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A FACILE SYNTHESIS OF ETHYL \( \alpha \)-CYANO-\( \beta \)-AMINOCRYLATES AND RELATED COMPOUNDS

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Ethyl-\( \alpha \)-cyano-\( \beta \)-aminocrylates (I) have been used as intermediates in the synthesis of pyrimidine derivatives\(^1,2\) and I (R=H, CH\(_3\), C\(_6\)H\(_5\)) 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 \( \alpha \)-cyano-\( \beta \)-aminocrylate (I, R=H), ethyl \( \alpha \)-cyano-\( \beta \)-aminocinnamates (I, R=C\(_6\)H\(_5\), -C\(_6\)H\(_4\)-CH\(_3\), -C\(_6\)H\(_4\)-NO\(_2\), p), ethyl \( \alpha \)-cyano-\( \beta \)-amino-\( \beta \)-benzylacrylate (I, R=CH\(_2\)C\(_6\)H\(_5\)), ethyl-\( \alpha \)-cyano-\( \Delta \)\(_4\)(3H), quinazolineacetate (II) and ethyl \( \alpha \)-cyano-\( \Delta \)\(_4\),\( \alpha \)-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 \( -\text{CC} - \) is intramolecularly...
hydrogen bonded to \(-\text{NH}\) and (I) have been assigned Z-configurations.

These results suggest that the adducts (IV) of carbothioamides and ethylbromocyanooacetate deprotonate to the corresponding thioacyl ylides (V) which through electrocyclic closure to thiirane derivatives (VI) desulphurise to I. Hence the thioacyl ylides generated from the adducts of bi or mono protic carbothioamides and ethylbromocyanooacetate behaved differently from those formed from nonprotic thioureas and ethylbromocyanooacetate which decompose to the parent thioureas and alkene\(^3\). This synthetic operation provides an alternative to Wittig reaction for the incorporation of a carboxthoxy, cyano methylidene moiety at carboxamide carbon via its carbothioamide derivative\(^4\) and parallels the multistep transformation of the thiones to alkenes via addition-extrusion reactions\(^5,6\).
Experimental

Ethylbromocyanooacetate (0.01 mole) in ethanol (2 ml) was added, with stirring, to a solution of the carbothioamide (0.01 mole) in appropriate amount of ethanol as such or containing sodium ethoxide (0.01 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 crystallized from methanol (Table).

References
4. 4-(Acyl and alkoxy carbonyl methylidene)-3,4-dihydroquinazolines have been obtained in an analogous manner. Harjit Singh, S.S. Narula, and C.S. Gandhi, Tetrahedron Letters, 3747 (1977).

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