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A NOVEL CLASS OF NITRILE YLIDE

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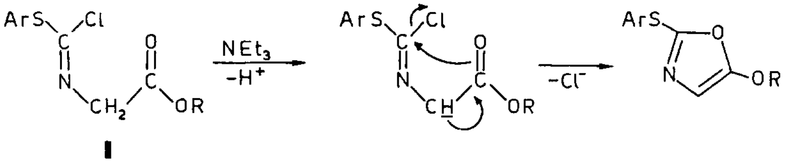
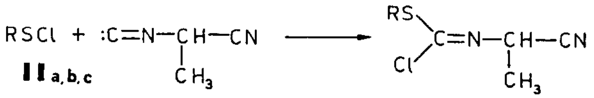
Abstract: Isothiocarbamoyl chlorides IV on treatment with NEt_3 afforded nitrile ylides V which reacted with dimethyl acetylenedicarboxylate to give 2*H*-pyrroles VI and with ethyl cyanoformate to give 4*H*-imidazoles VII.

In a previous paper[1] we reported a novel synthetic route to oxazoles by cyclization of N-alkoxycarbonylmethyl-S-arylisothiocarbamoyl chlorides I in the presence of triethylamine:



In continuation of our studies we decided to investigate the behaviour of some isothiocarbamoyl chlorides, unable to undergo ring-closure reaction, toward triethylamine.

As the isothiocarbamoyl chlorides we chose N-(1-cyanoethyl)-S-arylisothiocarbamoyl chlorides which were easily prepared, in almost quantitative yields by reacting sulfenyl chlorides II with 2-isocyanopropionitrile (III)[2] in methylene chloride at -50 °C:



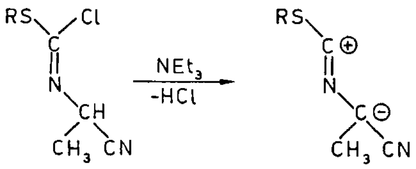
II a,b,c **III** **IV** a,b,c

a R = 4-chloro-2-nitrophenyl

b R = 2-nitrophenyl

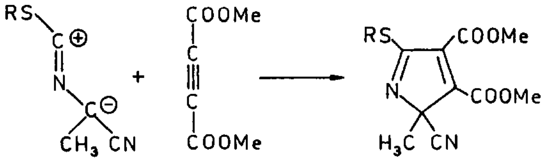
c R = 2,4-dinitrophenyl

On treatment of an ethereal solution of IV with triethylamine, triethylamine hydrochloride separated out and a solution containing the 1,3 dipolar species V was obtained:



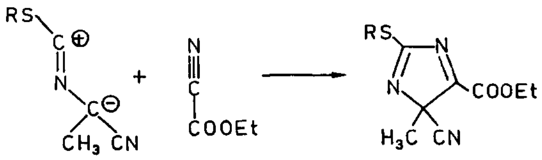
IV a,b,c **V** a,b,c

The presence of the 1,3 dipoles V, a hitherto unknown class of nitrile ylide, was confirmed by performing the reaction in the presence of dimethyl acetylenedicarboxylate: 1,3 dipolar cycloaddition took place giving 2*H*-pyrroles VI:



V a,b,c **VI** a,b,c

Analogously, employing ethyl cyanoformate as the dipolarophile, 4*H*-imidazoles VII were obtained:



V a,b **VII** a,b

A typical experimental procedure is as follows. Dry triethylamine (1.01 g, 10 mmoles) in Et_2O (10 ml) was added, during 2h, to a well-stirred solution of N-(1-cyanoethyl)-S-(4-chloro-2-nitrophenyl)isothiocarbamoyl chloride (Ia) (3.04 g, 10 mmoles) and dimethyl acetylenedicarboxylate (1.70 g, 12 mmoles) in dry Et_2O (35 ml). The reaction mixture was stirred for an additional hour and then evaporated to dryness. The residue was stirred with a little ethanol and filtered. The collected solid product was recrystallized from ethanol to give dimethyl 2-cyano-2-methyl-5-(4-chloro-2-nitrophenyl)-2*H*-pyrrole-3,4-dicarboxylate in 80% yield. Pale yellow crystals mp 165-166 °C.

The synthesis of 4*H*-imidazoles VII was accomplished following the procedure described for 2*H*-pyrroles VI except that benzene was employed as the solvent and the reaction was performed at 60 °C.

Physical and spectral data of compounds IV, VI and VII are summarized in the following Tables.

Table 1: N-(1-Cyanoethyl)-S-arylisothiocarbamoyl Chlorides IV.

Compound	Mp [a]/solvent	^{1}H-nmr (δ)[b]	
IVa	70-71 °C/hexane	4.77-4.58(q,1H,CH)	1.56-1.48(d,3H,CH_3)
IVb	41-42 °C/hexane	4.84-4.62(q,1H,CH)	1.57-1.48(d,3H,CH_3)
IVc	*c*	4.88-4.66(q,1H,CH)	1.61-1.53(d,3H,CH_3)

a) Uncorrected; *b*) Solvent $CDCl_3$, TMS as internal reference; *c*) The crude reaction product was employed for the successive reaction without purification.

Table 2: Dimethyl 5-Arylthio-2-cyano-2-methyl-2*H*-pyrrole-3,4-dicarboxylate VI.

Compound	Mp [a,b]	Yield	^{1}H-nmr (δ)[c]	ms[d]
VIa	165-166 °C	80%	3.96(s,6H,OCH_3(3)+OCH_3(4)) 1.78(s,3H,CH_3)	409
VIb	104-105 °C	65%	3.92(s,3H,OCH_3(3)) 3.88(s,3H,OCH_3(4)) 1.70(s,3H,CH_3)	375
VIc	144-146 °C	30%	3.97(s,3H,OCH_3(3)) 3.94(s,3H,OCH_3(4)) 1.76(s,3H,CH_3)	420

a) Uncorrected; *b*) Solvent EtOH; *c*) Solvent DMSO-d_6; TMS as internal reference
d) 70 eV, $|M|^+$ m/z values

Table 3: Ethyl 2-Arylthio-4-cyano-4-methyl-4*H*-imidazole-5-carboxylate VII.

Compound	Mp[a,b]	Yield	^{1}H-nmr (δ)[c]	ms[d]
VIIa	125-126 °C	66%	4.58-4.36(q,2H,CH_2) 1.75(s,3H,CH_3(4)) 1.55-1.38(t,3H,CH_3)	366
VIIb	137-138 °C	55%	4.54-4.33(q,2H,CH_2) 1.73(s,3H,CH_3(4)) 1.48-1.38(t,3H,CH_3)	332

a) Uncorrected; *b*) Solvent EtOH; *c*) Solvent DMSO-d_6; TMS as internal reference
d) 70 eV, $|M|^+$ m/z values.

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