Studies of Heterocyclic Compounds. Part 25.[1] Stable Indolizine and Pyrrolo[2,1-*b*]thiazole Carboselenaldehydes

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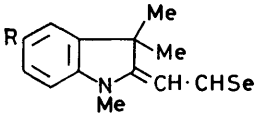
The reaction of indolizines and pyrrolo[2,1-*b*]thiazoles with phosphoryl chloride in dimethylformamide and treatment of the resulting Vilsmeier salts *in situ* with aqueous sodium hydrogen selenide gives indolizine and pyrrolo[2,1-*b*]thiazole carboselenaldehydes, many of which are stable crystalline compounds. ^{1}H N.m.r. and u.v. spectral data of the selenaldehydes are reported. 2,7-Dimethylindolizine-3-carboselenaldehyde and 5,6-dimethylpyrrolo[2,1-*b*]thiazole-7-carboselenaldehyde were reduced by lithium aluminium hydride–aluminium chloride to the corresponding trimethyl derivatives. 2,7-Dimethylindolizine-3-carboselenaldehyde and 5,6-dimethylpyrrolo[2,1-*b*]thiazole-7-carboselenaldehyde smoothly underwent Wittig reactions with isopropylidenetriphenylphosphorane in dimethyl sulphoxide–benzene solution at room temperature, and with acetylmethylenetriphenylphosphorane in boiling xylene.

It has gradually become evident † that the majority of compounds which have been formulated as selenaldehydes are either cyclic or linear selenaldehyde polymers or reduction products (selenols, selenides, diselenides) of selenaldehydes. The indole derivatives (1)

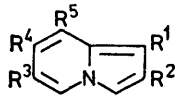


(1) R = H
(2) R = Me

and (2) [2] appear to be the only authentic selenaldehydes hitherto to have been prepared. They were obtained by reaction of the corresponding aldehydes with phosphorus pentaselenide, and were characterised by their melting points. In previous papers we described the preparation and characterisation of stable carbothioaldehydes in the indolizine [3] and pyrrolo[2,1-*b*]thiazole [4] series by a modification of the Vilsmeier aldehyde synthesis. We have also obtained [5] pyrrole-2- and pyrrole-3-carbothioaldehydes, and other workers [6] have recently prepared a 6-azaindolizinecarbothioaldehyde by this method. We now report a new application of the Vilsmeier reaction which gives stable heterocyclic selenaldehydes, and the characterisation of the selenaldehydes by spectroscopic and chemical methods.

Synthesis of Indolizine and Pyrrolo[2,1-b]*thiazolecarboselenaldehydes.*—Treatment of the indolizines (3)—(10) in dimethylformamide with phosphoryl chloride gave the corresponding Vilsmeier salts ($RCH{=}\overset{+}{N}Me_2{\cdot}PO_2Cl_2^-$, R = substituted 3-indolizine residue) which, when allowed to react *in situ* with aqueous sodium hydrogen selenide, afforded the indolizine-3-carboselenaldehydes (11)—(18), respectively. The carboselenaldehydes (11)—(15) were readily isolated as stable crystalline solids in yields of 28—46%. Samples of the carboselenaldehydes (11)—(15) which have been kept out of daylight show no sign of decomposition (t.l.c.; mass spectrum) more than seven years after preparation. Compound (16) was also obtained pure and crystalline but with difficulty, and the yield was low owing to extensive loss during purification. The carboselenaldehydes (17) and (18) were obtained as brown oils which did not crystallise and could not be satisfactorily characterised by elemental analysis. 2,3-Dimethylindolizine (19) gave the indolizine-1-carboselenaldehyde (20), which was much less stable than the indolizine-3-carboselenaldehydes, and which gradually decomposed.

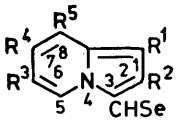
Selenoformylation of the pyrrolo[2,1-*b*]thiazoles (21)—(24) gave the corresponding pyrrolo[2,1-*b*]thiazole-7- and pyrrolo[2,1-*b*]thiazole-5-carboselenaldehydes (25)—(28), respectively, *via* the Vilsmeier salts ($RCH{=}\overset{+}{N}Me_2{\cdot}PO_2Cl_2^-$, R = 7- or 5-pyrrolo[2,1-*b*]thiazole residue). Compounds (25)—(27) were stable crystalline solids, but the carboselenaldehyde (28) was obtained as an oil which did not crystallise.



	R^1	R^2	R^3	R^4	R^5
(3)	H	Me	H	Me	H
(4)	H	Me	H	H	Me
(5)	Me	Me	H	H	H
(6)	H	Bu^t	H	Me	H
(7)	Me	Bu^t	H	H	H
(8)	H	Me	H	H	H
(9)	H	Me	Me	H	H
(10)	H	Bu^t	H	H	H

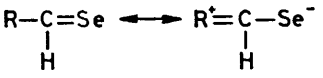
Since the carbothioaldehydes corresponding to the carboselenaldehydes (17), (18), (20), and (28) are stable compounds,[3,4] the range of stable carboselenaldehydes in the indolizine and pyrrolo[2,1-*b*]thiazole series is smaller than the range of stable carbothioaldehydes. Conjugation of the selenoformyl group with the electron-releasing indolizine nucleus at position 1 or 3 and with the pyrrolo[2,1-*b*]thiazole nucleus at position 5 or 7 increases the polarisation of the C=Se bond, delocalises the positive charge of the selenoformyl carbon atom, and

† A critical review is given by R. B. Silverman, in 'Organic Selenium Compounds: Their Chemistry and Biology,' ed. D. L. Klayman and W. H. H. Günther, Wiley–Interscience, New York, 1973, p. 245; see also K. J. Irgolic and M. V. Kudshadker, in 'Selenium,' ed. R. A. Zingaro and W. C. Cooper, Van Nostrand Reinhold, New York, 1974, p. 509.



