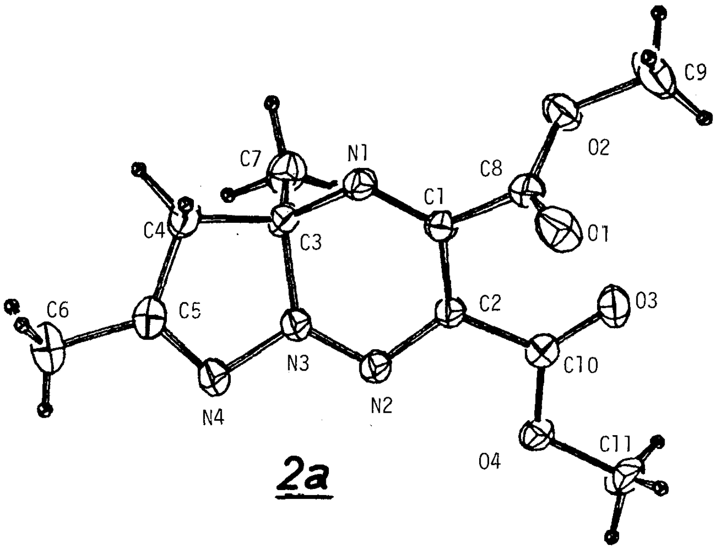
From these data the structure of 2a is proposed as 2,3-bis(carbomethoxy)-7,8a-dimethyl-8,8a-dihydropyrazolo[2,3-b][1,2,4]triazine. The structure was confirmed by a crystallographic study conducted as follows. X-Ray crystal analysis using CuKα radiation showed that the crystal 2a had a space group $P2_1/N$ and cell dimensions of a=13.717(6) Å, b=8.019(4) Å, c=13.152(6) Å, and β=113.75(2)°. The unit cell contained four molecules. The structure of the compound was determined by the direct method. The final R value for 1956 structure factors was 0.059, including anisotropic temperature factors for non-hydrogen atoms and isotropic factors for hydrogen atoms. The molecule geometry is shown in the figure on the next page.

The second product of the addition reaction was the Michael-adduct 3a, mp 153-156 °C, whose physical data were: PMR δ ($CDCl_3$) 2.31 (3H, s), 2.36 (6H, s), 3.72 (3H, s), 3.88 (3H, s), 6.18 (1H, s); IR (KBr) 1728, 1690, and 1550 cm^{-1}. The Michael-adduct, 3a, was not a precursor of the cycloadduct 2a because the former in solution did not give the latter when 3a was subjected to the conditions which provided 2a. The reaction of the 1b with DAC also gave similar adducts in the yields shown in Chart 1.$^{3)}$

Thus, it was found that the reaction of 1,2,3-triazine 2-imines with DAC afforded the unexpected adducts 2 which were probably formed via the primary adduct 6. Two mechanisms might be conceivable for the formation of the compound 2 from 6, the discriminative experiments presently being under consideration (Chart 2).

O1	-C8	1.198 (5)
O2	-C8	1.320 (4)
O2	-C9	1.461 (7)
O3	-C10	1.203 (5)
O4	-C10	1.328 (4)
O4	-C11	1.457 (6)
N1	-C1	1.298 (6)
N1	-C3	1.461 (5)
N2	-N3	1.295 (5)
N2	-C2	1.333 (5)
N3	-N4	1.396 (5)
N3	-C3	1.498 (4)
N4	-C5	1.293 (7)
C1	-C2	1.439 (5)
C1	-C8	1.498 (5)
C2	-C10	1.474 (6)
C3	-C4	1.536 (7)
C3	-C7	1.516 (6)
C4	-C5	1.502 (5)
C5	-C6	1.495 (8)

Bond lengths in Å



2a

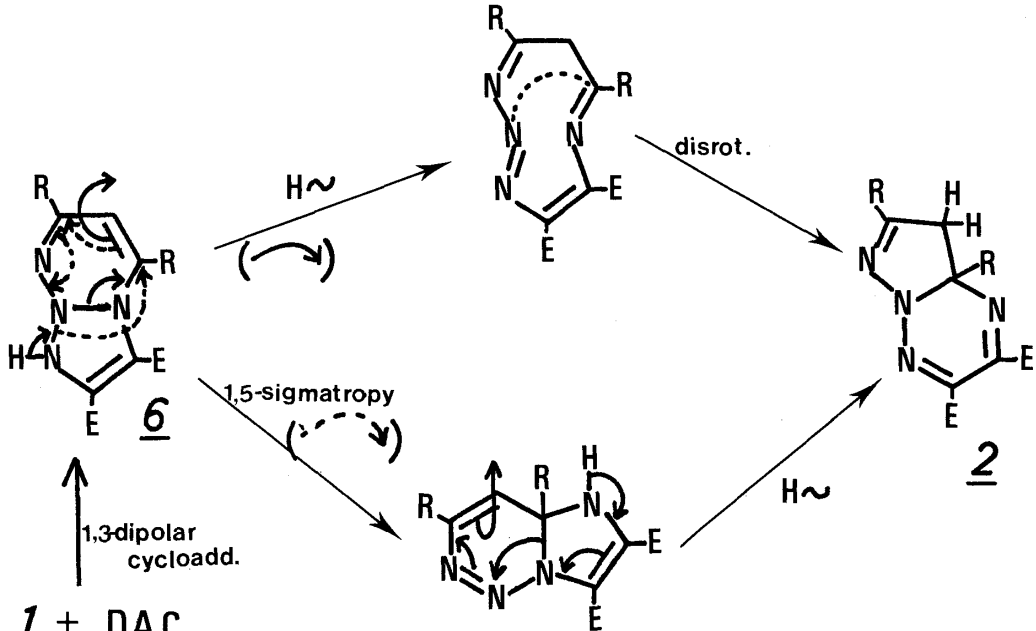


Chart 2

REFERENCES AND NOTES

1)For example, R.M. Acheson and N.F. Elmore, "Advances in Heterocyclic Chemistry," Vol.23, ed. by A.R. Katritzky and A.J. Boulton, Academic Press, New York, 1978, p. 263 and references cited therein.

2)The ylides 1 have been obtained from 1,2,3-triazines by the treatment with O-mesitylenesulfonylhydroxylamine followed by a neutralization with potassium carbonate. The 1-imine (regio isomer) was not obtained by this procedure. See H. Ohnishi, A. Ohsawa, H. Arai, Y. Abe, and H. Igeta, Heterocycles, 16, 163 (1981). Compound 1a was shown to exist in the monomeric form (osmometry in $CHCl_3$ presented the MW 116, vs. calcd MW 124). Synthesis and character of the compounds will be described in a full paper.

3)The reaction of 4-methyl-6-phenyl-1,2,3-triazine 2-imine with DAC afforded two adducts of type 2 which were distinguished from each other by the substitution position of the methyl and phenyl groups. The data were omitted in the present communication and will be described in a full paper.

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