EFFECTS OF THE ORTHO-SUBSTITUENTS IN THE ENAMIDE PHOTOCYCLIZATION

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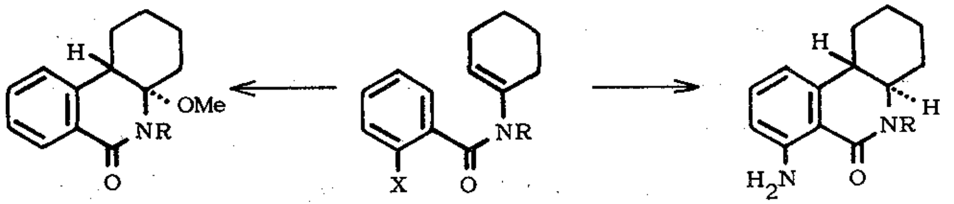
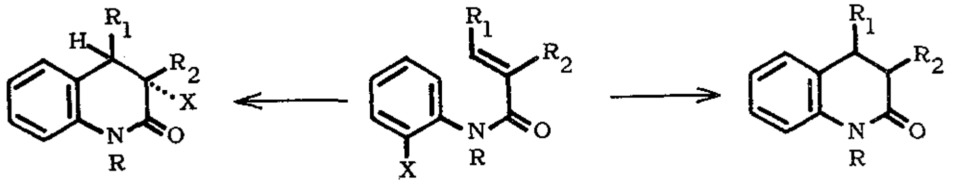
Irradiation of the ortho-methoxyl substituted enamide (Ia) of N-benzoylenamine and the ortho-carbonyl substituted enamides (IIa, b, c) of N-acylanilide types caused facile [1,5]-sigmatropic shift of these ortho-substituents to afford the products (III and V a,b,c) in moderate yields, respectively; whereas the ortho-amino substituted enamide (Ib) afforded the normally cyclized product (IV) due to hydrogen bonding. Further, the ortho-carboxyl substituted enamide (IIe) afforded the photocyclized product (VI), which however had no carboxyl group, but the enamide (IId), which has the ortho-carbamoyl group, afforded a mixture of the products (Vd and VI). With these results, the mechanism of the enamide photocyclization was discussed.



(III)   (Ia,b) (X=OMe, NH_2)   (IV)



(Va,b,c,d)   (IIa,b,c,d,e)   (VI)

(X=CO_2Me, Ac, CN, $CONH_2$, CO_2H)