Tetrahedron Letters No.21, pp. 2001-2002, 1967. Pergamon Press Ltd. Printed in Great Britain.

PARTICIPATION BY THE HYDROXYL GROUP IN THE ADDITION OF IODINE TO UNSATURATED ALCOHOLS

D.L.H. Williams.

University Science Laboratories, South Road, Durham, England.

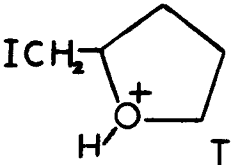
(Received 22 March 1967)

Participation by neighbouring groups, resulting in increased reaction rates and sometimes in the formation of cyclic or rearranged products, is very well established for many reaction types (1), particularly in nucleophilic substitution reactions in which a group can interact with the positive centre of an intermediate carbonium ion. Little kinetic work has been done on the effect of neighbouring groups on the stability of carbonium ions produced by electrophilic addition to olefins, although this has been demonstrated by product analysis on many occasions, e.g. in the formation of iodolactones from olefinic acids and iodine (2), and in the rearrangement of allylic halogen in the addition of hypohalous acids to allyl halides (3).

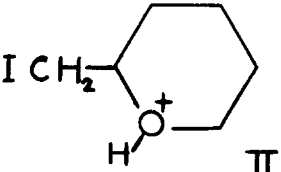
The following initial second-order rate coefficients (l.mole^{-1} min.$^{-1}$) have been determined for the reaction at $0^{\circ}C$ of iodine in aqueous potassium iodide with each of the following alcohols $CH_2=CH(CH_2)_nOH$.

n	1	2	3	4
k_2	0.011	0.023	2.2	0.38 ± 5% in each case

It was necessary to measure initial rate coefficients for compounds n = 1 and 2 since for both these reactions the rate coefficients dropped as reaction proceeded due to the reversibility of the reactions. The product from the reaction of compound n = 3 with iodine was identified as 2 iodomethyltetrahydrofuran. No iodine remained at equilibrium, but again the rate coefficient values decreased slightly as reaction proceeded, possibly due to the simultaneous formation of the cyclic product and a little of the diiodide (reversibly). No product analysis has yet been carried out for the case n = 4, but there was evidence of considerable autocatalysis after *ca.* 30% reaction suggesting that the product expected by neighbouring OH participation, 2 iodomethyltetrahydropyran (which as far as the author is aware has never been described) reacts further with iodine.



I



II

The results show clearly that OH-5 and OH-6 participation *via* intermediates I and II are involved in the reaction of iodine with 4 penten-1-ol and 5 hexen-1-ol respectively. The five-membered ring is more favoured than is the six-membered ring and there is no evidence for any participation through three- or four-membered rings. These conclusions parallel those found (4) for the hydrolysis in water of the chlorohydrins $Cl(CH_2)_nOH$. The rate maximum and the formation of a cyclic product occurred for n = 4. Shilov and co-workers (5) have also found a rate maximum corresponding to O^- - 5 participation in the reaction of iodine with the sodium salts of olefinic carboxylic acids.

References

1. B. Capon, *Quart. Revs.* **18**, 45 (1964).
2. E.E. van Temelen and M. Shamma, *J. Amer. Chem. Soc.* **76**, 2315 (1954).
3. P.B.D. de la Mare, P.G. Naylor and D.L.H. Williams, *J. Chem. Soc.* 3429 (1963).
4. H.W. Heine, A.D. Miller, W.H. Barton and R.W. Greiner, *J. Amer. Chem. Soc.* **75**, 4778 (1953).
5. E.N. Rengevich, V.I. Staninets and E.A. Shilov, *Dokl. Akad. Nauk.* **146**, 111 (1962).