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REACTION OF 1,2,3-TRIAZINE WITH DIENOPHILES

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Reactions of 4,6-dimethyl-1,2,3-triazine with electron rich acetylenes and acetylene equivalents at 180°C gave the mixtures of 2,4- and 2,6-dimethylpyridine derivatives. The formation of the latter products suggests the participation of the azete compound as the key intermediate.

KEYWORDS —— 1,2,3-triazine; inverse electron demand Diels-Alder reaction; azete (azacyclobutadiene); electron rich dienophile

Monocyclic 1,2,3-triazines[1] have high reactivity with nucleophiles. For example, by treating them with aqueous KOH at room temperature, their 4-positions are easily attacked by the hydroxide ion to give ring opening products (Chart 1).[2]

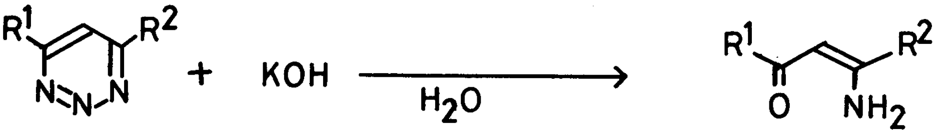

Chart 1

This type of nucleophilic attack seldom occurs in other azines or diazines, thus it appears that 1,2,3-triazines are highly electron deficient. On the other hand, they have a tendency to lose nitrogen molecules when heated[3] or on electron impact.[4]

Here we wish to report the reactivity of the 1,2,3-triazine with dienophiles, and the existence of azete (azacyclobutadiene, 4) as the reaction intermediate.

4,6-Dimethyl-1,2,3-triazine (1) (1 mmol) was adopted as a starting material, and was heated with an electron rich dienophile (4 mmol) in a sealed tube at 180°C for 1 h (Chart 2). The Table shows the yields of pyridines in the reaction by each dienophile. The relative yields of both pyridines (2 and 3) indicate that the inverse electron demand Diels-Alder reactions[5] occurred in this system. Although

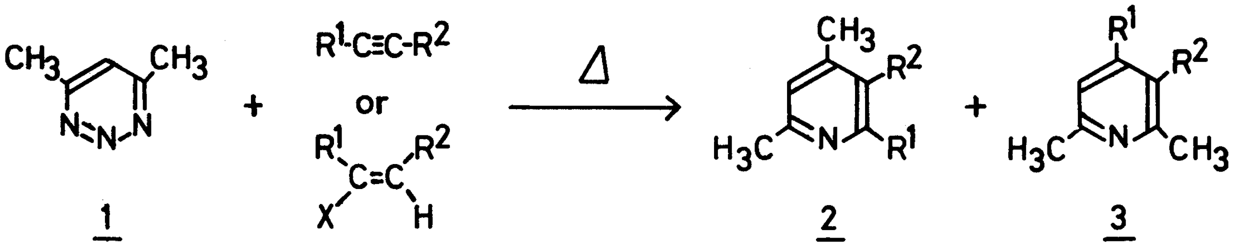

Chart 2

Table

Entry	Dienophile	Yield of (2)	Yield of (3)
1	$CH_3-C{\equiv}C-NEt_2$ $(R^1{=}NEt_2, R^2{=}CH_3)$	50 %	3 %
2	$C_6H_5-C{\equiv}C-H$ $(R^1{=}C_6H_5, R^2{=}H)$	38 %	6)
3	$CH_2{=}CHSOC_6H_5$ 7) $(R^1{=}R^2{=}H, X{=}SOC_6H_5)$	35 %	Trace
4	$CH_2{=}C(OEt)_2$ $(R^1{=}OEt, R^2{=}H, X{=}OEt)$	4 %	31 %
5	$H-C{\equiv}C-COOEt$ $(R^1{=}H, R^2{=}COOEt)$	0	0

