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Two Paths for the Acid Catalysed Interaction of Carbonyl Compounds with Nitriles

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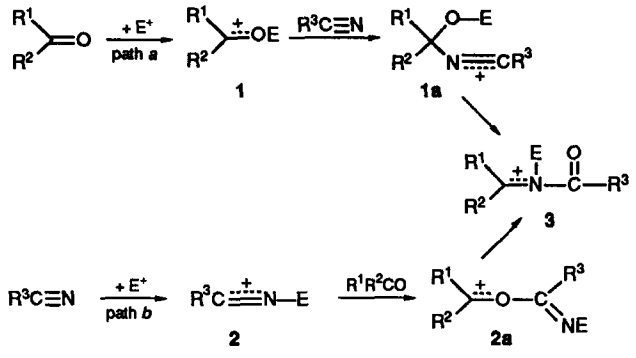
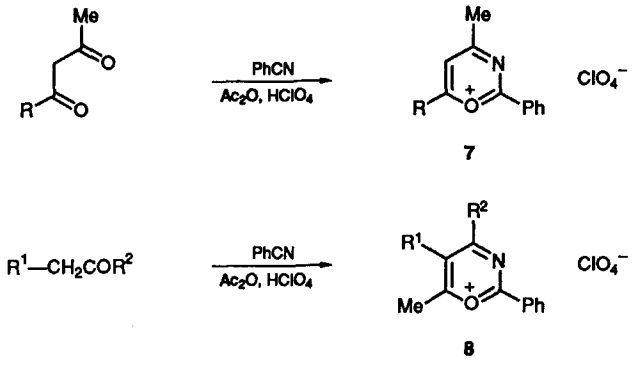
The acid catalysed interaction of carbonyl compounds with nitriles has been shown, on the basis of experimental data and AM1 quantum chemical calculations, not to be a variant of the Ritter reaction, in contrast to earlier proposals, but to be an independent reaction.

The acid catalysed interaction of carbonyl compounds with nitriles has recently been shown to have wide synthetic perspectives for obtaining various heterocyclic and polyfunctional compounds.[1–4] However, few examples of the reaction of aldehydes with nitriles are known.[1–5] Also, the intermolecular interaction of ketones with nitriles has not been described until now. In all publications on this problem the reactions are considered as nucleophilic additions of the nitriles to cationic particles **1** which are formed under the influence of electrophiles on the carbonyl compounds,[2,3,5] *i.e.* a Ritter-type reaction (path *a* in Scheme 1).

However, starting from the fact that nitriles add to electro-



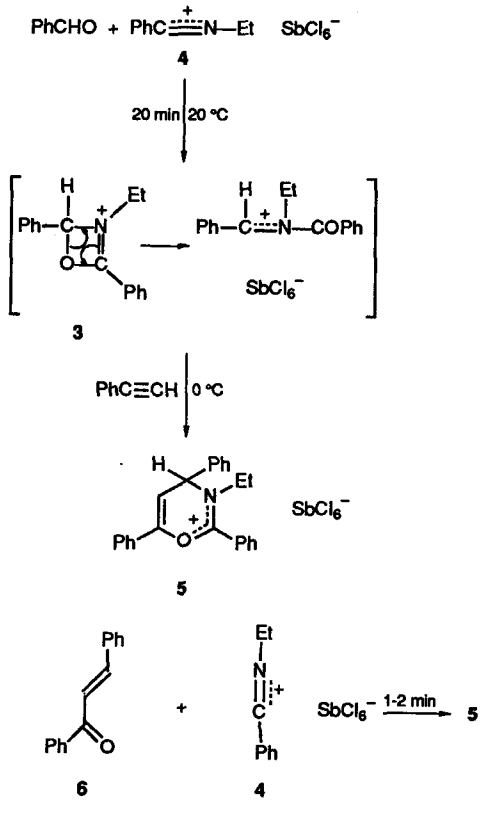
Scheme 1



Scheme 3

philic reagents to form nitrile salts[5] we assumed that the acid catalysed interaction of carbonyl compounds with nitriles could also occur *via* a mechanism involving electrophilic addition of nitrile salts **2** to the carbonyl group (path *b* in Scheme 1). We have found that the interaction of carbonyl compounds with nitrile salt **4** can pass through the intermediates **3**. Hence, intermixing a mixture of benzaldehyde with *N*-ethylbenzanitrilium hexachlorantimonate **4** in dichloroethane produces a solution which, on addition of phenylacetylene, leads to 3-ethyl-2,4,6-triphenyl-1,3-4*H*-oxazinium **5**. The same salt **5** has been made in a shorter time by boiling an equimolecular amount of chalcone **6** with the nitrile salt **4**. It is well known[7] that 1,3-4*H*-oxazinium salts of type **5** are formed by the reaction of acetylenes with *N*-acyliminium ions which are obtained by the ionization of *N*-(chloralkyl)amides.

Thus the possibility of the interaction of carbonyl compounds with nitriles *via* path *b* (Scheme 1) has been shown. On the other hand, we have recently discovered that the addition of acetic anhydride to a mixture of 1,3-diketone, benzonitrile, and



Scheme 2

$HClO_4$ gives rise to an intensive reaction leading to the 3-azapyrylium salts **7** which are difficult to obtain.[8] The same salts **8** have been made using arylalkylketones (Scheme 3).[4]

We explained these results in terms of the activation influence of the acyl cations forming in the reaction mixture as electrophilic reagents (E = Ac, path *a*, Scheme 1). Thus, the problem arises of the choice of a reaction mechanism for the electrophilic activation of interacting carbonyl compounds and nitriles, which possess comparable nucleophility. In order to solve the problem we have carried out AM1 semiempirical quantum chemical calculations for the systems [HCOH + HCN + H^+(A)] and [$H_2\dot{C}$—O—CHO + HCN and H_2C=O + HC$\dot{N}$CHO(B)] simulating proton and formyl catalysis, respectively.

The calculations have shown that under specific acid catalysed conditions path *b* (electrophilic activation of the nitrile part) is energetically preferable. At the same time, according to our calculations, path *a* becomes more favourable in the presence of formyl cation.

The results obtained indicate that the acid catalysed interaction of carbonyl compounds with nitriles cannot be considered, in general, to be a variant of the Ritter reaction. The interaction differs from the latter by two types of electrophilic activation of the reagents and by two types of rearrangements of nitrilium (**1a**→**3**) and carboxonium ions (**2a**→**3**) which have not been described previously. In addition the interaction occurs at oxidation level 2, while the Ritter reaction occurs at level 1[9]. Therefore, we consider that the interaction in question is an independent reaction, little investigated until now.

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