Preparation of 2,3-Dihydrothiazolo[2,3-*a*]isoquinolinium Salts and their Reactions with Complex Metal Hydrides

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3-Methyl-2,3-dihydrothiazolo[2,3-*a*]isoquinolinium perchlorate (3; R = Me) has been synthesised by the cyclisations of 1-allylthioisoquinoline (1) and β-hydroxypropylthioisoquinoline (4: X = H, OH: R = Me). 2,3-Dihydrothiazolo[2,3-*a*]isoquinolinium perchlorate (3; R = H) was obtained from β-hydroxyethylthioisoquinoline (4; X = H, OH; R = H) as well as 1-mercaptoisoquinoline and ethylene dibromide. Reduction of 3-methyl-2,3-dihydrothioazolo[2,3-*a*]isoquinolinium perchlorate (3; R = Me) and 3-methylthiazolo[2,3-*a*]isoquinolinium perchlorate (10; R = Me) with LAH or $NaBH_4$ gave 3-methyl-2,3-dihydro-10b*H*-thiazolo[2,3-*a*]isoquinoline (7), 3-methyl-2,3,5,6-tetrahydro-10b*H*-thiazolo[2,3-*a*]isoquinoline (8) and a minor component of undetermined structure. 3-Bromomethyl-2,3-dihydrothiazolo[2,3-*a*]isoquinolinium perchlorate (12) obtained from (1) and bromine was hydrogenolysed with LAH to (7) and (8).

THE Hantzsch thiazole synthesis [1] has been extensively used in synthesising a variety of thiazolo-heterocyclics [2] and their salts.[3] In these reactions, the formation of intermediate hydroxythiazolines [2a,4] and hydroxythiazolinium salts [3a,5] by the attack of N at an electrophilic carbonyl carbon have been reported. Here we both report the use of an alcohol and an alkene-carbonium ion for the synthesis of 2,3-dihydrothiazolo[2,3-*a*]isoquinolinium perchlorates and describe the behaviour of these compounds towards complex metal hydrides.

In 1-allylthioisoquinoline (1), the allylic side-chain can provide a secondary carbonium ion (2) at the carbon, appropriately placed for attack of N to form the thiazole ring. As alkylation in heterocyclic thioureas where the thio-function is exocyclic proceeds at S,[2a] (1) was obtained from allyl chloride and 1-mercaptoisoquinoline. Its n.m.r. spectrum showed the characteristic vinylic proton absorptions. Its mass spectrum, where the characteristic peaks appeared at *m*/*e* 201 (M^+), *m*/*e* 200, 174 (predominant γ-fission in 1-alkylisoquinolines,[6,7] loss of H· and $\dot{C}H=CH_2$), *m*/*e* 186 (*m**, *m*/*e* 172·1, *a*) and *m*/*e* 168 (*m**, *m*/*e* 140·3, *b*) further corroborated the structure.

Compound (1) cyclised smoothly to 3-methyl-2,3-dihydrothiazolo[2,3-*a*]isoquinolinium perchlorate (3; R = Me) in polyphosphoric acid although it failed in ethanolic HCl and sulphuric acid. Compound (3;

[1] R. H. Wiley, D. C. England, and L. L. Behr, *Org. Reactions*, 1951, **6**, 367.

[2] (*a*) A. F. Alper and A. Taurin, *Canad. J. Chem.*, 1967, **45**, 2903 and references therein; (*b*) H. Singh, S. L. Jain, V. K. Sharma, and K. S. Narang, *Indian J. Chem.*, 1969, **7**, 765; (*c*) C. K. Bradsher and H. F. Andrew, *J. Heterocyclic Chem.*, 1967, **4**, 577; (*d*) G. Doleschall, *Acta Chim. Acad. Sci. Hung.*, 1967, **53**, 385.

