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TAUTOMERIZATION AND A NOVEL REARRANGEMENT IN 2-NITROINDENES

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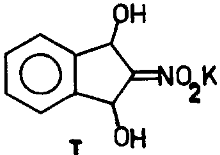
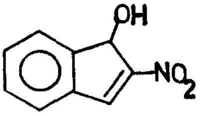
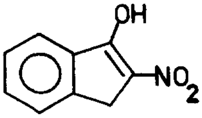
Phthaldehyde reacts with nitromethane in alcoholic potassium hydroxide solution to produce potassium 1,3-dihydroxy-2-aci-nitroindane (I)[1] which after treatment with aqueous hydrochloric acid is converted to 1-hydroxy-2-nitroindene (II)[1,2]. This product was for many years, until its NMR spectrum was recorded[2], considered to be 3-hydroxy-2-nitroindene (III) and/or its keto-tautomer, 2-nitroindane-1-one (IV)[3,4]. This conclusion was mainly based on the fact that II gives a 2,4-dinitrophenylhydrazone when reacted with 2,4-dinitrophenylhydrazine. It appeared to the present author that in this process II might have undergone a tautomerization to IV. In connection with a similar study in the thiophene series[5], occasion was given to test this idea. Others have shown[1] that sodium hydroxide does not bring about this tautomerization, but instead a Michael addition takes place producing 1,3-dihydroxy-2-nitroindane. It was, however, considered likely that tertiary amines would be the bases of choice to convert II to IV, and this indeed proved to be the case. With triethylamine in benzene solution, II was in few minutes completely converted to a product which mainly consisted of IV. Even catalytic amounts of pyridine suffice to promote this reaction.



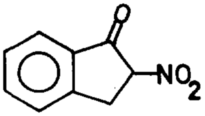
I



II



III

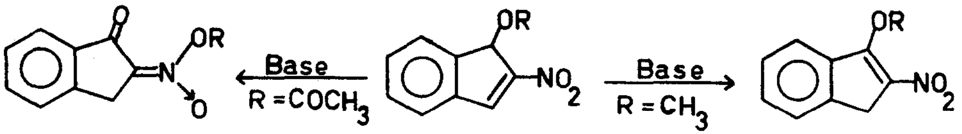


IV

The product from the rearrangement was isolated. The IR spectrum (KBr) showed strong bands at 1730 cm^{-1} (CO) and 1550 cm^{-1} (NO_2) with a weaker one at 1365 cm^{-1} (NO_2). This is in good agreement with the reported values for 2-nitroindane-1-one (IV)[6]. The melting point (72-74°) is lower than the reported one (80.0-81.5°)[6]. The explanation for this discrepancy may be that some of the enol III was present in the product. A positive ferric chloride test (negative for II) supports this hypothesis. It is however quite clear from the NMR spectrum of the crude material that the ketone IV is the main (>90%) product. The spectrum ($CDCl_3$) was rather complicated, but three multiplets with relative intensities 4:1:2 centered at τ=2.4, τ=4.6 and τ=6.2 ppm were distinguishable. These bands are assigned to the aromatic hydrogens, the methine and the methylene hydrogens respectively. (2-Benzoylindane-1-one displays corresponding signals at τ=2.5, τ=5.2 and τ=6.3 ppm)[7]. The MS spectrum (direct inlet) is not in disagreement with the above conclusion, giving the correct molecular ion peak at m/e 177 (12%), and the base peak at m/e 130, corresponding to the loss of HNO_2 from the molecular ion.

