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REACTIONS OF TRIKETO COMPOUNDS. Part-I

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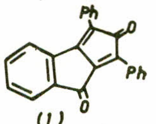
Condensation of ninhydrin with diphenyl ketone gives Indanocyclone (I), with urea it forms ninhydrylurea (II), whereas, acetamides react to give indeno [2, 1-b] pyrroles (III). It is now reported that ninhydrin reacts with dimethyl ketone to form cyclopent [a] indene dione (IV) in acidic media.

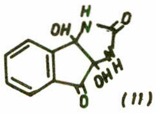
Key words: Cyclopent [a] indene-2, 8-dione; Ninhydrin accetone.

INTRODUCTION

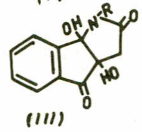
Ninhydrin has been reported to condense with 1, 3-diphenyl-acetone to yield 2, 8-dioxo-1, 3-diphenyl-2, 8-dihydro-cyclopent [a] -indene (I)[1,2] by the elemination of two moles of water molecules. However, urea has been reported to react with ninhydrin to form ninhydryl-urea (II)[3], without elemination of any water molecule. Similarly, acetamide and N-alkyl acetamides form indeno [2, 1-b] pyrroles (III)[4]. We wish to report the reaction of ninhydrin with aliphatic ketone to form 9,10-dihydroxy, cyclopent [a] indene-2, 8-diones-without elemination of water molecules (IV).



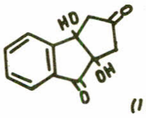
(I)



(II)



(III)



(IV)

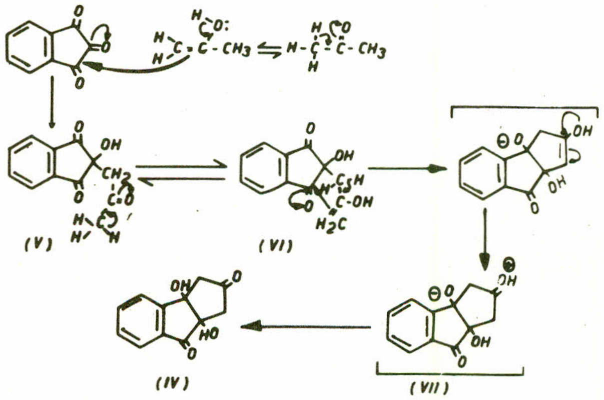
MATERIALS AND METHODS

Ninhydrin (17 gms) in acetone (58 ml) was refluxed on waterbath with hydrochloric acid concentrated (1 ml) for eight hours. The excess acetone was distilled off (40 ml) and the solid so obtained was crystallized by ethanol: water mixtue (3 : 1). An off white crystals were filtered, m.p. 140°. Yield 14 gms. (Found : C-66.4 %, H-4.7 %; 0-28.9 %; Required : C-66 %, H-4.58 %, 0-29.37 %).

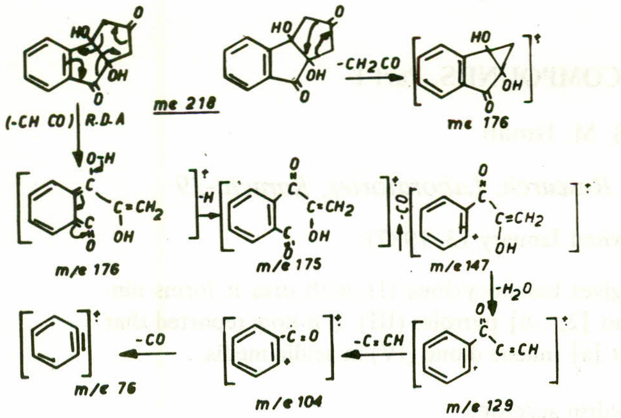
RESULTS AND DISCUSSIONS

Ninhydrin in dimethyl ketone was refluxed for 8 hours in presence of an acid. Excess of acetone was recovered and the solid so obtained was crystallised to give an off white crystals, m.p. 140°. Infrared spectra shows peaks at λ_{max}^{Nujo} 1730 cm^{-1} and 1620 cm^{-1}, suggesting the presence of two keto groups, consistent with those expected for the cyclopent [a] indene-2, 8-dione. The Ultravoilet spectra indicated the presence of 1-indanone chromophore [5]. The I.R. & U.V. spectra resembles closely with those reported for 2, 3, 3a, 8a-tetrahydro-3a, 8a-dihydroxyl-1-methyl indeno [2, 1-b] pyrrole-2, 8-dione (III, R = CH_3), formed by the reaction of N-methylacetamide with ninhydrin [4] indicating a cyclic structure for (IV).

In acidic media the enol tautomer of the acetone is probably involved, initially, in the generation of corresponding isomer (V) in a concerned electronic movement with ninhydrin. This possibly then undergoes into another enol tautomer to form an equilibrium with (VI). This equilibrium (V) = (VI) may then be broken irreversibly in favour of (VI) by intramolecular Aldol-type condensation to afford intermediate (VII) followed by proton transfer to give (IV).



The mass spectra of the compound (IV) showed the presence of ions at m/e 76,104,129,147,175,176 & 218. The prominent ion at m/e 176 suggests the fragmentation of (IV), as shown below, either by Retro-Diels-Alder method or by involving cyclopentane ring.



CONCLUSION

The fragmentation pattern suggest cyclic structure for the compound (IV). The product was identified as 1, 2, 3, 8, 9, 10-hexahydro-9, 10-dihydroxycyclopent [a] indene-2, 8-dione by its mass (m/e 218) as well as P.M.R. spectra. [rl. 9 – 2.4 (4H, m, aromatic protons), r2.6 – 2.95 (2H, s, 20H, exchangeable with D_2O) and r 6.3 – 6.95 (4H, Two doublets, geminal hydrogens)].

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