[3] (*a*) B. Stanovnik, M. Tisler and A. Vrbanic, *J. Org. Chem.*, 1969, **34**, 996, and references therein; (*b*) C. K. Bradsher and W. J. Jones, jun., *Rec. Trav. chim.*, 1968, **87**, 274; (*c*) C. K. Bradsher and H. F. Andrew, *J. Heterocyclic. Chem.*, 1966, **3**, 282; (*d*) C. K. Bradsher and W. J. Jones, *J. Org. Chem.*, 1967, **32**, 2079; (*e*) C. K. Bradsher and D. F. Lohr, jun., *J. Heterocyclic Chem.*, 1967, **4**, 71; (*f*) K. Undheim and K. R. Reistad, *Acta Chem. Scand.*, 1970, **24**, 2956, and references therein.

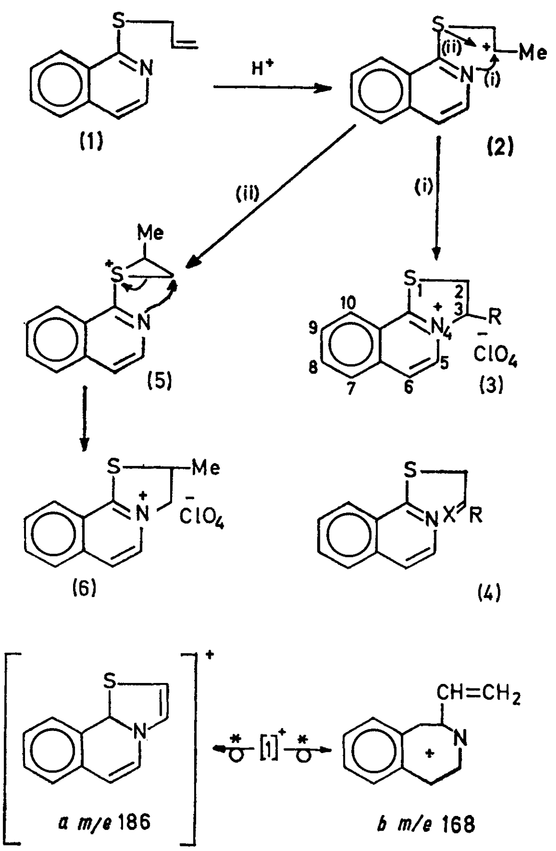
[4] (*a*) H. Singh and S. Singh, *Tetrahedron Letters*, 1970, 585; (*b*) H. Alper, *Chem. Comm.*, 1970, 383; (*c*) H. Alper and A. E. Alper, *J. Org. Chem.*, 1970, **35**, 835; (*d*) H. Alper, E. C. H. Keung, R. A. Partis, *J. Org. Chem.*, 1971, **36**, 1352.

[5] R. S. Egan, J. Tadanier, D. L. Garmaise, and A. P. Gaunce, *J. Org. Chem.*, 1968, **33**, 4422.

[6] G. Spiteller, *Adv. Heterocyclic Chem.*, 1966, **7**, 301.

[7] (*a*) H. Budzikiewics, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, pp. 287—288; (*b*) p. 309.

R = Me), was alternatively obtained by the cyclisation of (4; R = Me, X = H,OH), which was obtained by sodium borohydride reduction of (4; R = Me, X = O).[3e] The u.v. spectrum of (3; R = Me), which was different from that of the perchlorate of (1) (Figure), and its n.m.r. spectrum where vinylic protons were absent, corroborated the cyclic structure. In both these cases the possible formation of 2-methyl-2,3-dihydrothiazolo-[2,3-*a*]isoquinolinium perchlorate (6) through the intermediate (5) was ruled out (see later). The versatility which the use of alcohols allowed in preparing these systems was further illustrated by the cyclisation of (4; R = H, X = H, OH) to 2,3-dihydrothiazolo[2,3-*a*]-isoquinolinium perchlorate (3; R = H); this was also obtained by condensation of 1-mercaptoisoquinoline and dibromoethane. Compound (4; R = H, X = H, OH) was obtained from ethylene chlorohydrin and 1-mercaptoisoquinoline.



