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AZAFULVENES 6[1]. CYCLOADDITION REACTION OF 8-AZAHEPTAFULVENE TO ISOCYANATE AND ISOTHIOCYANATE

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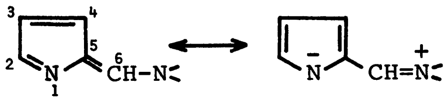
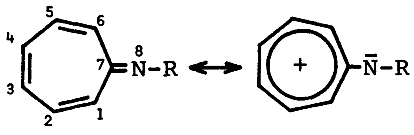
Eight-alkyl- and 8-aryl-8-azaheptafulvenes, generated *in situ* or isolated by treatment of the 8-azaheptafulvenium fluoroborates with base, reacted with phenyl, methyl, benzoyl and thiobenzoyl isocyanate to give the corresponding [8+2] cycloadducts, 1,2,3,3a-tetrahydrocyclohept[d]imidazol-2-one derivatives, in good yields. The similar reactions with phenyl and methyl isothiocyanate afforded the different type of cycloadducts, 2-imino-8aH-2,3-dihydrocyclohept[d]thiazoles, which were taken to be derived from addition of the C=S bond in isothiocyanates across the 8π system in 8-azaheptafulvenes. On the other hand, with benzoyl isothiocyanate 8-azaheptafulvenes gave the [8+4] cycloadducts, 10aH-4,5-dihydrocyclohept[f]-[1,3,5]oxadiazepine-4-thiones, in quantitative yields.

It has been found that 6-amino-1-azafulvenes reacted with heterocumulenes[2,3], electron-deficient olefins[4] and acetylenes[4,5] in the manner of [6+2] cycloaddition reactions in which azafulvene behaved only as a 6π component. This reactivity is probably because a dipolar structure in which a negative charge locates in the five-membered ring contributes in resonance hybrids. As shown from the result of molecular orbital caluculation[6], dipole moment of heptafulvene is directed toward the carbon atom at 8-position from the seven-membered ring contrary to that of fulvene. In 8-azaheptafulvene 1, a nitrogen analog of heptafulvene, electrons from the seven-membered ring of 1 will be drawn toward the external nitrogen atom, resulting in a



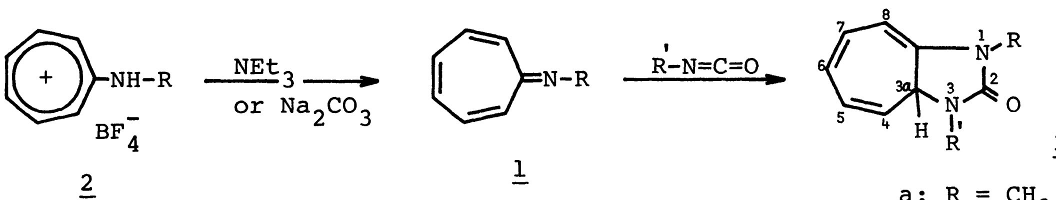


greater separation of positive and negative charge and, consequently, in an increase of dipole moment. Therefore electrophilic addition to the 8-position of 1 will occur easier than to the same position of the carbon analog. No any example of cycloaddition reaction of 8-azaheptafulvene 1, however, has so far been reported. The reactions of tropone with activated isocyanates gave cyclohept[d]imidazol-2-ones whose formation was rationalized by [8+2] cycloaddition of the isocyanates to not isolated 8-azaheptafulvenes7,8). The authors would like to communicate the first example of [8+2] and [8+4] cycloaddition reactions of 1, generated *in situ* or isolated from the 8-azaheptafulvenium fluoroborates 2 by treatment with bases, to isocyanates and isothiocyanates.

The reaction of 8-(p-chlorophenyl)-8-azaheptafulvene 1b9) with an equivalent amount of phenyl isocyanate in dry benzene gave the colorless 1:1 adduct 3b in quantitative yield. The IR spectrum of 3b showed no NH band but the characteristic one to a five-membered carbonyl group at 1735 cm^{-1} as sharp and strong absorption. This product 3b was deduced to be 1-(p-chlorophenyl)-3-phenyl-1,2,3,3a-tetrahydrocyclohept[d]imidazol-2-one which corresponds to the [8+2] cycloadduct of phenyl isocyanate to the cross-conjugated 8π system in 1b on the basis of the mass and PMR spectrum as well as above result. In the mass spectrum, the base peak appeared at m/e 181 is ascribed to the fragment that is produced from the parent peak (m/e; 334 and 336) by the elimination of p-chlorophenyl isocyanate (ClC_6H_4NCO). The PMR spectrum of 3b is also compatible to the proposed structure.

