

A NOVEL REACTION OF 2-PHENACYLDIMEDONE WITH
N,N-DISUBSTITUTED HYDRAZINES^{1,2}

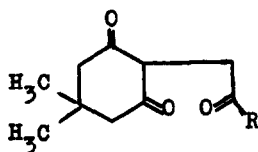
K. Nagarajan and R.K. Shah

CIBA Research Centre, Goregaon, Bombay 63, India.

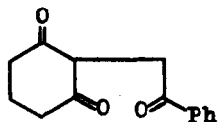
(Received in UK 23 February 1972; accepted for publication 2 March 1972)

The reaction of acetyldimedone (I) and 2-phenacyl-1,3-cyclohexanedione (II) with primary amines constitutes the basis for the synthesis of 'ketotetrahydroindoles' of type III³ which have been further usefully exploited⁴. We wish to report that the reaction of 2-phenacyldimedone (IV) with N,N-dimethylhydrazine does not lead to the expected pyrrole V, but an anomalous product of structure VI. Addition of 2-3 molecular equivalents of the hydrazine to IV resulted in an exothermic reaction. The initially formed paste became a crystalline solid. The reaction was completed by adding alcohol and refluxing the mixture for $\frac{1}{2}$ hr. The product, C₁₈H₂₂N₂O, m.p. 255-257°, was obtained in about 60% yield. Its U.V. (95% EtOH) [λ_{\max} 248, 276, 320 (inflex) nm (log ϵ 4.21, 4.25, 3.84)], IR (nujol mull) (bands at 1620, 3200 cm⁻¹) and NMR spectra (in DMSO-d₆ on Varian A60; TMS internal standard) [signals at δ 1.07 ppm (s, -C-Me₂), 2.27 (s, CH₂), 2.67 (8H, NMe₂, CH₂), 7.1-7.6 (m, 3 aromatic H), 7.7-8.0 (m, 2 aromatic H) and 11.2 (broad s, NH, washed out by D₂O)] were in agreement with structure VI. With N-aminomorpholine, IV likewise gave in 51% yield, the morpholino pyrrole VII, C₂₀H₂₄N₂O₂, m.p. 297-8°, forming an oxime, m.p. 285°(d), and with N,N-dibenzylhydrazine, the 3-dibenzyl-aminopyrrole VIII, m.p. 205-7°, in 43% yield. The U.V. spectra of VI, VII and VIII resembled those of the pyrroles X and XI, which were prepared by standard procedures³.

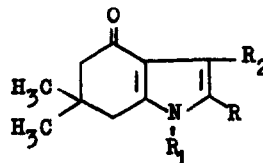
Catalytic debenylation of VIII afforded IX, m.p. 221-3°, whose diazonium sulfate on being heated in boiling alcohol, yielded X, m.p. 235-6°, thus confirming the structures of these novel products.

I R = CH₃

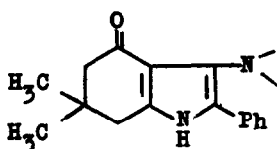
IV R = Ph



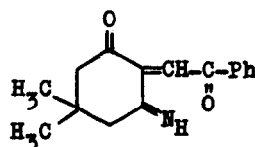
II



III

V R = Ph; R₁ = NMe₂; R₂ = HX R = Ph; R₁ = R₂ = HXI R = Ph; R₁ = H; R₂ = CH₃

VI N < = NMe

VII N < = VIII N < = N(CH₂Ph)₂IX N < = NH₂

XIII

Reaction of 1 mole of IV with 3 moles of *N,N*-dimethylhydrazine and 10 moles of morpholine yielded a mixture of VI and VII in the approximate ratio of 1:3. Pure VII was isolated from this mixture and identified. VII was also obtained from 3-amino-5,5-dimethyl-2-cyclohexenone, phenyl glyoxal and morpholine, thus making it conceivable that XIII was the key intermediate in the formation of VII from IV with *N*-aminomorpholine. Experiments are in progress to elucidate the mechanism and scope of this novel reaction.

We are thankful to Dr. T.R. Govindachari, Director, CIBA Research Centre, for his interest in this work and to Dr. S.Selvavinayakam for analytical and spectral data.

References

1. Contribution No.280 from CIBA Research Centre.
2. Presented before the Convention of Chemists, Bombay, October 27-November 1, 1971.
3. H. Stetter and R. Lauterbach, *Ann.*, **655**, 20 (1962).
4. H.J. Weiss et al in *Topics in Heterocyclic Chemistry* edited by Raymond N. Castle, Wiley-Interscience, 1969, p.195.