

AZAFULVENES 3.¹ CYCLOADDITION REACTION OF 6-AMINO-1-AZAFULVENE
TO ELECTRON-DEFICIENT OLEFIN AND ACETYLENE

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6-Amino-1-azafulvene (1) reacted with the electron-deficient olefins such as acrylate, vinyl ketone, acrylonitrile and N-aryl-maleimide affording the regio- and stereospecific [6+2] cycloadducts (4a-4g), some of which were readily deaminated to give the corresponding 3H-pyrrolizines (5a-5c). On the other hand, 1 gave the 1:2 cycloadduct with acetylenedicarboxylate.

We have previously reported^{2,3} that 6-amino-1-azafulvene generated by deprotonation from the iminium perchlorate or by pyrolysis of the dimer of 6-amino-1-azafulvene reacted as a 6 π -addend in the [6+2] cycloaddition reaction with isocyanate and isothiocyanate or in the [6+6] cyclodimerization reaction.

In this paper we would like to describe the cycloaddition reactions of 6-(N-pyrrolidiny1)-1-azafulvene (1), regenerated by pyrolysis from the corresponding dimer (2), either to such electron-deficient olefins as acrylic acid esters, methyl vinyl ketone, acrylonitrile and N-(p-substituted phenyl)maleimides or to diester of acetylenedicarboxylic acid.

Heating 2, the dimer of 1, in excess of ethyl acrylate (3a) under reflux gave

an oily product in quantitative yield. This product 4a was found to be a 1:1 adduct (M^+ ; m/e 248) of 1 and 3a, which was characterized as *trans*-2,3-dihydro-2-ethoxycarbonyl-1-(N-pyrrolidinyl)-1H-pyrrolizine on the basis of the spectral data. The most definitive evidence for the structure of 4a was afforded by its nmr spectrum in deuteriochloroform ($CDCl_3$), which showed the pyrrole ring protons at τ 3.52, 3.85 and 4.14, the methine proton at 1-position (1-H) as a doublet ($J = 4.0$ Hz) at 5.78, the methine proton at position 2 (2-H) as a double triplet ($J = 4.0$ and 6.5) at 6.42 and two methylene protons as a doublet ($J = 6.5$) at 5.83, besides ethyl and pyrrolidiny1 protons. The coupling constant of 4.0 Hz between two methine protons (1-H and 2-H) indicates these two protons are located in *trans* positions to each other. The ir spectrum revealed the stretching vibration band of carbonyl bond at 1730 cm^{-1} (Table 1).

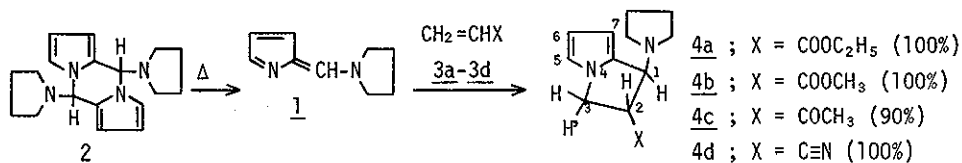


Table 1. 2,3-Dihydro-1-(N-pyrrolidinyl)-2-substituted-1H-pyrrolizines (4a-4d).

Ir (cm^{-1})	Nmr at 100 MHz in $CDCl_3$								
	Chemical Shift ; τ				Coupling Constant ; Hz				
	1-H	2-H	3-H	3'-H	J_{1-2}	J_{2-3}	$J_{2-3'}$	$J_{3-3'}$	
<u>4a</u>	1730(C=O)	5.78 ^d	6.42 ^{dt}	5.83 ^d	4.0	6.5	-	-	
<u>4b</u>	1730(C=O)	5.55 ^d	6.29 ^{dt}	5.78 ^d	4.0	7.0	-	-	
<u>4c</u>	1700(C=O)	5.78 ^d	6.75 ^{ddd}	6.42 ^{dd}	5.99 ^{dd}	4.0	8.0	4.0	11.0
<u>4d</u>	2240(C≡N)	5.53 ^d	6.36 ^{ddd}	5.59 ^{dd}	5.88 ^{dd}	4.8	9.0	6.0	10.5

a) ; The nmr spectrum was determined in hexadeuteriobenzene (C_6D_6).

Attempts to purify the product 4a by vacuum distillation⁴ or column chromatography over alumina were unsuccessful and thus 4a was brought about its conversion into the deaminated product, 2-ethoxycarbonyl-3H-pyrrolizine (5a), as a viscous oil. The easy deamination would be based on the location of two adjacent eliminating groups in *cis* positions and also on being activated of the hydrogen atom by the ester group on the same carbon atom. The above result and the nmr spectrum of 5a, in which an olefinic proton newly formed appeared as a singlet at τ 2.51, seem to substantiate the assignment of stereochemistry of the original cycloadduct 4a.

