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REACTIVITY OF THE (C_2–) BENZYLIC GROUP OF 4–OXOQUINZOLINES TOWARDS CARBONYL COMPOUNDS

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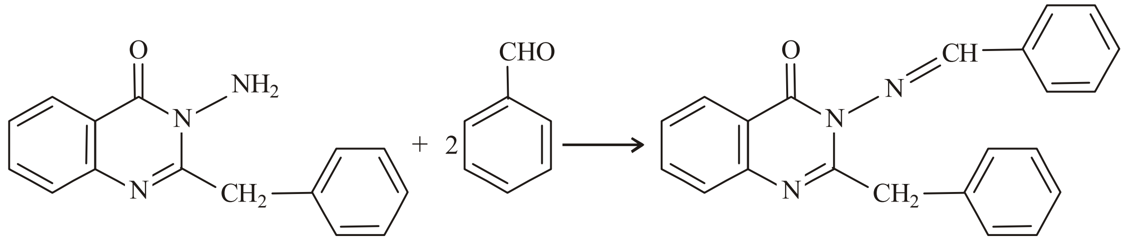
ABSTRACT

As our projected schemes of building tricyclic ring systems required condensations involving the ($N_{(3)}$–NH_2) and the (C_2–) benzylic methylene groups, it was necessary to examine the reactivity of the latter towards carbonyl compounds and others.

Key words: Quinazolones, Benzylic methylene, Benzaldehyde, Condensation.

INTRODUCTION

In view of the above considerations, the quinazolone **(I)** was reacted with 2 mol of benzaldehyde. The product from this reaction was; however, the mono (N_3–) benzylideneamino derivative **(II)**.



(I) **(II)**

The benzylic methylene group at $C_{(2)}$ remained unaffected although heating was continued for a longer time. This reaction was also carried out in ethanolic solution in the presence of piperidine but no further reaction took place after condensation of 1 mol of

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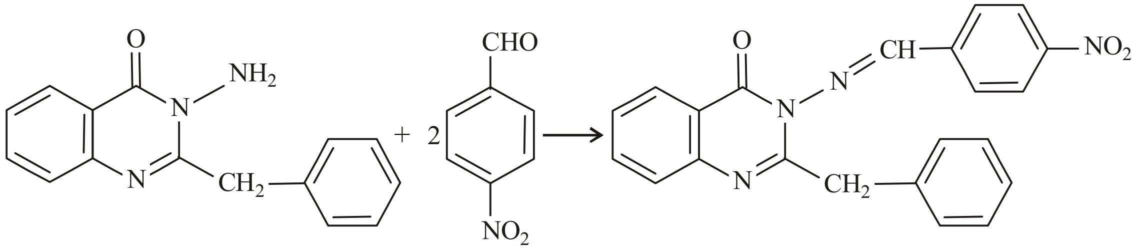
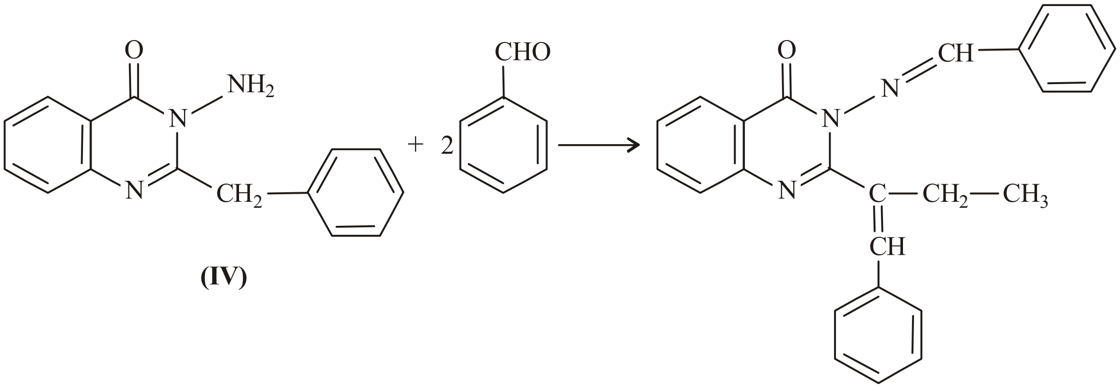
benzaldehyde with the $N_{(3)}–NH_2$ group. The same product **(III)** was obtained, when benzaldehyde was replaced by more reactive p- nitrobenzaldehyde in this reaction.



