Dehydrogenation of Indolines to Indoles *via* Azasulphonium Salts or *N*-Chloramines

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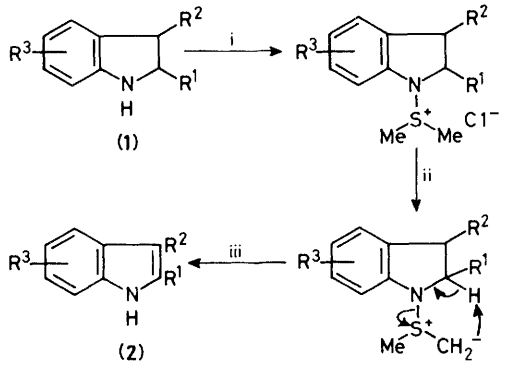
The dehydrogenation of indolines to indoles without using mineral oxidising reagents is described. The conversion was achieved *via* either azasulphonium salts or *N*-chloramines, the former route involving milder conditions but a more complex procedure.

Indoles bearing various substituents on the benzene ring often have potent physiological activities and can also be useful intermediates for the synthesis of indole alkaloids. We wanted to establish a new method for the introduction of various functions onto the benzene ring after the formation of the indole ring. To do this, we chose the following synthetic strategy: (i) reduction of the indoles to indolines,[1] (ii) substitution of the benzene ring,[2] and (iii) dehydrogenation of the indoline ring to give the indoles.† The third step has been studied extensively[3] and is usually carried out by chemical oxidation with active manganese dioxide,[4] cupric chloride in refluxing pyridine,[5] chloranil,[6] palladium on charcoal,[7] or cobalt(salen).[8] However, many of these methods require carefully controlled conditions, or are not generally applicable, or give low yields (in the case of functionalised indolines). For example, it is reported[4,8] that the most readily available reagent, active manganese dioxide, does not dehydrogenate 2,3-disubstituted indolines to the corresponding indoles and is not suitable for the large-scale production of indoles owing to the difficulty of safely disposing of large quantities of manganese dioxide. In an earlier communication,[9] we briefly reported a versatile method for the dehydrogenation of indolines to give indoles without using mineral oxidising agents; we now report a full account of the preliminary work and additional studies of dehydrogenation using *N*-chloramine intermediates; the scope and limitations of these dehydrogenation reactions are discussed.

Results and Discussion

Dehydrogenation of Indolines via *Azasulphonium Salt Intermediates.*—The dehydrogenation of indolines was attempted by the elimination of a suitable leaving group, substituted on a ring nitrogen, together with the hydrogen of C-2; it has been reported[10] that 1-phenylsulphinyl- and 1-phenoxyselenenyl-indolines are converted into indoles by this method. However, it is assumed that the dehydrogenation can be achieved under the mildest conditions when it takes place *via* an intramolecular cyclic transition state (Scheme).

Johnson *et al.*[11] found that an azasulphonium tetrafluoroborate salt could be synthesised from *p*-bromothioanisole and *N*-ethylidenemethylamine, and identified by hydrolysis and subsequent formation of the 2,4-dinitrophenylhydrazone. When aromatic amines are used instead of diethylamine, the alkylation of the aromatic moiety may occur by a Sommelet–Hauser rearrangement, and Gassman *et al.*[12] applied this to the synthesis of indoles. We presumed that azasulphonium salts produced from indolines, dimethyl sulphides, and t-butyl hypochlorite would undergo intramolecular attack of the carbanion, generated with base, at the C-2 hydrogen (rather than at the aromatic ring), to yield indolenines which are spontaneously converted into indoles by proton transfer (Scheme). Several such dehydrogenations were carried out, as described below.



