CHEMISTRY LETTERS, pp. 763-766, 1983.

CYCLOADDITION REACTION OF IMIDAZO[1,2-c]THIA^{IV}ZOLE TO ACETYLENIC DIPOLAROPHILES AND NOVEL CONVERSION OF CYCLOADDUCTS INTO 4,9c-DIAZAPENTALENO[1,6a,6 : ab]NAPHTHALENES

Otohiko TSUGE,* Shuji KANEMASA, and Takayoshi HAMAMOTO
Research Institute of Industrial Science, and Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences,
Kyushu University, Kasuga, Kasuga-shi, Fukuoka 816

A nitrogen-bridged tetravalent sulfur compound, 1,3,6-triphenylimidazo[1,2-c]thia^{IV}zole, reacts with several acetylenic dipolarophiles giving excellent yields of regio- and periselective [3 + 2] cycloadducts to the azomethine ylide 1,3-dipole of the thia^{IV}zole. These cycloadducts undergo, in the presence of triethylamine, a rare desulfurization and a subsequent 10π cyclization yielding the derivatives of a new heterocyclic system, 4,9c-diazapentaleno[1,6a,6 : ab]-naphthalene.

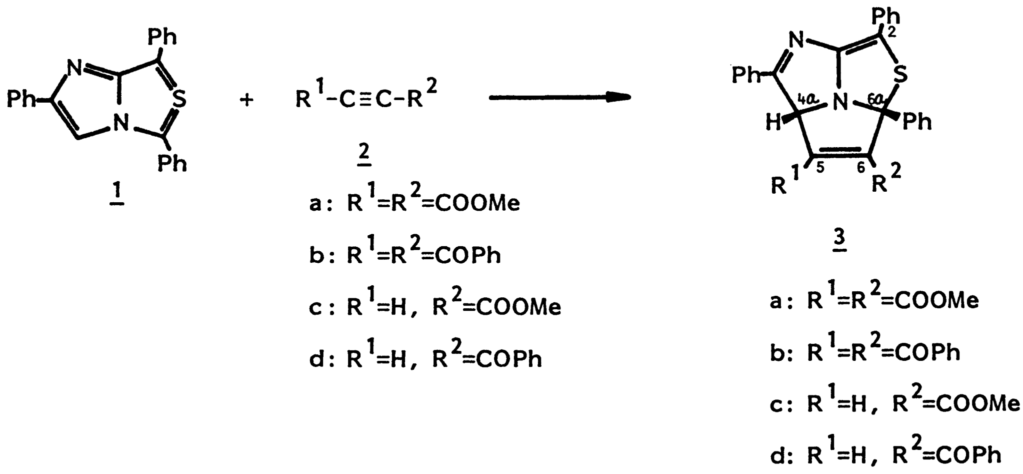
Two kinds of 1,3-dipolar forms, an azomethine ylide and a thiocarbonyl ylide, are masked along the periphery of 1,3,6-triphenylimidazo[1,2-c]thia^{IV}zole 1. A biperifunctional character of 1 has been first demonstrated in the cycloaddition reaction to N-(p-tolyl)maleimide whose cycloadduct to the azomethine ylide of 1 changes into that to the thiocarbonyl ylide through a retro 1,3-dipolar cycloaddition reaction.[1] As a succeeding study, several examples for the cycloaddition reaction of 1 to olefinic dipolarophiles have been investigated: The imidazo[1,2-c]thia^{IV}zole 1 undergoes a stereospecific cycloaddition reaction to symmetrically substituted olefins across the both ylides,[2] and a regio- and periselective cycloaddition reaction to unsymmetrically substituted olefins across the thiocarbonyl ylide.[3]

So far there are two similar systems known, a thia^{IV}zolo[3,4-b]indazole[4] and pyrrolo[1,2-c]thia^{IV}zole,[5] whose cycloaddition reaction affords the cycloadducts of different types depending upon the nature of dipolarophiles used. Thus, an acetylenic dipolarophile (dimethyl acetylenedicarboxylate) reacts across the azomethine imine (or ylide) 1,3-dipole, whereas an olefinic dipolarophile (N-phenylmaleimide) prefers the thiocarbonyl ylide.

In the present communication, we would like to show the cycloaddition reaction of 1,3,6-triphenylimidazo[1,2-c]thia^{IV}zole 1 to some acetylenic dipolarophiles giving the regio- and periselective [3 + 2] cycloadducts to the azomethine ylide 1,3-dipole of 1, and the novel conversion of the cycloadducts through a desulfurization and 10π cyclization leading to a new heterocyclic system, 4,9c-diazapentaleno[1,6a,6 : ab]naphthalene.

