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Synthesis of Nitriles and Symmetrical Organic Sulphides from Biprotic Carbothioamides and an α -Halogenated Ketone, Ester or Nitrile

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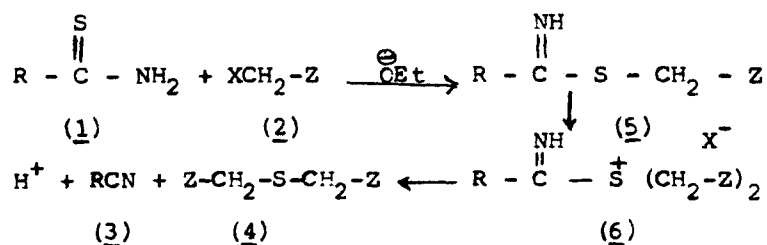
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SYNTHESIS OF NITRILES AND SYMMETRICAL ORGANIC
SULPHIDES FROM BIPROTIC CARBOETHIOAMIDES AND AN
 α -HALOGENATED KETONE, ESTER OR NITRILE

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Thioacetamide has been used as an elegant sulphur transfer reagent for C-S-C coupling of reactive halides.¹⁻⁴ Sulphur extrusion of biprotic carboethioamides to form corresponding nitriles has been reported with the help of (i) dichlorocarbene,⁵ (ii) triphenylphosphine, carbon tetrachloride, triethylamine,⁶ (iii) diethyl azocarboxylate, triphenylphosphine,⁷ and (iv) soft metal ions.⁸ Here, we report that under non-hydrolytic conditions viz. DMF/ OEt , EtOH/ OEt and DMF/ Et_3N , biprotic carboethioamides (1, R=CH₃, C₆H₅, CH₂C₆H₅) react with bromoacetophenone (2, Z=CC₆H₅), ethyl bromoacetate (2, Z=CCOEt)

and chloroacetonitrile (2, Z=CN) to furnish the C-S-C coupled products-2,2"-thiodiacetophenone (4, Z=CC₆H₅), ethylthiodiacetate (4, Z=COCC₂H₅), thiodiacetonitrile (4, Z=CN), respectively and the nitriles (3, R=CH₃, C₆H₅, CH₂C₆H₅) in good yields (table). These reagents like (iii) are also specific towards carbothioamides and do not react with amides. These results suggest that the reactions proceed by the cleavage of adducts (6), formed by the interaction of initial coupled intermediates (5) with (2).



Experimental

A solution of alpha-halogenated ketone, ester or nitrile (2, 0.02 mole) and carbothioamide (1, 0.01 mole) in anhydrous DMF (30 ml) containing sodium ethoxide (0.01 mole) was stirred. The reaction was complete in 4-5 h as shown by tlc monitoring. At this stage, the amount of nitrile formed was determined by glc analysis of a sample of the reaction mixture. The reaction mix-

Table

<u>1</u> (R)	<u>2</u> (Z)	Reac- tion condi- tions	G.l.c. <u>3</u> (%)	Column chromatography <u>3</u> (%) ^b	<u>4</u> (%) ^b
-C ₆ H ₅	-COC ₆ H ₅	c	70	32	67
		d	67	30	65
		e	71	36	63
-C ₆ H ₅	-COOC ₂ H ₅	c	80	35	70
		d	75	30	68
		e	82	38	72
-C ₆ H ₅	-CN	c	85	31	79
		d	80	27	75
		e	82	34	80
-CH ₃	-COC ₆ H ₅ ^g	c	80	f	73
-CH ₃	-COOC ₂ H ₅	c	90	f	82
-CH ₃	-CN	c	90	f	85
-Benzyl	-COOC ₂ H ₅	c	72 ^h	40	65
-Benzyl	-CN	c	76 ^h	45	67

(a) The yields are not optimized (b) The products were characterised by comparison (R_f , mp, ir, nmr) with authentic samples (ref. 2) (c) DMF/sodium ethoxide (d) Ethanol/triethylamine (e) Ethanol/sodium ethoxide (f) Acetonitrile could not be isolated by column chromatography. (g) A small amount of 2-methyl-4-phenyl thiazole was also formed. (h) Since the DMF and benzyl cyanide have almost same retention times, the amount of benzyl cyanide was determined from the chloroform extract after work up.

ture was diluted with water (150 ml) and was extracted with chloroform (3x75 ml). The extract was washed with water (3x100 ml), dried (anhydrous sodium sulphate) and the solvent was removed. The oily residue was chromatographed over a column of silica gel. The nitriles were eluted with pet. ether (40-60°) and the sulphides with chloroform. Similarly, these reactions were performed in sodium ethoxide (.02 mole)/ethanol (30 ml), and triethylamine (.02 mole)/ethanol (30 ml) (table).

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