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THE REACTIONS OF ISOTHIOAMIDES AND THIOAMIDIUM IODIDES

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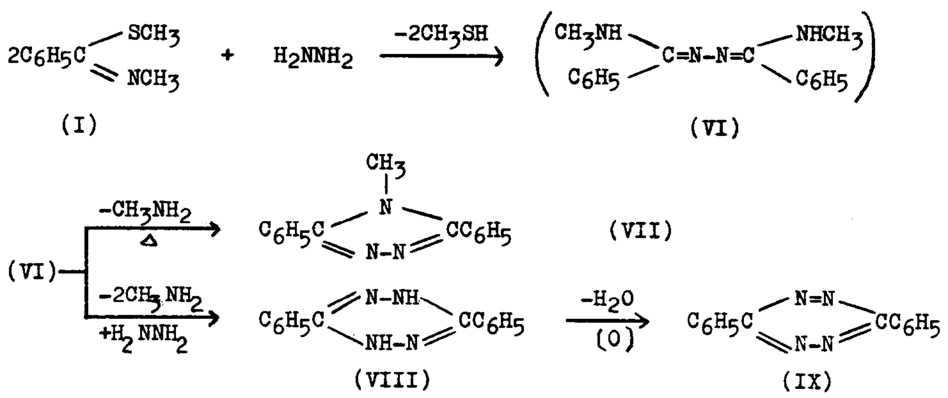
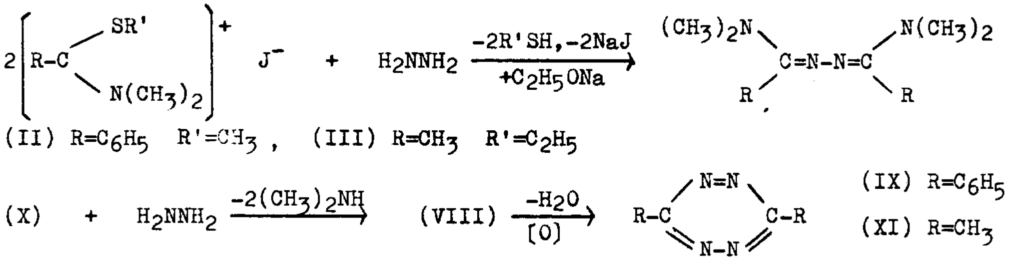
Concerning the reactions of isothioamides and thioamidium iodides, there has been reported that form- and aceto-isothioamide condensed with malonitrile or ethylcyanoacetate to give the enamine derivatives1). It has been shown in the preceding paper2) that N,N-dimethyl-S-methylthiobenzamidium iodide reacted with active hydrogen compounds such as active methylen compounds and amines to give the corresponding condensation products.

In the present experiment, the reactions of N-methyl-S-methylbenzisothioamide(I), N,N-dimethyl-S-methylthiobenzamidium iodide(II), N,N-dimethyl-S-ethylthioacetamidium iodide(III), S,S'-dimethyldithioterephthalamidium iodide(IV), 7-methylthio-tetrahydro-2H-azepine(V) with active hydrogen compounds such as hydrazine, phenyl hydrazine, malonitrile, 2-(phenylthio) acetophenone were investigated. One mole of anhydrous hydrazine immediatly reacts with two moles of (I) at room temperature with evolution of methyl mercaptan to give a white condensation product (VI) which becomes brown within a few minutes under exposure in the air and is too unstable to be purified. Heating of (VI) at 80°C for 4 hours gave 4-methyl-3,5-diphenyl-1,2,4-triazole (VII)3) (m.p. 242°C) in 78% yield with evolution of one mole of monomethylamine, detected as N-methyl-N'-phenylthiourea by treating with phenyl isothiocyanate. On the other hand, it was found that 1,4-dihydro-3,6-diphenyl-1,2,4,5-tetrazine(VIII)4) (m.p. 184°C in a sealed capillary) was obtained in 90% yield by refluxing a solution of (VI) and hydrazine in ethanol for 1 hour. (VIII) was easily converted to 3,6-diphenyl-1,2,4,5-tetrazine (IX)4) (m.p. 195°C) in 97% yield by the oxidation with mercuric oxide or with oxygen. Similarly, N,N-dimethylbenzamide azine (X)5) (m.p. 141°C) was obtained in a quantitative yield by the reaction of two moles (II) and sodium ethoxide with one mole of hydrazine at room temperature. Further

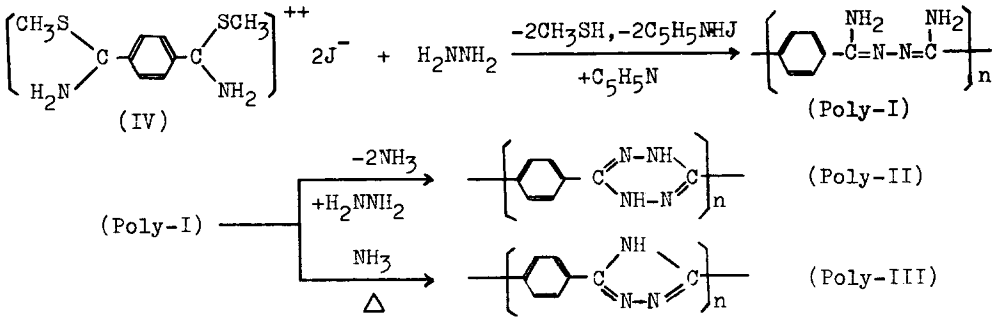


treatment of (X) with hydrazine gave dihydrotetrazine (VIII) in 93% yield. Tetrazine (IX) was obtained in a quantitative yield by the oxidation of (VIII). In the same way, (III) afforded an ethanolic solution of 1,4-dihydro-3,6-dimethyl-1,2,4,5-tetrazine. The solution was oxidized according to the R.A. Carboni's method[4] to give 3,6-dimethyl-1,2,4,5-tetrazine (XI)[4] (very volatile and deep red needles, m.p. 73°C) in 26% yield.

