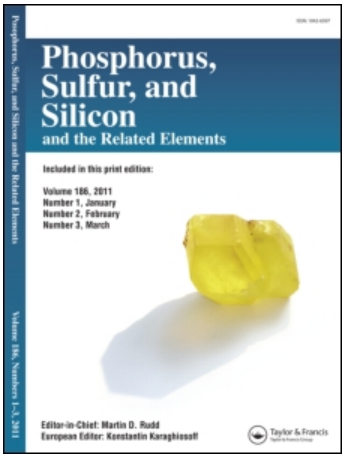

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M. M. Krayushkin[a]; L. G. Vorontsova[a]; M. G. Kurella[a]; E. Yu. Zvezdina[a]; M. A. Kalik[a]
[a] N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia

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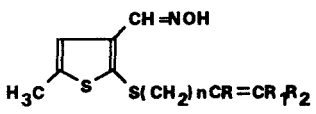
STRUCTURAL FEATURES OF PRODUCTS OF INTRA-MOLECULAR CYCLIZATION OF THIOPHENECARBO-NITRILE OXIDES

M.M.KRAYUSHKIN, L.G.VORONTSOVA, M.G.KURELLA, E.Yu.ZVEZDINA, and M.A.KALIK
N.D.Zelinsky Institute of Organic Chemistry, Moscow, Russia

Abstract Synthesis of new tricyclic systems and their X-ray data are discussed.

Intramolecular 1,3-dipolar cyclizations of 3-thiophenecarbonitrile oxides having unsaturated fragments in the position 2 of thiophene ring allow new annelated tricyclic systems to be obtained. Synthesis of starting thiophenecarbaldoximes **1-4** have been accomplished by transalkylation of 2-methyltio-5-methyl-3-thiophenecarbaldoxime[1,2].



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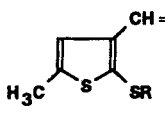
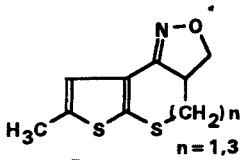


R = C≡CCH3, CH=C=CH2, CH2C≡CH

2 **3** **4**

Oxidation of the oximes with NaOCl leading quantitatively to respective nitrile oxides results in fused structures **5-10** in good yields[2,3].



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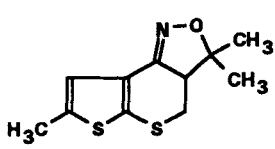

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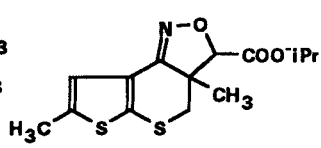

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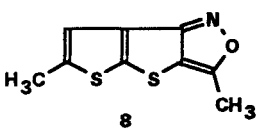

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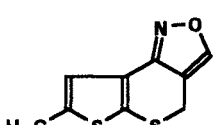

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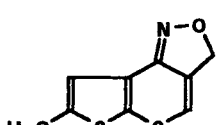

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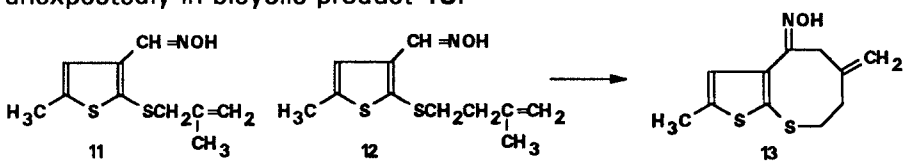
The yields of cyclization products **5** depend strictly on the length of unsaturated fragment and the substrate concentration in the solution.

The molecular structures of compounds **5** (n=1,2), **6** and **7** have been investigated by X-ray analysis. Unusually large deformation of isoxazoline rings in **5** (n=1,2) has been established. One can see

that the existence of methyl group in the position 4 of isoxazoline cycle will lead to greater steric changes.

Thus, we failed in preparation of usual products of cyclization on oxidation of oximes with methyl groups in β–positions of ethylene moiety. Oxidation of oxime **11** gave only non-identified mixture of polymeric products whereas an oxidation of oxime **12** resulted unexpectedly in bicyclic product **13**.



These abnormalities could be caused by not electronic but steric factors. It should be mentioned that there are known some cases of intramolecular cyclization of β-methyl fragments with nitrile oxide functions.

The reasons of obtaining products **6** and **7** are discussed. In these cases the isoxazoline envelopes proved to be bent that gave possibility to decrease deviations from standard bond angles in **6** and **7** as compared with **5** (n = 1,2).

Thus, cyclization is an useful method for the synthesis of annelated structures containing besides thiophene and isoxazoline (isoxazole) cycles also thiopyrane, thiepine and thiocine rings.

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