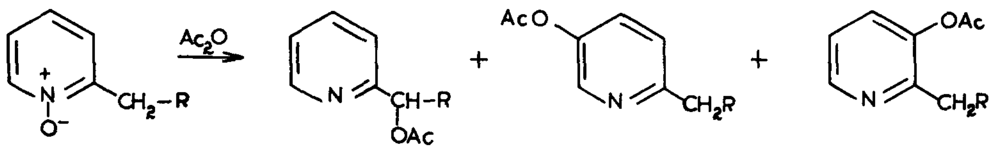
Tetrahedron Letters No.3, pp. 257-260, 1968. Pergamon Press. Printed in Great Britain.

NEW REARRANGEMENT TYPES IN REACTIONS OF ACETIC ANHYDRIDE WITH 2-ALKYLPYRIDINE 1-OXIDES (1)

R. Bodalski (2) and A.R.Katritzky

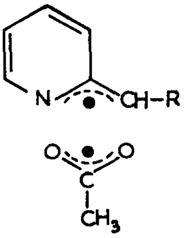
School of Chemical Sciences, University of East Anglia, Norwich

(Received in UK 19 October 1967)

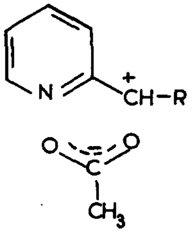


I II III a III b

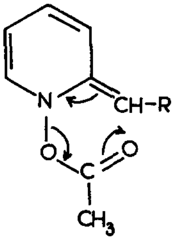
The mechanism of the rearrangement of 2-alkylpyridine 1-oxides (I) into 2-α-acetoxyalkylpyridines (II) has been the subject of considerable controversy since its discovery in 1953 (3). Oae (4) investigated the reaction of 2-picoline 1-oxide with ^{18}O-labelled acetic anhydride and concluded that an intimate radical pair (IV) was an intermediate. Oae's experimental findings could have also resulted (a) from scrambling of the label either before or after the arrangement proper, or alternatively, (b) from neglect of the considerable proportions of by-products of type (III) present (5) in the product. We have carried out ^{18}O-labelling experiments on a variety of 2-alkylpyridine 1-oxides, separated the products by preparative v.p.c., and excluded both these possibilities (6), and thus confirm Oae's experimental findings.