	R^1	R^2	R^3	R^4	R^5
(11)	H	Me	H	Me	H
(12)	H	Me	H	H	Me
(13)	Me	Me	H	H	H
(14)	H	Bu^t	H	Me	H
(15)	Me	Bu^t	H	H	H
(16)	H	Me	H	H	H
(17)	H	Me	Me	H	H
(18)	H	Bu^t	H	H	H

reduces the tendency of the carboselenaldehydes to polymerise. We think that other heterocyclic, carbocyclic, and organometallic systems will also be found capable of forming stable selenaldehydes, provided that



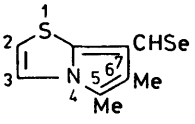
they are strongly electron-releasing and are able conjugatively to stabilise the selenoformyl group.

^{1}H *N.M.R. Spectra of Indolizine and Pyrrolo*[2,1-b-]*thiazole Carboselenaldehydes*.—A characteristic feature of the ^{1}H n.m.r. spectra of indolizine and pyrrolo[2,1-*b*]thiazole carboselenaldehydes (see Table 1) is the low-field signal which arises from the selenoformyl proton. This signal occurs in the range δ 12.04—12.78 for the indolizine-2-carboselenaldehydes (11)—(18), and in the range δ 11.94—12.24 for the pyrrolo[2,1-*b*]thiazole-5-carboselenaldehydes (26)—(28). The signal of the 1-selenoformyl proton in 2,3-dimethylindolizine-1-carboselenaldehyde (20) occurs at considerably lower field (δ 13.00) than that of the 3-selenoformyl proton in compounds (11)—(18), and the 7-selenoformyl proton (δ 12.59) in 5,6-dimethylpyrrolo[2,1-*b*]thiazole-7-carboselenaldehyde (25) is more deshielded than the 5-selenoformyl proton in compounds (26)—(28).

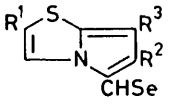
By comparing the spectra of the selenaldehydes (11)—(18), (20), and (25)—(28) with those of the corresponding thioaldehydes,[3,4] it is seen that for each selenaldehyde–thioaldehyde pair the selenoformyl proton is much more deshielded than the thioformyl proton (Δδ 1.63—2.05).

A comparison of the chemical shifts of the selenoformyl proton in the pairs of indolizine-3-carboselenaldehydes (11) and (14), (13) and (15), and (16) and (18) shows that substitution of a 2-methyl group by a 2-t-butyl group results in a downfield shift (Δδ 0.35—0.52) of the 3-selenoformyl proton signal. We attribute this to van der Waals deshielding of the selenoformyl proton by the t-butyl group.

The 3-selenoformyl group in the indolizine carboselenaldehydes (11)—(18) exerts a strong diamagnetic anisotropic deshielding effect on 5-H, which is seen by comparing the chemical shift of 5-H in 2,3-dimethylindolizine-1-carboselenaldehyde (20) (δ 8.13) with that of 5-H in the 3-carboselenaldehydes (11)—(18) (δ 11.68—12.33). Likewise the 5-selenoformyl group in the pyrrolo[2,1-*b*]thiazolecarboselenaldehydes (26)—(28) strongly deshields 3-H (δ 9.83—10.17) [*cf.* (25): 3-H, δ 7.47].

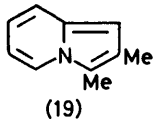


(25)

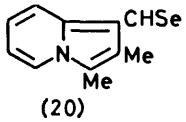


	R^1	R^2	R^3
(26)	H	Me	Me
(27)	H	Me	H
(28)	Me	Me	H

U.v. Spectra of Indolizine and Pyrrolo[2,1-b]*thiazole Carboselenaldehydes* (*see Table* 2).—Solutions of the selenaldehydes in hydrocarbon and weakly polar solvents are green. Two broad absorption bands occur in the visible region and doubtless have their origin in the C=Se n→π* transition. For indolizine-3-carboselenaldehydes these bands occur in the regions 704—683 nm (log ε 2.55—2.71) and 652—631 nm (log ε 2.28—2.55). The n→π* transitions of the corresponding thioaldehydes[3] occur at shorter wavelength [λ_1(C=Se) — λ_1(C=S), 138—151 nm; λ_2(C=Se) — λ_2(C=S), 120—135 nm]. The C=Se *n*—π* absorption of pyrrolo[2,1-*b*]thiazolecarboselenaldehydes occurs at shorter wavelength than that of indolizinecarboselenaldehydes (see Table 2).



(19)



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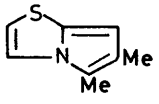

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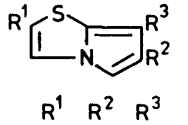
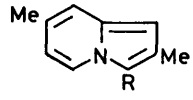
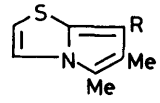


	R^1	R^2	R^3
(22)	H	Me	Me
(23)	H	Me	H
(24)	Me	Me	H



(29)	R = Me
(30)	R = Me_2C:CH
(31)	R = MeCO·CH:CH

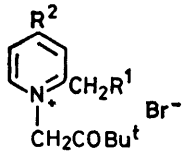


(32)	R = Me
(33)	R = Me_2C:CH
(34)	R = MeCO·CH:CH

The u.v. spectra of indolizine-3-carboselenaldehydes are similar in pattern to those of the corresponding 3-thioaldehydes.[3] They show four band groups of intense absorption (log ε 3.4—4.6), each band group comprising one or more absorption maxima or shoulders. These groups occur in the regions 490—465, 390—320, 280—260, and 240—230 nm.

