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HYDANTOINS, THIOHYDANTOINS, GLYCOCYAMIDINES.
THE REACTION OF THE 3-METHYL-2,5-BIS/METHYLTHIO/-4,4-DIPHENYL-4H-IMIDAZOLIUM CATION WITH SIMPLE POTENTIAL CARBANIONS.
A NOVEL S-DEALKYLATION REACTION OF A CYCLIC ISO-THIURONIUM COMPOUND.

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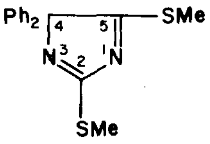
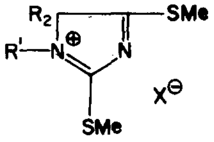
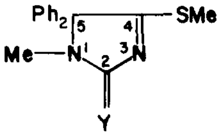
In continuation of our investigations into the reactivity of S-alkyl derivatives of thiohydantoins against nucleophyles, cf. eg.[1], an attempt has been made to bring these S-alkyl derivatives, eg. 2,5-bis/methylthio/-4,4-diphenyl-4H-imidazole /I/ into reaction with different/potential/ carbanions, eg. ethyl malonate, acetylacetone, sodium cyanide etc.; all our attempts to realize this aim, however, failed.



I



II
/R= Ph, R' = Me,
x= SO$_4$Me/



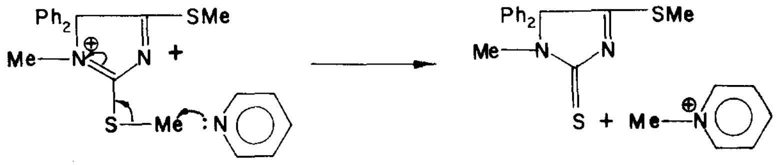
III /Y=0/
IV /Y=S/

Since, by quaternarization of either of the nitrogen atoms of I, the reactivity of both carbon atoms bearing the methylthio groups against nucleophyles must become enhanced, a quaternary methyl derivate II /mp. 180-181 C°, from a mixture of chloroform and petrolether; found C 52,46 H 4,87 N 6,48 S 21,72; $C_{19}H_{22}N_2O_4S_3$ requires C 52,05 H 5,06 N 6,39 S 21,90/ has been synthesised by refluxing I with methyl sulphate in chlorobenzene and subjected subsequently to reaction with potential carbanions. The structure of II, viz. the site of quaternarization of I follows from hydrolysis experiments carried out by us and leading, depending on the conditions applied/ neutral and acidic medium, respectively/, either to 1-methyl-4-methylthio-5,5-diphenyl-3-imidazolin-2-one /III, mp.: 229-230C°, lit.[2]: 235 C°/ or to 1-methyl-5,5-diphenyl-hydantoin /mp.: 226-227 C°, lit.[3]: 224-226 C°/. It should be pointed out that the first step of the hydrolysis of II which leads to III proceeds under much more mild conditions than the similar partial hydrolysis of I, thereby proving our assumption regarding the enhancement of the reactivity against nucleophyles by quaternarisation.

Analoges of II with aliphatic R groups had, in the form of tosylates, already been prepared but, without purification and isolation, had been subjected to subsequent condensation with potential carbanions as N-methylrhodanine, 1-phenyl-3-methyl-5/4H/-pyrazolinone etc. yielding thereby important dyes of the cyanine type[4]. We too condensed II, by heating in pyridine solution, with carbanions of the type mentioned, achieving thereby similar results, but in addition, also with simple carbanions as ethyl malonate, ethyl acetoacetate, acetylacetone, benzoylacetone, dimethyl-dihydroresorcinol /dimedon/ and malononitrile. With the first five reagents the same compound resulted in all cases and, by mp., mixed mp., analysis and UV spectrum, could be identified with an authentic sample of 1-methyl-4-methylthio-5,5-diphenyl-3-imidazoline-2-thione /IV, mp.: 203 C°, lit.[2]: 205 C°; found

C 65,32 H 4,72 N 9,12 S 20,20; $C_{17}H_{16}N_2S_5$ requires C 65,37 H 5,16 N 8,97 S 20,49; yield: 60-80%.

Thus in these cases a simple S-demethylation of II at the methylthio group in position 2 took place. Since the same result may be achieved by heating II simply with pyridine /yield: 85%, the potential carbanions applied, evidently, do not participate in the reaction, the mechanism of it being consequently

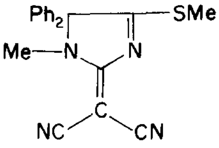


II IV

Preliminary findings indicate that the N-methyl-pyridinium cation is indeed formed as requested by the mechanism proposed.

This S-dealkylation reaction of a cyclic iso-thiuronium compound is a novel reaction, two cognates of which have been described recently[5,6].

With malonitrile the reaction of II took another, namely a "normal" course as a result of which 2-dicyanomethylen-1-methyl-4-methylthio-5,5-diphenyl-3-imidazoline



V

/V, mp.: 241-242°C, from an ethanol-pyridine mixture; found C 70,05 H 4,50 N 16,12 S 9,30; $C_{20}H_{16}N_4S$ requires C 69,75 H 4,68 N 16,27 S 9,29/ could be isolated in 85% yield.

That malononitrile reacts in a different manner as the other potential carbanions applied is caused by its smaller size and by its well known[7] greater tendency to form the corresponding anion.

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