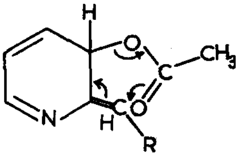
IV



V

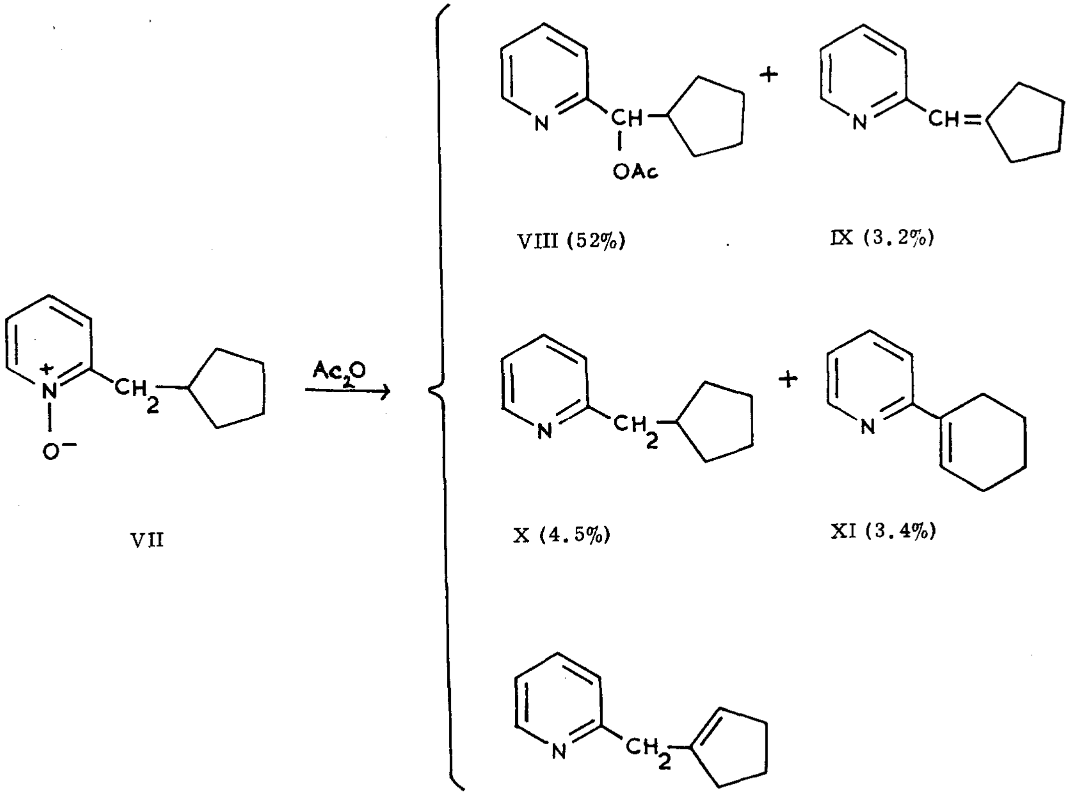


VI a



VI b

However, we do not agree with Oae's interpretation of the labelling results. This work excludes the rearrangement (VIa) as the route to (II) but there are still two other mechanisms which would fit Oae's labelling work : (a) an intimate ion pair (V) as suggested by Cohen and Fager (7), and (b) a reaction sequence involving the formation, and further rearrangement, as indicated, of intermediates of type (VIb). The second possibility (b) is excluded by a detailed consideration of our own labelling results, particularly those involving the isotopic composition of the byproducts of type (III), as will be discussed in detail in the full paper. To test for the possibility (a) we have now studied compounds in which R was selected to allow easy rearrangement of the carbonium ion portion in the ion-pair intermediate (V).

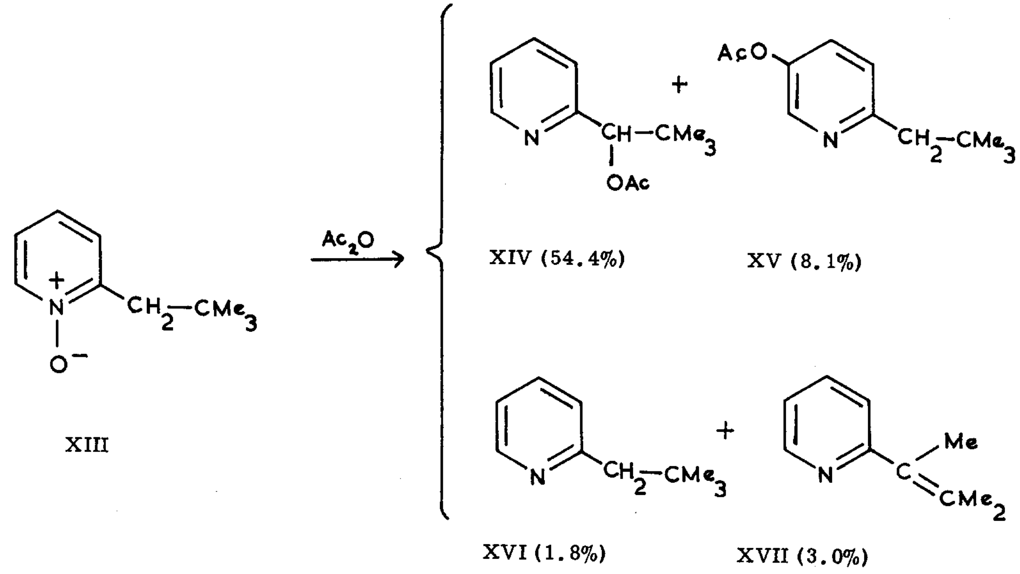


VII

VIII (52%) IX (3.2%)

X (4.5%) XI (3.4%)

XII (7.0%)



2-Cyclopentylcarbinyl- (VII) and 2-neopentyl-pyridine 1-oxide (XIII) were reacted with acetic anhydride and the products (VIII - XII) and (XIV - XVII) detected and analysed (8) by gas chromatography. Independent experiments confirmed the absence of the interconversions (VIII $\rightleftharpoons$ IX $\rightleftharpoons$ XI $\rightleftharpoons$ XII) and (XIV $\rightleftharpoons$ XVII) under the conditions of the reaction. Further, 2-n-propylpyridine 1-oxide yielded 15% of 2-propenylpyridine as well as the expected reaction products.

We consider that the significant proportions of rearranged products of type (XI) and (XVII) in the reaction mixtures afford evidence for the intermediate existence of carbonium ions, probably in the form of ion pairs of type (V). Carbonium ion rearrangements (similar to V → XI, XVII) are commonplace (9) but fast rearrangement of radicals of type (VI) would be unexpected (10).

Very recently (11) other evidence in favour of the ion-pair mechanism has been presented by Cohen and Decto.

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(6) Details will be reported in the full paper. We should like to thank Mr. P. Kelly, University of Newcastle, for help with the ^{18}O work.

(7) T.Cohen and J.H.Fager, J.Amer.Chem.Soc., 87, 5701 (1965).

(8) Satisfactory analytical data were obtained for all compounds reported. Products were identified by independent syntheses; these and the syntheses of the starting materials will be reported in the full paper.

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