Cycloaddition Reaction of 1,3,6-Triphenylimidazo[1,2-c]thia^{IV}zole 1 to Acetylenic Dipolarophiles 2.

The reaction of 1 with an equivalent amount of dimethyl acetylenedicarboxylate 2a in dry benzene, at room temperature for 24 h in a nitrogen atmosphere, gave the red 1:1 adduct 3a[6] in 98 % yield



Scheme 1

(Scheme 1). The structure of 3a was assigned as 5,6-bis(methoxycarbonyl)-2,4,6a-triphenyl-4a,6a-dihydro-1-thia-3,6b-diazacyclopenta[cd]pentalene, the cycloadduct to the azomethine ylide of 1, on the basis of the spectral data shown in Table 1. The ^{1}H-NMR spectrum shows a methine singlet at 5.72 ppm and the ^{13}C-NMR spectrum exhibits a methine (73.33 ppm) and a quaternary carbon (86.67 ppm). A low stretching vibration of ester carbonyls (1720 cm^{-1}) indicates that the both ester groups are conjugated, ruling out the 6,6a-dihydro structure.

A similar reaction between 1 and dibenzoylacetylene 2b under reflux in benzene for 1 h afforded the [3 + 2] cycloadduct 3b in 88 % yield (Table 1).

As mentioned above the thiocarbonyl ylide of 1 cycloadds to olefinic dipolarophiles in a highly regioselective manner.3) However a regioselectivity of the azomethine ylide of 1 in the cycloaddition reaction to unsymmetrical dipolarophiles is unknown.

Table 1. Cycloadducts of 1,3,6-Triphenylimidazo[1,2-c]thia$^{\text{IV}}$zole 1 to Acetylenic Dipolarophiles 2.

	Yield	mp	$\nu_{C=O}$	^{1}H-NMR [δ ppm]$^{a,b)}$			^{13}C-NMR [δ ppm]$^{a,c)}$					M^+
	[%]	[°C]	[cm^{-1}]	4a-H	5-R^1	6-R^2	2-C	2a-C	4-C	4a-C	6a-C	[m/e]
3a	98	192-194	1720	5.72s	3.41s Mc	3.75s Mc	107.79s	170.66s	155.00s	73.33d	86.67s	494
3b	88	179-181.5	1640	6.31s	- Bz	- Bz	108.26s	172.61s	156.57s	75.44d	89.29s	586
3c	78	185-187	1720	5.42d J_{4a-5}=1.2 Hz	7.01d H	3.62s Mc	107.21s	171.13s	155.52s	72.68d	86.00s	436
3d	87	199-200.5	1640	5.52d J_{4a-5}=2.0 Hz	6.53d H	- Bz	108.03s	171.84s	155.81s	73.21d	87.83s	482

a) Measured in $CDCl_3$.

