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DIAZAPOLYCYCLIC COMPOUNDS. IV. THE REACTION OF 1,2,4-TRIAZOLINE-3,5-DIONE WITH DIENES

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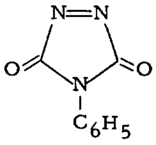
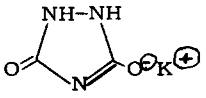
Although some 4-substituted 1,2,4-triazoline-3,5-diones (I) are known (1,2) and they are relatively stable compounds, with remarkable dienophilic properties (3,4,5,6), the parent compound 1,2,4-triazoline-3,5-dione (II) has not been characterized (1), nor studied as a dienophile.

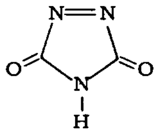
As a part of a continuing study on the synthesis of diazapolycyclic systems by 1,4-cycloaddition reactions (7,8,9), attempts were made to prepare stable solutions of II by the oxidation of the potassium salt of urazole (III) with t-butyl hypochlorite at low temperature.



I



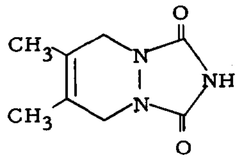
III



II

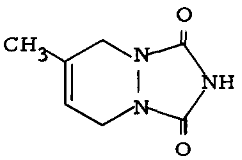
Thus, when a solution of t-butyl hypochlorite (3 g, 0.03 mole) and 30 ml of anhydrous acetone was cooled to -70º, and to it was added portionwise 3.7 g (0.03 mole) of III, two hours later a deep pink solution of II was obtained. No attempts were made to isolate II but instead it was trapped through reaction with several dienes.

The reactions of 1,2,4-triazoline-3,5-dione solutions at low temperature (∼-10) with equimolecular amounts of 2,3-dimethyl-1,3-butadiene, isoprene, 1,4-diphenyl-1,3-butadiene, α-phelandrene, cyclopentadiene, and 1-vinylcyclohexene were found to proceed with considerable ease to give the corresponding adducts (IV-IX) in yields up to 40 %, based on the starting III.



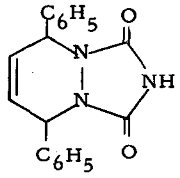
m. p. 216-217º (benzene)

IV



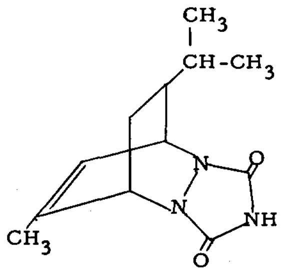
m. p. 204-206º (benzene)

V



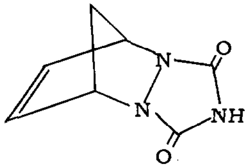
m. p. 284-285º (ethanol)

VI



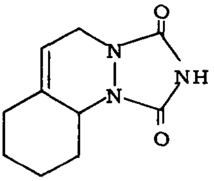
m. p. 174-175º (water)

VII



m. p. 214-216º (ethanol)

VIII



m. p. 181-183º (water)

IX

The adducts obtained above were characterized by their analytical data, NMR and IR spectra as the 1,4-addition products.

As pointed out already, this is the first time that (II) has been used as dienophile.

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