2,4-dimethylpyridines (2) are the normal products of these reactions (Chart 3), 2,6-dimethylpyridines (3) were also obtained unexpectedly. Especially, when 1 was heated with ketene diethylacetal, 2,6-dimethylpyridine derivative was the major product (Table, Entry 4). The formation of both 2,4- (2) and 2,6-dimethyl derivatives (3) are explained by the azete intermediate (Chart 4, 4), while the latter formation can't be elucidated by the direct Diels-Alder type additions between 1 and the dienophiles (Chart 3). In fact, the triazine was decomposed and an evolution of nitrogen gas was observed even when it was heated at 180°C in the absence of the dienophile. Thus, it appears that the formation of the azete, followed by the addition from the (A) or (B) side (Chart 4) produces 2,4- or 2,6-dimethylpyridines respectively. Since very little is known about the properties of monocyclic azete,8) our reaction system may be useful to probe its characteristics. Moreover, since 1,2,3-triazines function as electron deficient dienes, it may be possible for them to synthesize various pyridine derivatives.

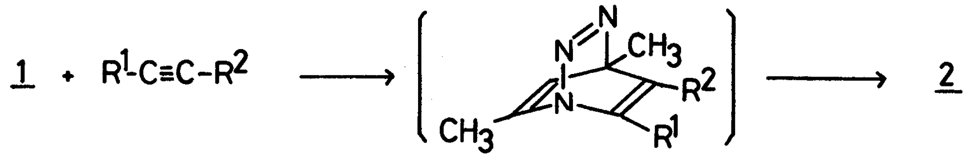

Chart 3

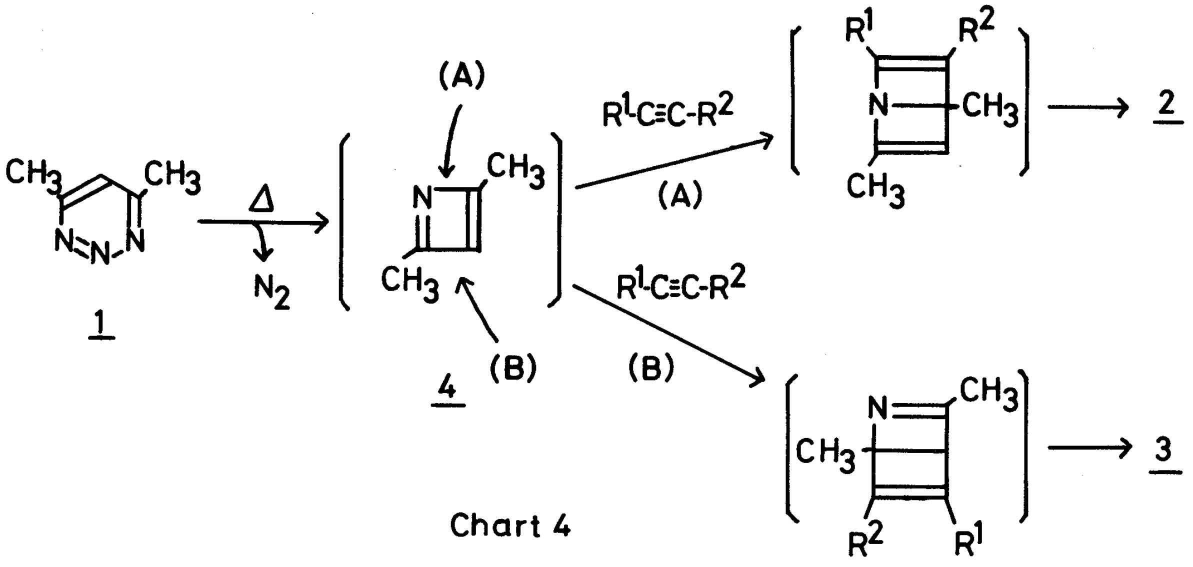

Chart 4

REFERENCES AND NOTES

1) A. Ohsawa, H. Arai, H. Ohnishi, and H. Igeta, J. Chem. Soc., Chem. Commun., 1981, 1174.

2) Unpublished data.

3) By flash vacuum thermolysis, 1,2,3-triazines afforded acetylenes and nitriles.

4) Dominant peak was $[M-N_2]^+$ instead of M^+ in EI-MS of 1,2,3-triazines.

5) D.L. Boger, Tetrahedron, 39, 2869 (1983).

6) Although the isomer was detected by GC-MS, the positions of the substituents were not determined.

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