

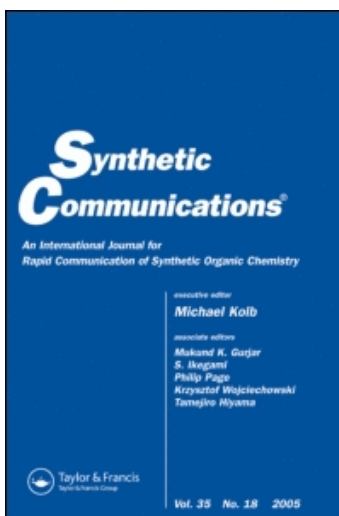
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A Facile Synthesis of Ethyl α -Cyano- β -amincacrylates and Related Compounds

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A FACILE SYNTHESIS OF ETHYL α -CYANO- β -AMINOACRYLATES
AND RELATED COMPOUNDS

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Ethyl- α -cyano- β -aminoacrylates (I) have been used as intermediates in the synthesis of pyrimidine derivatives^{1,2} and I (R=H, CH₃, C₆H₅) have been obtained by the condensations of ethyl cyanoacetate with amidines and iminoethers, in relatively poor yields.² We now report that both biprotic and monoprotic carbothioamides-thioformamide, thiobenzamides, phenylthioacetamide, quinazolin-4(3H)-thione and pyrrolidin-2(1H)-thione condense with ethyl bromocyanoacetate, with extrusion of sulphur, to form ethyl α -cyano- β -aminoacrylate (I, R=H), ethyl α -cyano- β -aminocinnamates (I, R=-C₆H₅, -C₆H₄-OCH₃, -C₆H₄-NO₂, p), ethyl α -cyano- β -amino- β -benzylacrylate (I, R=-CH₂C₆H₅), ethyl- α -cyano- Δ ^{4(3H)}, quinazolineacetate (II) and ethyl α -cyano- Δ ^{2, α} pyrrolidineacetate (III) (Table) respectively.

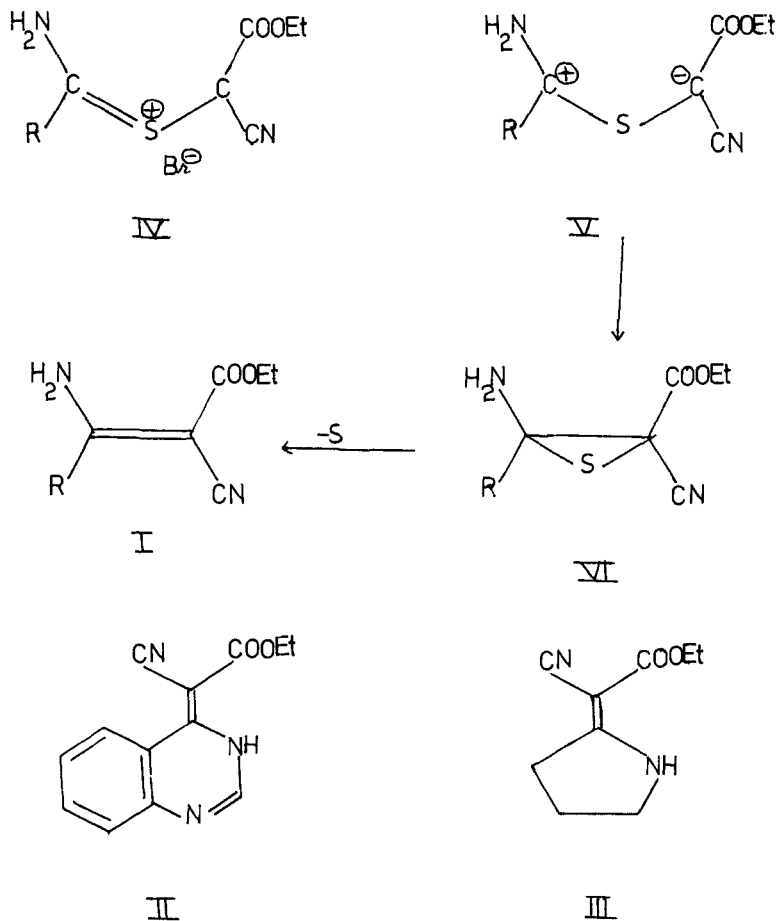
All these compounds gave satisfactory analytical and spectral data. The ethoxycarbonyl group absorptions (1670-80 cm⁻¹) of these products in i.r., did not undergo any change on dilution. Hence -CO- is intramolecularly

Table

Product	m.p.	Yield %
I, R=H	140 ^o	65- 67
I, R=C ₆ H ₅	123-24 ^o	65- 70
I, R=C ₆ H ₄ OCH ₃ -p	134-35 ^o	55- 60
I, R=C ₄ H ₄ NO ₂ -p	146-47 ^o	65-70
I, R=-CH ₂ -C ₆ H ₅	105 ^o	72-75
II	135 ^o	75-76
III	160 ^o	60-65

hydrogen bonded to -NH and (I) have been assigned Z-configurations.

These results suggest that the adducts (IV) of carbothioamides and ethylbromocynoacetate deprotonate to the corresponding thiocarbonyl ylides (V) which through electrocyclic closure to thiirane derivatives (VI) desulphurise to I. Hence the thiocarbonyl ylides generated from the adducts of bi or mono protic carbothioamides and ethylbromocynoacetate behaved differently from those formed from nonprotic thioureas and ethylbromocynoacetate which decompose to the parent thioureas and alkenes.³ This synthetic operation provides an alternative to Wittig reaction for the incorporation of a carbethoxy, cyano methyldene moiety at carboxamide carbon via its carbothioamide derivative⁴ and parallels the multistep transformation of the thiones to alkenes via addition-extrusion reactions.^{5,6}



Experimental

Ethylbromocyanoacetate (.01 mole) in ethanol (2 ml) was added, with stirring, to a solution of the carbothioamide (.01 mole) in appropriate amount of ethanol as such or containing sodium ethoxide (.01 mole) at room temperature. Sulphur separated out instantaneously and the reaction mixture was stirred for another two hours. Sulphur was

filtered off and the solvent was removed from the filtrate. The oily residue on treatment with pet. ether (20 ml) turned into a solid which was crystallied from methanol (Table).

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