Since we ultimately required a certain degree of saturation in ring B and ring rupture[8] accompanies the reductions of thiazolinium salts with complex metal hydrides, we studied the behaviour of (3; R = Me) upon reduction. With $NaBH_4$ and LAH it furnished three products bands I, II, and III in the approximate ratios of 1 : 3 : 6 and 5 : 1 : 5 respectively as monitored by t.l.c. Through repeated chromatographic separation on alumina, bands I and III (single spots on t.l.c.) could be isolated in sufficient amounts whereas pure band II was obtained in very small quantity. During this operation, the quantity of band I increased and that of band III decreased. The mass spectrum of component I (parent ion, *m/e* 203) showed the addition of only one H atom. Its n.m.r. spectrum indicated the presence of a C(5)–C(6) double bond as 5-H and 6-H appeared at δ 7·16 (1H, d, *J* 6 Hz) and 8·18 p.p.m. (1H, d, *J* 6 Hz) respectively; these were consistent with the 3-H and 4-H absorptions in the n.m.r. spectrum of (1). Evidently, the addition has taken place at C-10b and component I is 3-methyl-2,3-dihydro-10b*H*-thiazolo-[2,3-*a*]isoquinoline (7). In its mass spectrum, the base peak at *m/e* 202 (*M* — 1) may be due to fragment ion *C*.[7b] The parent ion at *m/e* 205 for component III suggested that it was 2,3,5,6-tetrahydro-3-methyl-10b*H*-thiazolo[2,3-*a*]isoquinoline (8) formed through the addition of two hydrogen atoms to (7). An alternative structure, (9), that could be formed by thiazolinium ring fission[8] was ruled out as the 3-H and 4-H absorptions were missing in its n.m.r. spectrum. The stereochemical assignment for 10b-H was made with the aid of C–H stretch region where the presence of three sharp Bohlmann bands[9] (2630, 2730, 2780 cm^{-1}) on the lower frequency side of the major C–H absorption indicated the presence of two α-hydrogens *trans*-diaxial to the unshared electron pair on the bridgehead nitrogen. Component II (mol. wt. 205) might be (9) or an isomer of (8) since an unambiguous structural assignment could not be made on the basis of the available spectral data.* From these structures the conversion of (8) into (7) during repeated chromatography, through oxidation, is understandable.

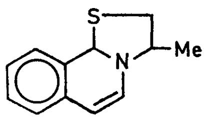
Bradsher[3e] reported the preparation of 3-methylthiazolo[2,3-*a*]isoquinolinium perchlorate (10; R = Me) from (4; R = Me, X = O). On reduction with LAH as well as $NaBH_4$, compound (10; R = Me) gave three identical products (R_F, i.r., mixed m.p. of picrate derivatives) with those obtained from (3; R = Me). The absence of any additional constituent in the reduction mixture from (10; R = Me) suggests that initial hydride attack at C-10b is followed by the reduction of the enamine [C(2)–C(3)] double-bond and finally the C(5)–C(6) double-bond is reduced. Since it was considered advisable to check the authenticity of the cyclodehydrated product (10; R = Me), the perchlorate of (4; R = Me, X = O) was prepared. It was found to be quite different from (10; R = Me) and upon dehydration it gave (10; R = Me) identical (mixed m.p. and u.v.) with the product obtained directly from (4; R = Me, X = O).[3e] Likewise, the perchlorate of (4; R = Ph, X = O) was dehydrated to (10; R = Ph), also obtained directly from (4; R = Ph, X = O). In the

* The available quantity precluded the determination of its n.m.r. spectrum and in its i.r. spectrum, the Bohlmann bands were absent.

[8] A. D. Clarke and P. Sykes, *J. Chem. Soc.* (*C*), 1971, 103.

[9] (*a*) F. Bohlmann, *Chem. Ber.*, 1958, **91**, 2157; (*b*) N. J. Leonard and W. K. Musker, *J. Amer. Chem. Soc.*, 1960, **82**, 5148; (*c*) W. E. Rosen, *Tetrahedron Letters*, 1961, 481; (*d*) E. Wenkert and D. Roychaudburi, *J. Amer. Chem. Soc.*, 1956, **78**, 6417.

i.r. spectra of the perchlorates of (4; R = Me, Ph, X = O), the carbonyl absorptions were missing and their u.v. spectra were identical with those of (3; R = Me); they were quite different from those of (10) (Figure).



