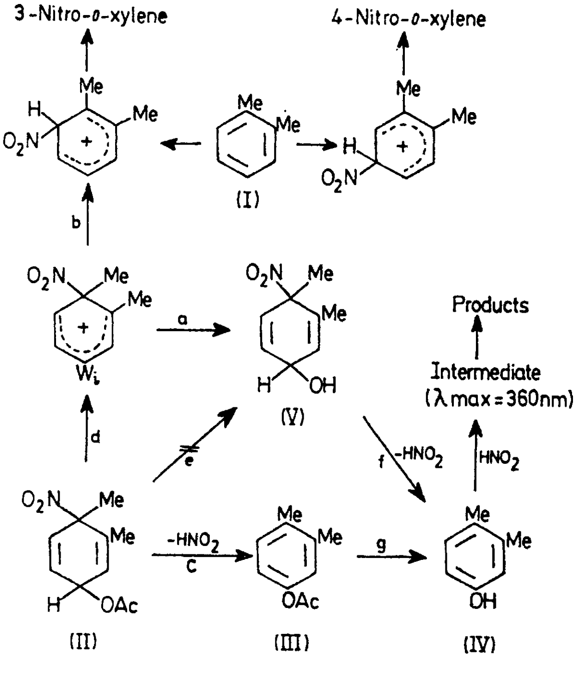
Relevance of the Acidolysis of 3,4-Dimethyl-4-nitrocyclohexa-2,5-dienyl Acetate to the Nitration of *o*-Xylene

By Hugh W. Gibbs, Roy B. Moodie,* and Kenneth Schofield
(*Chemistry Department, The University, Exeter* EX4 4QD)

Summary Acidolysis of 3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate in >55% sulphuric acid proceeds by the $A_{\mathrm{Al}}1$ mechanism, generating the *ipso*-Wheland intermediate which is also formed in the nitration of *o*-xylene; at these but not at lower acidities the results of the acidolysis are relevant to the outcome of nitration.

The yields of nitro-compounds obtained by nitrating methylbenzenes in H_2SO_4 vary with acidity.[1] This happens because the Wheland intermediates formed at *ipso*-positions (W_i's) are captured by nucleophilic attack of water at low acidities (Scheme, step *a*), but increasingly give nitro-compounds by 1,2-migration of the nitro-group (Scheme, step *b*) with rising acidity.[2] From *o*-xylene (I), 3-nitro-*o*-xylene is formed by direct nitration at C-3 and by rearrangement of W_i, so that the percentages of initial attack at the *ipso*- and 3-positions cannot be inferred from the yields of nitro-isomers, except when nucleophilic capture of W_i is complete.[1]



Independent evidence of the partitioning of W_i between capture and rearrangement is needed. Acidolysis of (II) gives 3-nitro-*o*-xylene in yields which increase with acidity.[1,2] The relevance of this to the nitration of *o*-xylene depends upon the extent to which the acidolysis proceeds *via* W_i, and we now report on this point.

Solutions of (II) in 25—32% H_2SO_4 containing 0·03 M urea showed initial spectra identical with that of 3,4-dimethylphenyl acetate (III). In a kinetically first order change the spectrum became that of 3,4-xylenol (IV), the rate constant being similar to that measured independently for the hydrolysis of (III). In 32—70% H_2SO_4 containing 0·03 M urea, to an increasing extent with increasing concentration of H_2SO_4, the initial spectrum was no longer that of (III). A new peak appeared rapidly at 360 nm and underwent first order decay. Independent experiments revealed that addition of aqueous $NaNO_2$ to a solution of (IV) in aqueous H_2SO_4 containing 0·03 M urea generated a peak with identical λ_{max} and first order rate constant for decay. When (II) was dissolved in >70% H_2SO_4 the peak at 360 nm became smaller and eventually negligible with increasing acidity, and the initial spectrum approximated to that of 3-nitro-*o*-xylene and did not change with time.

