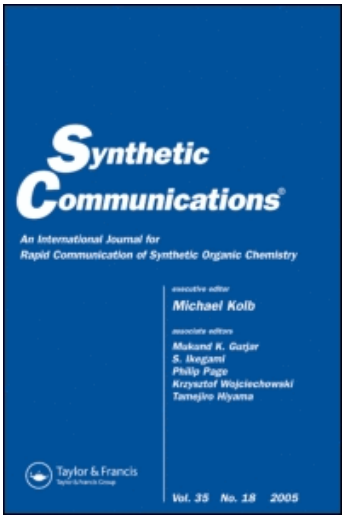

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An Iodine-Potassium t-Butoxide Catalysed Conversion of Thioamides and Thioureas to Their Oxygen Analogs

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AN IODINE-POTASSIUM t-BUTOXIDE CATALYSED CONVERSION OF THIOAMIDES AND THIOUREAS TO THEIR OXYGEN ANALOGS.

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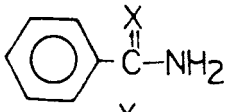
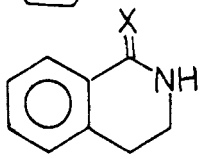
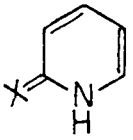
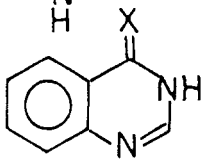
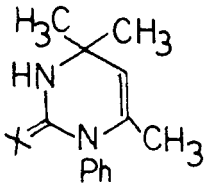
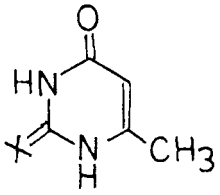
The title conversion, significant for its role in procuring modified nucleic acids[1] has been reported with bis(p-methoxyphenyl) telluroxide,[2] trimethyloxonium fluoborate,[3] DMSO/acids[4] and DMSO/iodine.[5] During the course of investigation of the reactions of heterocycles possessing thiourea and thioamide functionals, with iodocarbene generated from iodoform and potassium t-butoxide, we noticed the conversions of these substrates to their oxygen analogs.[6] Here, we report that the title conversion can be performed in a synthetically useful manner, under basic conditions, with the help of iodine/potassium t-butoxide in t-butanol solution. The reactions have been studied with both monoprotic

Table

Thioamides/ Thioureas (X = S)	Eluents	Reaction time in hours.	%age yield of the product (X = O)[a]
	$CHCl_3$:C_6H_6 (1:4)	40	90
	CH_3OH:C_6H_6 (1:4)	30	85[b]
	CH_3OH:$CHCl_3$ (1:9)	45	70
	CH_3CO_2Et:C_6H_6 (1:4)	48	35
	CH_3CO_2Et:C_6H_6 (1:4)	36	90
	---	30	95

a) All the products were identified by comparison (mmp, nmr, ir) with authentic samples.

b) Satisfactory elemental and spectral data was obtained.

and biprotic thioamides and thioureas (Table) and proceeded equally well when the thioamide was added to a solution of iodine and potassium t-butoxide or the later was added to a solution of iodine and thioamide in t-butanol. In all these cases sulphur was isolated in almost quantitative yield and the mechanism might be similar to the one reported for a similar reaction of DMSO/iodine.[7] However, from the above observations, it cannot be decided whether the reaction was initiated by the attack of iodine at S of thioamide or at O of t-butoxide.

These conversions did not occur with potassium t-butoxide in the absence of iodine and with sodium ethoxide and methoxide even in the presence of iodine.

Experimental

A catalytic amount of iodine (∽ 15 mg) was added to a solution of thioamide or thiourea (.001 mole) in t-butanol (60 ml) containing potassium t-butoxide (5 gm). A brisk reaction took place till iodine was dissolved. The reaction mixture was refluxed on a water bath and the progress of the reaction was monitored through tlc of the aliquot portion of the reaction mixture drawn at regular intervals. After the completion of the reaction,

the solvent was removed and the residue was dissolved in minimum amount of water. It was centrifuged and sulphur was separated. The aqueous portion was extracted with ethyl acetate (2 x 50 ml).[8] The extract was dried (Na_2SO_4) and the solvent was removed. The products were isolated through column chromatography of the residues over silica gel using eluents (Table).

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6. H.Singh and coworkers, unpublished results.
7. J.B.Chattopadhyaya and A.V. Rama Rao, Tetrahedron Letters, 3735 (1973).
8. 6-Methyl uracil was isolated as a precipitate formed after acidification of aqueous solution.