It was now of interest to see if this rearrangement took place with the methyl and acetyl derivatives[3], e.g. Va and Vb. When Va was treated with base (triethylamine or pyridine), it rearranged completely to the enol ether VIa. The structural assignment is based on spectroscopic evidence (NMR, IR and MS) as well as on elementary analysis. The compound was isolated as faint yellow plates, m.p. 85-86°. NMR ($CDCl_3$): τ=2.3 ppm (m, 1H: H_4); τ=2.6 ppm (m, 3H: H_{567}) τ=5.63 ppm (s, 3H: OCH_3) and τ=6.13 ppm (s, 2H: CH_2). The IR spectrum (KBr) contained strong bands at 1595 cm^{-1} (C=C), 1570 cm^{-1} (NO_2) and 1370 cm^{-1} (NO_2). The MS spectrum had dominant peaks at m/e 191 (76%) and m/e 145 (100%) corresponding to the molecular ion and the fragment M^+-NO_2 respectively.

When Vb in the same manner was treated with catalytic amounts of triethylamine in benzene solution, a product was isolated from the dark green mixture as colourless needles, m.p. 90° (dec.). The spectroscopic data were not compatible with the expected enol acetate corresponding to VIa, but rather with the nitronic anhydride VIb. The NMR spectrum ($CDCl_3$) possessed three

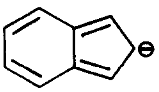


VIb Va Vb VIa

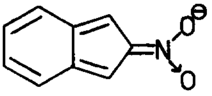
bands with intensities 4:2:3 at $\tau=2.4$ (m), $\tau=6.03$ (s) and $\tau=7.63$ ppm (s), due to the aromatic, the methylene and the acetyl hydrogens respectively. The IR spectrum (KBr) exhibited strong bands at 1805 cm^{-1} (acetyl carbonyl), 1710 cm^{-1} (ring carbonyl) and 1610 cm^{-1} (C=N[8]). The MS spectrum gave the right molecular weight and the base peak at m/e 43 (acetyl). The elementary analysis was in accordance with calculated values. It is thus the IR spectrum that disproves the conjugated enol acetate structure, which is expected to give only one strong band in the carbonyl region. It may be added that the positions of the given bands are almost the same when the spectrum is recorded in methylene chloride solution.

This type of rearrangement, in which an acetyl group migrates from an ester position to an oxygen of a nitro group, has tothe author's knowledge not been observed before. A limited number of nitronic anhydrides have been described in the literature[8-10]. They are prepared by acylation of the salts of secondary nitro compounds. Only the more conjugated ones are stable at room temperature[10], e.g. O-benzoyl-1-aci-nitroindene[8] is a crystalline solid, m.p. 120°.

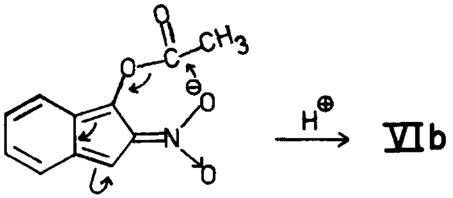
Due to the work of Bergson and his collaborators, the 1,3-tautomeric proton transfer in deuterated and alkyl substituted indenes is well documented[11]. With aliphatic amines in non--dissociating solvents (e.g. pyridine) the reactions were found to be intramolecular and stereospecific. In these cases indenyl-ammonium ion pairs were proposed as intermediates. In the rearrangement from position 1 to position 3, an intermediate in which the ammonium ion lies - above position 2 of the indenyl ion VII was calculated to be important[12]. If a similar mechanism is applicable in the cases reported in this paper, one has a ready explanation for the rate of these extremely rapid tautomerizations by simple consideration of the extra resonance stabilization due to the nitro group in the 2 position (resonance structure VIII). The observed colours (mostly dark green) during the rearrangements may be of significance in this connection. The fact that the acetoxy compound Vb gave the nitronic anhydride VIb upon rearrangement is also indicative of an intermediate analogous to VIII (cf. IX). Here a nucleophilic attack from the



VII



VIII



IX

negatively charged nitro oxygen on the carbonyl carbon and an acyl-oxygen cleavage in the ester group followed by protonation at the 1 position explains the observed acetyl migration. The possibility that the conjugated enol acetate (analogous to VIa) is formed first and then rapidly rearranges to VIb is considered less likely because similar enol acetates are known to be stable under comparable conditions[13].

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