We interpret these results as follows. (i) The decomposition of (II), at all acidities too rapid to follow, occurs by two competing pathways: elimination of HNO_2[3] (Scheme, step *c*) to give (III) which is then hydrolysed to (IV), and hydrolysis (Scheme, step *d*) to give a mixture of (IV) and 3-nitro-*o*-xylene. In the case of the analogue of (II) derived from 1,2,3-trimethylbenzene the rate of decomposition in aqueous ethanol[3] is proportional to the solvent parameter *Y*. Extrapolation of the results suggests that decomposition would be rapid under our conditions. (ii) Step *d* (Scheme) becomes increasingly important with increasing acidity. In >40% H_2SO_4, (IV) (from step *d*) and HNO_2 are present almost immediately, and react to give the intermediate responsible for the peak at 360 nm. The decay of this intermediate, formed in independent experiments with HNO_2 and 3,4-xylenol under the conditions used in the acidolysis of (II), produced 3,4-dimethyl-2- and 3,4-dimethyl-6-nitrophenol and unidentified minor products. We cannot yet identify the intermediate, but note that intermediates have been observed in other nitrosations.[4] (iii) In >70% H_2SO_4 not only is step *c* (Scheme) negligible by comparison with step *d*, but also W_i gives almost entirely 3-nitro-*o*-xylene (step *b*) and no (V). Good yields of 3-nitro-*o*-xylene are obtained. (iv) The process competing with step *c* (Scheme) in the decomposition of (II) must be fast enough to produce (IV) almost immediately at acidities as low as that represented by 48% H_2SO_4. This supports its identification as step *d* ($A_{\mathrm{Al}}1$ hydrolysis[5]) rather than step *e* ($A_{\mathrm{Ac}}2$ hydrolysis[5]). $A_{\mathrm{Ac}}2$ hydrolysis is rather insensitive to substituents, and in the known examples is relatively slow at this acidity. $A_{\mathrm{Al}}1$ hydrolysis can be fast when there is stabilisation by resonance of the carbonium ion formed (as in the present case), and its rate is steeply acidity-dependent.[5]

Measurements of the yields of 3-nitro-*o*-xylene formed by acidolysis of (II) are only relevant to elucidation of the processes occurring in the nitration of *o*-xylene, in particular to the partitioning of W_i between capture (Scheme, step *a*) and rearrangement (step *b*), when in the acidolysis step *c* does not compete effectively with step *d*. In 49—54% H_2SO_4 the initial peak at 360 nm observed in the solvolysis of (II) arises only because of reaction of HNO_2 with (IV) derived *via* route *d–a–f* (Scheme), and not with that which is formed more slowly *via* route *c–g*. When (III) is treated with $NaNO_2$ in the same media, no such peak is obtained. The initial absorbance at 360 nm, corrected for the known amount of 3-nitro-*o*-xylene formed, can be used to measure the extent of the decomposition of (II) which follows step *d*. This is 60($\pm$10)% in 54%, and *ca.* 100% in 58% H_2SO_4 At higher acidities step *c* is negligible. We hope to make these estimates more precise through experiments using ^{18}O-labelling, but it is now possible to say that the estimates of the partitioning of W_1 used previously,[1] from the yield of 3-nitro-*o*-xylene formed by acidolysis of (II) and assuming decomposition to occur entirely by the $A_{Al}1$ mechanism, were substantially correct for 60 and 70% H_2SO_4, but not for 50% H_2SO_4. Because of the relative unimportance in the nitration of *o*-xylene of step *b* in 50% H_2SO_4, the estimate of the percentage of initial attack at the *ipso*-position in this medium (ref. 1, Table 5) is changed only from 64 to 67%.

(*Received, 2nd April* 1976; *Com.* 345.)

---

[1] J. W. Barnett, R. B. Moodie, K. Schofield, and J. B. Weston, *J.C.S. Perkin II*, 1975, 648.

[2] P. C. Myhre, *J. Amer. Chem. Soc.*, 1972, **94**, 7921.

[3] P. C. Myhre, 'Some Representative Chemistry of *Ipso* Ions Formed During Aromatic Nitration' in 'Industrial and Laboratory Nitrations', eds. L. F. Albright and C. Hanson, American Chemical Society Symposium Series, No. 22, 1976, pp. 87—94.

[4] A. R. Butler and A. P. Sanderson, *J.C.S. Perkin II*, 1974, 1671.

[5] K. Yates, *Accounts Chem. Res.*, 1971, **4**, 136.