Reactions of Indolizine and Pyrrolo[2,1-b]*thiazole Carboselenaldehydes.*—The monomeric nature of the selenaldehydes was reflected in the chemical behaviour of selected derivatives. Reduction of the selenaldehydes (11) and (25) with lithium aluminium hydride–aluminium chloride gave the trimethyl derivatives (29) and (32), respectively. The selenaldehydes (11) and (25) readily took part in Wittig reactions. They reacted with isopropylidenetriphenylphosphorane in dimethyl sulphoxide–benzene solution at room temperature to give the olefins (30) (56%) and (33) (78%), and with acetylmethylenetriphenylphosphorane in boiling xylene they gave the ketones (31) (77%) and (34) (79%).

The previously unknown indolizines (6) and (7) were prepared by quaternisation of 2,4-dimethylpyridine and 2-ethylpyridine, respectively, with bromopinacolone, and cyclisation of the resulting bromides (35) and (36) with sodium hydrogen carbonate.



(35) R^1 = H, R^2 = Me
(36) R^1 = Me, R^2 = H

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. absorption spectra were measured with a Unicam SP 800 spectrophotometer. Light absorption data refer to solutions in cyclohexane. ^{1}H N.m.r. spectra were determined at 100 MHz for 0.4M-solutions in deuteriochloroform, unless otherwise indicated, with tetramethylsilane as internal reference. Unless otherwise stated, δ values refer to singlet absorptions. *J* Values were measured on the 100-Hz scale. Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with alumina (activity II, pH *ca.* 9.5, 100—200 mesh). Solvent mixtures are described in ratios by volume. Throughout ether denotes diethyl ether.

Materials.—Light petroleum was of boiling range 40—60 °C. Dimethylformamide was dried for *ca.* 1 week over powdered calcium hydride and then distilled at 15 mmHg. Aqueous 1M-sodium hydrogen selenide was prepared by passing hydrogen selenide in a slow stream of nitrogen through aqueous 1M-sodium hydroxide until an excess of hydrogen selenide emerged in quantity in the exit gas. Hydrogen selenide was generated by the action of 5M-hydrochloric acid on crushed aluminium selenide. 2-Methyl-,[7] 1,2-dimethyl-,[7] 2,3-dimethyl-,[7] 2,6-dimethyl-,[8] 2,7-dimethyl-,[7] 1,2-dimethyl-,[8] and 2-t-butyl-indolizine,[3] and 6-methyl-,[9] 2,6-dimethyl-,[9] 5,6-dimethyl-,[9] and 6,7-dimethylpyrrolo[2,1-*b*]thiazole [9] were prepared as described in the references cited.

Preparation of 7-Methyl-2-t-butyl- (6) *and 1-Methyl-2-t-butyl-indolizine* (7).—A mixture of the 2-alkylpyridine (100 mmol), bromopinacolone (13.5 ml, 100 mmol), and acetone (5 ml) was heated under reflux in a water-bath at 80 °C for 1.5 h. Gradual addition of ether to the cooled mixture precipitated the salt which was then filtered off, washed with ether, and dried *in vacuo*. 2,4-Dimethylpyridine and 2-ethylpyridine gave the bromides (35) (20.7 g, 72%) and (36) (28 g, 98%), respectively, which were cyclised without further purification.

A solution of the bromide (35) (14.31 g, 50 mmol) in water (200 ml) was extracted with ether, the ether extract was discarded, and sodium hydrogen carbonate (16.8 g, 200 mmol) was added to the aqueous solution. The mixture was steam-distilled, and the distillate was extracted with ether. Sublimation of the residue from the washed (× 1), dried, and evaporated extracts at 110—115 °C and 0.2 mmHg (block) afforded 7-methyl-2-t-butylindolizine (8.83 g, 94%) as spars which become blue in air and light, m.p. 80—81 °C (Found: C, 83.3; H, 8.9; N, 7.6. $C_{13}H_{17}N$ requires C, 83.4; H, 9.2; N, 7.5%); δ($CDCl_3$; 60 MHz) 1.32 (9 H, Bu^t), 2.21 (3 H, 7-Me), 6.15 (2 H, br, $J_{6,8}$ 1.8 Hz, 1- and 6-H), 7.00 (2 H, br, 3- and 8-H), and 7.69 (1 H, d, $J_{5,6}$ 7.2 Hz, 5-H); δ(CF_3·CO_2H, 60 MHz; spectrum of the 7-methyl-2-t-butyl-3*H*-indolizinium cation) 1.41 (9 H, Bu^t), 2.70 (3 H, 7-Me), 5.41 (2 H, 3-H_2), 6.78 (1 H, 1-H), 7.52 (1 H, dd, $J_{6,5}$ 6.6 Hz, $J_{6,8}$ 1.4 Hz, 6-H), 7.71 (1 H, m, 8-H), and 8.65 (1 H, d, $J_{5,6}$ 6.6 Hz, 5-H).

Cyclisation of the bromide (36) (8.58 g, 30 mmol) with sodium hydrogen carbonate (10 g) in water (100 ml) according to the procedure of the preceding experiment, and distillation of the product at 105—110 °C and 0.1 mmHg (block) gave 1-methyl-2-t-butylindolizine (4.67 g, 83%) as a pale yellow oil which rapidly becomes blue in air and light (Found: C, 83.7; H, 9.0; N, 7.3. $C_{13}H_{17}N$ requires C, 83.4; H, 9.2; N, 7.5%); δ($CDCl_3$; 60 MHz) 1.39 (9 H, Bu^t), 2.40 (3 H, 1-Me), 6.36 (2 H, br,m, 6- and 7-H), 7.01 (1 H, 3-H), 7.18 (1 H, d, $J_{8,7}$ 8.2 Hz, 8-H), and 7.66 (1 H, d*, $J_{5,6}$ 6.6 Hz, 5-H); δ(CF_3·CO_2H; 60 MHz; spectrum of the 1-methyl-2-t-butyl-3*H*-indolizinium cation) 1.48 (9 H, Bu^t), 2.42 (3 H, t, $J_{1\text{-Me},3\text{-}H_2}$ 1.8 Hz, 1-H), 5.40 (2 H, m, 3-H_2), 7.80 (2 H, m, 6- and 7-H), 8.38 (1 H, m, $J_{8,7}$ 7.6 Hz, 8-H), and 8.80 (1 H, d*, $J_{5,6}$ 6.1 Hz, 5-H).

