CYCLOADDITION REACTIONS OF 7-SUBSTITUTED ACENAPHTHO[1,2-*d*]PYRAZOLO[1,2-*a*]BENZOTRIAZOLES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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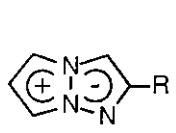
Abstract - The reactions of the title 7-phenyl- and 7-methylacenaphtho-pyrazolobenzotriazoles (triazapentalenes) with dimethyl acetylene-dicarboxylate gave a mixture of the corresponding initial azomethine imidic cycloadduct and its isomeric pyrazinopyrimidine, whose yields greatly depended on the reaction conditions. Structures of both the initial and isomeric products were determined by X-ray crystallographic analyses. The initial cycloadduct readily isomerized to the pyrazinopyrimidine. It has been found that the methyl-substituted pyrazinopyrimidine underwent the Micheal-type addition reaction.

Heteropentalenes characterized by the presence of two nitrogen atoms at the bridged positions are betainic aromatic compounds which are isoconjugate with the pentalenyl dianion, and belong to class B in Ramsden's classification.[1] These compounds are intrinsically interesting, particularly from the point of view of their electronic structure and their participation in 1,3-dipolar cycloaddition reactions. The pyrazolo[1,2-*a*][1,2,3]triazole (1,3a,6a-triazapentalene[2]), a heteropentalene of Ramsden's class B, may be behaved as both azomethine ylide and azomethine imine 1,3-dipole. It is known that bicyclic 1,3a,6a-triazapentalene system (**1**) (R=Me, Ph)[3] undergoes cycloaddition with dimethyl acetylenedicarboxylate (DMAD) onto the azomethine ylide



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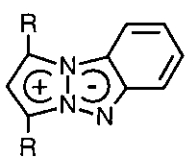

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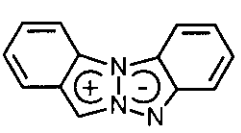

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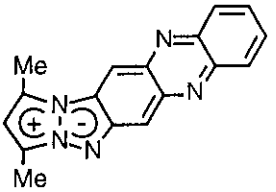

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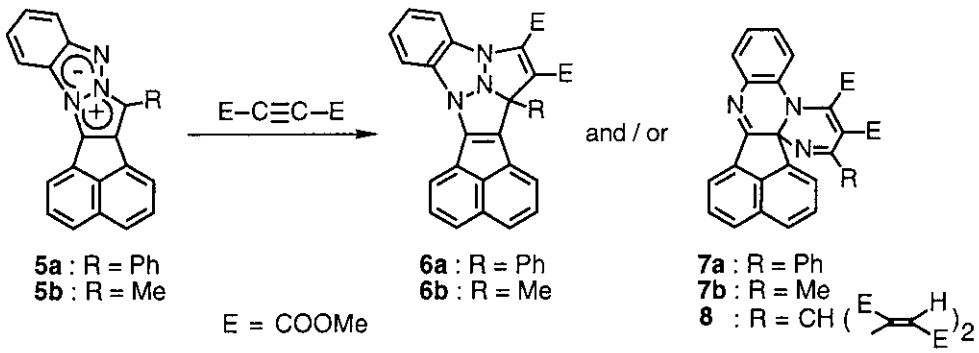
moiety, whereas dimethyl-substituted 2,3-benzo-fused tricyclic (**2**) (R= Me)[4] and 2,3-and 4,5-dibenzo-fused tetracyclic 1,3a,6a-triazapentalene (**3**)[5] react exclusively at the azomethine imine moiety; however, the azomethine imidic cycloadduct from **3** is thermally stable, but that from **2** spontaneously decomposes. On the other hand, the reactions of unsubstituted **2** (R=H)[6] and 2,3-phenazine-ring fused pentacyclic 1,3a,6a-triazapentalene (**4**)[7] with DMAD are somewhat complex: **2** gave a complex mixture containing an azomethine imidic cycloadduct and Micheal adduct at 4-position,[8] whereas **4** gave a mixture of azomethine ylidic cycloadduct and its isomeric pyrazinopyrimidine compound derived from an initial attack of DMAD at 1-position.[8]

Thus, a slightly structural change in 1,3a,6a-triazapentalene systems sensitively affected not only on the periselectivty, but also on the stability of cycloadduct. In addition, the reaction of 1,3a,6a-triazapentalene fused a ring other than benzo-ring at 4,5-position with DMAD has not been investigated yet. It therefore appeared of interest to investigate the periselectivity of cycloaddition of a novel 1,3a,6a-triazapentalene system in which condensed a cyclopentadiene ring in place of 4,5-benzo ring in **3** and the stability of product(s).