The treatment of 8-(p-chlorophenyl)-8-azaheptafulvenium fluoroborate 2b9) with phenyl isocyanate in the presence of triethylamine yielded the same product. Therefore the following cycloaddition reactions were carried out by using 8-azaheptafulvenium fluoroborates 2 as precursors for 8-azaheptafulvenes.

Thus 8-methyl- 1a10), 8-(p-chlorophenyl)- 1b and 8-(p-tolyl)-8-azaheptafulvene 1c9,11) were offered to the reactions with phenyl and methyl isocyanate affording



a: R = CH_3
b: R = p-ClC_6H_4
c: R = p-$CH_3C_6H_4$

a: R = CH_3, R' = C_6H_5
b: R = p-ClC_6H_4, R' = C_6H_5
c: R = p-$CH_3C_6H_4$, R' = C_6H_5
d: R = p-ClC_6H_4, R' = CH_3

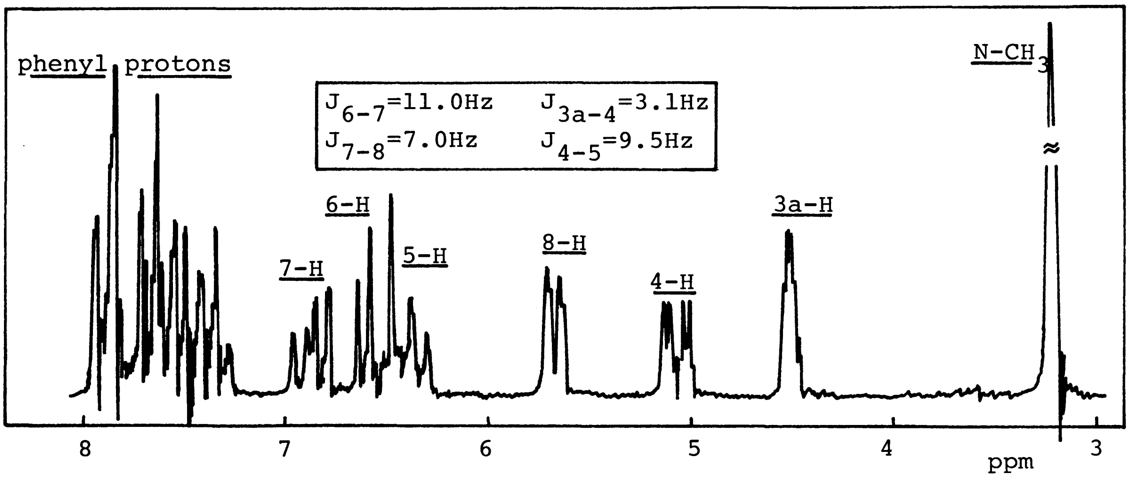
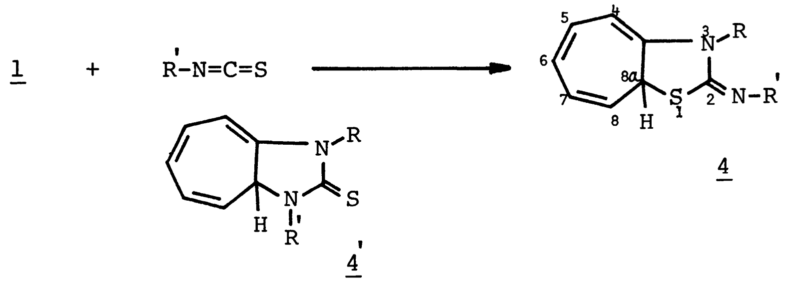


Fig. 1. The PMR Spectrum of 3a in $CDCl_3$.

the corresponding [8+2] cycloadducts 3a-3d whose yields and spectral data were summarized in Table 1 and 2. The PMR spectrum of 3a was illustrated in Fig. 1 as a typical example for those of the cycloadducts. The assignment of the each signal was made by double resonance experiments.

The reactions with isothiocyanates were also investigated under the similar conditions as above. On refluxing 2b with phenyl isothiocyanate in the presence of triethylamine in dry benzene was given the 1:1 adduct, after chromatographed over alumina. A resemblance of the PMR spectral pattern for the protons on seven-membered ring to those of 3 will propose two possible structures for this product: 2-imino-cyclohept[d]thiazole 4b and cyclohept[d]imidazole-2-thione 4b' arising from the combination of 8π system in 1b with C=S and C=N bond in phenyl isothiocyanate, respectively. The IR spectrum beared no similarity to those of 3 in terms of absorption pattern around whole wave numbers and in addition showed no any characteristic absorption to thioamide group at ca. 1500 cm^{-1} and thiocarbonyl group at ca. 1250 cm^{-1}, which should be observed for the latter 4b'. Instead, the appearance of strong absorption bands at 1635, 1610 and 1590 cm^{-1} might imply the existence of C=N group



a: R = CH_3, R' = C_6H_5
b: R = p-ClC_6H_4, R' = C_6H_5
c: R = p-$CH_3C_6H_4$, R' = C_6H_5
d: R = p-ClC_6H_4, R' = CH_3
e: R = p-$CH_3C_6H_4$, R' = CH_3

in the molecular structure of this product. As mentioned above, the PMR spectrum is quite similar to those of 3 only with a slight difference in chemical shift for the condensed methine-hydrogen atom (3a-H for 3 and 8a-H for 4). These results indicate the structure of this product to be not cyclohept[d]imidazole-2-thione 4b' but 2-iminocyclohept[d]thiazole 4b.