The reaction of 1 with methyl acrylate (3b) gave quantitatively the [6+2] cycloadduct (4b) which was also an oily substance and underwent a deamination reaction on heating or by its treatment with methanolic solution of sodium hydroxide to afford the yellow needles (5b), mp 84-86°C.

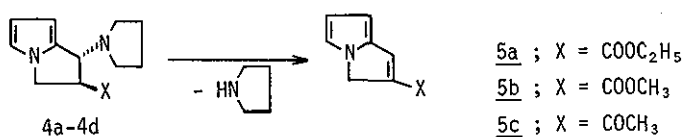


Table 2. 2-Substituted-3H-pyrrolizines (5a-5c).

Ir (cm ⁻¹)	Nmr at 100 MHz in CDCl ₃ ; τ			
	<u>-CH=CX</u> ^{a)}	<u>N-CH₂-CX</u> ^{a)}	pyrrole ring protons ^{b)}	other protons
<u>5a</u> 1690(C=O)	2.51 ^S	5.56 ^S	3.48, 3.71 and 3.80	5.76 ^q (-CH ₂ CH ₃) 8.68 ^t (-CH ₂ CH ₃)
<u>5b</u> 1690(C=O)	2.48 ^S	5.52 ^S	3.42, 3.67 and 3.80	6.19 ^S (CH ₃)
<u>5c</u> 1640(C=O)	2.56 ^S	5.55 ^S	3.49, 3.73 and 3.80	7.65 ^S (COCH ₃)

a) ; These protons appeared as broad singlets by a mutual long-range coupling.

b) ; All protons on pyrrole ring formed each multiplets.

Similarly, methyl vinyl ketone (3c) added easily to 1 in the manner of the regioselective and stereospecific [6+2] cycloaddition reaction. Tracing this reaction by taking nmr spectra showed that the rate of the formation of the 1:1 cycloadduct (4c) in benzene was approximately equal to that in chloroform, and that the deamination reaction progressed appreciably faster in chloroform than in benzene. Similar independence of the reaction rate upon the polarity of solvents was observed in the reactions of 1 with 3a and 3b. The 1:1 cycloadduct 4c (viscous oil) and its deaminated product 5c (yellow prisms, mp 67°C) were assigned to be *trans*-2,3-dihydro-2-acetyl-1-(N-pyrrolidinyl)-1H-pyrrolizine and 2-acetyl-3H-pyrrolizine by their spectral data, respectively. However the susceptibility of 4c to its pyrolytic deamination into 5c made itself impossible to be isolated as a pure form.

Acrylonitrile (3d) also reacted with 1 to yield the corresponding [6+2] cycloadduct (4d), mp 58-61°C as yellow prisms, which was found to be considerably stable against a deamination reaction. The structural assignment for the product 4d was given from the nmr spectral data as *trans*-2,3-dihydro-2-cyano-1-(N-pyrrolidinyl)-1H-pyrrolizine.

Moreover, the reactions of 1 with N-phenyl- (3e), N-(p-methylphenyl)- (3f) and N-(p-nitrophenyl)maleimide (3g) gave the corresponding [6+2] cycloadducts (4e-4g) in quantitative yields. The spectral data of 4e-4g are summarized in Table 3. Although the products 4e (mp 94-96°C (decomp) as colorless grains) and 4f (mp 139-142°C (decomp) as colorless needles) were obtained as pure forms by recrystallization from petroleum benzine after being chromatographed over alumina, 4g could not be purified in the similar way. In the nmr spectrum of pure 4f shown in Fig. 1, the coupling constant between two methine protons at 3a- and 8a-position is 7.8 Hz and one between 8a- and 8-H is 1.6 Hz. This spectrum is compatible with the structure having two hydrogen atoms at 8- and 8a-position in *trans* positions to each other.

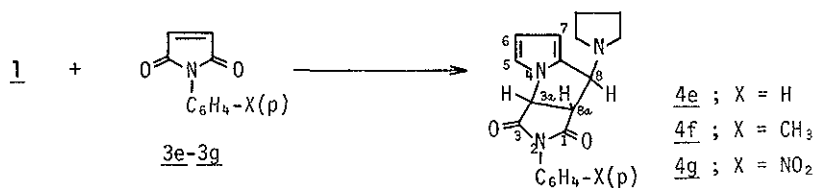


Table 3. 1,2,3,3a,8,8a-Hexahydro-8-(N-pyrrolidinyl)-2-arylpyrrolo[3,4-b]-pyrrolizine-1,3-diones (4e-4g).