In this paper we would like to report the reaction of 7-phenyl- and 7-methylacenaphtho[1,2-*d*]pyrazolo[1,2-*a*]benzotriazoles[9] (hereafter abbreviated as 7-phenyl- (**5a**) and 7-methyltriazapentalenes (**5b**), respectively), hexacyclic triazapentalenes, with DMAD as the study along this line.

The reaction of 7-phenyltriazapentalene (**5a**) with DMAD was first investigated under various conditions (Scheme 1, Table 1). Although the reaction of **5a** with a slight excess of DMAD in *m*-xylene under reflux for 5 h gave no adducts, in the reactions using excess DMAD two 1:1 adducts, (**6a**) (mp 230 °C) and (**7a**) (mp 226-227 °C) as both red prisms, whose relative yields depended on the reaction conditions, were formed. The yield of **7a** increased by the decreased yield of **6a** meaning that **6a** isomerized to **7a**.



Scheme 1

7-Methyltriazapentalene (**5b**) was more reactive to DMAD than **5a**. The reaction using a slight excess of DMAD in chloroform even at 25 °C afforded a good yield of 1:1 adduct (**6b**) (mp 164-165 °C) as red prisms. In the same reaction in THF under reflux, another 1:1 adduct (**7b**) (mp 210-211 °C) as red prisms was formed together with **6b**, and a prolonged reaction time resulted in an increase in the yield of **7b**. The cycloaddition in chloroform proceeded faster than that in THF or *m*-xylene. Thus, the cycloaddition reaction appears to be a non-concerted process. Such a solvent effect has been also observed in cycloaddition reactions of other triazapentalenes with DMAD.[6,7] On the other hand, the reaction using an excess of DMAD in refluxing THF for 2 days gave **7b** along

Table 1. Reactions of Triazapentalenes (**5**) with DMAD

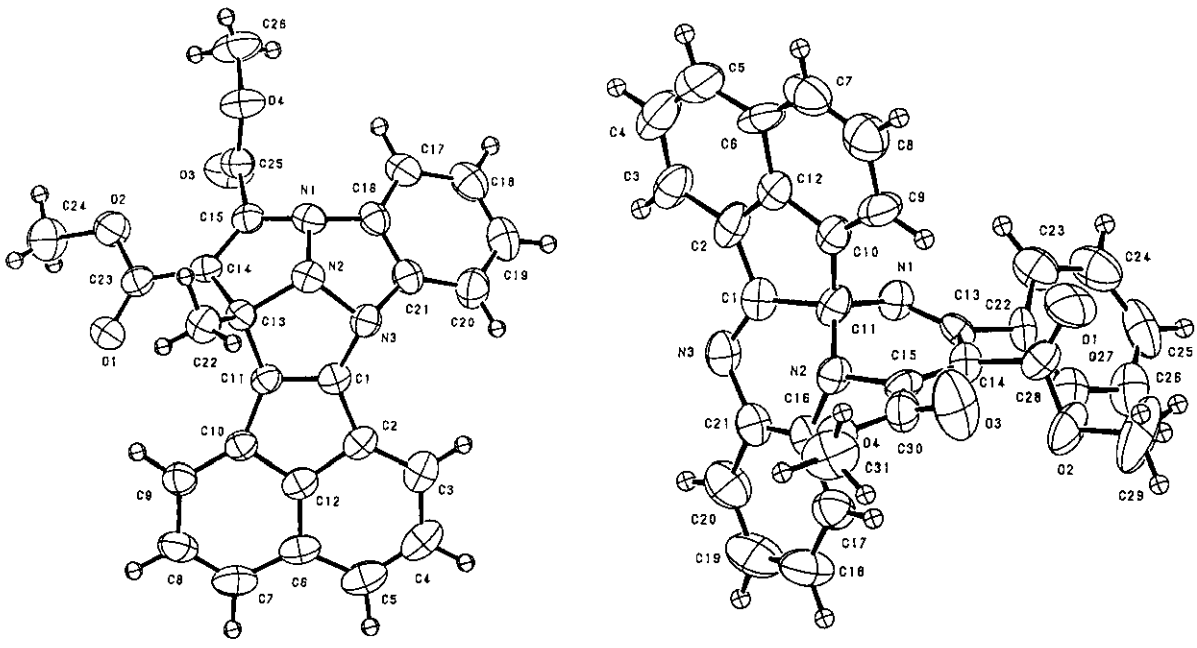
Entry	**5**	DMAD/**5**	Reaction conditions			Products/%		
		mol/mol	Solvent	Temp/°C	Time/h	**6**	**7**	**8**
1[a)]	**5a**	1.1	*m*-Xylene	reflux	5	-	-	-
2[a)]	**5a**	3.1	THF	reflux	60	trace	5	-
3	**5a**	3.0	*m*-Xylene	reflux	3.5	10	60	-
4	**5a**	3.0	*m*-Xylene	reflux	5	-	79	-
5	**5b**	1.2	$CHCl_3$	25	24	72	-	-
6	**5b**	1.2	THF	reflux	10	46	23	-
7	**5b**	1.2	THF	reflux	42	-	78	-
8	**5b**	3.1	THF	reflux	48	-	60	10
9	**5b**	3.5	*m*-Xylene	reflux	12	-	-	68