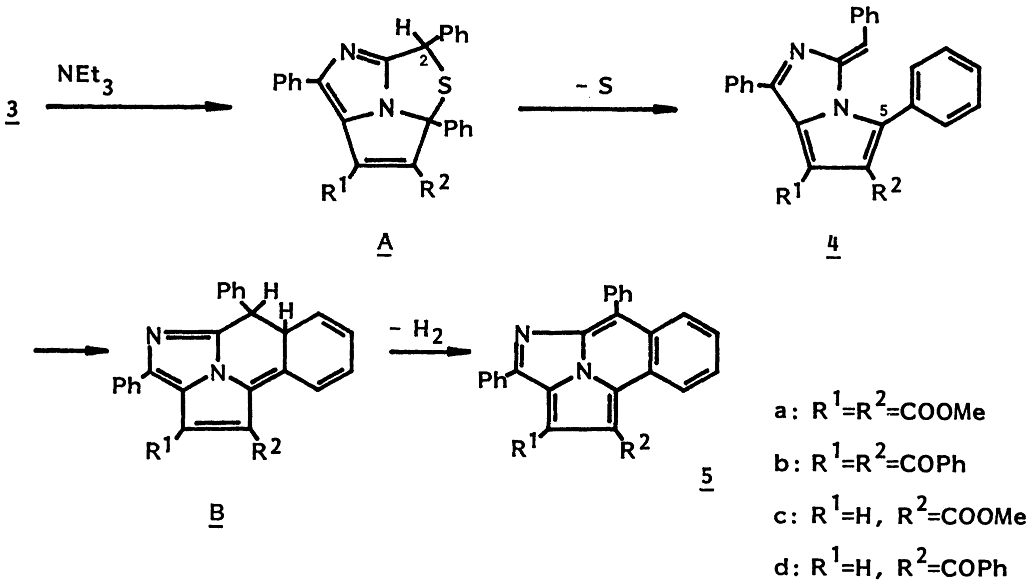
b) Mc: methoxycarbonyl; Bz: benzoyl

c) The carbonyl carbons are observed as follows: 3a: 162.28 and 165.03; 3b: 192.63 and 194.27; 3c: 162.80; 3d: 192.21 ppm.

The reactions of 1 with methyl propiolate 2c (under reflux in benzene for 2 h) and benzoylacetylene 2d (at room temperature for 24 h) gave the similar [3 + 2] cycloadducts 3c (78 %) and 3d (87 %) as the single products, respectively. The regiochemistry was determined as shown in Scheme 1 on the basis of the vicinal couplings between the 4a-H and 5-H (Table 1). These small coupling constants are consistent with the values estimated from a dihedral angle of the two hydrogens.[7] A high regioselectivity of the azomethine ylide of 1 was again observed in the carefully controlled reaction of 1 with acrylonitrile.[8]

Conversion of Cycloadducts 3 into 4,9c-Diazapentaleno[1,6a,6 : ab]naphthalenes 5.

Unlike the cycloadducts of olefinic dipolarophiles to the azomethine ylide of 1, all the cycloadducts 3 obtained above did not isomerize into the thiocarbonyl ylide cycloadducts but decomposed giving a complex mixture of products when heated in toluene or xylene. A clean reaction occurred, however, to give two products 4 and/or 5 depending upon the reaction conditions when 3 was treated with an equivalent amount of triethylamine in benzene (Scheme 2 and Table 2). The products 4 and 5 correspond to compounds derived from 3 with an elimination of elemental sulfur and of hydrogen sulfide, respectively. It is clear that the compound 5 has been formed via 4 through a dehydrogenation because i) the relative yields of 4 and 5 depend upon the reaction conditions and ii) the compound 4 is quantitatively convertible into 5 (Table 2). The structures of 4 and 5 were assigned as the 3(H)-methylenepyrrolo[1,2-a]imidazole and 4,9c-diazapentaleno[1,6a,6 : ab]naphthalene, respectively, on the ground of the spectral data.[9]



a: $R^1=R^2=COOMe$
b: $R^1=R^2=COPh$
c: $R^1=H$, $R^2=COOMe$
d: $R^1=H$, $R^2=COPh$

Scheme 2

The formation of 4 and 5 is explained by a sequence of reactions shown in Scheme 2. A 1,5-hydrogen shift, induced by triethylamine, of the 4a-H of 3 to the 2-position forms A. A rare elimination of elemental sulfur leads to the isolable intermediate 4 that, in some cases, is not stable enough to be purified by recrystallization. A phenyl group at the 5-position of 4 participates in a 10π cyclization forming B. A dehydrogenation of B gives a new azacycl[3.2.2]azine system, 4,9c-diazapentaleno[1,6a,6 : ab]naphthalene 5.

Table 2. Conversion of Cycloadducts 3 into 3(H)-Methylenepyrrolo[1,2-a]imidazoles 4 and 4,9c-Diazapentaleno[1,6a,6 : ab]naphthalenes 5.

3	Conditions[a]		Products [%] 4	5		
3a	room temp.	24 h	25	58	4a → 5a (92 %)	reflux 24 h[b]
	reflux	24 h	-	90		
3b	reflux	24 h	-	86		
3c	reflux	24 h	84	-	4c → 5c (100 %)	reflux 72 h[b]
	reflux	48 h	36	49		
	reflux	72 h	-	81		
3d	room temp.	24 h	67	13	4d → 5d (92 %)	reflux 24 h[b]
	reflux	24 h	-	78		

a) In benzene with triethylamine. b) In benzene without triethylamine.

