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AZAFULVENES 7(1). CYCLOADDITION REACTION OF 8-AZAHEPTAFULVENE TO KETENE

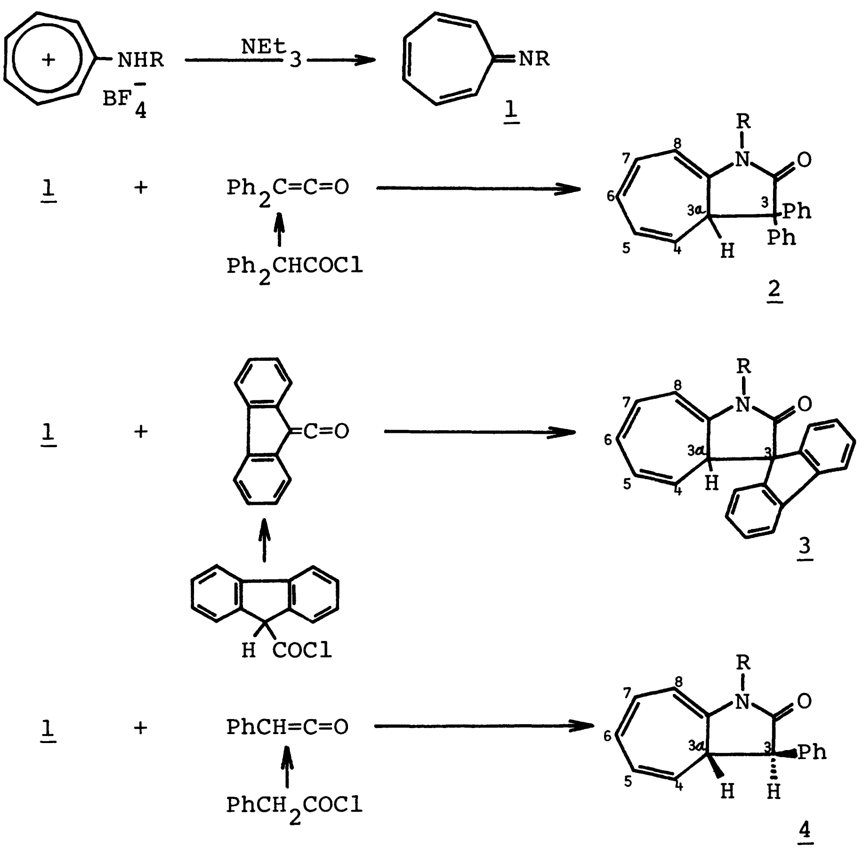
Kikuo YAMAMOTO, Shoji KAJIGAESHI, and Shuji KANEMASA*
Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube 755

8-alkyl- and 8-aryl-8-azaheptafulvenes reacted with diphenyl- and biphenyleneketene affording the corresponding [8+2] cycloadducts in good yields. Similarly the reactions with phenylketene gave only *trans* [8+2] cycloadducts.

It is known that tropone, one of the representatives of heteroheptafulvenes, generally gives Diels-Alder cycloadducts with many 2π components2-5) but exceptionally reacts with ketene to yield unusual [8+2] cycloadducts6, 7). Recently tropone-thione was found to behave as 8π addend in the reaction with maleic anhydride and acetylenedicarboxylate8). Furthermore the first example of cycloaddition reaction of 8-azaheptafulvene, which had yielded [8+2] or [8+4] cycloadducts to isocyanate and isothiocyanate, has been reported9). This reaction unfortunately gave no any information on its stereochemistry because of a possible inversion around the nitrogen atom at 3-position in the cycloadduct. Several ketenes were employed here as addends to 8-azaheptafulvene with a view to making the stereochemistry of cycloadduct in this type of reaction clear and applying 8-azaheptafulvene to syntheses of new heterocycles containing a fused cycloheptatriene ring.