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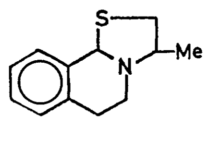

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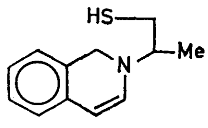

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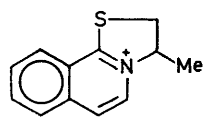

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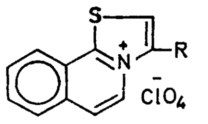

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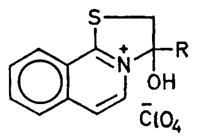

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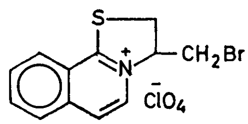

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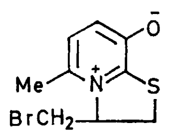

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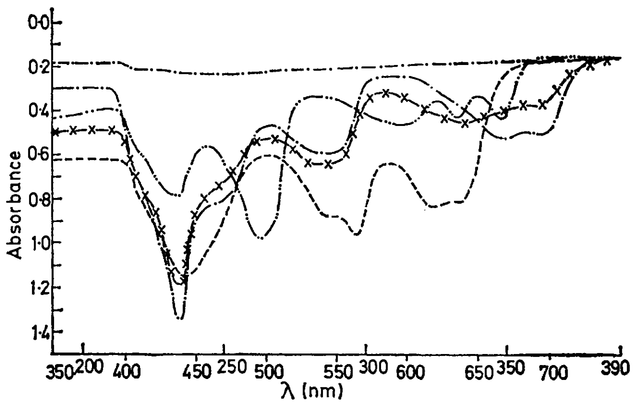

FIGURE 3 U.v. spectra of perchlorate of (1), (- - - -); (3; R = Me), (—·—·—); (10; R = Me), (—··—··—); and (11; R = Me), (—×—×—)

These spectral observations coupled with their ready dehydrations (characteristic of tertiary alcohols) suggested the cyclic structure (11) formed through preferred O protonation over N protonation [10] and subsequent cyclisation.

Undheim [11] established the formation of 3-bromoethyl-5-methyl-2,3-dihydrothiazolo[2,3-*a*]pyridinium 8-oxide (13) by bromination of 2-allylthio-6-methyl-3-hydroxypyridine. Likewise (1) was transformed into 3-bromomethyl-2,3-dihydrothiazolo[2,3-*a*]isoquinolinium perchlorate (12), which on hydrogenolysis with LAH [12] gave (7) and (8) (1 : 3). These transformations of (3; R = Me), (12), and (10; R = Me) to identical products provide substantial chemical evidence for the assignment of the methyl group to the 3-position, (3), rather than the 2-position (6).

EXPERIMENTAL

M.p.s were determined in capillaries. I.r. spectra were recorded for potassium bromide discs with a Perkin-Elmer 337 grating spectrophotometer. Elemental analyses were performed at Central Drug Research Institute, Lucknow. N.m.r. spectra were determined with Varian A-60 and HA-100 instruments and electronic spectra were measured in 95% ethanol and are qualitative. For t.l.c., plates were coated with silica gel G and spots were developed with iodine.

1-*Allylthioisoquinoline* (1).—A solution of 1-mercaptoisoquinoline (0·01 mol) in anhydrous ethanol (30 ml) containing sodium ethoxide (0·01 mol) and allyl chloride (0·01 mol) was refluxed for 2 h. The solvent was removed and the residue was treated with water and extracted with ether. The solvent was removed from the dried extract (Na_2SO_4) and the solution of the residue (yield 90%) in methylene chloride (10 ml) was passed through a small column filled with alumina (3 g). The product (single spot on t.l.c.) could not be distilled under reduced pressure. Equally good yields were obtained by keeping the reaction mixture overnight but use of sodium methoxide gave relatively poor yields, $\nu_{max.}$ (neat) 1642, 992, and 920 cm^{-1} (terminal vinyl); mass spectrum: $M^{+\cdot}$, *m/e* 201, n.m.r. δ ($CDCl_3$) 4·02 (2H, d, *J* 7·0 Hz, CH_2), 4·95—5·75 (3H, ABX m, $CH=CH_2$), 7·21 (1H, d, *J* 6 Hz, 4-H), 8·21 (1H, d, *J* 6 Hz, 3-H), 7·3—7·7 and 8·0—8·15 p.p.m. (4H, m, ArH).