Scheme. Assumed dehydrogenation mechanism. *Reagents:* i, Me_2S, Bu^tOCl; ii, base; iii, $-Me_2S$

To determine the optimum conditions, various sets of reaction conditions were investigated. According to Gassman,[12] anilines react with t-butyl hypochlorite to give *N*-chloroanilines, which, on addition of dimethyl sulphide to the reaction mixture, give azasulphonium salts. On the other hand, Claus *et al.*[13] reported that the initial addition of t-butyl hypochlorite into the aniline solution resulted in considerably lower yields of the final azasulphonium salts than when the hypochlorite was added last; we also found that the order in which the reagents are mixed has a profound effect on the yields of the indoles (Table 1), and the optimum yields were obtained by adding the t-butyl hypochlorite last to the reaction mixture, in agreement with Claus *et al.* However the reason for this effect on the yield is still unclear.

The effects of the solvent, reaction temperature, and the presence of various bases on the yield of (**2a**) were then investigated. As shown in Table 2, the optimum yield of compound (**2a**) was obtained in run 5; several indolines were dehydrogenated to give the corresponding indoles under these conditions. Table 3 shows the results of the dehydrogenation of 2- and/or 3-substituted indolines, which give the corresponding indoles in good yields. With compounds (**1h**) and (**1i**), triethylamine was used instead of sodium ethoxide to prevent racemisation (optical purity ≧95% in both cases).

The advantages of this method are that the procedure is simple (a one-pot reaction), the reagents used are readily available and inexpensive, and the reaction conditions are mild enough to be applied to indolines with substituents which would be unstable at higher temperatures, and sensitive to the presence of acids or strong bases.

† We used $CuCl_2$ in refluxing pyridine for the dehydrogenation of the indolines to give the indoles in 50—60% yields.

Table 1. Effect of the sequence of addition of the reagents on the yield from the dehydrogenation of indoline (**1a**) to give indole (**2a**)

$$(\mathbf{1a}) \xrightarrow[\text{mol equiv.), } -65\ ^\circ\text{C}]{\text{i, ii, iii}} (\mathbf{2a})$$

Reagents: i, (**1a**) (1 mol equiv.)–Me_2S (1.5 mol equiv.), then Bu^{t}OCl (1 mol equiv.); ii, (**1a**)–Bu^{t}OCl, then Me_2S; iii, Me_2S–Bu^{t}OCl, then (**1a**)

Addition order of reagents	Yield (%)[a] of (**2a**)
i	66(22)
ii	2(17)
iii	5(54)

[a] Figures in parentheses indicate recovery (%) of starting material.

Table 2. Dehydrogenation of indoline (**1a**) to give indole (**2a**) under various conditions

Run	Solvent	Reaction temp. (°C)	Base (3 mol equiv.)	Yield (%)[a] of (**2a**)
1[b]	CH_2Cl_2	−70	NaOEt	12(74)
2[c]	CH_2Cl_2	−65	NaOEt	59(32)
3	CH_2Cl_2	−40	NaOEt	40(55)
4	CH_2Cl_2	−68	Et_3N	42(45)
5[d]	CH_2Cl_2	−65	NaOEt[e]	82(9)
6[d]	DME[f]	−65	NaOEt[e]	73(22)
7[d]	THF[g]	−65	NaOEt[e]	24(61)
8[d]	DMF[h]	−65	NaOEt[e]	0(68)
9[d]	CH_2Cl_2	−65	Et_3N	63(35)
10[d]	CH_2Cl_2	−65	aq. $NaHCO_3$	47(42)

[a] Figures in parentheses indicate recovery (%) of starting material. [b] Tetrahydrothiophene was used as the sulphide; in the other runs dimethyl sulphide was used. [c] *N*-Chlorosuccinimide was used as the chlorinating agent; in the other runs t-butyl hypochlorite was used. [d] Et_3N (1 mol equiv.) was added to the solvent before addition of the reagents. [e] 5 Mol equiv. [f] Dimethoxyethane. [g] Tetrahydrofuran. [h] Dimethylformamide.

