Tetrahedron Letters No. 19, pp 1603 - 1606, 1975. Pergamon Press. Printed in Great Britain.

OXINDOLYLIDENENITROMETHANE AND THE REARRANGEMENT OF THE RELATED NITROBICYCLO[2,2,1]HEPTENE TO A BENZENE DERIVATIVE

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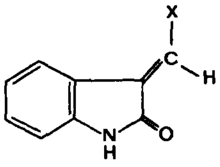
(Received in UK 24 March 1975; accepted for publication 3 April 1975)

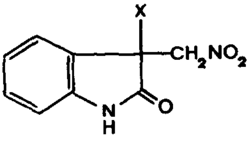
Previous attempts to prepare[1] oxindolylidenenitromethane (Ia) were frustrated by failure to dehydrate the intermediate (IIa) obtained from isatin and nitromethane. As we required this compound in order to extend our studies[2] of the dienophilic behaviour of oxindolylidene derivatives, we utilised a procedure described[3] by Tacconi to obtain the chloro compound (IIb), which we dehydrochlorinated (95% yield) by brief treatment with triethylamine followed by the rapid quenching of the reaction mixture with water. A selection of other bases gave only amorphous brown solids and prolonged exposure to all basic conditions converted the nitro compound (Ia) to a brown polymer.

The use of lithium chloride/dimethylformamide for this reaction gave only oxindolylidenechloromethane[4] (Ib), presumably by an addition-elimination reaction of the initially-formed nitro compound as the same product was obtained from the nitro compound when it was subjected to these conditions. Analogous nucleophilic displacements of the vinylic substituents of oxindolylidene derivatives have been reported[4,5], while Cheeseman and Roy have observed[6] a similar displacement of a nitro group while using lithium chloride in dimethylformamide. Pmr spectra show[7] that both oxindolylidenenitromethane and oxindolylidenechloromethane exist solely as the E-isomers.

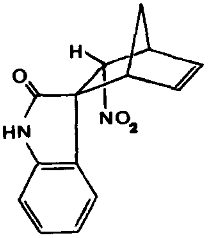
E-Oxindolylidenenitromethane proved to be an excellent dienophile, reacting very rapidly with cyclopentadiene to give, in 95% yield, the nitro adduct (III), one of the two possible[2] isomers. The same product was obtained by 'titrating' an ethereal solution of cyclopentadiene and 3-chloro-3-(nitromethyl)oxindole (IIb) with triethylamine, the transient red colour of the dienophile acting as an indicator. The adduct dissolved in boiling aqueous sodium hydroxide to form a solution which, if cooled immediately, deposited the sodium nitronate (IV), but from which separated an 88% yield of 3-phenyloxindole (VI) if heating was continued. The structure of this product was inferred from its pmr and infra red spectra and its identity confirmed by comparison with a specimen prepared[8] unambiguously. This rearrangement also occurred when an aqueous solution of the nitronate was heated and during the mass spectrometric examination of the salt; the largest mass ion observed was that corresponding to 3-phenyloxindole or its precursor (V). The appended mechanism is suggested for this conversion.



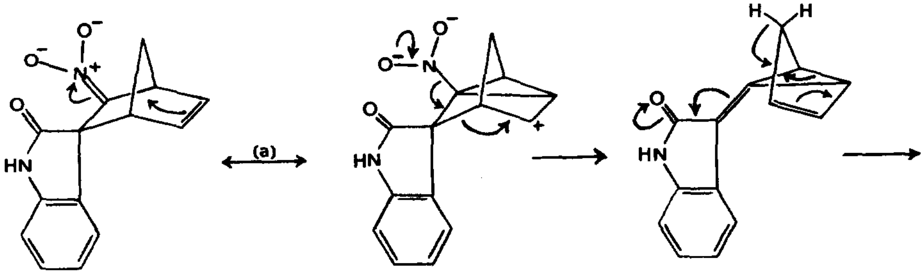
Ia, X = NO_2
Ib, X = Cl



IIa, X = OH
IIb, X = Cl

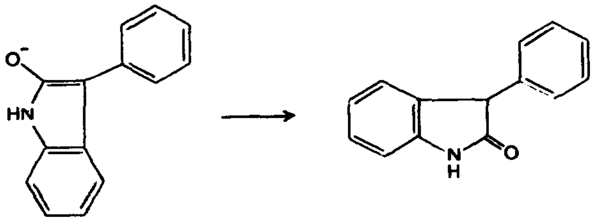


III

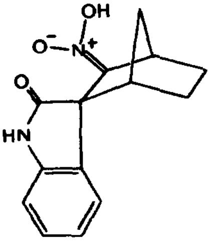


IV

V



VI



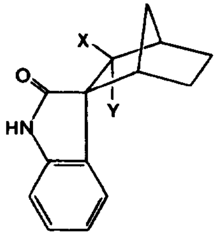
VII

Precedent for step (a) may be found in the suggestion[9] that homoallylic resonance is responsible for the failure of nitronorbornenes to undergo the Nef reaction.

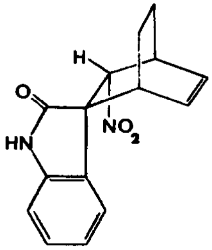
Catalytic hydrogenation of the adduct (III) gave the nitrobicycloheptane (VIIIa), the nitro group of which proved resistant both to catalytic and metal/acid reduction. The dihydro adduct readily formed a sodium nitronate which was stable to prolonged heating, confirming the participation of the norbornene double bond in the above rearrangement.

A mixture of the two trans-5-nitro-6-phenylbicyclo[2,2,1]hept-2-enes did not similarly rearrange when boiled with sodium hydroxide. This result indicated that a suitably situated electron-withdrawing group is also a requirement for this rearrangement; the scope and mechanism are being investigated.

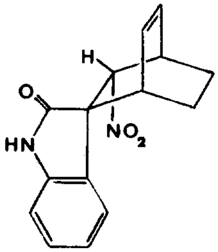
Acidification of an aqueous solution of the reduced nitronate during an attempted Nef reaction gave the acid (VII). The behaviour of this compound contrasts with that normally observed[10] for nitronic acids; no trace of its tautomers, or of any decomposition, has been observed over 22 months. Bornane-2-nitronic acid has a half-life of a few minutes[11]. No ketonic material was formed when the acid (VII) was heated in boiling water for one hour, but tautomerisation to a 3:1 mixture of the epimers (VIIIa and VIIIb) occurred. Complete epimerisation was effected when the endo-nitro adduct (VIIIa) was allowed to stand with a small amount of triethylamine for 7 days an unusual result as base-catalysed epimerisation of simple exo-nitronorbornanes gave[12] mixtures of endo-and-exo-derivatives.



VIIIa, X = H, Y = NO_2
VIIIb, X = NO_2, Y = H



IX



X

Oxindolylidenenitromethane(Ia) also reacted with cyclohexa-1,3-diene to produce a 40% yield of the two bicyclo[2,2,2]octene adducts (IX and X) in a ratio of 4:1. Attempts to improve the yield of this reaction were nullified by the thermal instability of the dienophile which also prevented any adduct formation with butadiene, cycloheptatriene and 1,3-diacetoxycyclohexa-1,3-diene.

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