Three ketenes and five 8-azaheptafulvenes used in the following cycloaddition reactions were generated, not isolated, from the corresponding acyl chlorides and 8-azaheptafulvenium fluoroborates by use of triethylamine as base, respectively. Thus a solution of 8-methyl-8-azaheptafulvenium fluoroborate and diphenylacetyl chloride in dry dichloromethane was treated with triethylamine and then the resulting mixture was stirred at room temperature for 15 hrs. After usual work-up, the products were chromatographed over alumina with benzene as eluent. A colorless product 2a isolated in 78% yield was found to be a 1:1 adduct of 8-methyl-8-azaheptafulvene 1a to diphenylketene. The PMR spectrum is closely similar in spectral patterns for protons on the seven-membered ring to the [8+2] cycloadduct[9)] of 1 to phenyl isocyanate. The IR spectrum revealed the carbonyl stretching vibration characteristic of five-membered carbonyl group at 1720 cm^{-1}. A consideration of these results indicates this product 2a to be the [8+2] cycloadduct, 1-methyl-2-oxo-3,3-diphenyl- 1,2,3,3a-tetrahydro-1-azaazulene.

Similarly, 8-n-propyl- 1b, 8-(p-anisyl)- 1c, 8-(p-tolyl)- 1d and 8-(p-chlorophenyl)-8-azaheptafulvene 1e gave the corresponding [8+2] cycloadducts 2b-2e with diphenylketene. These results and the PMR spectral data were summarized in Table 1 and 2, respectively. Thermal lability of 8-alkyl-8-azaheptafulvenes 1a and 1b would give rise to a decrease in yields of the products. On the other hand, 8-aryl homologs 1c-1e are enough stable to be isolated[10)] and with diphenylketene gave the cycloadducts in quantitative yields.



a: R = CH_3
b: R = $CH_3CH_2CH_2$
c: R = $P-CH_3OC_6H_4$
d: R = $p-CH_3C_6H_4$
e: R = $p-ClC_6H_4$

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The reactions of 8-azaheptafulvenes 1c-1e with biphenyleneketene under the same conditions as above gave spiro [8+2] cycloadducts 3a-3c in excellent yields whose structures were confirmed on the basis of the spectral data shown in Table 1 and 2.

As a typical example of unsymmetrically substituted ketene, phenylketene was

Table 1. The Cycloadducts of 8-Azaheptafulvenes to Ketenes

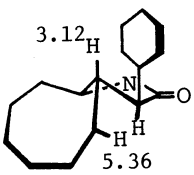
	R	Yield$^{a)}$ (%)	Mp(°C)	IR(cm^{-1}) $\nu_{C=O}$	IR(cm^{-1}) $\nu_{C=C}$	Mass M^+(m/e)
2a	CH_3	78	108-109	1720	1630	313
2b	$CH_3CH_2CH_2$	59	88-90	1715	1625	341
2c	p-$CH_3OC_6H_4$	100	178	1720	1620	405
2d	p-$CH_3C_6H_4$	100	204-204.5	1720	1625	389
2e	p-ClC_6H_4	98	177-177.5	1725	1620	409, 411
3a	p-$CH_3OC_6H_4$	93	194-194.5	1720	1630 1615	403
3b	p-$CH_3C_6H_4$	93	204-204.5	1720	1630 1615	387
3c	p-ClC_6H_4	90	231-232	1725	1620	407, 409
4a	CH_3	48	97-98	1710	1625	237
4b	p-$CH_3OC_6H_4$	97	152.5-153	1715	1625	329
4c	p-$CH_3C_6H_4$	91	137-137.5	1720	1625	313
4d	p-ClC_6H_4	93	129-130	1710	1625	333, 335

a) Yields based on the corresponding 8-azaheptafulvenium fluoroborates.