1-*Allylthioisoquinolinium Perchlorate*.—This compound, m.p. 107—109° (CH_3OH) (yield 60%), was obtained by cooling a solution of compound (1) and 60% $HClO_4$ in methanol. Use of $HClO_4$–ether (1 : 1 v/v) gave better yields, $\nu_{max.}$ 2680 ($\overset{+}{N}$–H), 1170—1070 (ClO_4) cm^{-1}; $\lambda_{max.}$ 237s, 286sh, 297, 325, and 336 nm (Figure) (Found: N, 5·1. $C_{12}H_{12}ClNSO_4$ requires N, 4·65%). Similar procedures were used for the preparations of the following compounds.

1-β-*Hydroxyethylthioisoquinoline* (4; R = H, X = H, OH). This was prepared from ethylene chlorohydrin and 1-mercaptoisoquinoline. It was purified by chromatography and could not be distilled (yield 83%).

1-β-*Hydroxyethylthioisoquinolinium perchlorate*.—This compound had m.p. 142—145° (MeOH–ether; 1 : 1), yield 40% $\lambda_{max.}$ 226, 245sh, 274sh, 283, 294, and 310—340 nm (broad hump) (Found: N, 4·8. $C_{11}H_{12}ClNOSO_5$ requires N, 4·6%).

(*Isoquinolin*-1-*ylthio*)*acetone* (4; R = Me, X = O).[3e]—This compound had $\nu_{max.}$ (neat) 1705 (CO) cm^{-1}.

3-*Methyl*-3-*hydroxy*-2H-*thiazolo*[2,3-a]*isoquinolinium Perchlorate* (11; R = Me)*.—This compound had m.p. 145—146° from [CH_3CN–ether, 1 : 1 (v/v)], yield 60%, $\nu_{max.}$

[10] H. V. Berde, V. N. Gogte, C. I. Jose, and B. D. Tilak, *Ind. J. Chem.*, 1970, **8**, 801.

[11] K. Undheim and K. R. Reistad, *Acta chim. Scand.*, 1970, **24**, 2949.

[12] N. G. Gaylord, *J. Amer. Chem. Soc.*, 1954, **76**, 285.

3400br (OH) and 1615(C=N) cm^{-1}, $\lambda_{max.}$ 235s, 252sh, 280—292, 327—337, 350, and 364 nm (Figure), n.m.r. δ ($CDCl_3$) 2·0 (3H, s, CH_3), 4·22 (2H, s, CH_2), and 7·1—8·2 p.p.m. (6H, m, ArH).

2-(*Isoquinolin*-1-*ylthio*)*acetophenone* (4; R = Ph, X = O).—This compound had m.p. 100—101° (from CH_3OH), yield 60%, and was obtained from bromoacetophenone and 1-mercaptoisoquinoline; $\nu_{max.}$ 1695 cm^{-1} (C=O) (Found: N, 5·1. $C_{17}H_{13}NOS$ requires N, 5·0%).

3-*Phenyl*-3-*hydroxy*-2H-*thiazolo*[2,3-a]*isoquinolinium Perchlorate* (11; R = Ph)*.—This compound had m.p. 160—161°, yield 25%, $\nu_{max.}$ 3220 (OH) and 1605 (C=N) cm^{-1}, $\lambda_{max.}$ 232s, 270—290, and 310—330 nm, n.m.r. δ ($CF_3 \cdot CO_2H$) 4·10 (2H, s, CH_2) and 7·3—8·9 p.p.m. (11H, s, ArH) (Found: N, 3·5. $C_{17}H_{14}ClNO_4S$ requires N, 3·8%).

