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α-HALOAMIDE REACTIONS. III[1]. THE REACTION OF α-CHLORO-α-α-DIPHENYLACETANILIDE WITH SODIUM HYDRIDE

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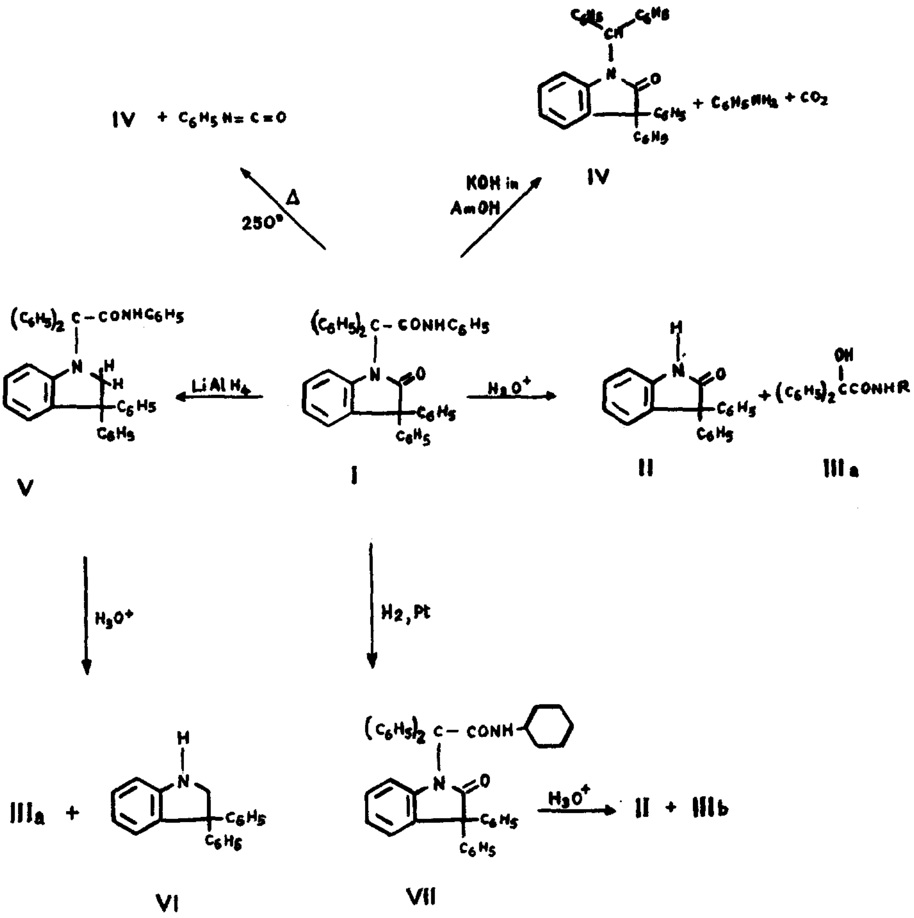
In this communication we show that the correct structure of product obtained in the reaction of α-chloro-α,α-diphenylacetanilide with sodium hydride[1b] is that of 1-[diphenylmethylcarbanilide]-3.3-diphenyloxindole (I)[2]. We found a molecular weight of 567 ± 5 (Calcd. for $C_{40}H_{30}N_2O_2$: 570) for the product (I) melting at 213-214°[3], by use of vapor pressure osmometer (Mechrolab VPO Model 301A), in benzene at 37°. The assignment of structure follows: i) from its hydrolysis in 10% hydrochloric acid in 80% acetic acid, giving a 1.3:1 mixture of 3.3-diphenyloxindole (II)[4] and α-hydroxy-α,α-diphenylacetanilide (IIIa)[4]; ii) its alkaline hydrolysis in boiling amylalcohol, providing 1-diphenylmethyl-3.3-diphenyloxindole (IV) [m.p.223°[5] ; anal. found: C,87.7; H,5.6; N,3.1; mol.wt., 451 (mass spectrum); $^{EtOH}_{max}$ 260 mμ (4.02)]; iii) on $LiAlH_4$ reduction in boiling N-ethylmorpholine only the lactam carbonyl was affected, resulting in a $C_{40}H_{32}N_2O$ compound (75%), m.p.177°(V). This was evidenced from its acid hydrolysis, furnishing a 1:1 mixture of (IIIa) and 3.3-diphenyl-2.3-dihydroindole (VI, m.p.205-206°) being characterized as a picrate, m.p.212-214° (*anal.* found : C.62.6; H,4.1; N,11.3); iv) its platinum-promoted hydrogenation (uptake, 3 moles H_2) resulted in the reduction of the aniline group only (VII, m.p.204-205°; *anal.* found for $C_{40}H_{36}N_2O$: C,83.5; H,6.4; N,4.8), yielding upon acid hydrolysis a 1:1 mixture of II and N-cyclohexyl-α-α-diphenyl-acetamide (IIIb)[4]. (I) tends to undergo easy fragmentation on heating above its m.p., giving IV and phenylisocyanate[6].

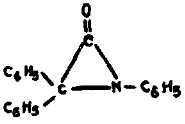
Chart 2 portrays in outline a mechanism for the formation of I. It is assumed that 1.3.3-triphenylaziridone-2 (α-lactam) (VIII), produced in the first stage of the reaction, undergoes an unusual dimerization into I. This involves cyclization of VIII with concomitant attack of the heterocyclic nitrogen on the carbon atom of another molecule of α-lactam to yield a zwitter-ionic intermediate (IX), which is then stabilized by shift of proton following the route IX → I. Dimerization of VIII into the respective hexaphenyldiketopiperazine[7] does not seem to occur, probably due to steric factors. The formation of I in the reaction of phenyl isocyanate and diphenyldiazomethane[8] under the influence of ultraviolet light is likely to proceed by the same mechanism.

CHART I

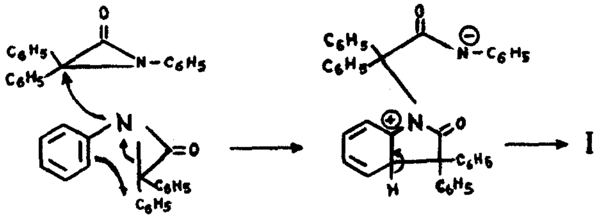


IIIa $R = C_6H_5$ IIIb $R = C_6H_{11}$

CHART 2



VIII



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2. S.Sarel and J.T.Klug, ibid., preceding paper.
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4. The products showed identity with authentic samples prepared according to literature, as to m.p., mixture m.p. and infrared spectra.
5. C.H.Hassall and A.E.Lippman, J.Chem.Soc., 1059 (1953) give for 1-diphenylmethyl-3.3-diphenyloxindole m.p.219.5-220 and λ_{max}^{EtOH} 260 mμ (3.98).
6. Compare, T.Mukauyama, H.Takei and Y.Koma, Bull.Chem.Soc.Japan, 36, 95 (1963)
7. The correct structure of the thermal dehydrochlorination product of α-chloro-α-diphenylacetanilide, first described by H.Klinger [Ann., 390, 367 (1912)] and then in our previous paper[1b] proved to be 3.3-diphenyloxindole (II), rather than hexaphenyldiketopiperazine as formulated by Klinger [S.Sarel, E.Breuer, and H.Leader, unpublished results].
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