

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

Kikuo Yamamoto, Shoji Kajigaeshi, and Shuji Kanemasa
Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube 755, Japan

8-Alkyl- and 8-aryl-8-azaheptafulvene, generated in situ or isolated from the azaheptafulvenium fluoroborate and base, reacted with phenyl and methyl isocyanate to give the corresponding [8+2] cycloadduct, 1,2,3,3a-tetrahydrocyclohept[d]imidazol-2-one derivative, in good yield.

The similar reaction with phenyl and methyl isothiocyanate, however, afforded the different type of cycloadduct, whose structure was determined to be 8aH-2,3-dihydrocyclohept[d]thiazol-2-one on the basis of the spectral data and which was taken to be derived by the addition of C=S bond in isothiocyanate to 8 π system in 8-azaheptafulvene.

Although a formation of [8+4] cycloadduct is expected by the reaction of 8-azaheptafulvene with benzoyl and thiobenzoyl isocyanate, the product was unexpectedly 3-acyl- or 3-thioacyl-1,2,3,3a-tetrahydrocyclohept[d]imidazol-2-one, the similar [8+2] cycloadduct to that from phenyl and methyl isocyanate. On the other hand, with benzoyl isothiocyanate 8-azaheptafulvene gave the [8+4] cycloadduct, 10aH-4,5-dihydrocyclohept[f][1,3,5]oxadiazepine-4-thione, in a quantitative yield.

This is the first example of cycloaddition reaction of 8-azaheptafulvene.