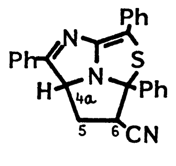
References

1) O. Tsuge, S. Kanemasa, and T. Hamamoto, Chem. Lett., 1982, 1491.
2) O. Tsuge, S. Kanemasa, and T. Hamamoto, Chem. Lett., 1983, 85.
3) O. Tsuge, S. Kanemasa, and T. Hamamoto, Heterocycles, 20, No 4, to be published.
4) K. T. Potts and J. L. Marshall, J. Org. Chem., 41, 129 (1976).
5) J. M. Kane, J. Org. Chem., 45, 5396 (1980).

6) All the compounds described in this communication gave satisfactory elemental analyses.

7) An inspection of the Dreiding molecular model shows that the dihedral angle is about 70°.

8) The reaction of 1 with three equivalents of acrylonitrile in benzene at 70 °C for 4 h gave the azomethine ylide cycloadduct 6 in 20 % yield together with the thiocarbonyl ylide cycloadduct (35 %) and the recovered 1 (18 %).
6: orange crysts., mp 140.5-142 °C. ^{1}H-NMR (CDCl$_3$) δ 2.03 (1H, ddd, J=13.0, 4.0, and 3.5 Hz, one of the 5-CH$_2$), 2.34 (1H, ddd, J=13.0, 9.0, and 8.0 Hz, the other of the 5-CH$_2$), 2.34 (1H, dd, J=8.0 and 3.5 Hz, 6-H), and 4.86 ppm (1H, dd, J=9.0 and 4.0 Hz, 4a-H).



6

9) The physical properties and spectral data of 4 and 5 are given as follows:
4a: yellow crysts., mp 151.5-153.5 °C (decomp.). IR (KBr) 1740 and 1700 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 3.64, 3.80 (each 3H, s, COOMe), 6.07 (1H, s, =CHPh), and 7.00-8.02 ppm (15H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 51.67, 52.37 (each q, COOMe), 110.43 (s, 7-C), 114.89 (d, =CH-), 160.16 (s, 3-C), 163.85, and 165.56 ppm (each s, COOMe); MS m/e 462 (M$^+$).
4c: yellow crysts., mp 137-139 °C (decomp.). IR (KBr) 1710 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 3.65 (3H, s, COOMe), 5.99 (1H, s, =CHPh), 7.01 (1H, s, 7-H), and 7.08-8.40 ppm (15H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 51.02 (q, COOMe), 105.03 (d, 7-C), 112.37 (d, =CH-), 158.75 (s, 3-C), and 164.45 ppm (s, COOMe); MS m/e 404 (M$^+$).
4d: yellow crysts., mp 154-155.5 °C (decomp.). IR (KBr) 1640 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 6.28 (1H, s, =CHPh), 6.91 (1H, s, 7-H), and 7.00-8.32 ppm (20H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 106.39 (d, 7-C), 112.74 (d, =CH-), 159.37 (s, 3-C), and 192.03 ppm (s, COPh); MS m/e 450 (M$^+$).
5a: yellow needles (benzene-hexane), mp 251.5-253 °C. IR (KBr) 1715 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 4.00, 4.05 (each 3H, s, COOMe), 7.36-8.38 (13H, m, ArH), and 9.64 ppm (1H, br d, 9-H); ^{13}C-NMR (CDCl$_3$) δ 52.48, 52.84 (each q, COOMe), 158.16 (s), 164.86, and 166.27 ppm (each s, COOMe); UV (MeCN) λmax (log ε) 294 (4.27), 298 (4.27), 380 (4.20), and 428 nm (3.71); MS m/e 460 (M$^+$).
5b: yellow needles (benzene-hexane), mp 272-273 °C. IR (KBr) 1645 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 7.02-8.44 (23H, m, ArH) and 8.90 ppm (1H, br d, 9-H); MS m/e 452 (M$^+$).
5c: yellow needles (benzene-hexane), mp 241-242 °C. IR (KBr) 1700 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 4.08 (3H, s, COOMe), 7.22 (1H, s, 2-H), 7.40-8.50 (13H, m, ArH), and 10.00 ppm (1H, br d, 9-H); MS m/e 402 (M$^+$).
5d: yellow needles (benzene-hexane), mp 290-291 °C. IR (KBr) 1630 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 7.21 (1H, s, 2-H), 7.36-8.20 (18H, m, ArH), and 9.74 ppm (1H, br d, 9-H); UV (MeCN) λmax (log ε) 245 (4.26), 320 (4.32), 383 (4.19), 412 (3.79), and 437 nm (3.73); MS m/e 448 (M$^+$).

(Received March 7, 1983)