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CYCLISATION OF MONO- AND DISUBSTITUTED BIGUANIDES WITH PHENYL-ISOTHIOCYANATE

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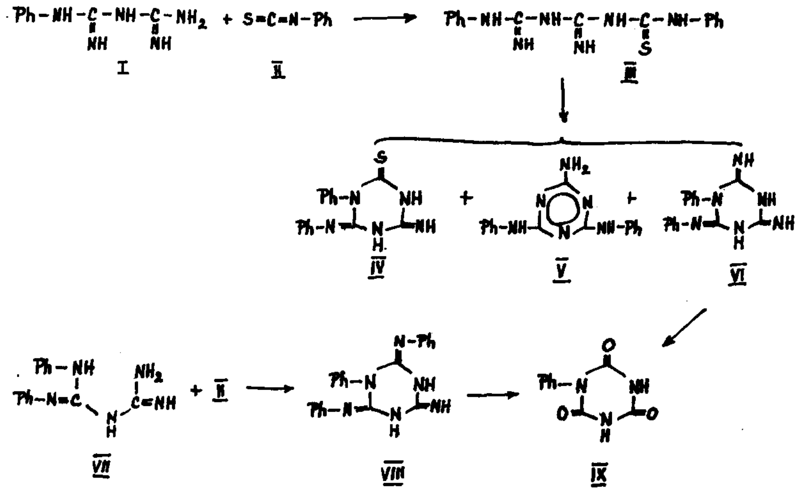
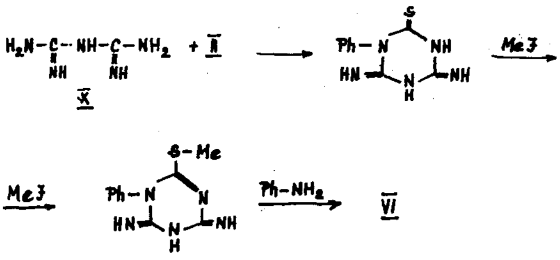
As an extension of our works on 1-phenylbiguanides /1/ and mustard-oils /2/ respectively we have investigated the reaction of 1-phenylbiguanide /I/ with phenylisothiocyanate /II/.

Equimolecular quantities of I and II heated on steam-bath for 5 hours in pyridine gave 30-35% of crystalline 1,2-diphenyl-isomelamine /VI/, mp. 257-259° which when purified by dissolving in 1% hot acetic acid solution and precipitating with ammonium hydroxide melted at 274-275° [+]



[+] All melting points determined on a Kofler hot-stage apparatus are uncorrected.

/found C 63,41; H 5,41; N 30,20; $C_{15}H_{14}N_6$/278,31/ requires C 64,73; H 5,07; N 30,20/. Kurzer and Pitchfork /3/ synthesized this compound by the following series of reactions:



but they gave mp. 250-252° /80% EtOH/ and no analytical data for VI and proved its structure by comparing with an authentic material, what they obtained by another but not published way.

From the mother liquor of VI we obtained about 15% of 2,4-diphenyl-melamine /V/, mp. 217-218° /found C 64,40; H 4,97; N 30,81; required as for VI/ giving the same IR-spectrum and no mp.-depression when compared with an authentic /4/ material.

The reaction between I and II gave also a third, sulphur containing compound presumably 1-phenyl-2-phenylimino-4-imino-6-thiono-hexahydro-s-triazine /IV/ whose identification is in progress.

We succeeded also in isolating of the intermediate addition product /III/, mp. 130,5-133° obtained in abs. dioxane at room temperature in a quantitative yield. This intermediate could not be set free from dioxane perfectly by heating or purified by recrystallisation, because it generated slowly hydrogen sulphide upon longer standing even at room temperature. It was transformed upon heating in pyridine or abs. ethanol or 70% acetic acid giving VI in a 30-40% yield.

The above reaction between substituted biguanide and II was found also suitable for the preparation of other phenylated isomelamine derivatives. Pyridine solution of 1,2-diphenyl-biguanide /5/ /VII/ and equimolecular II refluxed for 8-9 hours without the isolation of the crystalline addition product formed during the reaction gave 87% of 1,2,6-triphenyl-isomelamine /VIII/, mp. 271-272,5° /found C 71,77; H 5,19; N 22,58; $C_{21}H_{18}N_6$ /354,40/ requires C 71,17; H 5,12; N 23,72/; the same compound obtained previously by Kurzer and Pitchfork /6/ from the reaction of N,N'-diphenyl-carbodiimide with guanidine melts at 270-271° /decomp./.

The structures of VI and VIII are supported by their mode of formation and their hydrolysis with concentrated hydrochloric acid at 160° to 1-phenyl-isocyanuric acid, in a 60% yield, mp. 310° /Lit. /7/ mp. 310-311°/ /found C 52,87; H 3,82; N 21,08; $C_9H_7N_3O_3$/205,17/ requires C 52,68; H 3,44; N 20,48/ obtained previously by Rathke /8/ from 1,2,4-triphenyl-isoammeline with the same procedure.

Some details of these results and the proof of structure IV supposed as well as other investigations made on IV and VI will be published elsewhere.

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