CARBONYL TO THIOCARBONYL CONVERSIONS USING TERTIARY AMINE-SOLUBILISED PHOSPHOROUS PENTASULPHIDE

C. Someswara Rao and M. P. Dave

(*Medicinal Chemistry Division, Sarabhai Research Centre, Wadi Wadi, Baroda* 390 007)

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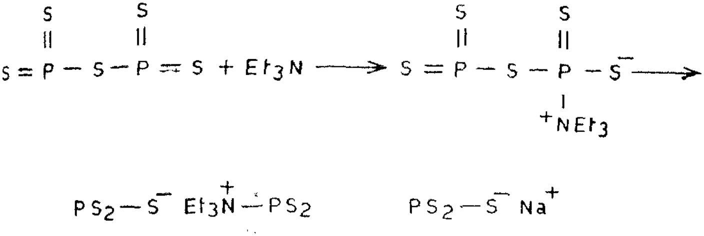
Abstract

In continuation of our earlier work on carbonyl to thiocarbonyl conversions using triethylamine-solubilised phosphorous pentasulphide in acetonitrile at room temperature it was found that the use of triethylamine and phosphorous pentasulphide in equimolar proportions rather than in a 2:1 *ratio gave very high yields of thioamides. Use of bases other than triethylamine such as diazabicyclo-* [2.2.2] *octane and triethylammonium acetate in this reaction is also discussed.*

Key words: Tert. amine solubilised P_2S_5, high yields of thioamides at room temperature Dabco, triethylammonium acetate.

Introduction

It was recently shown by us[1] that phosphorus pentasulphide (P_2S_5) could be made soluble in acetonitrile or dichloromethane at room temperature or below by the addition of 2 molar eq. of Et_3N. The clear yellow solution obtained proved to be highly reactive in the conversion of amides to thioamides at r.t. Addition of 1 eq. of Et_3N gave only a partial solution and at the time it was deemed necessary to add 2 eq. of Et_3N. This work was based on known high reactivities associated with tetraalkylammonium salts of carbanions[2] as compared to their alkali metal salts and constitutes an extension of this fact to mercaptide anion types. The reaction of a tert. amine with P_2S_5 can be depicted as in Fig. 1 and a tetraalkylammonium type salt (I) is possibly the reactive species which has already been shown to be much more reactive than the corresponding sodium salt (II) generated by the addition of $NaHCO_3$ to P_2S_5 in acetonitrile.[3]



$$S{=}\overset{S}{\overset{\|}{P}}-S-\overset{S}{\overset{\|}{P}}{=}S + Et_3N \longrightarrow S{=}\overset{S}{\overset{\|}{P}}-S-\underset{{}^{+}NEt_3}{\overset{S}{\overset{\|}{P}}}-S^{-} \longrightarrow$$

$$PS_2-S^{-}\ Et_3\overset{+}{N}-PS_2$$

I

$$PS_2-S^{-}\ Na^{+}$$

II

FIG. 1. Suggested course of reaction between Et_3N and P_2S_5.

III, R = H, X = O

IV, R = Ph, X = O

V, R = H, X = S

VI, R = Ph, X = S

VII, X = O

VIII, X = S

FIG. 2. The amides used and the thioamides obtained from them.

RESULTS

The results obtained in the present study along with some from our earlier work are summarised in Table I. All the reactions were carried out in acetonitrile as solvent at room temperature. The yields reported in the table refer to products after chromatography and/or crystallisation.

TABLE I

Carbonyl to thiocarbonyl conversions using t-amine-solubilised P_2S_5

Thioamide	Base (eq)	Time (hr)	m.p. (°C)	Yield (%)	Yield (%) by other methods
V	Et_3N (2)	24	123–125	72	
V	$NaHCO_3$ (2)	24	„	60	
V	Et_3N (1)	24	„	90	80[4]
V	Dabco (1)	48	„	85	
V	Dabco (0·5)	48	„	87	
V	$Et_3\overset{\pm}{N}H\ \overset{-}{O}Ac$ (2)	24	„	63	
V	$Et_3\overset{+}{N}H\ \overset{-}{O}Ac$ (1)	24	„	53	
VI	Et_3N (2)	24	188–90	75	
VI	$NaHCO_3$ (2)	24	..	.. *	
VI	$Et_5\overset{+}{N}H\ \overset{-}{O}Ac$ (2)	24	..	.. *	
VI	Et_3N (1)	24	188–90	85	
VIII	Et_3N (2)	48	130–31	20 †	
VIII	Dabco (1)	48	„	38 †	
VIII	Dabco (0·5)	48	„	94	50[6]
VIII	$NaHCO_3$ (2)	48	„	90	
VIII	$Et_3\overset{+}{N}H\ \overset{-}{O}Ac$	48	„	40	
VIII	Et_3N (1)	48	„	94	

* Starting amide recovered.

† Product isolated by column chromatography on silica gel using 10% ethylacetate in benzene.

MATERIALS AND METHODS

‘Riedel P_2S_5’ was used in this work. Acetonitrile was dried by distilling over P_2O_5.

The thioamides prepared in this work have already been characterised[1] by us by elemental analysis and IR and NMR spectra.

GENERAL PROCEDURE FOR THE CONVERSION OF AMIDES TO THIOAMIDES

The carbonyl compound in acetonitrile (10% solution) was treated with P_2S_5 followed by the tert. amine (in 2 or 3 portions) with occasional cooling in ice water to moderate the exothermic reaction. The resulting mixture was stirred 2–3 hr at r.t. and left at r.t. for 24–48 hr. The reaction mixture was poured into water and the product was isolated by filtration and purified by crystallisation from benzene or benzene-pet. ether. Reactions using Dabco were worked up by pouring the reaction mixture into excess of saturated $NaHCO_3$ solution followed by stirring for 1 hr.

The thiono compound VIII did not show any amide carbonyl peak in the IR (Found: S, 35·46. $C_8H_7NS_2$ requires S, 35·36%).

DISCUSSION

As can be seen from the table superior yields of thioamides of high purity could be obtained by the use of equimolar amounts of Et_3N and P_2S_5. 2H–1, 4-benzoxazine-3 (4 H)-thione (V) could not be prepared at all, as claimed earlier[4], using P_2S_5 in refluxing xylene or toluene, whereas it can now be obtained readily in 90% yield. The utility of this procedure was dramatically illustrated by the preparation of 2H–1, 4-benzothiazin-3 (4 H)-thione (VIII) in 94% yield whereas it was obtained in 20% yield with a 2 : 1 ratio of Et_3N and P_2S_5 and in 50% yield using P_2S_5 in refluxing toluene[5] starting from VII.[6]

Diazabicyclo (2.2.2) octane (Dabco) formed an insoluble complex with P_2S_5 but it was as effective as Et_3N although longer reaction times (48 hr) were necessary. The use of $NaHCO_3$ and P_2S_5 in a 2 : 1 ratio also gave the thione (VIII) in 90% yield.

Triethylammonium acetate could also solubilise P_2S_5 in acetonitrile but such solutions gave lower yields of product (63% of V) and was totally unreactive towards the rather sterically hindered amide (IV). Further experiments are in progress to evaluate the reactivity of true tetra-alkylammonium salts such as $PS_2\text{–}\bar{S}\ \overset{+}{N}Bu_4$.

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