a) **5a** was recovered in 90 and 82% in Entries 1 and 2, respectively.

with a new 1:3 adduct (**8**) (mp 291-292 °C (decomp.)), which was the sole isolated product in *m*-xylene under reflux (Table 1).

The above results indicate that the initial adduct (**6b**) isomerizes to **7b**, which further reacts with DMAD to give **8**: In fact, the initial adduct (**6b**) readily isomerized thermally or photochemically to **7b**, and the reaction of **7b** with two equivalents of DMAD gave **8** as mentioned below (Scheme 2).

As spectroscopic data did not allow us unequivocally to assign the structures of both the 1:1 adducts (**6**) and (**7**),[10] X-ray crystallographic analyses were carried out. It could be thus determined that the initial adduct (**6**) is

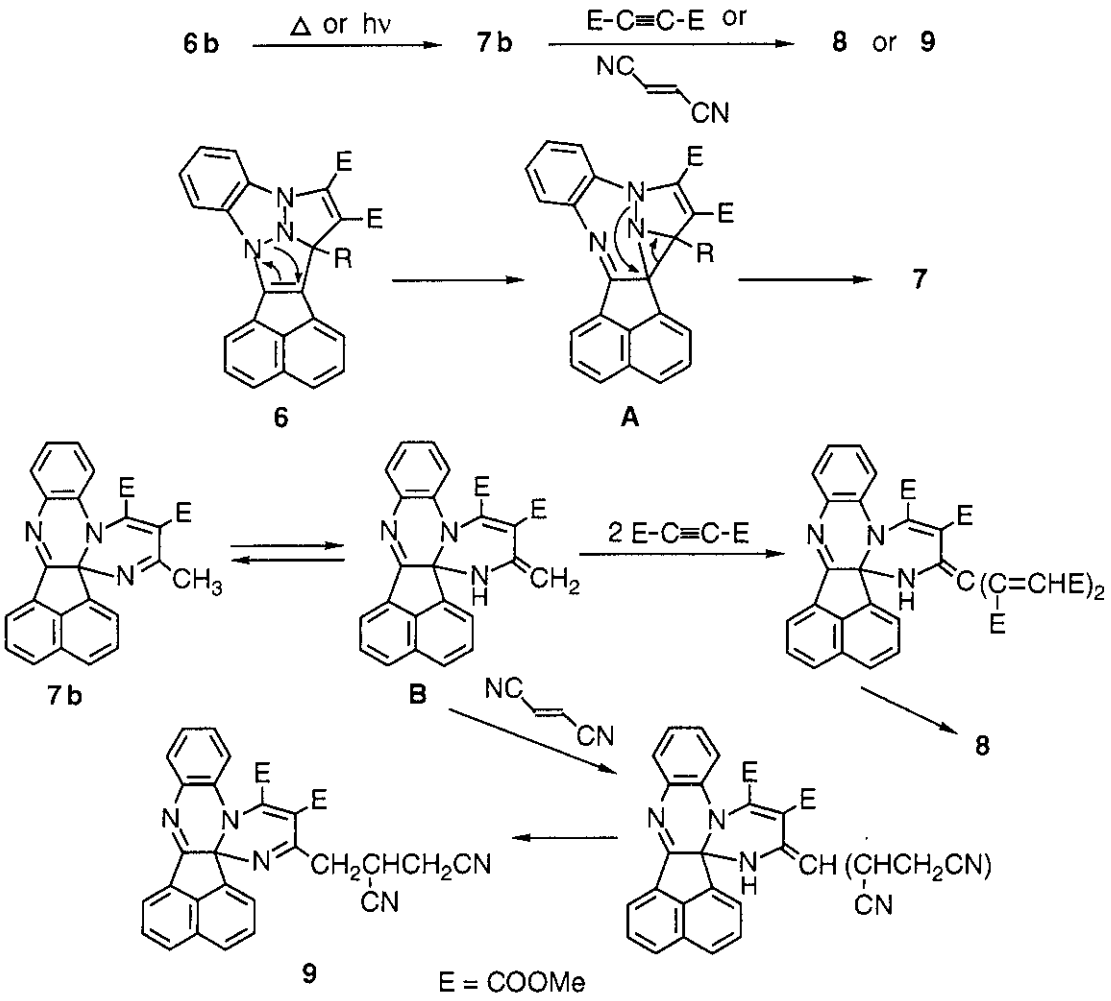


6b **7a**

Figure 1. ORTEP drawings of **6b** and **7a**

the [3+2] cycloadduct across the azomethine imine 1,3-dipole of **5**, whereas **7** is the isomeric pyrazinopyrimidine ring system. ORTEP drawings of **6b** and **7a** are shown in Figure 1.[11]

On heating in refluxing *m*-xylene for 10 h or irradiation with a 100-W high pressure mercury lamp in benzene at 25 °C for 2 h **6b** converted into **7b** in 83 and 90% yields, respectively. The pathway of novel rearrangement of **6** to **7** was tentatively deduced as illustrated in Scheme 2: The initial cycloadduct (**6**) undergoes 1,3-sigmatropic shift to form an aziridine intermediate (**A**) followed by concurrent cleavages of C-C and N-N bonds to evolve the stable pyrazinopyrimidine (**7**). Although