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AZAFULVENES 1. A NOVEL GENERATIVE METHOD OF 6-AMINO-1-AZAFULVENE AND ITS CYCLOADDITION REACTION WITH ISOCYANATE AND ISOTHIOCYANATE

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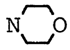
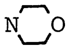
Pyrrole-2-carboxaldehyde reacted with sec. amines affording dipyrrolo[1,2-a:1',2'-d]pyrazines which corresponded to the dimers of 6-amino-1-azafulvenes. Pyrolytic decomposition of the pyrazine derivatives in the presence of dienophiles such as phenyl isocyanate, phenyl-isothiocyanate and benzoyl isocyanate gave pyrrolo[1,2-c]imidazoles. These results can be interpreted by the initial formation of 6-amino-1-azafulvenes on pyrolysis following the [6+2]cycloaddition reactions with dienophiles.

In recent years a number of cycloaddition reactions of fulvene have been developed. Most of them were Diels-Alder type [4+2]cycloaddition reactions in which fulvene behaved as a diene[1] but in a few examples fulvene reacted as a 6π-component to give [6+4]cycloadduct[2]. As known, fulvene has a relatively large value of dipole moment directed toward the fulvene ring[3]. In the case of 6-amino-1-azafulvene with strongly electron donating amino group at the 6-position of fulvene ring a larger moment should be observed. If so, it is expected that 6-amino-1-azafulvene will add to a polar multi-bond in a manner of [6+2]cycloaddition reaction. Nevertheless, neither synthetic method nor cycloaddition reaction of 6-amino-1-azafulvene has been reported.

We have studied the syntheses of 6-amino-1-azafulvenes from pyrrole-2-carboxaldehyde and sec. amines and we wish to report the novel generative method of 6-amino-1-azafulvenes and the first cycloaddition reactions to phenyl isocyanate, phenyl isothiocyanate and benzoyl isocyanate with the formation of the corresponding [6+2]cycloadducts.

By refluxing pyrrole-2-carboxaldehyde 2 with morpholine 3a in benzene for 3 hrs colorless prisms 4a, mp 190-193°C(decomp.), were obtained in 59% yield. This product was identified as 5,10-dihydro-5,10-dimorpholinodipyrrolo[1,2-a:1′,2′-d]pyrazine 4a on the basis of the following spectroscopic data as well as the result of elemental analysis; nmr in $CDCl_3$: τ2.99(2H,dd,pyrrole ring protons), 3.75(4H,m,pyrrole ring protons), 4.17(2H,s,methine) and 6.34, 7.50(each 8H,m,methylene); ir as KBr disks: 1110, 1000 and 710 cm^{-1}; mass at 75 eV: m/e 328(M^+), 242(M^+- ), 164(6-morpholino-1-azafulvene, base peak) and 156(242^+- ). Piperidine 3b reacted with 2 under the same conditions to afford the similar dimer 4b. However heating pyrrolidine 3c with 2 gave two isomeric dimer, 4c and 4c′. The ir spectra of these products are very similar to each other and nmr spectrum of 4c showed the methine protons of pyrazine ring at τ3.91(2H,s) but 4c′ at 3.91 and 4.15(each 1H,s). From the spectroscopic data shown in Table 1 the structures of 4a-4c and 4c′ were confirmed to be trans and cis isomers, respectively.

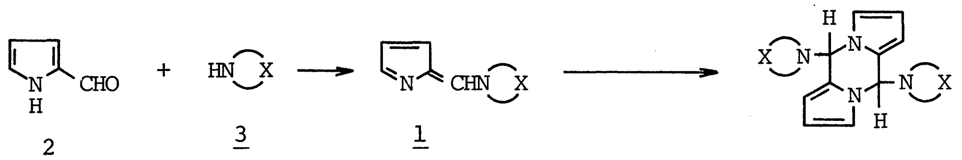
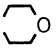


Table 1. 5,10-Dihydro-5,10-diaminodipyrrolo[1,2-a:1′,2′-d]pyrazines 4

	X	mp(°C)a)	yield(%)	nmr in $CDCl_3$; τ		M^+(m/e)
				pyrrole ring protons	methine protons	
4ab)		190-193	59	2.99(2H,m), 3.75(4H,m)	4.17(2H,s)	328
4bb)		162	40	3.01(2H,m), 3.79(4H,m)	4.18(2H,s)	324
4cb)		95-98	d)	3.06(2H,m), 3.81(4H,m)	3.91(2H,s)	296
4c′,c)		65-68	d)	3.06(2H,m), 3.81(4H,m)	3.91, 4.15(each 1H,s)	296

a); All the compounds melted with decomposition.