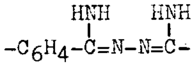
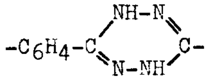
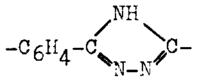


Further, the reaction was extended to the preparation of polymeric substances from bifunctional thioamidium iodide and hydrazine. A polycondensation product (Poly-I) deposited by the reaction of (IV) with an equimolar amount of hydrazine in pyridine at room temperature. The solid (Poly-I) was washed with cold pyridine and methanol,and dried in vacuum. When (Poly-I) was further treated with hydrazine in pyridine at 105-110°C for 6 hours, (Poly-II) was gradually separated from the solution with a loss of ammonia. Heating of (Poly-I) at 270°C gave (Poly-III). These poly-I, -II, -III were confirmed to be poly-azine, -dihydrotetrazine, -triazole, respectively, by means of elemental analysis and i.r. spectrum. The yields and properties are listed in the table.

Next, the reactions of (V), a cyclic isothioamide, with active hydrogen compounds were tried. One mole of hydrazine immediately reacts with two moles of



TABLE

Polymer	Repeating unit	Yield (%)	Elemental analysis (%) C	H	N	S	Molecular weight*	Color
I	 $-C_6H_4-\overset{HNH}{C}=N-N=\overset{HNH}{C}-$	95	f.58.74 c.59.98	4.86 5.03	32.50 34.98	0.28	11,400	Yellow-orange
II		95	f.60.55 c.60.75	4.79 3.82	33.22 35.43	0.28	11,400	Red
III		97	f.66.22 c.67.12	3.57 3.52	27.55 29.36	0.26	12,300	Grey

Polymer	Thermal properties decomposition temp.	weight loss‡	Inherent viscosity*‡	Solubility**** S	F	DMF	DMSO
I	270-280, gave Poly-III	-	0.42	+	(+)	-	(+)
II	>400, discolored at 330	2%	-	(+)	-	-	-
III	>400,	2%	0.40	+	-	-	-

*. based on sulfur analysis, assuming one sulfur atom per chain.

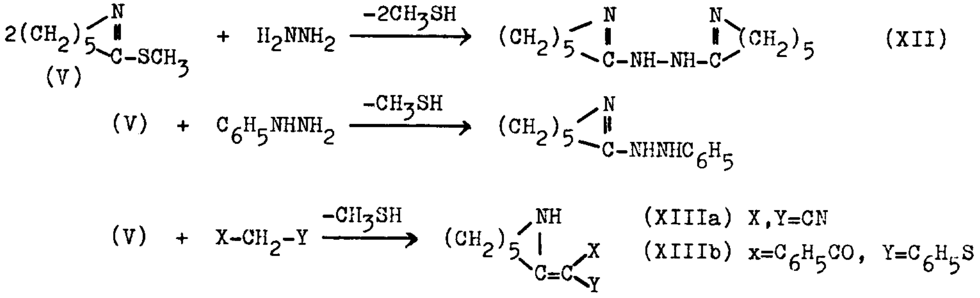
‡. after heating at 280°C for 8 hours.

*‡. 0.5 gr/dl in conc sulfuric acid at 35°C.

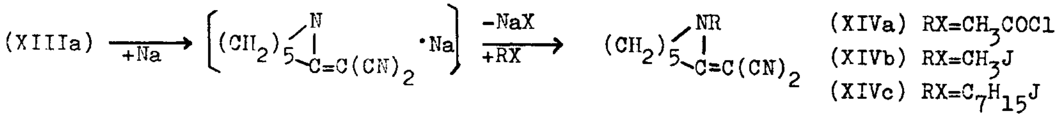
****. determined only sulfuric acid(S), formic acid(F), DMF and DMSO.
code: + soluble, (+) soluble in hot solvent, - insoluble.

(V) at 60°C to give 7,7'-dihydrazo-bis [tetrahydro-2H-azepine] (XII)$^{5)}$(m.p. 125.5°C) in 96% yield. Under the same condition, phenyl hydrazine and (V) afforded 7-phenylhydrazino-tetrahydro-2H-azepine$^{6)}$(m.p. 108°C) in 62% yield. Further, malonitrile reacts with (V) under ice cooling to give 7-dicyanomethylidene-hexahydro-1H-azepine (XIIIa)$^{5)}$(m.p. 108°C) in 97% yield. Heating of a mixture of 2-(phenylthio)acetophenone and (V) at 80°C for 2 hours gave 7-(2-phenylthio)-

phenacylidene-hexahydro-1H-azepine(XIIIb)⁵⁾(m.p. 173°C) in 55% yield.



In addition, a fine powdered salt of (XIIIa) was produced by treating (XIIIa) with metallic sodium in ethanol. When acetyl chloride was added to a suspension of this salt in ether, 1-acetyl-7-dicyanomethylidene-1H-azepine (XIVa)⁵⁾(m.p. 247-248.5°C) was obtained. In a similar way, the salt reacted with methyl iodide and n-heptyl iodide to give 1-methyl-7-dicyanomethylidene-1H-azepine(XIVb)⁵⁾(m.p. 81°C, 35% yield) and 1-heptyl-7-dicyanomethylidene-1H-azepine(XIVc)⁵⁾(m.p. 200°C, 32% yield).



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