Alternatively compounds (4; R = Me or Ph, X = O) and (11; R = Me or Ph) were obtained by refluxing a solution of 1-mercaptoisoquinoline and the appropriate α-halogeno-ketone in ethanol for 6—7 h. After evaporating the solvent, the residue was distributed in ether and water. The ethereal layer gave compound (4; R = Me or Ph, X = O) whereas the aqueous layer on treatment with 60% $HClO_4$ gave (11; R = Me or Ph).

1-β-*Hydroxypropylthioisoquinoline* (4; R = Me, X = H, OH).—$NaBH_4$ (100 mg) was added with stirring to a methanolic solution of (4; R = Me, X = O) during 15 min. After 1 h it was successively acidified and basified with acetic acid and sodium hydroxide and was extracted with chloroform. The extract was dried (Na_2SO_4) and the solvent was removed; the residue was used as such for cyclodehydration; $\nu_{max.}$ (neat) 3335 cm^{-1} (OH).

3-*Methyl*-2,3-*dihydrothiazolo*[2,3-*a*]*isoquinolinium Perchlorate* (3; R = Me).—(*a*) A solution of compound (1) (0·8 g) in freshly prepared PPA (4—5 g) was heated at 140—145° for 4 h under anhydrous conditions. It was taken up in hot water and the solution was filtered. The filtrate was treated with 60% $HClO_4$ (1 ml) and then set aside overnight. The product (0·7 g, 60%) crystallised from methanol as shining plates, m.p. 150—151°. $\lambda_{max.}$ 235s, 252sh, 280—294, 322—340, 350, and 365 nm (Figure), $\lambda_{max.}$ 1615 (C=N), 1050—1110 cm^{-1} (ClO_4); n.m.r. δ($CDCl_3$) 1·5 (3H, d, *J* 6·5 Hz), 2·7 (2H, s), diffused multiplet centred at 4·3 (1H), 7·0—8·0 p.p.m. (m, 6H, ArH) (Found: C, 48·35; H, 4·6; N, 4·75. $C_{12}H_{12}NSClO_4$ requires C, 47·85; H, 4·0; N, 4·65%).*

(*b*) Alternatively a solution of compound (1) in H_2SO_4 was set aside overnight. It was washed repeatedly with cold anhydrous ether and the oily residue was taken up in hot water and filtered. The filtrate on treatment with $HClO_4$ gave only intractable tar.

(*c*) A solution of compound (1) in ethanol saturated with anhydrous HCl gas was refluxed for 6 h. On work-up it gave the perchlorate of compound (1) identical (mixed m.p.) with the authentic sample.

(*d*) Compound (4; R = Me, X = H, OH) when heated in polyphosphoric acid (PPA) gave a product identical (mixed m.p.) with (3; R = Me) obtained in (*a*).

2,3-*Dihydrothiazolo*[2,3-a]*isoquinolinium Perchlorate* (3; R = H).—(*a*) Compound (4; R = H, X = H, OH) was cyclised by heating it both in PPA (yield 60%) as well as in H_2SO_4 (yield 70%). The product was crystallised from methanol, m.p. 163—165°, $\lambda_{max.}$ 232s, 252sh, 264—290, and 320—340 nm (Found: N, 4·96. $C_{11}H_{10}NSClO_4$ requires N, 4·88%).

(*b*) A solution of the sodium salt of 1-mercaptoisoquinoline (0·8 g) in acetone was treated with 1,2-dibromethane and the mixture was kept overnight. The solvent was removed and the residue was dissolved in water. On treatment with $HClO_4$, it deposited the product which was identical with that obtained in (*a*).

3-*Methylthiazolo*[2,3-a]*isoquinolinium Perchlorate* (10; R = Me).—This compound, m.p. 212—213° (CH_3OH), was identical with Bradsher's product[3e] and obtained by cyclising compound (4; R = Me, X = O) in PPA; $\nu_{max.}$ 1610 (C=N), 1050—1110 cm^{-1} (ClO_4); $\lambda_{max.}$ 222sh, 233, 264, 268sh, 300—322, 334, and 349 nm (Found: C, 48·55; H, 3·65; N, 4·8. $C_{12}H_{12}NSClO_4$ required C, 48·15; H, 3·35; N, 4·7%).