Preparation of Indolizine and Pyrrolo[2,1-b]*thiazole Carboselenaldehydes.*—Indolizines were selenoformylated by the following general procedure. A solution of phosphoryl chloride (0.5 ml, 5.5 mmol) in dimethylformamide (5 ml) was added dropwise during 30 min to a stirred solution of the indolizine (5 mmol) in dimethylformamide (5 ml). The temperature of the solution was kept at −50 °C during the addition in the case of indolizines unsubstituted at both positions 1 and 3, in order to avoid disubstitution, and at room temperature in the case of 1- or 3-substituted indolizines or 2-t-butylindolizines. The reaction mixture was stirred at this temperature for a further 30 min or, in the case of 2-t-butylindolizines, for a further 2 h. Aqueous 1M-sodium hydrogen selenide (20 ml) was added and then benzene, and the mixture was poured into water. The resulting mixture was extracted *rapidly* with benzene, and the extracts were washed with water (× 6), dried, and evaporated. The residue was dissolved in benzene and chromatographed. Details are given in Table 3. In all cases elution was first carried out with benzene; this brought through yellow eluates which were discarded. The solvent used subsequently to elute the selenaldehyde varied and is given in each case (Table 3). The homogeneous green eluates were evaporated and the selenaldehyde was recrystallised from benzene–cyclohexane, unless otherwise indicated. In several cases a further quantity of the selenaldehyde was obtained by evaporation of the mother-liquors from the recrystallisation, rechromatography of the residue,

* Components broadened.

TABLE 1

^{1}H N.m.r. spectral data for the indolizine carboselenaldehydes (11)—(18) and (20) and the pyrrolo[2,1-*b*]-thiazole carboselenaldehydes (25)—(28) in $CDCl_3$ (100 MHz, unless otherwise stated)

Compound	δ values; *J* in Hz
(11)	2.31 (3 H, 7-Me), 2.32 (3 H, d, 2-Me), 6.32 (1 H, 1-H), 6.87 (1 H, dd, 6-H), 7.24 (1 H, br, 8-H), 11.73 (1 H, d, 5-H), and 12.04 (1 H, CHSe); $J_{1,2\text{-Me}}$ 0.9, $J_{1,5}$ 0.6, $J_{5,6}$ 7.0, $J_{5,8}$ 0.7, $J_{6,8}$ 1.8, $J_{7,8\text{-Me}}$ 0.8
(12)	2.34 (3 H, d, 2-Me), 2.52 (3 H, 8-Me), 6.43 (1 H, 1-H), 6.95 (1 H, t, 6-H), 7.55 (1 H, d, 7-H), 11.68 (1 H, d, 5-H), and 12.35 (1 H, CHSe); $J_{1,2\text{-Me}}$ 0.8, $J_{1,5}$ 0.6, $J_{5,6}$ 6.9, $J_{5,7}$ 1.1, $J_{6,7}$ 7.3
(13)	2.15 (3 H, 1-Me [a]), 2.27 (3 H, 2-Me [a]), 7.05 (1 H, td, 6-H), 7.45 (1 H, dt, 8-H), 7.81 (1 H, ddd, 7-H), 11.93 (1 H, dt, 5-H), and 12.09 (1 H, CHSe); $J_{\text{Me,Me}}$ 0.6, $J_{5,6}$ 6.6, $J_{5,7}$ *ca.* 0.8, $J_{5,8}$ 0.7, $J_{6,7}$ 7.2, $J_{6,8}$ 1.5, $J_{7,8}$ 8.4
(14)	1.48 (9 H, Bu^t), 2.33 (3 H, 7-Me), 6.41 (1 H, 1-H), 6.91 (1 H, dd, 6-H), 7.28 (1 H, m, 8-H), 12.03 (1 H, d, 5-H), and 12.39 (1 H, CHSe); $J_{1,5}$ 0.6, $J_{5,6}$ 7.0, $J_{5,8}$ 0.9, $J_{6,8}$ 1.9
(15)	1.60 (9 H, Bu^t), 2.36 (3 H, 1-Me), 7.06 (1 ,H, td, 6-H), 7.53 (1H,dt, 8-H), 7.83 (1 H, ddd, 7-H), 12.33 (1H, dt, 5-H), and 12.61 (1 H, CHSe); $J_{5,6}$ 6.6, $J_{5,8}$ 0.6, $J_{6,7}$ 7.1, $J_{6,8}$ 1.5, $J_{7,8}$ 8.4
(16)	2.30 (3 H, d, 2-Me), 6.37 (1 H, q, 1-H), 6.97 (1 H, td, 6-H), 7.40 (1 H, d,[b] 8-H), 7.72 (1 H, ddd, 7-H), 11.84 (1 H, d,[b] 5-H), and 12.33 (1 H, CHSe); $J_{1,2\text{-Me}}$ 1.0, $J_{5,6}$ 6.9, $J_{5,7}$ 1.2, $J_{6,7}$ 7.6,[c] $J_{7,8}$ 7.6,[c] $J_{6,8}$ 1.8
(17) [d]	2.31 (3 H, 2-Me), 2.41 (3 H, 6-Me), 6.32 (1 H, 1-H), 11.85 (1 H, br, 5-H), and 12.25 (1 H, CHSe) [e,f]
(18) [d]	1.49 (3 H, Bu^t), 6.50 (1 H, 1-H), 7.06 (1 H, 6-H), 7.46 (1 H, 8-H), 7.79 (1 H, 7-H), 12.14 (1 H, d, 5-H), and 12.78 (1 H, CHSe) [f]
(20) [d]	8.13 (1 H, d, 5-H) and 13.00 (1 H, br, CHSe) [g]
(25)	2.23 (3 H, q, 6-Me [a]), 2.28 (3 H, q, 5-Me [a]), 7.09 (1 H, d, 2-H), 7.47 (1 H, d, 3-H), and 12.59 (1 H, CHSe); $J_{2,3}$ 4.0, $J_{\text{Me,Me}}$ 0.8
(26)	2.09 (3 H, 7-Me), 2.14 (3 H, 6-Me), 6.96 (1 H, d, 2-H), 10.17 (1 H, d, 3-H), and 11.94 (1 H, CHSe); $J_{2,3}$ 4.1
(27)	2.24 (3 H, d, 6-Me), 6.38 (1 H, m, 1-H), 6.97 (1 H, d, 2-H), 10.16 (1 H, dd, 3-H), and 12.24 (1 H, CHSe); $J_{2,3}$ 4.0, $J_{3,7}$ 0.6, $J_{6\text{-Me},7}$ 0.8
(28) [d]	2.21 (6 H, 2- and 6-Me), 6.22 (1 H, 7-H), 9.83 (1 H, 3-H), and 12.04 (1 H, CHSe)

