New Heterocyclic Ring Systems. XII. Synthesis of [1,4]Thiazinocarbazoles (1)

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Five [1,4]thiazinocarbazoles have been synthesized from 6-, 7- and 8-amino-2*H*[1,4]benzothiazin-3(4*H*)ones by the Jaap-Klingemann reaction with 2-hydroxymethylenecyclohexanone followed by Fischer indolisation of the resulting hydrazones. The structures of the hitherto unknown ring systems have been confirmed by pmr spectral data.

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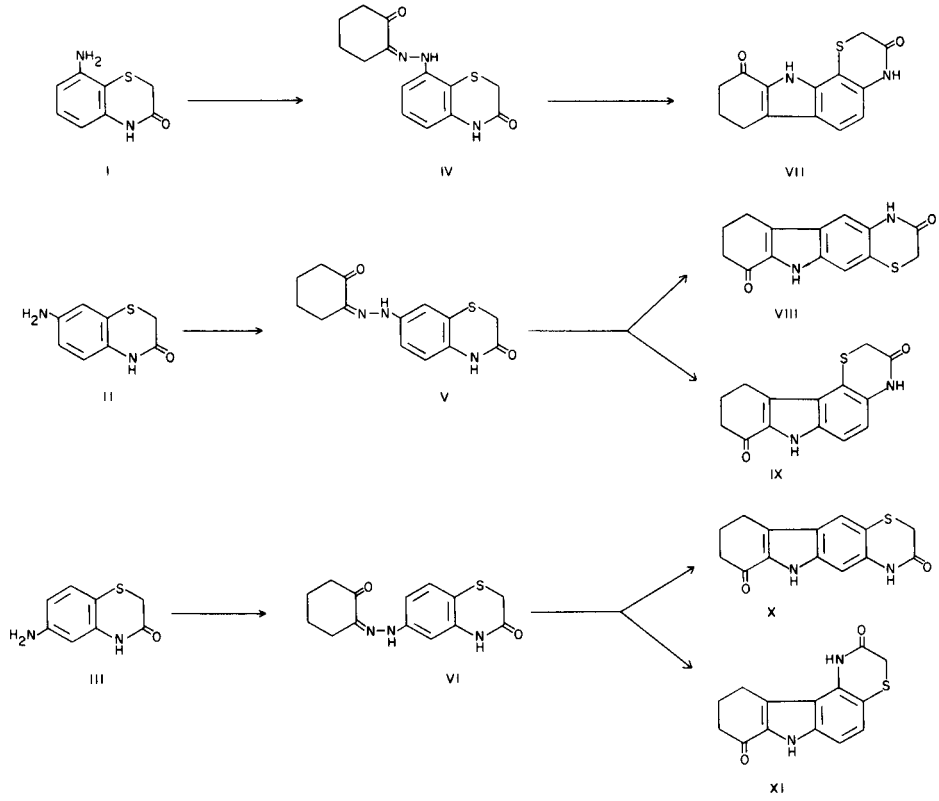
The thiazinocarbazoles represent interesting molecules which have remained pratically unexplored. The literature gives only one reference (2) which deals with the formation of [1,4]thiazino[2,3,4-*jk*]carbazole by a photho reaction of *N*-phenyl-2-benzothiazolinone.

As part of a research program on the synthesis of polyheterocycles with possible pharmacological activities (3), we now wish to report the preparation of some new [1,4]-thiazinocarbazole derivatives starting from the isomeric amino[1,4]benzothiazines I, II and III previously described by us (4,5). These amines were subjected to the Jaap-Klingemann reaction with 2-hydroxymethylenecyclohexanone to afford the corresponding hydrazones IV, V and VI which, by Fischer indolisation with glacial acetic acid and hydrochloric acid, furnished the hitherto unknown [1,4]thiazinocarbazoles VII-XI. 8-Amino-2*H*-[1,4]benzothiazin-3(4*H*)one (I) gave the steroidal analogue 2,3,4,7,8,9,10,-11-octahydro[1,4]thiazino[2,3-*a*]carbazole-3,10-dione (VII) whose structure was easily confirmed by the pmr spectrum revealing the presence of two aromatic protons as an AB quartet with J = 9 Hz. 7-Amino- (II) and 6-amino-3,4-dihydro-2*H*-[1,4]benzothiazin-3-one (III) afforded in each case a mixture of two products, namely the linear tetracyclic structures (VIII and X) and the angular ones (IX and XI). The two pairs of isomers could be separated by fractional crystallization. In fact, as expected, the



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