the formation of analogous pyrazinopyrimidine compound[12] *via* a betaine intermediate followed by twice N-N bond cleavages has been reported in the reaction of triazapentalene (**4**) with DMAD,[7] the two ester groups are located at 9- and 9a-positions in the pyrazinopyrimidine ring.[12] However, the two ester groups in **7** are situated at 3- and 4-positions of pyrazinopyrimidine moiety. Thus, the formation path for **7** apparently differs from that for the pyrazinopyrimidine from **4**.



Scheme 2

Contrary to **6**, the azomethine imidic cycloadduct of **3** having benzo ring in place of a cyclopentadiene ring of **6** is thermally stable. In the azomethine imidic cycloadduct of **3** a 1,3-sigmatropic shift to an aziridine intermediate such as **A** will be difficult because of the loss of aromaticity of benzo ring: This seems to be attributable to its greater stability.

The reaction of **7b** with two equivalents of DMAD in *m*-xylene under relux for 10 h afforded **8**[13] in 63% yield. This reaction can be reasonably understood as the Michael-type addition reaction via a key intermediate, enamine tautomer (**B**) of **7b**, as illustrated in Scheme 2. The participation of **B** was also strongly supported by the reaction of **7b** with fumaronitrile giving the Michael-type adduct (**9**)[14] (Scheme 2).

REFERENCES AND NOTES

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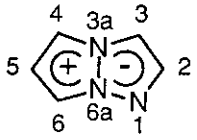
2. The triazapentalene nomenclature is empolyed and the following numbering system is adopted in this paper.



