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A NOVEL DEHYDROGENATION SEQUENCE

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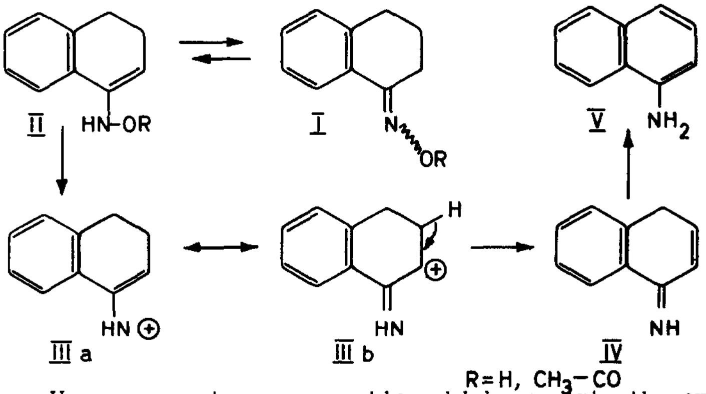
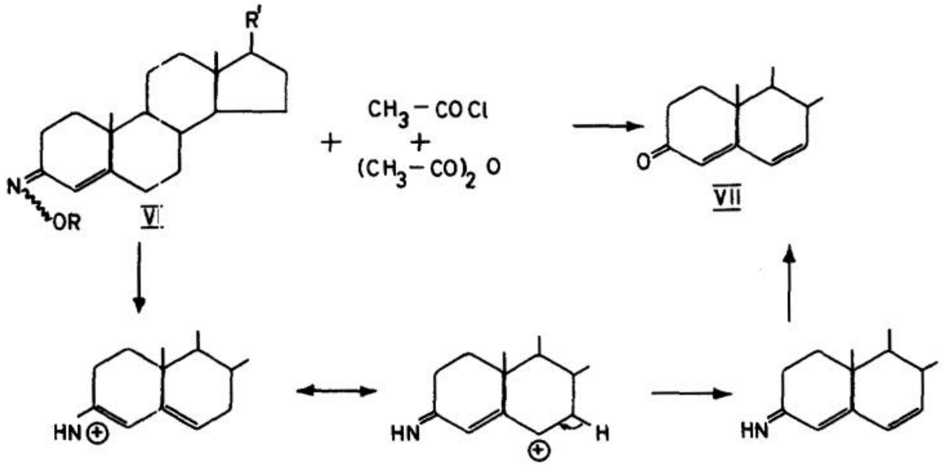
ONE of the suggestions[1] concerning the mechanism of Wolff-Semmler reaction[2] involved the intermediacy of a mesomeric-α-iminocarbonium ion (IIIa and IIIb) which upon elimination of a proton, is transformed into an imine of dienone or its analogue, e.g. IIIa,b is converted to IV, in the case of tetralone oxime. This view has been fruitful in indicating the possibility of a novel dehydrogenation sequence when the chance for concommitant aromatization does not exist.



We now report a new reaction which converts the oxime of an α,β-unsaturated ketone (IV) to a dienone (VII).



R=H-, CH_3-CO-
R', a=$C_8H_{17}-$, b=OH, C=$CH_3-CO-O-$

Cholestenone oxime VIa (R=H) was converted to its acetyl derivative VIa (R=CH_3-CO) with acetic anhydride and pyridine. It was treated without isolation, with a solution acetylchloride in aceticanhydride under ice cooling and stirring. After heating on a waterbath for 4 hrs., the reaction mixture was treated with water and extracted with benzene. The benzene extract was washed successively with conc. hydrochloric acid, water, brine and dried over sodium sulphate and the solvent was evaporated. The residue was taken up in acetic acid, treated with dinitrophenylhydrazine, and warmed for 5 min. on a waterbath, cooled, and the solid was collected.[3] The crude mixture of DNPs obtained in 43% yield was chromatographed over silica gel. Elution with benzene-petrol (70:30) gave a product, m.p. 225-8°, which upon recrystallization from ethyl acetate yielded (32%) red needles, m.p. 230-1° alone or when mixed with DNP of authentic cholesta-4,6-diene-3-one (VII).[4] IR and UV spectra of both these derivatives were similar. The DNP was converted to the dienone, by a known procedure.[5] The yellow material on recrystallization furnished yellow neeldes, m.p. 77-8°, in 30% yield (based on cholestenone). Identity was proved by mixed m.p., and comparison of UV and IR spectra of the product with the authentic specimen of VII.[4]

The residual DNP that remained after chromatography and elution of DNP of VII, consisted of a mixture of at least three components as found by TLC on silica gel. We are now engaged in separating and characterizing these products.

In a similar manner the oxime of testosterone acetate was converted to 6-dehydrotestosterone, m.p. 205-7°, (uncorrected) Lit.[6] 209-11° (corrected) in about 30% yield. In this case also the dienone was isolated as the DNP derivative and later regenerated from it. The scope of this reaction, and effect of variations of experimental conditions are being explored.

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