Table 3. Dehydrogenation of the indolines (**1**) to give the indoles (**2**) *via* azasulphonium salts

$$(\mathbf{1}) \xrightarrow[-65\ ^\circ\text{C, } CH_2Cl_2]{\text{i, ii}} (\mathbf{2})$$

Reagents: i, Me_2S, Et_3N; ii, Bu^{t}OCl, NaOEt

Compound	Yield (%) of (**2**)	M.p. (°C) of (**2**)	Recryst. solvent	Lit. m.p. (°C) of (**2**)
(**1a**)	82	52—53	H_2O	52[a]
(**1b**)	91	94—95	ligroin	95[b]
(**1c**)	69	59—60	EtOH–H_2O	61[c]
(**1d**)	63	119—120.5	MeOH	117—118[d]
(**1e**)	74[e]	139.5—141	Benzene	137—138[f]
(**1f**)	73	93—94	Benzene	94[g]
(**1g**)	61	122—123	AcOEt	122—123[h]
(**1h**)	63[i,j]	107—110, 108—109[k]	Benzene–hexane	109—109.5[l]
(**1i**)	61[i,m]	116—122, 136—138[k]	Benzene	138—139[n]

[a] I. Fleming and M. Woolias, *J. Chem. Soc., Perkin Trans. 1*, 1979, 829. [b] I. Fleming and M. Woolias, *ibid.*, 1979, 827. [c] O. Kruber, *Ber.*, 1926, **59**, 2752. [d] C. U. Rogers and B. B. Corson, *J. Am. Chem. Soc.*, 1947, **69**, 2910. [e] CH_2Cl_2–DME (1:1, v/v) was used as solvent. [f] A. J. Ewins, *J. Chem. Soc.*, 1911, **99**, 270. [g] H. Plieninger, T. Suehiro, K. Suhr, and M. Decker, *Chem. Ber.*, 1955, **88**, 370. [h] Ref. 2c. [i] Et_3N was used as base. [j] $[\alpha]_D^{24}$ +48.0° (*c* 0.5, $CHCl_3$) {lit.,[17] $[\alpha]_D^{20}$ +50° (*c* 0.5, $CHCl_3$)}. [k] M.p. after recrystallization. [l] Ref. 17. [m] $[\alpha]_D^{21}$ +49.2° (*c* 0.5, $CHCl_3$) {lit.,[9] $[\alpha]_D^{21}$ +51.0° (*c* 0.5, $CHCl_3$)}. [n] Ref. 9.

Table 4. Dehydrogenation of the indolines (**1**) to give the indoles (**2**) by Somei's method[a]

Starting compound	NCS[b] (mol equiv.)	Et_3N (mol equiv.)	Reaction time (h)	Product	Yield (%) of product
(**1a**)	1.0	1.2	14	(**2a**)	48
(**1a**)	1.5	1.2	14	(**2a**)	28
(**1a**)	1.0	1.2	3	(**2a**)	52
(**1j**)	1.0	1.2	2	(**2j**)	8
				(**3**)	19
(**1k**)	1.0	1.2	4	*c*	

[a] Reaction conditions: solvent CH_2Cl_2 at room temp. [b] *N*-Chlorosuccinimide. [c] No products were characterised.

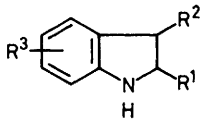
Table 5. Dehydrogenation of indoline (**1a**) to indole (**2a**) under various conditions

$$(\mathbf{1a}) \xrightarrow{\text{i or ii}} (\mathbf{4}) \xrightarrow{\text{iii or iv}} (\mathbf{2a}) + (\mathbf{5})$$

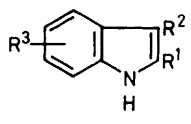
Reagents: i, Bu^{t}OCl–solvent; ii, Bu^{t}OCl–Et_2O–base; iii, base; iv, polar solvent

Run[a]	Solvent	Base (1.2 mol equiv.)	Yield (%) (**2a**)	Yield (%) (**5**)
1	Et_2O–DMF (1:1 v/v)	$NaHCO_3$	0	25[b]
2	CH_2Cl_2	Et_3N	26	<5[c]
3	$ClCH_2CH_2Cl$	Et_3N	41	<5[c]
4	DMF	Et_3N	32	<5[c]
5	Et_2O–DMF (1:1 v/v)	Et_3N	66	0
6	Et_2O–DMF (3:1 v/v)	Et_3N	63	0
7	Et_2O + CH_2Cl_2	Et_3N	51	0
8	Et_2O + DMF	Et_3N	55	0
9	Et_2O + DMF	DBU	75	0

[a] Reaction conditions: i and iii for runs 1—6; ii and iv for runs 7—9. [b] (**5**) [m.p. 90–91 °C (from light petroleum, lit.,[18] m.p. 94—95 °C)] was converted into the 1-benzoyl derivative [m.p. 97—98 °C (from EtOH, lit.,[18] m.p. 97—98 °C)] and characterised by m.p. [c] Determined by gas chromatography.