[a] The assignments of the Me signals are tentative and may require to be interchanged. [b] Signal further weakly split. [c] *J* value approximate. [d] 60 MHz. [e] Accurate δ values of 7- and 8-H not obtainable. [f] Accurate *J* values not obtainable. [g] Other δ and *J* values not obtainable owing to decomposition.

and recrystallisation. Yields (%) refer to the total quantity of recrystallised material.

The procedure for the selenoformylation of pyrrolo-[2,1-*b*]thiazoles was identical with that for the selenoformylation of indolizines, except that the pyrrolo[2,1-*b*]-thiazole was dissolved in a larger volume (7.5 ml) of dimethylformamide, and during the addition the temperature of the reaction mixture was kept at −35 °C in the case of pyrrolo[2,1-*b*]thiazoles unsubstituted at both positions 5 and 7, and at room temperature in the case of 5- or 7-substituted pyrrolo[2,1-*b*]thiazoles. The mixture was stirred at this temperature for a further 30 min before the addition of aqueous 1M-sodium hydrogen selenide.

Selenoformylation of 2,7-*dimethylindolizine* (3). Elution gave successively homogeneous green eluates [B→B–E (19 : 1)] and two-component green eluates [B–E (4 : 1)]. Recrystallisation of the residue from the homogeneous eluates afforded the selenaldehyde (11). The mother liquors from the recrystallisation and the two-component eluates were combined and evaporated, and the residue was rechromatographed to give a further quantity of product. Further details are in Table 3.

Selenoformylation of 2,6-*dimethylindolizine* (9). Elution from the column [alumina (25 × 2.2 cm)] with benzene–ether (49 : 1) afforded a brown oil (133 mg, 11%) which failed to crystallise. The oil was shown to be 2,6-dimethylindolizine-3-carboselenaldehyde (17) by its ^{1}H n.m.r. spectrum (details in Table 1) and its mass spectrum [*m/e* 237 (M^+)].

Selenoformylation of 2-*t*-*butylindolizine* (10). Elution from the column [alumina (30 × 2.2 cm)] with benzene followed by evaporation of the eluates at room temperature, finally at 0.1 mmHg, gave a brown oil which consisted of 2-t-butylindolizine-3-carboselenaldehyde (18) and a small quantity of benzene (n.m.r.). The oil could not be entirely freed from solvent without undergoing some decomposition. The ^{1}H n.m.r. spectrum (details in Table 1) and the mass spectrum [*m/e* 265 (M^+)] were consistent with the selenaldehyde structure (18).

Selenoformylation of 2,3-*dimethylindolizine* (19). Elution from the column [alumina (25 × 2.5 cm)] with benzene–ether (19 : 1→9 : 1) gave inhomogeneous eluates, the residue from which was rechromatographed [alumina (35 × 2.5 cm)]. The initial yellow eluates [B→B–E (19 : 1)→B–E (9 : 1)] were discarded, and the succeeding green eluates [B–E (9 : 1)] afforded 2,3-dimethylindolizine-1-carboselenaldehyde (20) (137 mg, 12%) as a brown oil [*m/e* 237 (M^+)] which gradually decomposed.

Selenoformylation of 5,6-*dimethylpyrrolo*[2,1-b]*thiazole* (21). Elution gave successively homogeneous green eluates and impure green eluates. The residue from the impure eluates was rechromatographed in the same manner to give a further quantity of homogeneous green eluates. Recrystallisation of the solid from the homogeneous eluates

TABLE 2

U.v. spectral data for the indolizine carboselenaldehydes (11)—(18) and (20) and the pyrrolo[2,1-*b*]thiazolecarboselenaldehydes (25)—(27)

