AZAFULVENES 4[1]. CYCLOADDITION REACTION OF 6-AMINO-1-AZAFULVENE TO ISOCYANATE, KETENE AND SULFENE

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6-Amino-1-azafulvene and its benzo analog, generated from the iminium perchlorate by deprotonation, reacted with isocyanate, ketene and sulfene affording the corresponding [6+2] cycloadducts.

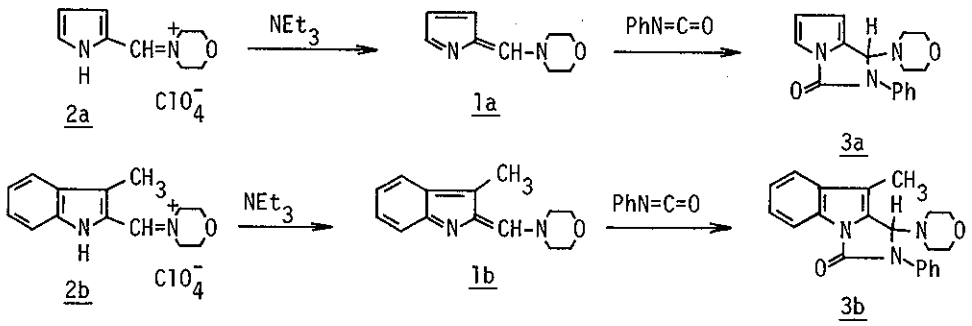
It was previously reported that 6-amino-1-azafulvene 1 could be regenerated by the pyrolysis of 5,10-dihydro-5,10-diaminodipyrrolo[1,2-a:1',2'-d]pyrazine, the dimer of 1, and was captured by isocyanate giving the corresponding [6+2] cycloadduct[2]. In addition, the treatment of the iminium perchlorate 2, synthesized from pyrrole- and indolecarbaldehyde with perchlorate of secondary amine, with some bases gave the dimer of 1[3]. This result indicates that deprotonation of 2 would lead to the generation of 1, followed by the dimerization.

In order to obtain a corroboratory evidence for the generation of 6-amino-1-azafulvene 1 by deprotonation from 2 and also to investigate the reactivity of 1 in its cycloaddition reaction, the reactions of 2 with base in the presence of isocyanate, ketene and sulfene were attempted in this communication.

A mixture of equivalent amount of N-(2-pyrrolylmethylene)morpholinium per-

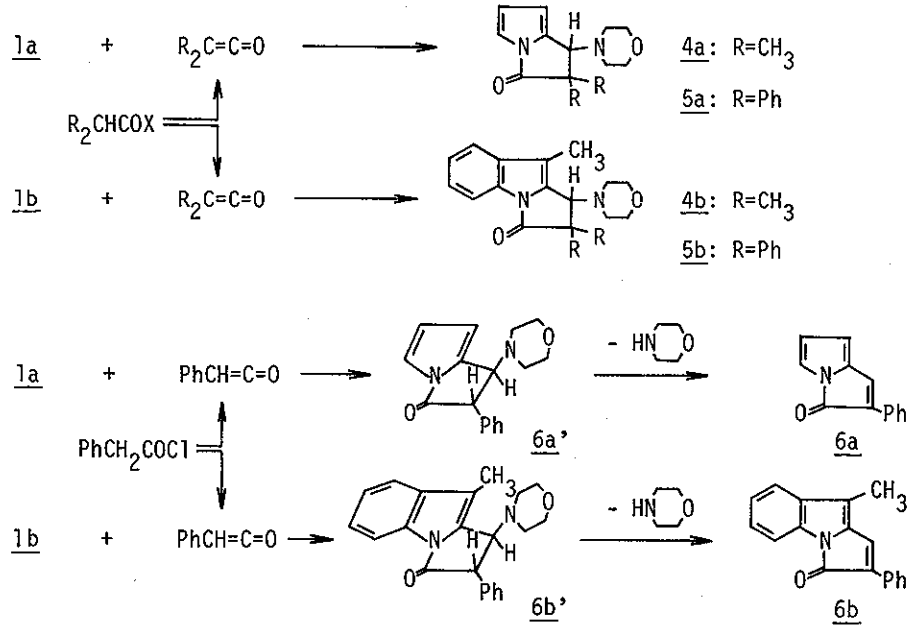
chlorate 2a and phenyl isocyanate in benzene was treated with triethylamine at room temperature to give the 1:1 adduct 3a in 72% yield which showed the identical ir and nmr spectrum with 2,3-dihydro-1-morpholino-2-phenyl-1H-pyrrolo-[1,2-c]imidazol-3-one already prepared by us[2]. After adding triethylamine to the suspension of the iminium salt 2a in methylene chloride at -50°C, the subsequent addition of phenyl isocyanate to this reaction mixture formed the same product 3a in 88% yield. This indicates that the iminium salt 2a liberated 6-morpholino-1-azafulvene 1a on the treatment with base, which is considerably stable at low temperature enough to permit the cycloaddition with phenyl isocyanate into the corresponding [6+2] cycloadduct.