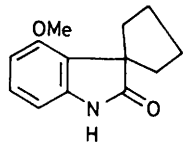


(**1**)

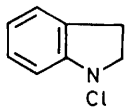


(**2**)

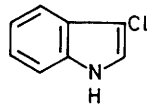
	R^1	R^2	R^3
a;	H	H	H
b;	H	Me	H
c;	Me	H	H
d;		$-(CH_2)_4-$	H
e;	H	$(CH_2)_2NHCOPh$	H
f;	H	H	6-Br
g;	H	$(CH_2)_2NHCOBu^t$	6-Br
h;	H	$CH_2CH(NHAc)CO_2Et$	H
i;		Z-L-Ala-2,3-dihydro-L-Trp-OMe	
j;		$-(CH_2)_4-$	4-OMe
k;	Me	CH_2CO_2Et	5-OMe
l;	H	H	6-NO_2



(3)



(4)



(5)

Table 6. Dehydrogenation of the indolines (**1**) to give the indoles (**2**) *via* *N*-chloramine intermediates

(**1**) $\xrightarrow{\text{i, ii}}$ (**2**)

Reagents: i, Bu^{t}OCl, DBU, Et_2O; ii, DMF

Compound	Yield (%) of (**2**)
(**1a**)	75, 84[a]
(**1c**)	79
(**1h**)	60[b]
(**1i**)	59[c]
(**1j**)	72
(**1k**)	40[d]
(**1l**)	81

[a] Larger scale operations were performed (see Experimental section). [b] Optical purity 100%. [c] Optical purity 88%. [d] Reaction temp. −78 °C.

Dehydrogenation of Indolines via N-*Chloramine Intermediates*.—The dehydrogenation method described above is the mildest of those tried, but requires a low reaction temperature and is not suitable for the large-scale production of indoles. We have also investigated a simpler method, by which most indolines can be dehydrogenated to give indoles at ambient temperature without particular care.

The chemistry of *N*-halogenoamines has been widely studied,[14] and it is known that a carbon–nitrogen double bond can be formed from *N*-chloramines by the elimination of hydrogen chloride.[15] However, there is only one report of the dehydrogenation of indolines to give indoles *via* *N*-chloramines, by Somei *et al.*,[16] and in this case a 1-chloroindoline derivative was dehydrogenated to give the indole derivative accompanied by considerable amounts of the nuclear chlorinated starting indoline. We examined Somei's reaction in detail, and the results are presented in Table 4. Indoline (**1a**) was dehydrogenated to give indole (**2a**) in moderate yield, but in other cases several products were detected by thin layer chromatography on silica gel and it was difficult to isolate the desired product in a pure state. Although the results were unsatisfactory, further studies were carried out to find the optimum conditions for the dehydrogenation of indoline (**1a**); the results are presented in Table 5 and show that the yield of indole (**2a**) is greatly affected by the solvent and base used. With polar solvents, indole (**2a**) was obtained in 25—40% yields and trace amounts of 3-chloroindole (**5**) were detected by gas chromatography (runs 2—4). As compound (**5**) must be derived from the chlorination of indole (**2a**) with 1-chloroindoline, it is speculated that the 1-chlorination of indoline (**1a**) and the dehydrogenation of 1-chloroindoline to give (**2a**) proceed concurrently in polar solvents, and the chlorination of (**2a**) occurs as a side reaction. However, 1-chloroindoline is less soluble in non-polar solvents; thus, if the reaction is carried out in, for example, diethyl ether, it accumulates and can then be converted directly into (**2a**) by the addition of a polar solvent, without occurrence of the side reaction. The yield of indole (**2a**) was not affected significantly by the addition of a polar solvent and fairly good yields were obtained in diethyl ether diluted with smaller amounts of dimethylformamide (runs 5 and 6). Therefore, dimethylformamide can also be added to the ether solution as a solubilising agent when the starting material is not soluble in ether alone. Several indolines were dehydrogenated to the corresponding indoles *via* 1-chloroindoline intermediates under the optimum conditions (run 9, Table 6). The 5-methoxyindoline derivative (**1k**), the 1-chloro derivative of which is unstable at ambient temperature, could be converted into the corresponding indole derivative (**2k**) at low temperatures.