The similar [8+2] cycloadducts 4a-4e were obtained from the reactions of 1a-1c with phenyl and methyl isothiocyanate whose results were summarized in Table 1. The proposed structure for 4 is consistent with the fact that the $\nu_{C=N}$ was shifted toward higher wave number (1655 and 1645 cm^{-1}) on the replacement of a methyl substituent for a phenyl one and that in all cases the chemical shifts for the methine proton at 8a-position were observed within a considerably constant value (3.81-4.00 ppm) regardless of the kind of substituent from isothiocyanate. If a methyl group is introduced into the 3-position of improbable 4', the methine proton at 3a-position shoul be shifted toward higher field by 0.5 ppm than those of phenyl derivatives as observed

Table 1. Cycloadducts of 8-Azaheptafulvenes to Isocyanates and Isothiocyanates

	R	R'	Yield[a] (%)	Mp[b] (°C)	IR (cm^{-1})	Mass M^+ (m/e)
					νC=O νC=C	
3a	CH_3	C_6H_5	38	93-95	1720, 1630, 1370	238
3b	p-ClC_6H_4	C_6H_5	100	137	1735, 1630, 1370	334, 336
3c	p-$CH_3C_6H_4$	C_6H_5	99	128-129	1730, 1630, 1370	314
3d	p-ClC_6H_4	CH_3	81	137.5-138.5	1725, 1630	272, 274
					νC=N νC=C	
4a	CH_3	C_6H_5	41	68-70	1635, 1610, 1585	254
4b	p-ClC_6H_4	C_6H_5	96	123-124	1635, 1610, 1590	350, 352
4c	p-$CH_3C_6H_4$	C_6H_5	100	101.5-103	1635, 1610, 1590	330
4d	p-ClC_6H_4	CH_3	78	117-118	1655, 1645, 1605	288, 290
4e	p-$CH_3C_6H_4$	CH_3	62	105-106	1655, 1645, 1600	268
					νC=O νC=X νC=C	
5a	p-ClC_6H_4		100	134	1750, 1670, 1635, 1330	362, 364
5b	p-ClC_6H_4		100	158-159.5	1750, 1270, 1635, 1320	378, 380
					νC=S νC=C	
6a	p-ClC_6H_4		93	172-172.5	1245, 1625, 1490, 1480	378, 380
6b	p-$CH_3C_6H_4$		100	170.5-171.5	1250, 1620, 1490, 1475	358

a; Yield based on the fluoroborates 2.

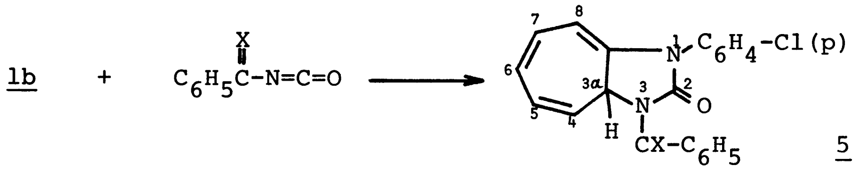
b; All the compounds melted with decomposition.

