

PHOTOADDUCTS OF N-METHYL-2-PYRIDONE WITH HALOETHYLENES
AND THEIR DERIVATIVES

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In order to obtain the informations of 1:2 cycloaddition between 2-pyridones and haloethylenes, formation of double bonds by successive elimination reaction to the adducts and valence isomerization into ten-membered heterocyclic compounds from the products, following approaches were examined.

Photoirradiation of N-methyl-2-pyridone [NP] with several haloethylenes gave a lot of halogenated 3-oxo-2-azabicyclo[4.2.0]oct-4-enes, 2-oxo-3-azabicyclo[4.2.0]oct-4-enes and others. Thus, photolysis of [NP] with trichloroethylene in the presence of xanthone led to 7,7,8-trichloro-2-methyl-3-oxo-2-azabicyclo[4.2.0]oct-4-ene [1], 7,8,8-trichloro-3-methyl-2-oxo-3-azabicyclo[4.2.0]oct-4-ene [2], 7,7,8-trichloro-2-methyl-3-oxo-2-azabicyclo[2.2.2]oct-5-ene [3] and others. The reactivities of the haloethylenes were as follows; 1,2-dichloroethylene < tetrachloroethylene < trichloroethylene < 1,1-dichloroethylene .

Those of cycloadditions between 4,4,6-trimethyl-5,6-dihydro-2-pyridone and chloroethylenes (trichloroethylene < 1,2-dichloroethylene) were very different from the upper data.

[1] and [3] were reduced by zinc dust to give 7-chloro-2-methyl-3-oxo-2-azabicyclo[4.2.0]oct-4,7-diene [4] and 6-chloro-2-methyl-3-oxo-2-azabicyclo[2.2.2]oct-5,7-diene respectively.

It was found that [4] gave thermally (at 110°C) a valence isomer, 3-chloro-8-methyl-7-oxo-8-azabicyclo[4.2.0]oct-2,4-diene. Similarly, 7,8-dichloro-2-methyl-3-oxo-2-azabicyclo[4.2.0]oct-4,7-diene gave 2,3-dichloro-8-methyl-7-oxo-8-azabicyclo[4.2.0]oct-2,4-diene at 120°C. But, 7,8-dichloro-3-methyl-2-oxo-3-azabicyclo[4.2.0]oct-4,7-diene and 4,4,6-trimethyl-2-oxo-3-azabicyclo[4.2.0]oct-7-ene did not afford valence isomers.