Ir (cm ⁻¹)	Mass M ⁺ (m/e)	Nmr at 100 MHz in CDCl ₃					
		Chemical Shift ; τ			Coupling Constant		
		pyrrole ring protons	8-H	8a-H	3a-H	J _{8-8a}	J _{3a-8a} (Hz)
<u>4e</u> 1710(C=O)	321	3.13, 3.68 and 3.96	5.40 ^d	5.98 ^{dd}	4.87 ^d	1.6	8.1
<u>4f</u> 1710(C=O)	335	3.18, 3.75 and 4.02	5.45 ^d	5.98 ^{dd}	4.88 ^d	1.6	7.8
<u>4g</u> 1710(C=O)	-	3.43, 3.96 and 4.22	5.57 ^d	6.03 ^{dd}	4.98 ^d	2.0	7.0

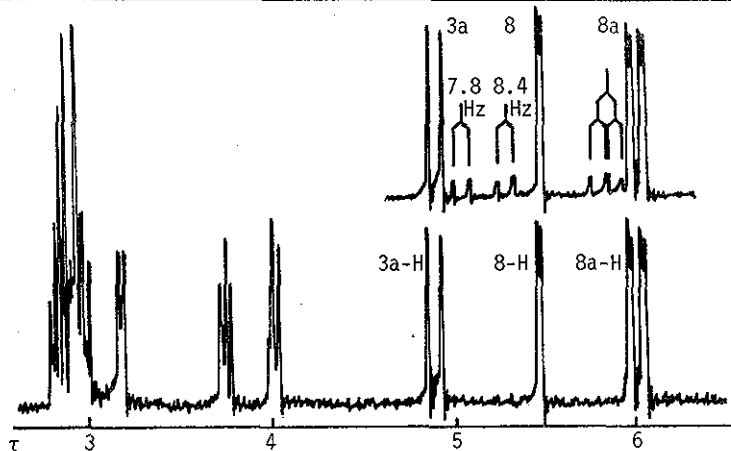
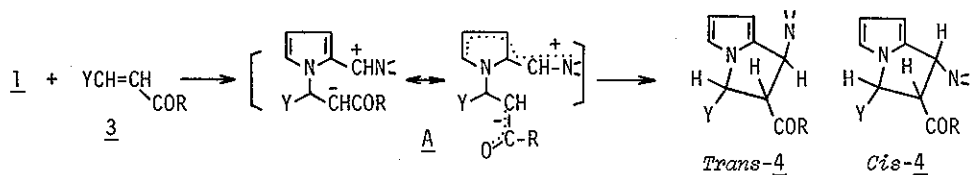


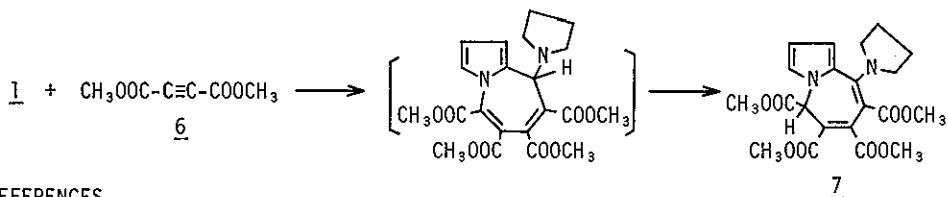
Fig. 1. Nmr spectra of pure 4f (bottom) and crude 4f (top) at 100 MHz in CDCl₃.

On the other hand, crude 4f showed three additional signals for methine protons whose coupling constants are 8.4 Hz (J_{8-8a}) and 7.8 (J_{3a-8a}). This seems to

indicate that the reaction of 1 with 3f (similarly 3e) gave not only *trans* cycloadduct 4f as a main product but a small amount of *cis* cycloadduct which could not be isolated as a pure form.



From these results, the reactions of 1 with the electron-deficient olefins 3 might proceed via dipolar intermediates A by the stepwise [6+2] cycloadditions⁵. In the intermediates A, the cyclization would occur generally in the less sterically hindered direction to yield the *trans* cycloadducts 4, but occasionally in the opposite direction to give the *cis* cycloadducts. This mechanism convinced us that the reaction of 1 with dimethyl acetylenedicarboxylate (6) afforded the 1:2 cycloadduct. This product (7), mp 172.5-174°C (decomp) as yellow prisms, was deduced to be 5H-pyrrolo[1,2-a]azepine derivative on the basis of its spectral data. The similar reaction has been reported by Sonnet⁶.



REFERENCES

1. For part 2 of this series, see reference 3.
2. M.Watanabe, T.Kobayashi, S.Kajigaeshi, and S.Kanemasa, *Chem.Lett.*, 1975, 607.
3. T.Kobayashi, S.Kajigaeshi, and S.Kanemasa, *Bull.Chem.Soc.Japan*, 1975, 48, 3255.
4. The compound 4a was distillable at 106°C/1 mmHg to give the mixture of 4a and deaminated product 5a.
5. The semi-empirical LCAO-SCF calculation of 1 shows that the energy level of the highest occupied (HO) π orbital lie close to that of the next to highest occupied (NHO) one. If NHO orbital is predominant in [6+2] cycloaddition reactions of 1, these reactions might proceed in a concerted manner.
6. P.E.Sonnet, *J.Heterocycl.Chem.*, 1974, 11, 811.

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