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SYDNONES—II

ACTION OF ALCOHOLIC KOH ON SOME SUBSTITUTED SYDNONE DERIVATIVES[1]

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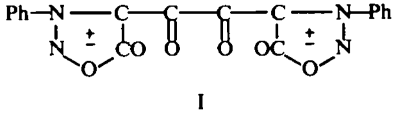
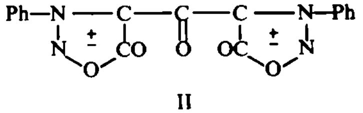
Abstract—The action of alcoholic KOH on 4,4'-bis(3-phenylsydnonyl) α-diketone (I), 4,4'-bis(3-phenylsydnonyl)ketone (II) and 4,4'-bis(3-phenylsydnonyl)carbinol (III) has been examined.

INTRODUCTION

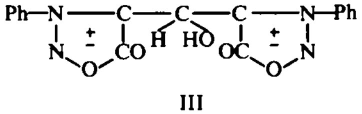
ALTHOUGH the sensitivity of sydnones towards nucleophilic agents is known,[2,3] the action of these reagents on sydnone derivatives having the reactive group directly bound to the sydnone ring has not been reported. The action of alcoholic KOH on the diketone 4,4'-bis(3-phenylsydnonyl)α-diketone[4] (I) the ketone 4,4'-bis(3-phenylsydnonyl) ketone (II) and the secondary alcohol 4,4'-bis(3-phenylsydnonyl)carbinol[1] (III) has now been investigated.



I



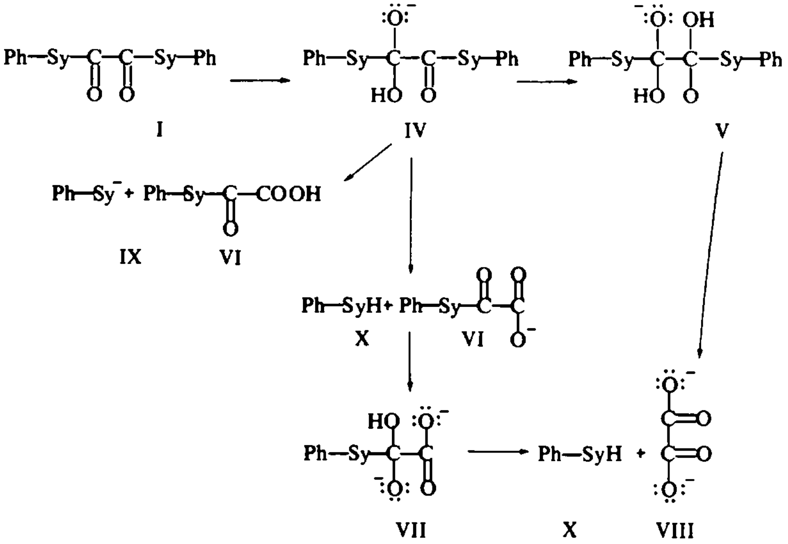
II



III

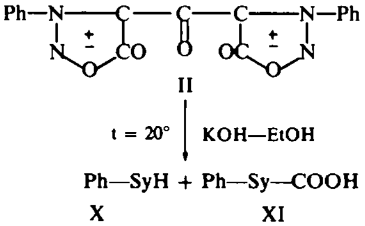
In the first case the product should have been potassium 4,4'-bis(3-phenylsydnonyl) hydroxymethane carboxylate, analogous to benzilic acid from a diketone of benzil type. Instead, a break of the carbon-sydnonyl bond resulted in the formation of oxalic acid and phenylsydnone. either by attack of the nucleophilic agent on (a) a single carbonyl group, leading to the anion IV; or (b) on the carbonyl group of the anion IV leading to the dianion V.

Both the formation of phenylsydnonyl glyoxylic anion VI from anion IV and that of the oxalic dianion VIII either from V or from VII may occur in one of two ways: (a) A proton may migrate from the oxygen to the carbon atom with the simultaneous cleavage of the carbon-carbon(carbonyl-sydnonyl)bond yielding phenylsydnone. (b) The phenylsydnonyl anion (IX) may be formed as intermediate in the stepwise breaking of the molecule. The experimental evidence available is insufficient to



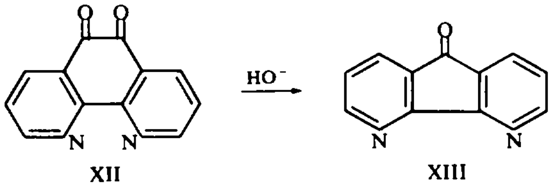
decide in favour of either mechanism, but the rupture of the bond between the two carbonylic carbon atoms may be ruled out since the 3-phenylsydnonyl 4-carboxylic acid (XI) formed is not decarboxylated during the reaction.

Since the 4,4′-bis(3-phenylsydnonyl)ketone (II) under analogous conditions yields phenylsydnonyl carboxylic acid and phenylsydnone (probably by a similar mechanism) the reaction probably takes place by nucleophilic attack on the C=O group.

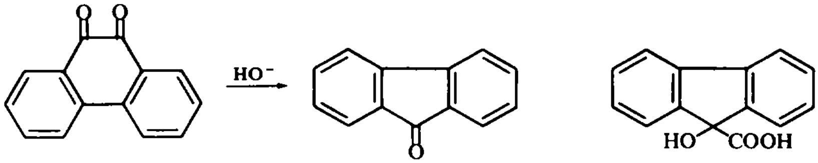


These observations are in agreement with the mechanism of the benzilic transposition. In fact, in anions of type IV, the migration of an aryl rest takes place together with its electrons. In this way, the above mentioned behaviour may be related to the uncommon stability of the phenylsydnonyl carbanion IX, which determines its separation from the molecule and its reaction with the medium.