Table 2. PMR Data for Cycloadducts 2-4 in Deuteriochloroform (δ ppm)

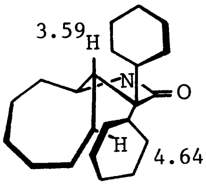
	3-H	3a-H	4-H	5-H	6-H	7-H	8-H	J_{3-3a}, Hz
2a		$3.53^{br.d}$	4.44^{dd}	5.91^{ddd}	6.29^{dd}	6.63^{dd}	5.61^{d}	
2b		3.49^{m}	4.35^{dd}	5.82^{ddd}	6.18^{dd}	6.53^{dd}	5.52^{d}	
2c		3.60^{m}	4.61^{dd}	6.01^{ddd}	6.23^{dd}	6.57^{dd}	5.52^{d}	
2d		3.60^{m}	4.63^{dd}	6.05^{ddd}	6.34^{dd}	6.58^{dd}	5.55^{d}	
2e		3.59^{m}	4.64^{dd}	6.04^{ddd}	6.37^{dd}	6.60^{dd}	5.56^{d}	
3a		3.94^{m}	4.89^{dd}	5.90^{m}	6.01^{m}	6.23^{m}	5.50^{d}	
3b		3.94^{m}	4.91^{dd}	5.91^{m}	6.00^{m}	6.26^{m}	5.52^{d}	
3c		3.88^{m}	4.92^{dd}	5.94^{m}	6.02^{m}	6.25^{m}	5.50^{d}	
4a	3.85^{d}	3.07^{m}	5.31^{dd}	6.24^{m}	6.24^{m}	6.55^{dd}	5.61^{d}	5.0
4b	4.00^{d}	3.11^{m}	5.35^{m}	6.11	———	6.51^{m}	5.44^{d}	5.0
4c	4.02^{d}	3.13^{m}	5.35^{dd}	6.09	———	6.48^{m}	5.45^{d}	5.0
4d	4.01^{d}	3.12^{m}	5.36^{m}	6.13	———	6.42^{m}	5.46^{d}	5.5

offered to this cycloaddition reaction. Thus the 8-azaheptafulvenes 1c-1e having aryl group at the 8-position gave the corresponding [8+2] cycloadducts 4b-4d in excellent yields as compared to the 8-methyl homolog 1a which afforded 4a only in 48% yield. No any changes were observed in the PMR spectra of products 4 before and after the purification. These spectra showed the product from the reaction with phenylketene not to be a mixture of *cis* and *trans* [8+2] cycloadduct but either of them. The coupling constants of 5.0-5.5 Hz between 3- and 3a-H in 4 are compatible with *trans* structure for 4. In order to ensure this assignment of configuration, Stuart models were constructed for the products 2e, 3c and 4d which are three kinds of [8+2] cycloadducts to 8-(p-chlorophenyl)-8-azaheptafulvene 1e. According to the inspection by use of the models, two phenyl groups at the 3-position in 2e seem to be restricted in rotation and, consequently, 4- and 3a-H are located right just above the first benzene ring and nearly within a plane of the second one, respectively. Direct joining between the o-positions of two phenyl groups in 2e leads to the [8+2] cycloadduct 3c, in which 4-H is apart from the shielding region owing to the first benzene ring and reversely 3a-H is closely within the plane of the second ring. On the other hand, substitution of a hydrogen atom for the phenyl group trans to 3a-H in 2e leads to the *trans* [8+2] cycloadduct 4d.



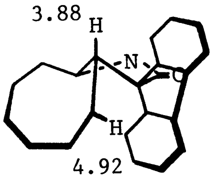
4d

With
Phenylketene



2e

Diphenylketene



3c

Biphenyleneketene

The PMR data shown in Table 2 provided a powerful evidence in confirmation of *trans* structure of 4. A remarkable shift of 4-H in 4 toward lower field (0.7 to 1.0 ppm lower than 2) would originate in removal of the phenyl group faced to this hydrogen atom. In addition, allowed rotation of the alternative phenyl group made 3a-H in 4 shift toward higher field.

Further work should be investigated to determine the mechanism of this reaction.

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