Thus, an improved version of Somei's method offers a versatile route for the dehydrogenation of indolines to give indoles under the usual conditions.

Experimental

All m.p.s are uncorrected. N.m.r. spectra (tetramethylsilane as internal standard) were obtained with a JEOL PS-PFT/EC-100 instrument, i.r. spectra with a Shimadzu IR-400 instrument, and mass spectra with a Shimadzu LKB-9000 spectrometer, and with a JMS-O1SG instrument for accurate mass measurements.

Reagents.—Indoline (**1a**) and 6-nitroindoline (**1l**) were purchased from Tokyo Kasei Kogyo Co. and other indolines were prepared by the literature method.[1] The physical data of the new compounds are as follows: 1,2,3,4,4a,9a-*hexahydro*-5-*methoxycarbazole* (**1j**), m.p. 59—60 °C (from ligroin) (Found: M^+, 203.1313; $C_{13}H_{17}NO$ requires M, 203.1311); $\nu_{max.}$(neat) 3 360 (NH) and 1 603 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.75—1.15 (8 H, m, aliphatic H), 2.75—3.90 (2 H, m, 4a- and 9a-H), 3.75 (3 H, s, OCH_3), 6.10—6.43 (2 H, d, 6- and 8-H), 7.00 (1 H, t, J 8 Hz, 7-H); 3-ethoxycarbonylmethyl-5-methoxy-2-methylindoline (**1k**), $\nu_{max.}$(neat) 3 360 (NH), 1 730 (CO), and 1 600 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.00—1.80 (6 H, m, 2-CH_3 and CH_2CH_3); m/z 247 (M^+, 6%), 174 (45), 162 (87), 161 (52), and 160 (100).

General Procedure for the Dehydrogenation of the Indolines (**1**) *to give the Indoles* (**3**) (*Table* 3).—To a vigorously stirred solution of N^{α}-acetyl-2,3-dihydro-L-tryptophan ethyl ester (**1h**) (320 mg, 1.16 mmol), dimethyl sulphide (0.13 ml, 1.74 mmol), and triethylamine (117 mg, 1.16 mmol) in dry CH_2Cl_2 (7 ml) under argon at −65 °C was added dropwise t-butyl hypochlorite (0.17 ml, 1.50 mmol) in dry CH_2Cl_2 (4 ml) during 1 h. Triethylamine (352 mg, 3.48 mmol) in dry CH_2Cl_2 (1—2 ml) was added for 10 min, and the reaction mixture was stirred for 2 h, during which time it was allowed to warm up to room temperature. To the solution, 5% HCl (20 ml) was added, and the reaction mixture was extracted with CH_2Cl_2 (30 × 2 ml). The combined extracts were washed with H_2O, saturated aqueous $NaHCO_3$, saturated aqueous NaCl, and dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel using benzene–acetone (4:1 v/v) as eluant to give N^{α}-acetyl-L-tryptophan ethyl ester (**2h**) (200.5 mg, 63%), m.p. 107—110 °C, $[\alpha]_D^{24}$ +48.0° (*c* 0.5, $CHCl_3$) {lit.,[17] m.p. 109—109.5 °C; $[\alpha]_D^{20}$ +50° (*c* 0.5, $CHCl_3$)}.

For compounds (**1a—g**), NaOEt solution [prepared from Na (5 mol equiv.) in EtOH] was added during 10 min, instead of trimethylamine in CH_2Cl_2.