Although this reaction appears similar to decarbonylation of α-diketones, it is nevertheless of a new type. Inglett and Smith[5] have shown that 1,10-phenanthroline-5, 6-quinone (XII) treated with KOH under much more drastic conditions yields 4,5-diazafluorenone (XIII).



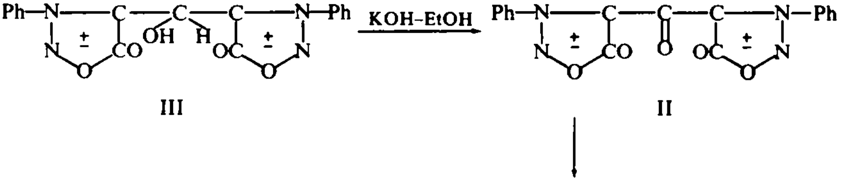
An analogous decarbonylation[6] is that of 9,10-phenanthrene-quinone (XIV) which on treatment with hot alkali is converted into fluorenone (XV) or 9-hydroxy-9-fluorene carboxylic acid (XVI) depending on the concentration of the alkali used.



XIV XV XVI

Gore and Hughes[7] considered that in the examples cited as well as in other similar cases a decarbonylation reaction takes place, the carbon monoxide being found among the reaction products as formic acid. The "formal" hydrolysis reactions described by Bachmann[8] and Mosher[9] for some mono ketones are similar to those for ketones I and II. This reaction though unexpected is the first case described of formal hydrolysis of an aromatic α-diketone. It is however less surprising in the case of ketone II. In contrast to the reactions described in literature, this proceeds rapidly and almost quantitatively at room temperature.

During the reaction of alcoholic KOH with carbinol III, no change of the sydnone ring[2,3] takes place, but the carbinol is converted into a ketone. The reaction proceeds faster than the corresponding reactions of secondary alcohols of the benzhydrol or fluorenol type.[10]



III II

X + XI

The reaction of the diketone I was carried out in a manner such that the disappearance of the characteristic absorption maximum at 340 mμ was continuously observed, simultaneously with the appearance of a maximum at 310 mμ characteristic for the phenylsydnone. After introducing KOH in the alcoholic solution of the carbinol III an absorption maximum at 380 mμ characteristic to the ketone II was seen to appear (neither III nor X or XI have maxima in this region of the spectrum). This disappeared gradually (in few minutes at room temperature) while X and XI were formed.

EXPERIMENTAL

Reaction of 4,4'-bis(3-phenylsydnonyl) α-diketone (I) *with alcoholic* KOH. To 0·5 g (1·32 mM) of I. 7 ml of 5–10% alcoholic KOH were added. The colour of the crystals changed immediately from yellow to white. After filtering, the mother liquor was concentrated *in vacuo* at room temp. The white ppt obtained was added to the one from the first filtration and both were washed with 10 ml water, acidified with HCl to pH = 6. After drying, 0·35 g of a slightly coloured ppt was obtained (yield 82% based on the diketone) m.p. 132° dec. alone and on admixture with phenylsydnone,[11] m.p. 134°.

After recrystallization from alcohol the m.p. was raised to 134° and the IR spectrum was identical with phenylsydnone. Addition of sat. $CaCl_2$ aq to the aqueous soln having pH = 6, precipitated 0·1 g of calcium oxalate, proved qualitatively by the colourimetric methods of Pesez[12] (treatment with Zn in H_2SO_4 soln and resorcinol gave a blue colour) and Paget and Berger[13] (after reduction with Zn and HCl, the glyoxylic acid obtained was condensed with phenylhydrazine and the product oxidized with potassium ferricyanide giving an intense red colour).

Reaction of 4,4'-*bis*(3-*phenylsydnonyl*) *ketone* (II) *with alcoholic* KOH. To 0·1 g (0·29 mM) ketone II, 3–5 ml of 5–10% alcoholic KOH was added. The colour changed from yellow to white. After filtering, the water washed ppt was recrystallized from water–alcohol yielding a product m.p. 134° (no depression with phenylsydnone m.p. 134°).

The alcoholic filtrate was acidified with HCl thus increasing the yield of phenylsydnone to 30 mg (65% based on the ketone). The acidified filtrate after evaporation *in vacuo* at room temp yielded crystals (40 mg) m.p. 165°. After recrystallization from water–alcohol this substance (m.p. 193°) proved to be identical with 3-phenylsydnonyl 4-carboxylic acid[14] (IR spectrum and mixed m.p.).

Reaction of 4,4'-*bis*(3-*phenylsydnonyl*)*carbinol* (III) *with alcoholic* KOH. The carbinol III (0·2 g; 0·57 mM) was suspended in 5 ml of 5–10% alcoholic KOH with formation of a yellow colour. The slightly coloured ppt, ≃ 70 mg, was of a mixture of II and III which after recrystallization from alcohol–chloroform yielded III m.p. 210° ≃ 50 mg.

The initial filtrate after acidifying with HCl filtering and evaporating part of the alcohol yielded X ≃ 50 mg, m.p. 134° alone and on admixture with authentic X.

By completely evaporating the filtrate after the separation of X and by extracting the residue with hot benzene, concentrating the extract and recrystallizing from alcohol a yellowish ppt was obtained, m.p. 185° alone and on admixture with authentic XI, m.p. 192°.

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