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3-Oxo-5-Phenylimino-1,2,4-thiadiazolidine and Its Some Aryl Analogues

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Certain 3-oxo-2-unsubstituted/aryl substituted-4-unsubstituted/aryl substituted-5-phenylimino-1,2,4-thiadiazolidines involving interaction of S-chloro-N-phenyl isothiocarbamoyl chloride and parent and mono- and di-aryl carbamides have been prepared. Their structural assignments have been made on the basis of certain chemical transformations and IR spectral analysis.

INTERACTION of S-chloro-N-phenyl isothiocarbamoyl chloride and certain thioamido group containing compounds leading to certain 5- and 6-membered heterocyclic compounds have been investigated[1-3]. It therefore appeared quite interesting to investigate the behaviour of this isothiocarbamoyl chloride towards carbamides. With this end in view the reactions of S-chloro-N-phenyl isothiocarbamoyl chloride and carbamides have been investigated and certain 3-oxo-5-phenylimino-1,2,4-thiadiazolidlnes(I) have been isolated which cannot be prepared by the usual ways. The present communication is the record of these investigations.

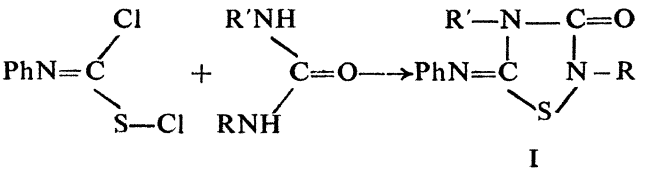
When the reaction of S-chloro-N-phenyl isothiocarbamoyl chloride and parent carbamide was carried out in boiling chloroform medium for 3 hr, evolution of hydrogen chloride was clearly observed. The insoluble solid was filtered and crystallised with aq. ethanol, m.p. 110°.

The product was assigned the structure 3-oxo-5-phenylimino-1,2,4-thiadiazolidine(Ia) on the basis of following facts :

The product was stable to boiling 8% alkali and also concentrated hydrochloric acid. It was not desulphurised when boiled with alkaline plumbite solution. On reaction with aniline in boiling ethanolic medium 1,3-diphenyl thiocarbamide, 152° and 1,3-diphenyl carbamide, 235° have been isolated. It was found stable to ethanolic ammoniacal hydrogen sulphide of moderate concentration. The IR spectrum of the product clearly indicated the presence of C=O, NH, C=N and C–S stretching frequencies.

When the reaction of this isothiocarbamoyl chloride has been extended to phenyl carbamide, 1,3-diphenyl carbamide, 1-phenyl-3-*p*-tolyl and 1-phenyl-3-*p*-Cl-phenyl carbamides, the related 1,2,4-thiadiazolidines(Ib-Ie) have been isolated. The structures of all these products have been assigned on the basis of usual chemical transformations and IR spectral analysis.

The formation of 1,2,4-thiadiazolidines may be represented as follows :



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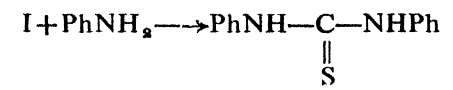

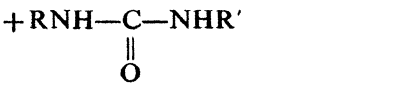

where (a) R = R′ = Hydrogen
(b) R = Phenyl and R′ = Hydrogen
(c) R = R′ = Phenyl
(d) R = Phenyl and R′ = *p*-tolyl
(e) R = Phenyl and R′ = *p*-Cl-Phenyl

S-chloro-N-phenyl isothiocarbamoyl chloride did not react with other mono- and di-aryl carbamides.

Experimental

The required S-Chloro-N-phenyl isothiocarbamoyl chloride was prepared by the usual procedure[1,5]. The parent carbamide used was of analytical grade. The mono-aryl and di-aryl carbamides were prepared by the interaction of aryl amines and carbamide and aryl amines and corresponding arylisothiocyanates, respectively.

Formation of 3-oxo-5-phenylimino-1,2,4-thiadiazolidine and the related compounds :

Details of a typical experiment (where R = R' = Hydrogen) are as follow :

Carbamide (3.0 g) was suspended in chloroform (10 ml) and to this was added a chloroform solution of S-chloro-N-phenyl isothiocarbamoyl chloride (11.0 g). The reaction mixture was refluxed over a boiling water bath for 4 hr. During the reaction evolution of hydrogen chloride was noticed. The resultant solid was filtered and washed several times with chloroform followed by petroleum ether (3.2 g) and crystallised from aq. ethanol, m.p. 110° (Found : C 49.2, H 3.5, N 21.33, S 16.38. $C_8H_7N_3SO$ requires ; C 49.74, H 3.62, N 21.76, S 16.58%). It was identified as a 3-oxo-5-phenylimino-1,2,4-thiadiazoline(Ia) on the basis of following facts :

The product was stable to 8% boiling aq. alkali and conc. hydrochloric acid. It did not desulphurise when boiled with alkaline plumbite solution. On thermal decomposition the odours of phenylisothiocyanate and ammonia were quite perceptible. The product (1 g) on reaction with aniline (2 ml) in boiling ethanolic medium 1,3-diphenyl carbamide and 1,3-diphenyl carbamide, m.p. 152° and 235° respectively, have been isolated. The product could not be degraded with boiling alcoholic ammoniacal hydrogen sulphide of moderate concentration. IR spectrum of the product clearly indicated the presence of NH (3310 cm^{-1}), C=O (1660 cm^{-1}), C=N (1570 cm^{-1}), C—S (780 cm^{-1}) bands.

When the reaction of S-chloro-N-phenyl isothiocarbamoyl chloride was extended to phenyl carbamide, 1,3-diphenyl carbamide, 1-phenyl-3-*p*-tolyl and 1-phenyl-3-*p*-Cl-phenyl carbamides under the identical reaction conditions the related substituted 1,2,4-thiadiazolidines(Ib-Ie) have been isolated. These have been listed in Table 1.

TABLE 1—3-OXO-5-PHENYLIMINO-1,2,4-THIADIAZOLIDINE AND ITS ARYL SUBSTITUTED ANALOGUES

Reaction Conditions : Refluxing chloroform medium. S-Chloro-N-Phenyl isothiocarbamoyl chloride taken about 0.05 mole.

Sl. No.	Carbamide (g)	1,2,4-thiadiazolidine(I) (g, m.p. °C)	IR Characteristics (cm^{-1})
1.	Carbamide (3 g)	3-Oxo-5-phenylimino-(Ia) (2 g), 110°	NH (3310), C=O (1660), C=N (1570)
2.	Phenyl- (6 g)	3-Oxo-4-phenyl-5-phenylimino-(Ib), (5 g), 354°	NH (3340), C=O (1670), C=N (1620)
3.	1,3-Diphenyl- (10 g)	3-Oxo-2,4-diphenyl-5-phenylimino-(Ic),(13.2 g),345°	C=O (1660), C=N (1630)
4.	1-Phenyl-3-*p*-tolyl-(11g)	3-Oxo-2-phenyl-4-*p*-tolyl-5-phenylimino-(Id)(11.2 g),334°	C=O (1640), C=N (1560)
5.	1-Phenyl-3-*p*-Cl-phenyl- (11 g)	3-Oxo 2-*p*-Cl-phenyl-4-phenyl-5-phenylimino-(Ie) (14.5 g), 295°	C=O (1720), C=N (1640)

All the compounds exhibited consistent C, H, N and S analysis.

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