The similar reaction of N-(3-methyl-2-indolylmethylene)morpholinium perchlorate 2b with triethylamine in the presence of phenyl isocyanate gave 2,3-dihydro-9-methyl-1-morpholino-2-phenyl-1H-imidazo[1,5-a]indol-3-one 3b in 76% yield. The structure of 3b was deduced on the basis of the spectral data shown in Table 1.



As well known, ketene and sulfene can be liberated from acyl halide and sulfonyl halide by the elimination of hydrogen halide, respectively. The reactions of 1 with ketene and sulfene were therefore carried out by use of the method in which the generation of 1 from 2 was made concurrently with that of ketene from acyl halide and that of sulfene from sulfonyl chloride by the action of base.

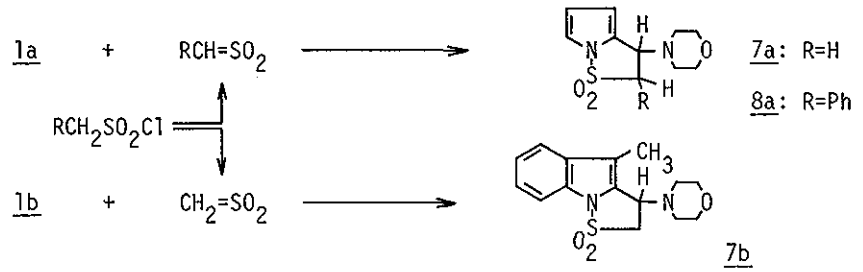
Thus the mixture of iminium salt 2a and α,α-diphenylacetyl chloride in benzene was treated with an excess of triethylamine and the resultant reaction mixture was chromatographed on alumina to afford the 1:1 adduct of 1a with diphenylketene in 67% yield. This product 5a was identified to be 2,3-dihydro-1-morpholino-2,2-diphenyl-1H-pyrrolizin-3-one by its ir and nmr spectrum in which the absorption band at 1740 cm^{-1} was assigned to the five-membered carbonyl group and three the protons on pyrrole ring appeared as each multiplet. Similarly 1a reacted with dimethylketene and 1b did with dimethyl- and diphenylketene to give the respective [6+2] cycloadducts, 4a, 4b and 5b. The reactions of 1a and 1b with phenylketene, however, resulted in no isolation of the [6+2] cycloadducts, 6a' and 6b', but formation of the deaminated products as red crystals. The ease of deamination would due to the trans conformation of the initially formed cycloadducts 6'. The comparable deamination reactions have been allowed in the case of the trans [6+2] cycloadducts of 1a with acrylates and methyl vinyl ketone[4].



The reactivity of 6-amino-1-azafulvene 1 in its cycloaddition to ketene is quite distinct from that of an ordinary fulvene which underwent the [2+2] cycloaddition to mono- and dichloroketene at the endocyclic double dond[5,6]. Only an example of the [6+2] cycloaddition of 1,4-diazafulvene to ketene has been reported by Rohr and his co-workers[7].

The first cycloaddition of fulvene to sulfene will be presented as follows: The treatment of the iminium salt 2a and methane sulfonyl chloride with triethylamine gave the [6+2] cycloadduct 7a whose structure was confirmed to be 2,3-dihydro-3-morpholinodipyrrolo[1,2-b]isothiazole-1,1-dioxide on the basis of the spectral data shown in Table 1. The yield of 7a was depended upon the reaction temperature. Similarly 1b reacted with sulfene to give the corresponding [6+2] cycloadduct 7b.

