Thermal Transacylations in a Series of Cyclic Enamines

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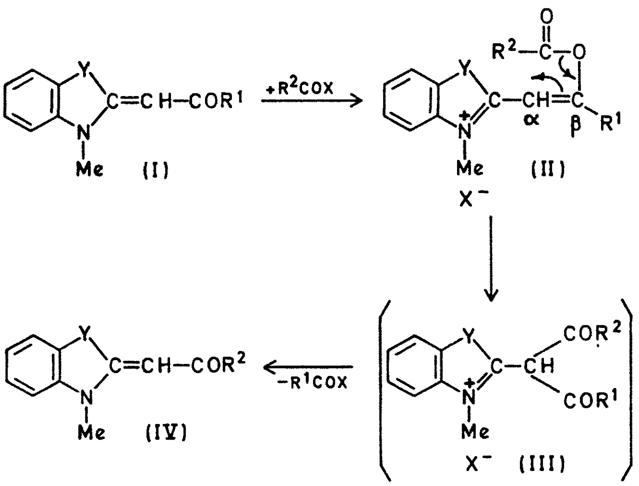
Summary 2-Acylmethylene derivatives of some N-heterocycles were transacylated by thermal rearrangement of the corresponding quaternary enol esters.

THE 2-acylmethylene derivatives (I) of benzthiazoline and benzimidazoline,[1,2] as well as those of 1,2-dihydropyridine[3] and 1,2-dihydroquinoline[4] react with acyl halides giving the corresponding *O*-acyl derivatives (II). These acylation reactions proceed smoothly at room temperature in acetone or benzene solution, their direction being determined by the general tendency of electrophiles to attack the carbonyl oxygen atom rather than the carbon atom of the acylmethylene group.



We have observed that the *O*-acyl derivatives (II) readily undergo a thermal reaction releasing a molecule of acyl halide. When $R^1 \neq R^2$, and R^2 is more electronegative than R^1, the acyl halide molecule eliminated so contains the less electronegative radical R^1, and the thermal reaction leads finally to the transacylated acylmethylene derivative (IV). For example, 3-methyl-2-[β-(*p*-nitrobenzoyloxy)propenyl]benzthiazolium iodide [(II; Y = S, R^1 = Me, R^2 = *p*-$NO_2C_6H_4$, X = I) m.p. 175—176° decomp.] on heating for some minutes at 180—185° is converted into 3-methyl-2-(*p*-nitrobenzoyl)methylenebenzthiazoline (IV; Y = S, R = *p*-$NO_2C_6H_4$; m.p. 300—301°). Similarly, 1,3-dimethyl-2-[β-(*p*-nitrobenzoyloxy)styryl]benzimidazolium chloride [(II; Y = MeN, R^1 = Ph, R^2 = *p*-$NO_2C_6H_4$, X = Cl) m.p. 179—180°] at 245—250° gives 1,3-dimethyl-2-(*p*-nitrobenzoyl)-methylenebenzimidazoline [(IV; Y = MeN, R = *p*-$NO_2C_6H_4$) m.p. 206—207], while 1-methyl-2-[β-(3′,5′-dinitrobenzoyloxy)styryl]quinolinium chloride {[II; Y = CH = CH, R^1 = Ph, R^2 = 3,5-$(NO_2)_2C_6H_3$, X = Cl] m.p. 95—96°} at 185—190° gives 1-methyl-2-(3′,5′,-dinitrobenzoyl)methylene-1,2-dihydroquinoline {[IV; Y = CH = CH, R = 3,5-$(NO_2)_2C_6H_3$] m.p. 320—321° decomp.]}

The mechanism of the reported transformations may be rationalized in terms of an acyl migration proceeding through a 4-centred cyclic transition state, similar to the thermal rearrangement of simple vinyl esters.[5,6] The diacyl intermediates (III) should be unstable[7] and able to eliminate an acyl halide molecule under the reaction conditions used.

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