Table 2. PMR Data for Cycloadducts in Deuteriochloroform

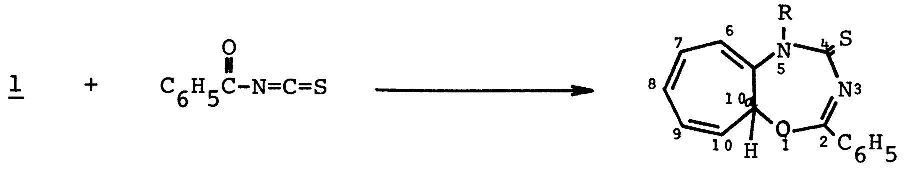
	Chemical shifts of ring protons						Other protons (δ; ppm)
	3a-$H^{br.d}$	4-H^{dd}	5-H^{m}	6-H^{m}	7-H^{dd}	8-$H^{br.d}$	
3a	4.48	5.04	6.30-6.68		6.85	5.66	3.20^{s}(N-CH_3), 7.28-7.96^{m}(Ar)
3b	4.45	5.02	6.12-6.46		6.55	5.58	7.04-7.72^{m}(Ar)
3c	4.47	5.02	6.12 —— 6.64			5.54	2.40^{s}(CH_3), 7.08-7.76^{m}(Ar)
3d	3.93	5.11	6.06 —— 6.56			5.51	3.08^{s}(N-CH_3), 7.20-7.46^{m}(Ar)
	8a-$H^{br.d}$	8-H^{dd}	7-H^{m}	6-H^{m}	5-H^{dd}	4-$H^{br.d}$	
4a	3.81	5.05	6.04	6.14	6.49	5.42	3.23^{s}(N-CH_3), 6.72-7.18^{m}(Ar)
4b	3.96	5.28	6.07 —— 6.57			5.28	6.92-7.52^{m}(Ar)
4c	3.96	5.24	6.02 —— 6.51			5.24	2.36^{s}(CH_3), 6.82-7.52^{m}(Ar)
4d	4.00	5.28	6.08 —— 6.60			5.18	3.13^{s}(N-CH_3), 7.20^{d}, 7.26^{d}(Ar)
4e	3.99	5.30	6.08 —— 6.56			5.21	2.41^{s}(CH_3), 3.16^{s}(N-CH_3), 7.12^{d}, 7.26^{d}(Ar)
	3a-$H^{br.}$	4-H^{dd}	5-H^{m}	6-H^{m}	7-H^{m}	8-$H^{br.s}$	
5a	4.86	5.25	6.07 —— 6.41			5.48	7.12-7.71^{m}(Ar)
5b	5.20	5.25	6.16 —— 6.51			5.57	7.13-7.57^{m}(Ar)
	10a-$H^{br.}$	10-H^{dd}	9-H^{m}	8-H^{m}	7-H^{m}	6-$H^{br.d}$	
6a	4.04	5.40	6.12 —— 6.54			5.48	7.20-7.60^{m}, 7.90-8.05^{m}(Ar)
6b	4.05	5.42	6.12 —— 6.70			5.51	2.48^{s}(CH_3), 7.12-7.48^{m}, 7.92-8.16^{m}(Ar)

in the case of 3, but the result did not fit in the fact. The products 4 were too stable against acid and base to be hydrolised.

Against our expectation of formation of the corresponding [8+4] cycloadduct as well as [8+2] cycloadduct, the reactions between 1 and benzoyl and thiobenzoyl isocyanate gave only the latter products 5 in quantitative yields. The structures of 5a and 5b were confirmed to be 3-benzoyl(or thiobenzoyl)-1-(p-chlorophenyl)-1,2,3,3a-tetrahydrocyclohept[d]imidazol-2-ones on the basis of the PMR and IR spectra, the latter of which afforded the definite evidence for the structure showing the band assignable to the five-membered carbonyl group at 1750 cm^{-1}.



5 a: X = O, b: X = S



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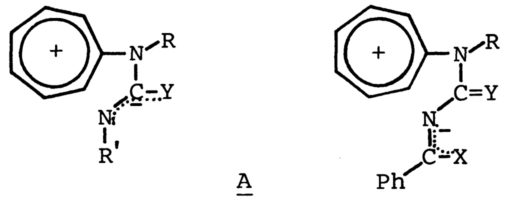
a: R = p-ClC_6H_4

b: R = p-$CH_3C_6H_4$

On the other hand, the IR spectra of the 1:1 adducts 6a and 6b yielded from the reactions of 1 with benzoyl isothiocyanate were entirely dissimilar to those of 3, 4 and 5 and showed no any carbonyl stretching vibration. Furthermore the existence of thioamide group (characteristic band at 1475-1490 cm^{-1}) indicates these products to be the corresponding [8+4] cycloadducts. The results of the PMR spectra are consistent in the given structures.

Thus a high sensitivity of 8-azaheptafulvene 1 to isocyanate and isothiocyanate resulted in the success of the cycloaddition reaction in which 1 behaved as 8π component in all cases. The formation of different types of cycloadducts in the reaction of 1 with isocyanate and isothiocyanate is rationalized by the mechanism containing the stepwise undergoimg cyclization *via* the zwitter-ionic intermediate A, namely in A the combination between positively charged carbon atom on seven-membered ring and negatively charged hetero atom would lead to 3, 4, 5 and 6.



Y=O or S A X=O or S

It is unusual result that benzoyl and thiobenzoyl isocyanate with tendency to act as 4π system[12] gave the [8+2] cycloadducts 4 and 5, on the other hand benzoyl isothiocyanate with tendency to behave as 2π component[12] afforded the [8+4] cycloadducts 6. The reason why these reagents showed different reactivities toward 8-azaheptafulvene is not clarified yet.

These are the first example for cycloaddition reaction of 8-azaheptafulvene.

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