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REACTION OF METHANE(TRI-CHLOROACETONE) UNDER FAVORSKII CONDITIONS: A DIRECT ENTRY TO THE TRIASTERANE STRUCTURE

E. Herranz and F. Serratosa[+]

Instituto de Química Orgánica de Barcelona. Patronato "Juan de la Cierva".
C.S.I.C. Barcelona-17. Spain

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Methane(triacetic) acid derivatives are useful starting materials for the synthesis of some unusual polycyclic cage structures.[1,2]

In the present communication we wish to report the reaction of methane(tri-chloroacetone)(I) -a compound easily accesible by the method we have recently described[2b]- under Favorskii conditions.

Dropwise addition of a solution of methane(tri-chloroacetone) in anhydrous THF to a solution of potassium ter-butoxide in ter-butyl alcohol affords, in 72% yield, a water soluble, highly crystalline, $C_{10}H_{10}O_3$ compound, m.p. 108º, that has been characterized by spectroscopic techniques (UV, IR, NMR and MS), as well as by mechanistic considerations and the preparation of some derivatives, as 1-hydroxymethyl-tetracyclo$[3.3.1.0^{2,8}.0^{4,6}]$nona-3,7-dione (II).

This one-step synthesis of a triasterane[3] derivative involves a series of intramolecular transformations (Scheme 1) that found precedents in the intermolecular base-induced reactions of mono-α-chloroketones:

i) proton abstraction from the more acidic CH_2 adjacent to both the carbonyl group and the chlorine atom[4],

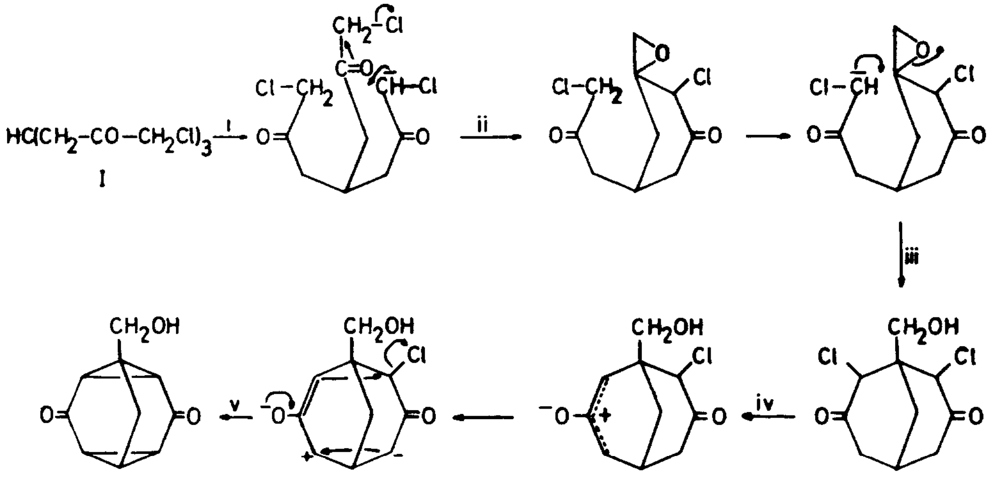
ii) intramolecular nucleophilic attack of the carbanion to the carbonyl group of another side chain, with simultaneous attack of the resulting alkoxide to the adjacent carbon atom and elimination of a chloride, to give an epoxide,[5]

iii) intramolecular nucleophilic attack of a second carbanion to the epoxide and formation of a bicyclic primary carbinol[5],

iv) dehydrochlorination of this bicyclic carbinol to give an oxyallyl dipolar ion[6], and

v) "anomalous Favorskii rearrangement" of the oxyallyl dipolar ion, induced by an intramolecular nucleophilic attack of a new carbanion, to give the triasterane II.

Confirmation of the triasterane structure for compound II could be obtained by addition of a lanthanide shift reagent, such as Eu(fod)$_3$, to the deuterochloroform solution, which produces a nearly first-order NMR spectrum.



Scheme 1

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