SUMMARY

The work embodied in this 'thesis' forms a contribution to the knowledge in the area of organic chemistry of sulphur, selenium and tellurium. 2-Chloro-4-cyano-3-vinylquinolines(6) were used as precursors and reacted with dihydrogen sulphide as well as with sodium hydrogen sulphide to give the corresponding 2,3-dihydro-4-cyanothieno(2,3-b)quinolines. Attempted dehydrogenation of the 4-cyano-dihydrothienoquinoline did not yield the expected dehydrogenated product viz., 4-cyanothieno(2,3-b)quinoline. This result was quite in contrast with the behaviour of its 4-H and 4-methyl analogues which readily underwent dehydrogenation with DDQ to give the corresponding thienoquinolines. The only product that was realized (in <10% yield) was (4-cyano-3-vinyl) quinolin-2yl-disulphide, for which transformation as well as for the failure of the 4-cyano-2,3-dihydrothienoquinoline to undergo dehydrogenation reaction, a mechanistic rationale has been put forth.

As an alternative way of obtaining 4-cyanothieno(2,3-b) quinolines, the 2-chloro-3-vinylquinolines(6) were converted into the corresponding quinoline-2(1H)-thiones. But when the thiones (132) were subjected to sequential treatment with bromine in chloroform and triethylamine, they did not yield the expected 4-cyanothienoquinolines. The product obtained was their dihydroderivative. Here again the result was in contrast with what
was realized in the case of 4-methyl-and 4-phenyl-substituted-quinoline-thiones. A mechanistic insight has been gained into this intriguing result. The intermediacy of a sulphenyl bromide in the above transformation is established. Isolation of the sulphenyl bromide and treatment then with triethylamine led to the dehydrogenated derivative. On hydrolysis followed by decarboxylation, the cyanoquinoline yielded the parent thienoquinoline.

Unlike the 3-vinyl-2-quinolinones, the 4-methyl-and 4-phenyl-thiones did not undergo acetoxy-cyclization reaction with iodine in the presence of silveracetate in acetic acid, but underwent oxidative dimerization to give the corresponding disulphide. The disulphides (realized using chloramine-T almost quantitatively) readily underwent chlorolysis with chlorine to give the corresponding sulphenyl-chlorides, which on boiling with triethylamine in chloroform gave the thieno(2,3-b)quinolines. Interestingly, when the 4-cyano-3-vinyl-2(1H)thiones (132) treated with the prevost reagent or chloramine-T, the outcome was not the disulphide-formation but the corresponding 2,3-dihydrothieno (2,3-b)quinolines. The role of the oxidant in this case is rationalized.

Another interesting aspect encountered with the 4-cyano series was that the 2-chloro-4-cyano-3-vinylquinolines, unlike their 4-H, 4-methyl and 4-phenyl and 4-carbomethoxy analogues
gave when treated sequentially with bromine and thiourea, the corresponding dihydro-thienoquinolines. The latter series as experienced earlier gave, with these reagents the corresponding dehydro-thienoquinolines. A mechanism interpretation is proposed.

The foregoing novel results were then tested in the selenium and tellurium series. The key precursor viz., 2-chloro-4-cyano-3-vinyl quinolines were then exploited for obtaining the synthesis of selenoloquinolines. The cyanoquinoline with sodium hydrogen selenide gave a mixture of diselenoloquinoline and 2,3-dihydroselenoloquinoline. With sodium diselenide they gave the dihydroselenoloquinolines. Here again the 2-chloro-3-vinylquinolines bearing a cyano group at the C4-position showed contrasting behaviour to that of the 4-alkyl or 4-phenyl substituted series. The results were mechanistically rationalized.

Another deviation that was observed was in the addition of bromine to the cyanoquinoline followed by heating the resulting dibromide with selenoureia in boiling ethanol, or with sodium hydrogen selenide or sodium diselenide in the same solvent. In all these experimentations, the product obtained was the 4-cyano dihydroselenolo(2,3-b)quinoline.

The 2-chloro-4-cyanoquinolines readily reacted with selenoureia but the resulting selenouranium salt when decomposed
with alkali followed by acidification gave the dihydroselenolo (2,3-b)quinoline. The 4-alkyl and 4-phenyl-2-chloro-3-vinylquinolines gave the corresponding selenoxo compounds when reacted with selenourea and base. The selenoxo compounds realized with 4-alkyl and 4-phenyl series when reacted with iodine in the presence of silver acetate or chloramine-T in glacial acetic acid, readily underwent oxidative cyclization to give the corresponding selenolo(2,3-b)quinolines.

With sodium telluride or sodium ditelluride 4-cyano-3-vinylquinoline gave a mixture of two products. One of them was identified to be a ditelluride and other could not be characterized.