Tetrahedron Letters No. 34, pp 2907 - 2908, 1974. Pergamon Press. Printed in Great Britain.

ON THE MECHANISM OF OXIDATION OF THIOUREAS

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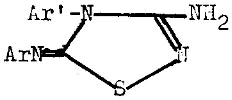
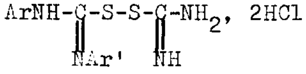
(Received in UK 30 May 1974; accepted for publication 3 July 1974)

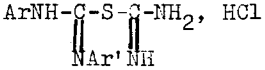
Oxidation of binary mixtures of s-diarylthioureas and thiourea is known to yield 3-amino-4-aryl-5-arylimino-1,2,4-Δ^2-thiadiazolines (Ia)[1]. The reaction has been envisaged to involve the intermediate formation of dithioformamidine (IIa), thioformamidine (IIIa), and amidinothiourea (IVa) salts. Similar intermediates have been isolated in the oxidation of certain aromatic thioureas[2]. During the rearrangement of IIIa to IVa, an unsubstituted amidino group preferentialy migrates to an aryl substituted nitrogen, due to the greater ease of delocalisation of a partial charge developed on that nitrogen. It is now found that when the aryl groups in the thioformamidine (III) are different, the unsubstituted amidino group shifts towards the nitrogen bearing the more electron releasing aryl group.



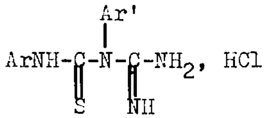
I


$\mathrm{ArNH{-}\underset{\underset{NAr'}{\|}}{C}{-}S{-}S{-}\underset{\underset{NH}{\|}}{C}{-}NH_2,\ 2HCl}$

II


$\mathrm{ArNH{-}\underset{\underset{NAr'}{\|}}{C}{-}S{-}\underset{\underset{NH}{\|}}{C}{-}NH_2,\ HCl}$

III


$\mathrm{ArNH{-}\underset{\underset{S}{\|}}{C}{-}\overset{\overset{Ar'}{|}}{N}{-}\underset{\underset{NH}{\|}}{C}{-}NH_2,\ HCl}$

IV

a) Ar=Ar'=C_6H_5-, o-$CH_3C_6H_4$-, or p-$CH_3C_6H_4$-
b) Ar=C_6H_5-; Ar'=p-$CH_3C_6H_4$-
c) Ar=o-$CH_3C_6H_4$-; Ar'=C_6H_5-
d) Ar=C_6H_5-; Ar'=o-$CH_3C_6H_4$-
e) Ar=p-$NO_2C_6H_4$-; Ar'=C_6H_5-

Oxidation of an equimolar mixture of 1-phenyl-3-p-tolylthiourea and thiourea yields 3-amino-5-phenylimino-4-p-tolyl-1,2,4-Δ^2-thiadiazoline(Ib), m.p.184°. Its structure is based on its reductive degradation to p-tolylguanidine and phenylisothiocyanate and on its analytical and spectral data. Similar oxidation of a mixture of 1-phenyl-3-o-tolylthiourea and thiourea yields two products, 3-amino-4-phenyl-5-o-tolylimino-1,2,4-Δ^2-thiadiazoline (Ic), m.p.154° (60-70% of the total) and 3-amino-5-phenylimino-4-o-tolyl-1,2,4-Δ^2-thiadiazoline (Id), m.p.214°,where as oxidation of a mixture of 1-p-nitrophenyl-3-phenylthiourea and thiourea affords 3-amino-5-p-nitrophenyl-4-phenyl-1,2,4-Δ^2-thiadiazoline (Ie), m.p.180°, only.

Regarding the mechanism of formation of these products, it is most likely that in the product determining rearrangement of the intermediate (III), the partial charge developed is better delocalised by the aryl substituents and hence the unsubstituted amidino carbon-sulphur bond ruptures. Simultaneously a partial bond is formed between the amidino carbon and the more nucleophilic of the two aryl substituted nitrogens. This nitrogen invariably is the one attached to an aryl group with strongly electron releasing substituents. The above observed results conform with the following order of electron releasing effects of the different aryl groups; p-tolyl ≈ o-tolyl > phenyl > p-nitrophenyl. Barring any rearrangement during the cyclisation of IV to form I, the migration of the unsubstituted amidino group to the more nucleophilic nitrogen explains the formation of the thiadiazolines Ib and Ie. However, in the case of the phenyl, o-tolyl analogue, migration of the amidino group to the o-tolyl substituted nitrogen is sterically unfavourable, so that migration to the phenyl substituted nitrogen occurs to a greater extent, yielding more of thiadiazoline, Ic.

The data gathered from these oxidation reactions can be utilised for the prediction of the substitution pattern in I,when such binary mixtures are used for the preparation of 1,2,4-thiadiazoles.

The author's sincere thanks are due to Dr.C.P. Joshua for his valuable guidance.

REFERENCES

1. C.P. Joshua and P.N. Kesavan Nambisan, Indian J. Chem., 11, 1273 (1973)
2. a. K.S. Suresh, J. Indian Chem. Soc., 37, 483 (1960)
   b. F. Kurzer and P.M. Sanderson, J.Chem. Soc. 3336 (1963)