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ADDITION OF SULFENYL CHLORIDES TO THE CYANOGEN BOND IN ACTIVATED NITRILES

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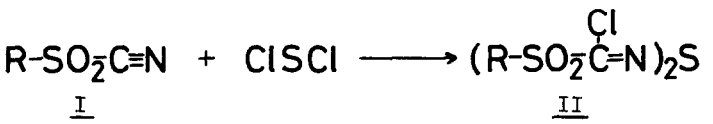
It is known (1) that sulfenyl halides are capable of undergoing addition reactions with compounds having C≡N triple bond, such as nitriles, cyanates, cyanogen and cyanogen chloride.

With nitriles, however, the addition was restricted to particular cyano compounds, such as cyanoethylenes and mercapto-cyanoethylenes.

We now wish to report the readily occuring addition of sulfur dichloride and methanesulfenyl chloride to activated cyano groups in sulfonyl cyanides I (2,3) and dichloromalononitrile IV (4).

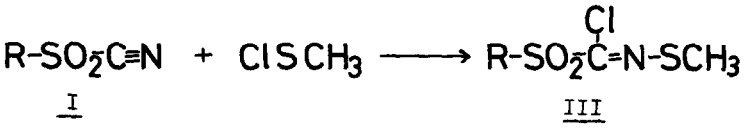
The reaction was carried out at 0° C in THF, using catalytical amounts of tetraethylammonium chloride.



I II

THIOBIS-(SULFONYL FORMIMIDOYL CHLORIDE) (II)

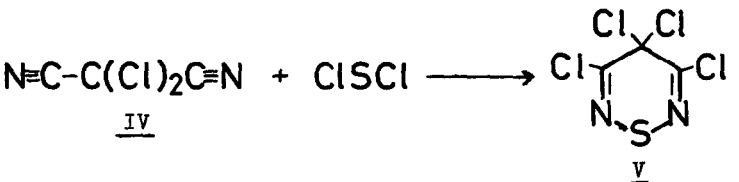
R	m.p.	yield(%)	compound
CH_3	233°	90	IIa
C_6H_5	156°	89	IIb
p-$CH_3C_6H_4$	143°	90	IIc



I III

N-METHYLTHIO SULFONYL FORMIMIDOYL CHLORIDE (III)

R	m.p.	yield(%)	compound
C_6H_5	80°	93	IIIa
p-$CH_3C_6H_4$	110°	91	IIIb
p-ClC_6H_4	133°	75	IIIc



IV V

3,4,4,5-TETRACHLORO-4H-1,2,6-THIADIAZINE (V)
b.p. 100 / 6mm. yield: 92 %.

All new compounds had elemental analyses and spectroscopic properties in full agreement with the assigned structures.

Compounds II, III and V are stable under normal condition.

REFERENCES

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