Compound	$\lambda_{max.}$/nm (log ε)
(11)	683 (2.71), 631 (2.55), 477 (4.56), 470 (4.56), 370 (3.53), 351 (3.61), 328 (4.00), 272 (3.95), 263 (3.89), 241 (4.34), 237br (4.25)
(12)	697 (2.65), 643 (2.38), 476 (4.51), 468 (4.51), 360 (3.72), 351 (3.77), 326 (4.08), 314sh (3.88), 271 (4.11), 263 (4.01), 252sh (3.95), 239 (4.31), 233sh (4.30)
(13)	691 (2.71), 638 (2.42), 489 (4.57), 478 (4.49), 386 (3.40), 375infl (3.50), 364 (3.64), 338 (4.09), 325sh (4.02), 277 (4.08), 268 (3.98), 238br (4.32)
(14)	691 (2.71), 637 (2.46), 477 (4.60), 471sh (4.58), 370 (3.40), 350infl (3.56), 327 (4.03), 271 (3.91), 263 (3.89), 237br (4.40)
(15)	706 (2.68), 652 (2.41), 610sh (2.07), 485 (4.57), 478sh (4.51), 336 (4.06), 325sh (3.90), 277 (4.01), 269infl (3.94), 239br (4.34)
(16)	700 (2.55), 645 (2.28), 472 (4.40), 467 (4.42), 371 (3.53), 360infl (3.57), 350 (3.60), 327 (4.01), 316sh (3.83), 271 (3.97), 263 (3.90), 236br (4.31)
(17) *	697, 688sh, 641, 479, 471, 375, 368, 357, 331
(18) *	704, 652, 473, 469sh, 349sh, 328, 272, 263, 237br
(20) †	723, 666
(25)	651 (2.43), 630 (2.36), 451 (4.28), 442 (4.26), 305 (3.61), 255 (3.97), 236 (4.25)
(26)	667 (2.66), 622 (2.40), 465 (4.52), 348 (3.86), 229 (4.19)
(27) *	672, 625, 454, 343, 330, 224

* Log ε values were not determined owing to slight decomposition (deposition of selenium) in solution. † Owing to decomposition only the long wavelength (n→π*) bands could unequivocally be assigned to the selenaldehyde (20); log ε values were not determined.

gave the selenaldehyde (25), and rechromatography of the residue from the mother liquors yielded a further quantity of product. Further details are in Table 3.

Selenoformylation of 2,6-dimethylpyrrolo[2,1-b]*thiazole* (24). Elution with benzene yielded 2,6-dimethylpyrrolo[2,1-*b*]thiazole-5-carboselenaldehyde (28) (126 mg, 10%), which failed to crystallise. The ^{1}H n.m.r. spectrum (details in Table 1) and the mass spectrum [*m/e* 243 (M^+)] were recorded, but the compound gradually decomposed and was not further investigated.

Reduction of Selenaldehydes with Lithium Aluminium Hydride–Aluminium Chloride.—A solution of the selenaldehyde (2 mmol) in benzene (50 ml) was added dropwise during 10 min to a stirred solution of lithium aluminium hydride (266 mg, 7 mmol) and aluminium chloride (1.86 g, 14 mmol) in ether (50 ml). The mixture was stirred for 50 min before being poured into ice-cold 0.07M-sulphuric acid (250 ml). The resulting mixture was basified (Na_2CO_3) and extracted with ether (× 4), and the residue from the washed (× 1), dried, and evaporated extracts was distilled. 2,7-Dimethylindolizine-3-carboselenaldehyde (11) gave 2,3,7-trimethylindolizine (29) (216 mg, 74%) as an oil, b.p. 85—90 °C at 0.2 mmHg (block), which solidified to crystals, m.p. 33—34 °C (Found: C, 83.2; H, 8.3; N, 8.6. $C_{11}H_{13}N$ requires C, 83.0; H, 8.2; N, 8.8%), δ($CDCl_3$; 60 MHz) 2.23 (3 H, 2-Me), 2.29 (6 H, 3- and 7-Me), 6.08 (1 H, 1-H), 6.24 (1 H, dd, $J_{6,5}$ 7.1 Hz, $J_{6,8}$ 1.8 Hz, 6-H), 7.00 (1 H, m, 8-H), and 7.48 (1 H, d, $J_{5,6}$ 7.1 Hz, 5-H). 5,6-Dimethylpyrrolo[2,1-*b*]thiazole-7-carboselenaldehyde (20) afforded 5,6,7-trimethylpyrrolo[2,1-*b*]thiazole (32) (252 mg, 76%) as an oil, b.p. 90—95 °C at 0.2 mmHg (block) [lit.,[9] b.p. 130—135 °C at 10 mmHg (block)], whose ^{1}H n.m.r.

