

SYNTHESIS OF SOME DIAZA AND TRIAZASTEROIDIC COMPOUNDS.
(Diels-Alder reactions of diazoline- and triazolone-diones.
Diaza and triaza cyclopentenophenanthrene derivatives).

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In previous work (1), we reported the synthesis of a perhydro-5,6-diazasteroid by Diels-Alder reaction of pyridazine-3,5-dione and 'cis'-2,3,3a,4,5,7a-hexahydro-7-vinyl indene, followed by hydrogenation of the adduct formed in the cycloaddition.

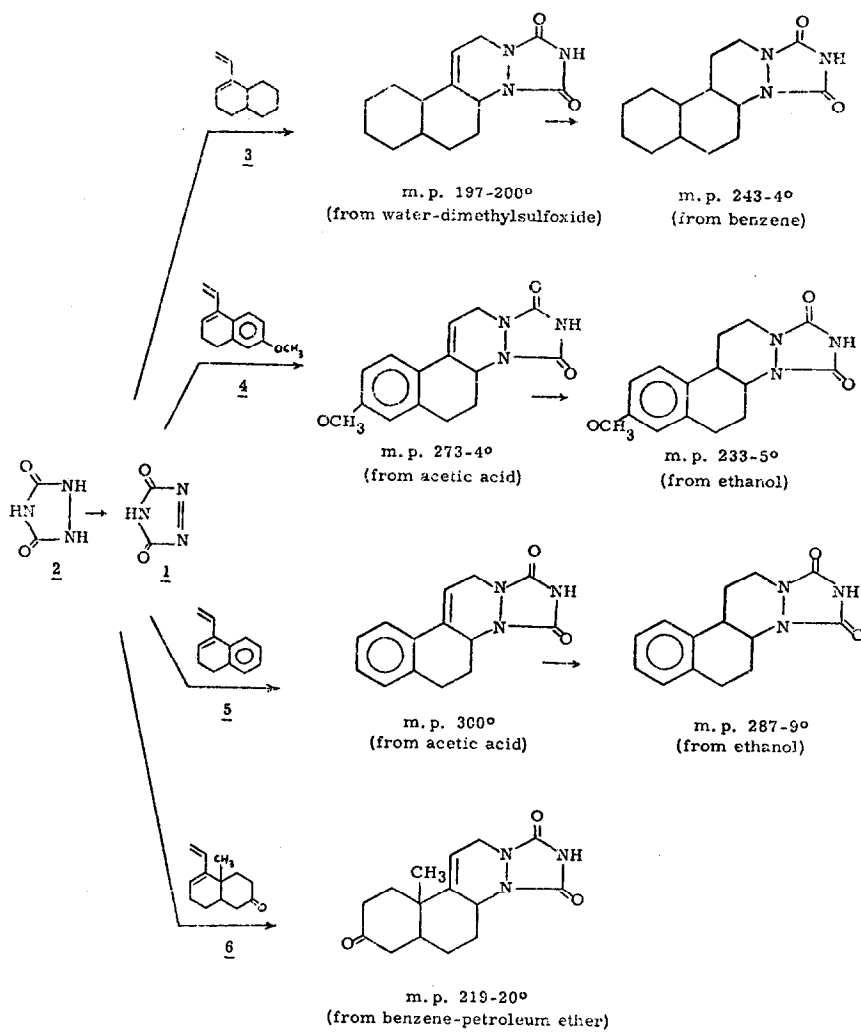
Diazasteroids and triazasteroids with the nitrogen atoms situated in different positions have now been synthesized by taking advantage of the great dienophylic character shown by the triazolone-3,5-dione and diverse monosubstituted pyrazoline-3,5-diones, when reacting with dienes like 2,3-dimethyl and 1,6-diphenyl-1,3-butadienes, α -phelandrene, 1-vinylcyclohexene and cyclopentadiene (2,3).

Reaction of the 1,2,4-triazolin-3,5-dione, 1 (obtained by t-butyl-hypochlorite oxidation of the 1,2,4-triazolidine-3,5-dione (2), with diverser 1-vinyl-hydronaphthalene derivatives 3, 4, 5, 6 gave the expected adducts, which by hydrogenation yielded the 13,14,16-triazasteroids shown in Scheme 1.

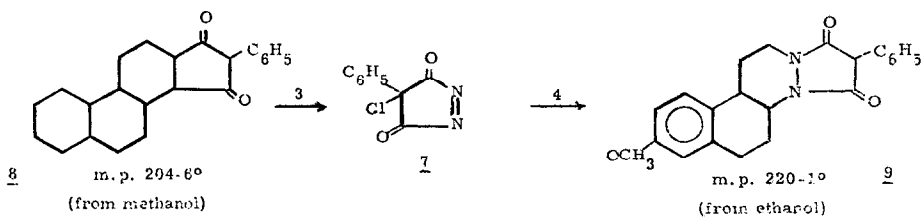
Similarly, pyrazoline-3,5-diones can be obtained by oxidation of the cyclic hydrazines of the corresponding substituted malonic acids with t-butyl hypochlorite. In this reaction, substitution of the hydrogen at C-4 by a chlorine atom is usually observed. By this procedure the 4-phenyl-4-chloro pyrazoline-3,5-dione, 7, was isolated as a crystalline solid, m.p. 220-22^o C. Treatment of 1 either with 3 and 4 led to the corresponding chlorinated adducts which, by hydrogenation of the double bond (and loss of the chlorine atom by hydrogenolysis) afforded the 13,14-diazasteroids 8 and 9 (Scheme 2).

The adducts were always formed by adding an acetone solution of the diene to the respective dienophylic in acetone, at temperature between -60 and -70^oC. Solvent was removed and the residue separated as a solid or oil and crystallised, to give adduct yields of 15-20% (yield rises up to 40% in 3). The hydrogenation products were obtained in quantitative yields.

All the compounds above described were identified by elemental analysis and IR and NMR spectroscopy, on the basis of the spectroscopic data known from adducts previously studied.



SCHEME 1



SCHEME 2

REFERENCES

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