

ON THE STRUCTURE OF THE PRODUCTS FROM
THIOPHOSGENE AND DIAZOKETONES.

1,3,4 - THIADIAZOLES

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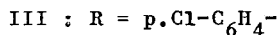
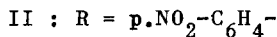
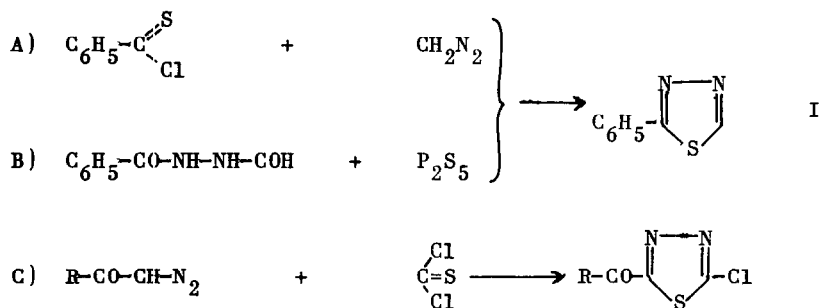
In a work published in 1957 (1) we wrote about the reaction between thiobenzoyl chloride and diazomethane. At that time we had established that the carbon atom of the diazocompound binds itself to the sulphur atom of the C=S group, because the final product of the reaction is the 2-phenyl-1,3,4-thiadiazole (eq. A). This fact confirmed a similar experience of Staudinger (2), who had assigned the structure of 2-carbethoxy-5-phenyl-1,3,4-thiadiazole to the product obtained from diazoacetic ester and thiobenzoyl chloride. Recently Ried and Cow. (3) studied the reaction of thiophosgene with diazoketones, and assigned the structure of 1,2,3-thiadiazole derivatives to some of the products obtained.

It seemed to us rather singular that the thiophosgene behaved so differently from the chloride of the thiobenzoic acid, or that the behaviour of the diazoketones was so different from that of diazomethane and diazoacetic ester. Moreover we did not find the proofs given to support the 1,2,3-thiadiazolic structure and exclude the isomeric 1,3,4-thiadiazolic, re-

cognised as possible by Ried (3), convincing.

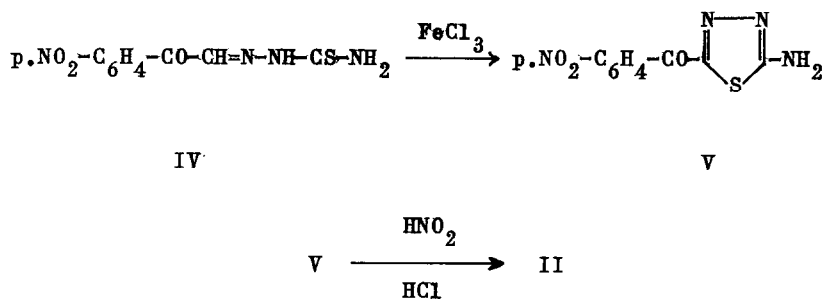
Then we repeated the procedure described (1) to obtain the 2-phenyl-1,3,4-thiadiazole, and we found that this now well known compound (4), besides not lowering the melting point of a mixture with an authentic sample obtained from N-benzoyl-N'-formyl-hydrazine and P_2S_5 (eq. B), shows the same I.R. spectrum, where we could identify all the bands assigned by Katrizky (5) to the normal vibrations of the 1,3,4-thiadiazolic ring.

Then we decided to revise the structure of the thiadiazoles obtained by Ried (3), and we prepared two samples according to the process he had employed (eq. C). We compared their properties and those of some derivatives with those of samples obtained by independent syntheses, and we found they are 1,3,4- and not 1,2,3-thiadiazoles.