TABLE 3

Preparation of indolizine and pyrrolo[2,1-*b*]thiazole carboselenaldehydes

Starting material	Column dimensions (cm)	Elution solvent *	Product	Yield (%)	Form †	M.p. (°C)	*m/e* (%) ‡	Formula	Found (%) / Required (%) C	H	N	S	Se
(3)	25 × 2.2	B→B–E(19 : 1)→B–E(4 : 1) [a]	(11)	46	Green	141—143 [b]	237 (63),[c,§] 236 (100),[d,§] 157 (35),[e] 156 (21),[f] 155 (12), 154 (24)	$C_{11}H_{11}NSe$	55.9 55.9	4.6 4.7	5.8 5.9		33.4 33.4
(4)	25 × 2.2	B–E(49 : 1)	(12)	28	Dark green	132—136 [b]	237 (65),[c,§] 236 (100),[d,§] 157 (30),[e] 156 (18),[f] 155 (11), 154 (20)	$C_{11}H_{11}NSe$	55.7 55.9	4.6 4.7	6.2 5.9		
(5)	32 × 2.2	B	(13)	43	Dark red	139—140	237 (71),[c,§] 236 (100),[d,§] 157 (20),[e] 156 (51),[f] 78 (35)	$C_{11}H_{11}NSe$	55.9 55.9	4.8 4.7	6.2 5.9		33.3 33.4
(6)	30 × 2.5	B–E(99 : 1)→B–E(49 : 1)→B–E(19 : 1)	(14)	37	Dark blue [g,h]	109—111	279 (100),[c,§] 278 (91),[d,§] 199 (15),[e] 198 (67) [f]	$C_{14}H_{17}NSe$	60.1 60.4	6.0 6.2	5.1 5.0		27.8 28.4
(7)	30 × 2.5	B–E(97 : 3)	(15)	40	Bronze	167—169	279 (80),[c,§] 278 (100),[d,§] 199 (9),[e] 198 (44) [f]	$C_{14}H_{17}NSe$	60.7 60.4	6.5 6.2	5.3 5.0		
(8)	40 × 2.2	B	(16)	2.5	Dark brown [i]	63—67	223 [j]	$C_{10}H_9NSe$	54.1 54.0	4.1 4.1	6.1 6.3		
(21)	32 × 2.5	B–E(9 : 1) [a]	(25)	43	Dark red	143—145	243 (72),[c,§] 242 (41),[d,§] 163 (37),[e] 162 (100),[f] 59 (47),[k] 58 (59),[l] 44 (77)	C_9H_9NSSe	44.4 44.6	3.8 3.7	6.0 5.8	13.3 13.2	33.2 32.6
(22)	20 × 2.7	B	(26)	11	Red	146—149	243 (55),[c,§] 242 (27),[d,§] 163 (46),[e] 162 (100),[f] 59 (45),[k] 58 (38),[l] 44 (16)	C_9H_9NSSe	44.4 44.6	3.8 3.7	6.0 5.8	13.1 13.2	32.3 32.6
(23)	15 × 2.7 (twice)	B–E(9 : 1), B	(27)	15	Brown [h]	*m*	229 [j]	C_8H_7NSSe	41.6 42.1	3.0 3.1	6.0 6.1		

* B = benzene, E = ether. † Needles unless otherwise stated. ‡ Peaks which result from the loss of alkyl substituents or from processes which involve the modification of alkyl substituents are not included. § The modifications of $RCHSe^{+\cdot}$ and $RCSe^+$ which result from the presence of ^{82}Se, ^{80}Se, ^{78}Se, ^{77}Se, ^{76}Se, ^{74}Se, and ^{13}C give rise to a cluster of peaks at unit *m/e* intervals between $M + 3$ and $M - 7$ (M = $RCH^{80}Se$; R = 3-indolizine or 5- or 7-pyrrolo[2,1-*b*]thiazole residue).

[a] Non-standard procedure; further details are in the Experimental section. [b] With decomposition. [c] $M^{+\cdot}$ ($RCH^{80}Se^{+\cdot}$). [d] $R–\overset{+}{C}=Se \longleftrightarrow R–C\equiv\overset{+}{Se} \longleftrightarrow \overset{+}{R}=C=Se$. [e] $RCH^{+\cdot}$; exact structure not known. [f] RC^+; exact structure not known. [g] Plates. [h] From cyclohexane. [i] From benzene–light petroleum. [j] Spectrum not analysed. [k] $C_2H_3S^+$. [l] $C_2H_2S^{+\cdot}$. [m] Gradual decomposition on being heated.

spectrum in $CF_3 \cdot CO_2H$ {spectrum of the 5*H*-5,6,7-trimethylpyrrolo[2,1-*b*]thiazolium cation} was identical with that of 5*H*-5,6,7-trimethylpyrrolo[2,1-*b*]thiazolium perchlorate.[10]

Reactions of Selenaldehydes with Wittig Reagents.—2,7-*Dimethylindolizine-3-carboselenaldehyde* (11) *with isopropylidenetriphenylphosphorane.* A solution of 2-iodopropane (9.35 g, 5.5 ml, 55 mmol) and triphenylphosphine (13.1 g, 50 mmol) in dimethylformamide (50 ml) was heated at 120 °C (oil-bath) for 12 h. Addition of ether (500 ml) to the cooled solution precipitated isopropyltriphenylphosphonium iodide as an oil which gradually crystallised. The solid was filtered off, washed with ether, and dissolved in ethanol (40 ml); perchloric acid (7 ml, 83 mmol) was then added to the solution. Gradual addition of ether precipitated a solid, which was filtered off, washed with ether, and redissolved in ethanol (60 ml). Perchloric acid (7 ml) was added to the resulting solution. Precipitation with ether, filtration, and washing with much ether gave *isopropyltriphenylphosphonium perchlorate* (8.88 g, 44%) as spars from ethanol, m.p. 182—183 °C (Found: C, 62.1; H, 5.5. $C_{21}H_{22}ClO_4P$ requires C, 62.3; H, 5.5%).

A solution (13.1 ml) of n-butyl-lithium (3.8 mmol) in light petroleum (b.p. 30—40 °C) was added to a solution of isopropyltriphenylphosphonium perchlorate (1.62 g, 4 mmol) in dimethyl sulphoxide (10 ml) and benzene (10 ml) in an atmosphere of nitrogen. A solution of the selenaldehyde (11) (474 mg, 2 mmol) in benzene (50 ml) was added to the red solution which thereupon rapidly became pale yellow. The resulting solution was diluted with water and extracted with benzene; the extracts were then washed with water (× 4), dried, and evaporated. Distillation of the residue at 115—120 °C and 0.1 mmHg afforded 3-(2,2-*dimethylvinyl*)-2,7-*dimethylindolizine* (30) (224 mg, 56%) as a pale yellow oil which rapidly became green in air and light (Found: C, 84.4; H, 8.5; N, 6.7. $C_{14}H_{17}N$ requires C, 84.4; H, 8.6; N, 7.0%); δ($CDCl_3$; 60 MHz) 1.61 (3 H, d, $J_{H>=<Me}$ 1.0 Hz, $^{H>=<Me}$), 1.97 (3 H, d, $J_{H>=<Me}$ 1.3 Hz, $^{H>=<Me}$), 2.16 (3 H, 2-Me), 2.33 (3 H, 7-Me), 6.06 (1 H, br,m, C*H*:CMe_2), 6.13 (1 H, 1-H), 6.22 (1 H, dd, $J_{6,5}$ 7.1 Hz, $J_{6,8}$ 1.6 Hz, 6-H), 7.06 (1 H, br, 8-H), and 7.53 (1 H, d, $J_{5,6}$ 7.1 Hz, 5-H). In $CDCl_3$–D_2O compound (30) undergoes H–D exchange at position 1.