(I) **(III)**

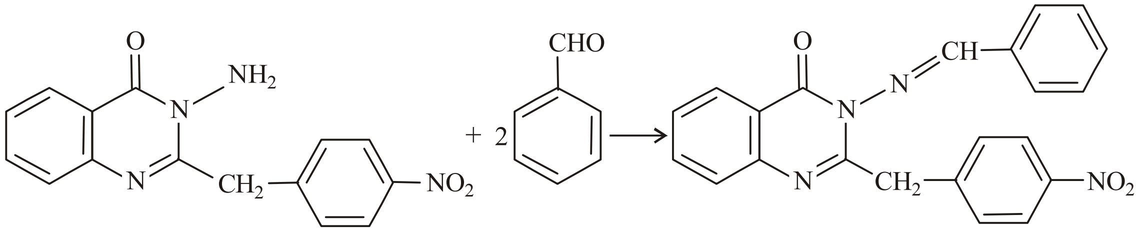
EXPERIMENTAL

It was found by some Egyptian workers that condensation occurs at both $N_{(3)}–NH_2$ and $C_{(2)}–CH_2$ in the quinazolone **(IV)**, when it was reacted with 2 mol of aromatic aldehyde in the presence of acetic acid-acetic anhydride mixture.



(IV)

Contrary to expectations, the methylene group in 3-amino-2-benzyl-4-oxoquinazoline **(I)** and 3-amino-2-p-nitrobenzyl-4-oxoquinazoline **(V)** failed to condense with aromatic aldehydes.

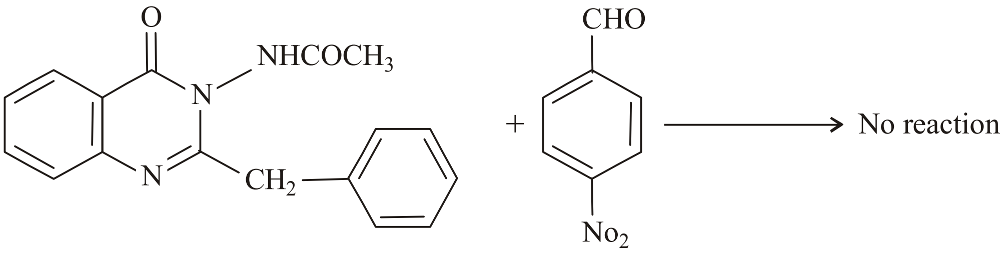


(V)

RESULTS AND DISCUSSION

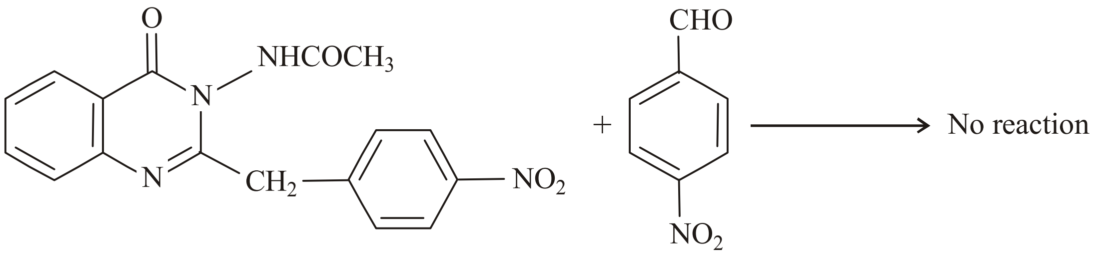
Another approach was made to bring about condensation at the $C_{(2)}$–benzylic methylene group under more forcing conditions. For this, the $N_{(3)}$–NH_2 was protected by acetylation.

The acetamido derivative **(VI)** was treated with p-nitrobenzaldehyde successively in ethanol, pyridine, acetic acid- acetic anhydride mixture and ethanol containing fused zinc chloride. In each case, the quinazolone **(V)** was recovered unchanged with the benzylic methylene group remaining unaffected even under rigorous conditions.



(VI)

Similarly, the following reaction also did not take place.



The non-reactivity of the benzylic methylene in the quinazolones; **(I)** and **(V)**, at first appeared to be very surprising. The methylene group at $C_{(2)}$– is activated because of the electron withdrawing influence of the pyrimidine ring, to which it is attached. This reactivity could be enhanced by a phenyl group, and even more by a p-nitrophenyl group attached to it.

CONCLUSION

It was clear that the steric factors must account for the failure of the methylene group to react and a possible explanation may be as follows: The non-reactivity of the benzylic methylene in the quinazolones; **(I)** and **(V)** at first appeared to be surprising, and it has already been pointed out that the methylene at $C_{(2)}$– is subject to electron withdrawing influence of the pyrimidine ring to which it is attached. The reactivity of this methylene group can be increased, when p-nitrophenyl group is attached to it. Steric factors, must, therefore be responsible for the lack of reactivity shown by the group. If the $C_{(2)}$– methylene were to condense with an aromatic aldehyde, the methylene carbon is sp^2 hybridized with its three bonds extending at angles of 120^0 with each other. This would push one of the aryl groups very close to the group attached to $N_{(3)}$–N. The steric strain caused on account of this would preclude the formation of an arylidene group at $C_{(2)}$– carbon.

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