With asymmetrically substituted sulfene, phenylsulfene, 1a afforded the stereospecific [6+2] cycloadduct 8a. This compound 8a should be either cis or trans isomer, while the coupling constant of 7.0 Hz between two the methine protons at 1- and 2-position failed to determine the geometrical structure.



Although the unisolated [6+2] cycloadducts 6' from the reactions with phenylketene readily eliminated morpholine to yield the deaminated products 6 as described above, the deamination reaction from the [6+2] cycloadducts with sulfenes (7 and 8) could not occur even on heating or treatment with base. An inspection using Dreiding model showed that the eliminating groups in 6' are

located in nearly eclipsed position which favors to promote the cis elimination, whereas showed the difficulty of the deamination from 7 and 8 with the eliminating groups in staggered positions.

The low yield of the [6+2] cycloadducts from benzoazafulvene 1b would owe to the tendency to dimerization under the reaction conditions. In fact, a considerable amount of the dimer of 1b was isolated in almost all cases.

Table 1. The Reactions of 1 with Isocyanate, Ketenes and Sulfenes.

	Mp (°C)	Yield (%)	Reaction temp.	Ir (cm^{-1})	Nmr at 100 MHz in $CDCl_3$ δ (ppm)	M^+ (m/e)
With Isocyanate						
3a	180-182 decomp.	72 88	R.T. -50°C	1720 νC=O	2.46, 3.50(each 4H,m,CH_2), 5.77(1H,s,CH), 6.04, 6.28, 6.92-7.48(8H,m,pyrrolyl and phenyl protons)	283
3b	140-142 decomp.	76	R.T.	1720 νC=O	2.32(3H,s,CH_3), 2.53, 3.53(each 4H,m,CH_2), 5.95(1H,s,CH), 7.20-8.05(9H,m,indolyl and phenyl protons)	347
With Ketenes						
4a	oil	40	R.T.	1750 νC=O	1.36(6H,s,CH_3), 2.33, 3.67(9H,m,CH and CH_2), 6.15, 6.43, 6.99(each 1H,m,pyrrolyl protons)	-
4b	110-112	21	R.T.	1720 νC=O	1.28, 1.39, 2.34(each 3H,s,CH_3), 2.41, 3.63 (each 4H,m,CH_2), 3.79(1H,s,CH), 7.16-8.00 (4H,m,indolyl protons)	298
5a	105-106	67	R.T.	1740 νC=O	2.18, 3.18(each 4H,m,CH_2), 4.71(1H,s,CH), 6.18, 6.42, 6.98-7.72(13H,m,pyrrolyl and phenyl protons)	358
5b	213-215 decomp.	19	-50°C	1720 νC=O	2.49(3H,s,CH_3), 2.40, 3.29(each 4H,m,CH_2), 4.94(1H,s,CH), 7.16-8.16(14H,m,indolyl and phenyl protons)	422
6a	110-112	7	-50°C	1720 νC=O	5.92, 6.83(3H,m,pyrrolyl protons), 7.05(1H, s,-CH=), 7.24, 7.64(5H,m,phenyl protons)	195

Table 1. *Continued*

6b	113-115	16	-50°C	1700 $\nu C{=}O$	2.08(3H,s,CH_3), 7.00(1H,s,-CH=), 6.80-7.80 (9H,m,indolyl and phenyl protons)	259
With Sulfenes						
7a	133-135	44 83	R.T. -70°C	1330 νSO_2	2.51, 3.65(each 4H,m,CH_2), 3.85(2H,m,SO_2CH_2), 4.64(1H,dd,J=6.0, 7.0Hz,CH), 6.04, 6.32, 6.85 (each 1H,m,pyrrolyl protons)	242
7b	156-158 decomp.	36 20	80°C R.T.	1330 νSO_2	2.32(3H,s,CH_3), 2.59, 3.79(each 4H,m,CH_2), 3.89, 3.96(each 1H,m,SO_2CH_2), 4.99(1H,dd, J=5.0, 8.0Hz,CH), 7.26-7.86(4H,m,indolyl protons)	302
8a	163-164	14 88	R.T. -40°C	1340 νSO_2	2.57, 3.63(each 4H,m,CH_2), 4.94(1H,d,J=7.0Hz, CH-N), 5.15(1H,d,J=7.0Hz,CHPh), 6.15, 6.48, 7.03(each 1H,m,pyrrolyl protons), 7.44(5H,m, phenyl protons)	318

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