5,6-*Dimethylpyrrolo*[2,1-b]*thiazole-7-carboselenaldehyde* (20) *with isopropylidenetriphenylphosphorane.* The procedure was identical with that of the preceding experiment, with 5,6-dimethylpyrrolo[2,1-*b*]thiazole-7-carboselenaldehyde (484 mg, 2 mmol) in place of compound (11). Distillation gave 7-(2,2-*dimethylvinyl*)-5,6-*dimethylpyrrolo*[2,1-b]-*thiazole* (33) (321 mg, 78%) as an oil, b.p. 120—125 °C at 0.2 mmHg, which solidified to crystals, m.p. 45—48 °C (Found: C, 70.2; H, 7.2; N, 6.7. $C_{12}H_{15}NS$ requires C, 70.2; H, 7.4; N, 6.8%); δ($CDCl_3$; 60 MHz) 1.76 (3 H, d, $J_{H>=<Me}$ 0.9 Hz, $_{H>=<Me}$), 1.92 (3 H, d, $J_{H>=<Me}$ 1.2 Hz, $_{H>=<Me}$), 2.07 (3 H, 6-Me), 2.31 (3 H, 5-Me), 6.07 (1H, br,m, C*H*:CMe_2), 6.52 (1 H, d, $J_{2,3}$ 4.1 Hz, 2-H), and 7.16 (1 H, d, $J_{3,2}$ 4.1 Hz, 3-H).

2,7-*Dimethylindolizine-3-carboselenaldehyde* (11) *with acetylmethylenetriphenylphosphorane.* A solution of the selenaldehyde (11) (474 mg, 2 mmol) and acetylmethylenetriphenylphosphorane [11] (762 mg, 2.4 mmol) in xylene (10 ml) was boiled for 2 h. The cooled solution was chromatographed [alumina (25 × 1.9 cm)]. Successive elution with benzene (200 ml), benzene–ether (9 : 1; 200 ml), and benzene–ether (1 : 1; 100 ml) gave pale yellow eluates which contained (t.l.c.) triphenylphosphine selenide and were discarded. Subsequent elution with ether gave yellow eluates (800 ml) which were evaporated, and the residual solid was rechromatographed [alumina (15 × 1.9 cm)] with ether. The yellow eluates afforded 2,7-*dimethyl*-3-(3-*oxobut*-1-*enyl*)*indolizine* (31) (320 mg, 77%), as yellow needles from cyclohexane, m.p. 116—117 °C (Found: C, 78.9; H, 7.4; N, 6.8. $C_{14}H_{15}NO$ requires C, 78.8; H, 7.1; N, 6.6%); δ($CDCl_3$; 60 MHz) 2.28 (3 H, 2-Me), 2.32 (3 H, COMe), 2.42 (3 H, 7-Me), 6.22 (1 H, 1-H), 6.39 (1 H, d, $J_{2',1'}$ 15.9 Hz, 2'-H), 6.50 (1 H, dd, $J_{6,5}$ 7.3 Hz, $J_{6,8}$ 1.8 Hz, 6-H), 7.07 (1 H, br, 8-H), 7.85 (1 H, d, $J_{1',2'}$ 15.9 Hz, 1'-H), and 8.13 (1 H, d, $J_{5,6}$ 7.3 Hz, 5-H).

5,6-*Dimethylpyrrolo*[2,1-b]*thiazole-7-carboselenaldehyde*(20) *with acetylmethylenetriphenylphosphorane.* A solution of the selenaldehyde (20) (484 mg, 2 mmol) and acetylmethylenetriphenylphosphorane (762 mg, 2.4 mmol) in xylene (10 ml) was boiled for 1.5 h. The cooled solution was chromatographed [alumina (25 × 1.9 cm)]. Successive elution with benzene (200 ml) and benzene–ether (9 : 1; 200 ml) gave colourless eluates which yielded triphenylphosphine selenide (543 mg, 80%), as spars from cyclohexane, m.p. 186—188 °C (lit.,[12] 187—188 °C). Elution with benzene–ether (1 : 1; 100 ml) then gave pale yellow eluates which were discarded. Subsequent elution with ether (400 ml) brought through pale green eluates which contained (t.l.c.) a trace of the selenaldehyde (20). Continued elution with ether gave yellow eluates which yielded 5,6-*dimethyl*-7-(3-*oxobut*-1-*enyl*)*pyrrolo*[2,1-b]*thiazole* (34) (347 mg, 79%), as lemon yellow needles from cyclohexane, m.p. 167—168 °C (Found: C, 65.7; H, 6.1; N, 6.3. $C_{12}H_{13}NOS$ requires C, 65.7; H, 6.0; N, 6.4%); δ($CDCl_3$; 60 MHz) 2.22 (3 H, 6-Me), 2.34 (6 H, 5-Me and COMe), 6.18 (1 H, d, $J_{2',1'}$ 15.9 Hz, 2'-H), 6.90 (1 H, d, $J_{2,3}$ 4.0 Hz, 2-H), 7.35 (1 H, d, $J_{3,2}$ 4.0 Hz, 3-H), and 7.70 (1 H, d, $J_{1',2'}$ 15.9 Hz, 1'-H).

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