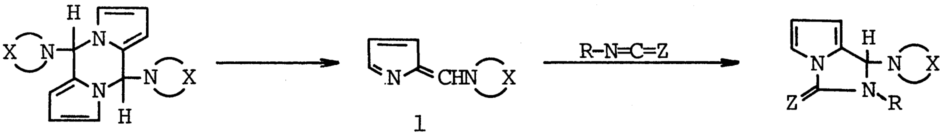
b); Trans isomer, c); Cis isomer

d); Isomer ratios depended on the reaction temperatuer as follows:

at 80°C: 22%(4c/4c′=3/10), at 70°C: 70%(4c/4c′=7/10), at room temp.: 58%(4c only)

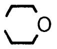
Although the reactions of 3 with 2 under milder conditions were carried out in order to isolate 6-amino-1-azafulvenes 1, 3a and 3b failed to react with 2 at room temperature. On the other hand, the dimer 4c was obtained by the treatment of 3c with 2 at room temperature and 4a was also obtained by stirring 3a with 2 at this temperature under the influence of catalyst such as $HClO_4$ or HBF_4.

The dimer 4 decomposed and turned red when heated in the melting point apparatus and this phenomenon seemed to indicate that 6-amino-1-azafulvene 1 could be generated by thermal decomposition of dimer 4. So the pyrolysis reaction of dimer 4 in an inert solvent in the presence of phenyl isocyanate was carried out. By heating the mixture of 4c and 4c′ with phenyl isocyanate in dry benzene for 1 hr colorless prisms 5c, mp 137-142°C(decomp.), were formed in a quantitative yield. The product 5c was confirmed to be [6+2]cycloadduct of 6-(N-pyrrolidinyl)-1-azafulvene to phenyl isocyanate on the basis of the spectroscopic data and the result of elemental analysis as shown in Table 2. That is, the nmr spectrum of 5c in $CDCl_3$ showed the characteristic signals of pyrrole ring protons(ABC pattern) and the band at 1720 cm^{-1} was assigned to the stretching vibration of the carbonyl group of five membered ring. The similar [6+2]cycloadducts 5a and 5b were obtained by the reactions of 4a in o-dichlorobenzene and 4b in xylene with phenyl isocyanate, respectively.



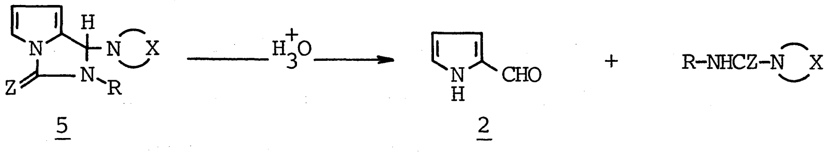
4 1 5

Table 2. The [6+2]Cycloadducts of 6-Amino-1-azafulvenes 1 to Phenyl Isocyanate, Phenyl Isothiocyanate and Benzoyl Isocyanate

	X	R	Z	mp(°C)[a]	yield(%)	reaction temperature and solvent used	ν_{CO} (cm^{-1})	τ(1-H)	M^+(m/e)
5a		Ph	O	157-158	62	180°C, o-dichlorobenzene	1720	4.23(1H,s)	283
5b		Ph	O	114-117	64	140°C, xylene	1720	4.36(1H,s)	281
5c		Ph	O	137-142	100	80°C, benzene	1720	3.97(1H,s)	267
5d		Ph	S	145-147	62	140°C, xylene		4.16(1H,s)	297
5e		Ph	S	99-101	58	80°C, benzene		3.76(1H,s)	283
5f		PhCO	O	169	92	80°C, benzene	1680 1635		295

a); All the compounds melted with decomposition.

These 1:1 cycloadducts 5a-5f were easily hydrolyzed to 2 and the corresponding ureas. Thus, it has become apparent that 6-amino-1-azafulvenes 1 could be generated



on pyrolysis of the dimer 4 and that 1 could easily add to the C=N bond of isocyanate. Therefore, the cycloaddition reactions of 1 to phenyl isothiocyanate and benzoyl isocyanate were further investigated. In particular, it is very interesting whether benzoyl isocyanate would act against these 1-azafulvenes as 2π- or 4π-component. Actually, the corresponding [6+2]cycloadducts 5d-5f were obtained by the reactions of phenyl isothiocyanate with 4b and 4c or of benzoyl isocyanate with 4c under the pyrolysis conditions as shown in Table 2. No isolation of the cycloadducts from the reactions of phenyl isothiocyanate with 4a and of benzoyl isocyanate with 4a or 4b could be realized probably because the melting points of the assumed products would be below the pyrolysis temperature. The structures of the [6+2]cycloadducts were confirmed by the spectroscopic data and the elemental analysis.

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