Tetrahedron Letters No.32, pp. 2813-2816, 1965. Pergamon Press Ltd.
Printed in Great Britain.

RESEARCHES ON THE REACTIVITY OF 9 BISPIDINONES (*)

Giovanni Gottarelli

Istituto di Chimica degli Intermedi Università di Bologna Italy

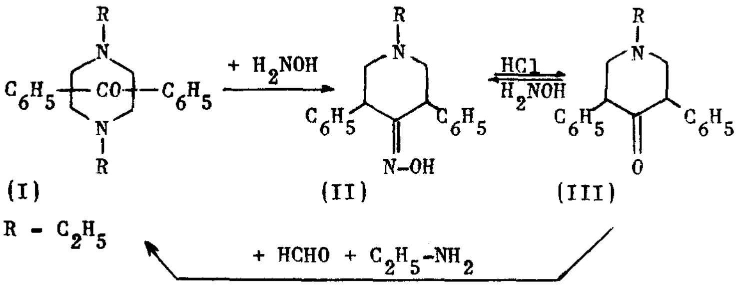
(Received 23 June 1965)

In the field of the preceding researches on the reactivity of Mannich's bases (1) in course in this Institute, the first results concerning the study of bicyclic systems (Bispidinones, form. I), obtained by Mannich's reaction on the 1,3-di-phenyl-acetone (2), are here reported. There have been particularly examined the reactions of hydroxylamine A), of some primary amines B), of alkali C) on bispidinones, or on the correspondent methyodide derivatives-IV.

Out of the study of these reactions it has emerged the possibility of synthetizing asymmetrical bispidinones, whose interest is evident even in the theoretical aspect.

A) The various attempts to put into evidence the carbonyl by the common reagents had previously failed (3). Though not leading to the expected oxime the reaction by hydroxilamine hydrocloride in presence of sodium acetate in acetic acid (3;1) during 8-10 hours at 100°C has supplied a product identified as the oxime of the γ-Piperidone (form. II):

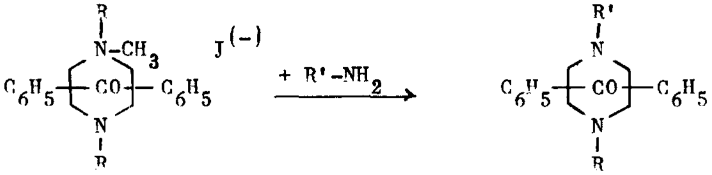
(*) This work was made possible by the C.N.R. fund.


(I) (II) (III)

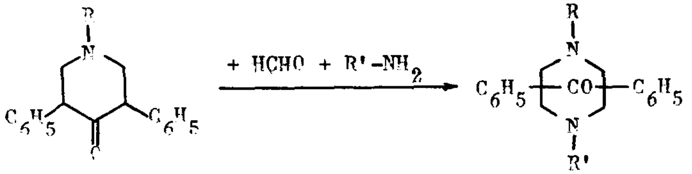
R - C_2H_5

The ketone III is probably the meso (bis-equatorial) compound as it is originated by the breaking of the bridged system (form. I) where the two phenyl are obliged in a bis-equatorial position. Every attempt to isomerize (III) into the trans derivative has not given results worth consideration. From this point of view for the oxime II two "geometrical enantiomorphic" isomers (4) might be possible.

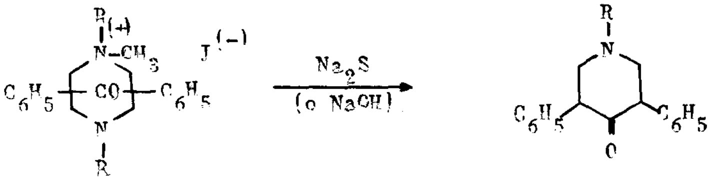
B) The primary alkylamines react with methyodides-IV to supply exchange products (form. V)


(IV) (V)

whose structure is confirmed by synthesis:



C) The action of alkali or sodium sulphide on methyodides-IV, is carried on with the elimination of a ring to give γ-piperidone-VI (III-VI):

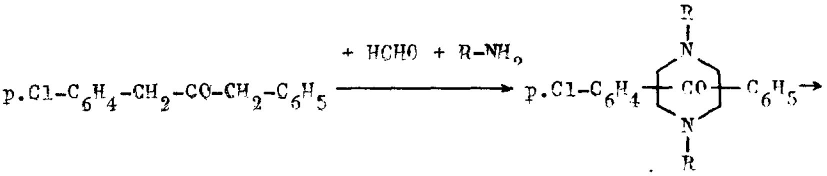


(IV)

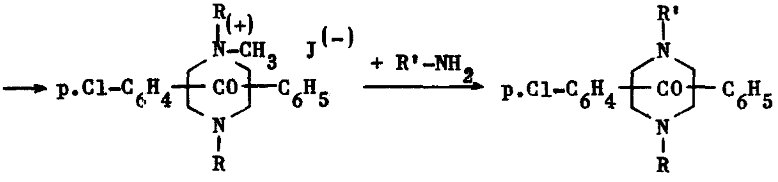
(VI)

$R = C_2H_5$

Among the above referred reactions, the aminolysis one shows useful to the synthesis of asymmetric bispidinones of type IX according to the following scheme:



(VII)



(VIII) (IX)

$R - C_2H_5$; $R' - C_6H_{11}$

The bispidinones IX has two asymmetrical carbon atoms, but only a DL pair must be expected for it, in so much as the bridge of the second ring is fixed on cis position. Researches for the separation and characterization of stereoysomers, of bispidinones IX and of the expected geometrical enontiomorphic isomers of oxime-II are in course.

"I am grateful to Prof. Renato Andrisano for useful discussion the subiect"

References

(1) A.S.Angeloni e M.Tramontini, Ann.Chim., 34, 645 (1964); R.Andrisano, A.S.Angeloni e M.Tramontini, Ann.Chim., 55, 143 (1965).
(2) Zu Yoong Kyi and Walter Wilson, J.Chem.Soc., 1951, 1706.
(3) Mannich and Veit, Ber., 68, 506 (1935); Zu Yoong Kyi and Walter Wilson, J.Chem.Soc., 1951, 1706; S.Chiavarelli, G.Settimy, H.Magalhès Alves, Gazz.chim.ital. 87, 109 (1957).
(4) R.H.Lyle and G.G.Lyle, J.Org.Chem., 24, 1679 (1959).