3-*Phenylthiazolo*[2,3-a]*isoquinolinium Perchlorate* (10; R = Ph).—This compound, m.p. 238—240° (MeOH) (yield 70%), was obtained by the cyclodehydration of (4; R = Ph, X = O) in PPA (Found: N, 3·75. $C_{17}H_{12}SNClO_4$ requires N, 3·9%). Compounds (10; R = Me, Ph) were also obtained by similar dehydrations of (11; R = Me, Ph).

Reduction of Compound (3; R = Me).—(a) *With* $NaBH_4$. To a solution of compound (3; R = Me) (100 mg) in methanol (10 ml), $NaBH_4$ (500 mg) was added portionwise, with stirring, during 20 min. The reaction mixture was stirred for an hour and solvent was then removed. The residue was treated with acetic acid and was then made alkaline with aqueous NaOH. The solution was extracted with dichloromethane and the extract was dried (Na_2SO_4); solvent was then removed. From the residue (100 mg), the following three constituents were isolated by repeated chromatography over alumina. Band (I): 3-*Methyl*-2,3-*dihydro*-10bH-*thiazolo*[2,3-a]*isoquinoline* (7) (picrate, m.p. 140—142°, from benzene), $M^{+\cdot}$, *m/e* 203; n.m.r. δ ($CDCl_3$) 1·79 (3H, d, *J* 6·5 Hz), 3·7—4·0 (1H, m), 5·8—6·2 (2H, m), 6·7—7·0 (1H, m), 7·16 (1H, d, *J* 6·5 Hz), 8·18 (1H, d, *J* 6·5 Hz), 7·9—8·04 (1H, m, ArH), 7·23—7·6 (3H, m, ArH). Band (II): $M^{+\cdot}$, *m/e* 205. Band (III): 3-*Methyl*-2,3,5,6-*tetrahydro*-10bH-*thiazolo*[2,3-a]*isoquinoline* (8) (picrate, m.p. 165—167°, benzene), $M^{+\cdot}$, *m/e* 205; $\nu_{max.}$ 2780, 2730, and 2680 cm^{-1}; n.m.r. δ ($CDCl_3$), broad signals at 1·1—1·4, 2·5—3·5; 3·7—3·8 (11H), and 6·85—7·15 p.p.m. (4H).

(b) *With* LAH. To a suspension of LAH (100 mg) in anhydrous THF (15 ml) was added dropwise, with stirring, a solution of (3; R = Me) (100 mg) under anhydrous conditions. The reaction mixture was stirred overnight and decomposed by addition of ethyl acetate and aqueous sodium hydroxide. The organic layer was dried (Na_2SO_4) and the solvent was removed. The residue contained three products identical (R_F) with those obtained in (a).

Compound (10; R = Me) was likewise reduced with $NaBH_4$ as well as LAH and the products obtained were identical with the ones obtained in the reductions of (3; R = Me).

3-*Bromomethyl*-2,3-*dihydrothiazolo*[2,3-a]*isoquinolinium Perchlorate* (12).—Bromine (0·01 mol) dissolved in CCl_4 (5 ml) was added dropwise to a solution of compound (1) (0·01 mol) in CCl_4 (20 ml). The separation of a yellow coloured product accompanied the addition and the temperature rose to 65°. The mixture was set aside for 1 h; solvent was decanted and the oily residue was dissolved in methanol and treated with $HClO_4$. The orange product

* Compound (11; R = Me) on recrystallisation, partly changed to (10) and an analytically pure sample could not be obtained.

(70%) was crystallised from methanol, m.p. 139—140° (Found: N, 3·9. $C_{12}H_{11}BrClNSO_4$ requires N, 3·7%).

Hydrogenolysis of Compound (12) *with* LAH.—A suspension of compound (12) (100 mg) and LAH (500 mg) in THF (50 ml) was refluxed for 16 h under anhydrous conditions. After work-up, the products were found to be identical with compounds (8) and (7).

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