So we prepared the chlorothiadiazoole (II) described with m.p. 133° (3) by reacting p-nitrobenzoyl-diazomethane and thio-

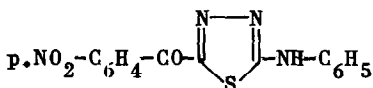
phosgene (eq. C). The reaction seems not to proceed by a simple pattern, because the principal product is always accompanied by some byproducts that lower the melting point, and among them we recognised the ω -chloro-p-nitroacetophenone. The same product (II) was obtained also by the following process:



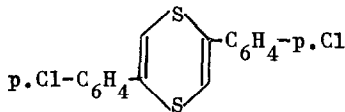
that proves it has a 1,3,4-thiadiazolic structure.

The thiosemicarbazone (IV) (6) was oxidized with an alcoholic solution of FeCl_3 and gave a compound melting at 240°C , whose analysis was in accord with the expected formula (V) (for $\text{C}_9\text{H}_5\text{N}_4\text{O}_3\text{S}$ calc. %: C=43,19; H=2,41; N=22,39. Found %: C=43,44; H=2,64; N=22,45). The aminothiadiazoole (V) was then treated with sodium nitrite in a solution of acetic and hydrochloric acids. By adding CuCl_2 the thiadiazoole (II), melting at 133°C , precipitated in a good yield. We recognised its identity with the product described by Ried (3) by comparing their I.R. spectra. To the contrary of what was previously observed (3), the compound (II) is very sensitive to the nucleophilic reactants (7). It reacted with aniline in ethanol, at room temperature, to give the anilino derivative (VI), melting at 295°C (for

$C_{15}H_{10}N_4OS$ calc. %: C=55,2; H=3,09; N=17,17. Found %:
C=55,36; H=3,27; N=17,40).



VI



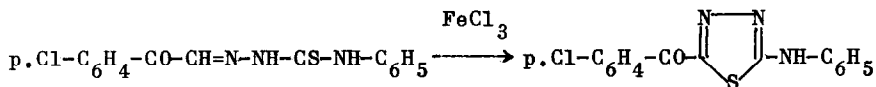
VII

It is interesting to observe that the properties of this derivatives are very different from those of the isomeric compound obtained from p-nitrobenzoyl-diazomethane and phenylisothiocyanate (8), and therefore it is correct to assign to the last product the structure of a 1,2,3-thiadiazolic derivative, already proposed by Ried (8).

Then we revised the reaction between p-chlorobenzoyl-diazomethane and thiophosgene, and we found that it has not a simple pattern. Besides the product (III) (8) we could isolate variable quantities, sometimes large, of ω -chloro-p-chloroacetophenone and the dithiadiazole (VII). This last compound, isolated by eluting the raw products (eq. C) adsorbed on alumina, shows a m.p. = 149-150° C, a percentage composition in agreement with the calculated one (for $C_{16}H_{10}Cl_2S_2$ calc. %: C=56,73; H=2,97; Cl=20,90; S=18,9. Found %: C=56,61; H=2,93; Cl=20,75; S=18,6) and a deep red-violet colour when treated with conc. H_2SO_4 . When heated at 190° C for 1½ hrs it gave sulphur and 2,4-bis-p-chlorophenyl-thiophene, melting at

139° C (9).

The 2-chloro-5-p.chlorobenzoyl-1,3,4-thiadiazole (III) with aniline in methanol gave the expected 2-anilino-derivative (IX) (m.p. = 278° C from methanol. For $C_{15}H_{10}ClN_3OS$ calc. %: C=57,2; H=3,17; N=13,31. Found %: C=57,12; H=3,21; N=13,10). The same product was also prepared by the following process:



VIII

IX

The phenyl-thiosemicarbazone (VIII) (m.p. = 168-169° C from benzene. For $C_{15}H_{12}ClN_3OS$ calc. %: C=56,76; H=3,78; N=13,23. Found %: C=57,39; H=3,67; N=13,11), prepared in a good yield from p.chlorophenylglyoxal and 4-phenylthiosemicarbazide, was treated with $FeCl_3$ in dilute dioxane and kept at the boiling point for 1/2 hr. The product (IX) so isolated was identical with that previously obtained.

It seems then evident, from our statements, that, in the reaction with the two diazoketones we considered, the thiophosgene shows a reactivity similar to that of the thio-benzoyl chloride with diazomethane and diazoacetic ester.

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