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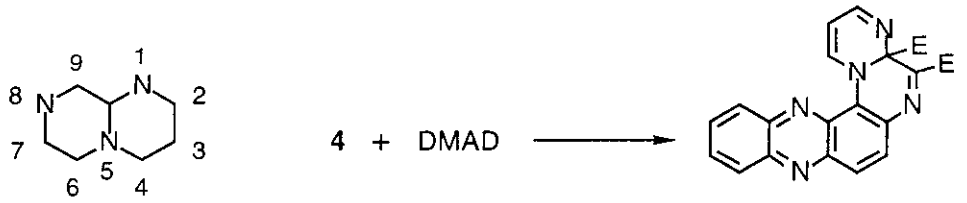
6. A. Albini, G. Bettinetti, and G. Monoli, J. Org. Chem., 1984, **49**, 2670.
7. A. Albini, G. F. Bettinetti, G. Minoli, and R. Oberti, J. Chem. Res. (M), **1980**, 4801; J. Chem. Res. Synop., **1980**, 404.
8. The position is indicated by the numbering of triazapentalene ring shown in ref. 2.
9. The triazapentalenes, (**5a**) and (**5b**), were prepared by reductive cyclization of the corresponding 3-substituted 1-(o-nitrophenyl)acenaphtho[1,2-d]pyrazoles (J. Heterocycl. Chem., 1994, **31**, 1283).
10. All the new compounds in this paper gave satisfactory elementary analyses. The spectral data of **6b** and **7b** are shown as selected ones. **6b**: Ir (KBr) 1746, 1702 cm^{-1}, ^1H nmr ($CDCl_3$) δ=2.06, 3.80, 3.90 (each 3H, s), 6.96-7.93 (10H, m); ^{13}C nmr ($CDCl_3$) δ=24.49, 51.81, 53.02, 114.88, 115.19, 122.38, 123.41, 125.01, 125.89, 126.23, 126.74, 127.50, 128.13, 128.63, 129.07, 131.72, 131.89, 137 05, 140.93, 147.31, 151.38, 161.48, 163.29; ms m/z 437 (M^+). **7b**: Ir (KBr) 1727 cm^{-1}; ^1H nmr (DMSO-d_6) δ=2.03, 3.91, 4.00 (each 3H, s), 6.69-8.27 (10H, m); ^{13}C nmr (DMSO-d_6) δ=21.41, 53.42, 53.89, 73.32, 115.66, 118.62, 120.65, 123.37, 126.54, 128.20, 129.00, 129.26, 130.38, 131.81, 132.20, 133.45, 135.26, 137.70, 157.42, 162.39, 162.97, 164.91; ms m/z 437 (M^+).
11. X-Ray crystallographic analyses were carried out on a Rigaku AFC5S diffractometer. The diffraction data were collected with the use of MoKα radiation and 5304 (for **6b**) and 4867 (for **7a**) independent reflections

were used the structures by the TEXSAN Program (TEXSAN TEXRAY, Structure Analysis Package, Molecular Structure Corporation), respectively. Crystal data for **6b**: $C_{26}H_{19}N_3O_4$ + 1/2C_6H_6 (benzene), F.W.=476.51, triclinic, space group P1 (#2), a=10.208(3)Å, b=13.822(3)Å, c=8.620(6)Å, α=97.53(3)°, β=92.84(4)°, γ=73.85(2)°, V=1158.0(9)Å^3, Z=2, Dcalc=1.367g/cm^3, μ(MoKα)=0.86 cm^{-1}, R=0.051, Rw=0.056. Crystal data for **7a**: $C_{31}H_{21}N_3O_4$, F.W.=499.52, monoclinic, space group $P2_1/c$ (#14), a=10.63(1)Å, b=16.652(2)Å, c=16.017(5)Å, β=108.43(4)°, V=2522(3)Å^3, Z=4, Dcalc=1.316g/cm^3, μ(MoKα)=0.83 cm^{-1}, R=0.052, Rw=0.052. The structure of **7b** was also determined by crystallographic analysis.

12. The numberring of pyrazinopyrimidine ring and the pyrazinopyrimidine[7] obtained from the reaction of **4** with DMAD are as follows.



13. **8**: Ir (KBr) 1744, 1702 cm^{-1}; ^{1}H nmr (CD_3CN) δ=3.49, 3.63, 3.72, 3.81, 3.84, 3.97 (each 3H, s), 4.15 (1H, s,), 5.22, 6.06 (each 1H, s), 6.50-7.13 (4H, m), 7.45-7.96 (6H, m); ^{13}C nmr (DMSO-d_6) δ=51.41, 52.12, 52.27, 52.42, 53.26, 60.42, 72.16, 79.69, 91.09, 97.64, 100.59, 111.42, 118.19, 119.13, 119.77, 120.44, 125.01, 126.46, 126.87, 128.74, 129.07, 130.05, 132.90, 138.21, 139.02, 139.79, 140.21, 141.90, 163.06, 163.29, 163.96, 166.36, 168.45, 170.81; ms m/z 721 (M^+).

14. The reaction of **7b** with 1.4 equivalents of fumaronitrile in refluxing *m*-xylene for 31 h afforded **9** (mp 225-226 °C (decomp.)) as orange needles, in 27% yield. **9**: Ir (KBr) 2256, 1740 cm^{-1}; ^{1}H nmr (CD_3CN) δ=2.31-3.28 (5H, m), 3.93, 3.99 (each 3H, s), 6.78-8.26 (10H, m); ms m/z 515 (M^+).

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