General Procedure for the Dehydrogenation of the Indolines (**1**) *to give the Indoles* (**2**) via N-*Chloramine Intermediates* (*Table* 6).—*Synthesis of* 1,2,3,4-*tetrahydro*-5-*methoxycarbazole* (**2j**). t-Butyl hypochlorite (0.14 ml, 1.2 mmol) was added dropwise to the mixture of 1,2,3,4,4a,9a-hexahydro-5-methoxycarbazole (**1j**) (200 mg, 0.99 mmol), 1,8-diazabicyclo[5.4.0]undec-4-ene (DBU) (0.18 ml, 1.2 mmol), and diethyl ether (10 ml) at 0 °C. After being stirred for 5 min, dimethylformamide (DMF) (10 ml) was added quickly and the reaction mixture was stirred for

30 min at room temperature. H_2O (30 ml) was added to the reaction mixture and it was extracted with AcOEt (30 × 2 ml). The combined extracts were washed with 5% HCl (25 ml) and with saturated aqueous NaCl (25 ml), dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel using benzene–hexane (1:1 v/v) for elution to give 1,2,3,4-tetrahydro-5-methoxycarbazole (**2j**) as a white solid (142 mg, 72%), m.p. 134—135 °C (from EtOH) (lit.,[19] m.p. 130—131 °C).

Synthesis of indole (**2a**). In a 1-l three-necked flask fitted with a stirrer, a dropping funnel, a thermometer, and a calcium chloride tube were placed indoline (**1a**) (3.00 g, 25 mmol), DBU (7.4 ml, 50 mmol), and dry diethyl ether (200 ml), and the mixture was cooled to −12 °C. t-Butyl hypochlorite (3.1 ml, 26 mmol) in dry diethyl ether (100 ml) was added dropwise to the reaction mixture, then the cooling bath was removed, warmed DMF (40 °C; 300 ml) was added quickly and the reaction mixture simultaneously warmed to room temperature. After being stirred for 30 min, H_2O (300 ml) was added to the mixture. The ethereal layer was separated and the aqueous layer was extracted with two 200-ml portions of diethyl ether. The combined ether extracts were washed with 2% HCl (200 ml) and saturated aqueous NaCl (300 ml), dried ($MgSO_4$), and concentrated. The residue was purified by flash column chromatography [40—63 μm (230—400 mesh), silica gel 60 (Merck No. 9385)] with benzene–hexane (2:1 v/v) as eluant to give indole (**2a**) as a white solid (2.49 g, 84%), m.p. 52—53 °C [from diethyl ether–light petroleum (1:10 v/v)] (lit.,[18] m.p. 52 °C).

Physical data of the new products. 3-Ethoxycarbonylmethyl-5-methoxy-2-methylindole (**2k**) was reported as an oil in the literature;[10] however, we obtained it as a solid; m.p. 69—70 °C (from EtOH) (Found: C, 67.7; H, 7.0; N, 5.4. $C_{14}H_{17}NO_3$ requires C, 67.99; H, 6.93; N, 5.66%); $\nu_{max.}$(neat) 3 400 (NH), 1 730 (CO), and 1 595 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.25 (3 H, t, *J* 7 Hz, CH_2CH_3), 2.35 (3 H, s, 2-CH_3), 3.65 (2 H, s, CH_2CO), 3.85 (3 H, s, OCH_3), 4.10 (2 H, q, *J* 7 Hz, CH_2CH_3), 6.75 (1 H, dd, *J* 2 and 8 Hz, 6-H), 7.00 (1 H, s, 4-H), 7.20 (1 H, d, *J* 8 Hz, 7-H), and 8.00 (1 H, br s, NH); *4-methoxy-2-oxoindoline-3-spirocyclopentane* (3), m.p. 169—170 °C (from diethyl ether) (Found: M^+, 217.1067. $C_{13}H_{15}NO_2$ requires *M*, 217.1103); $\nu_{max.}$(Nujol) 3170 (NH), 1700, 1620, and 1520 cm^{-1} (CONH); δ_H (100 MHz; $CDCl_3$) 1.93—2.24 (8 H, m, aliphatic H), 3.84 (3 H, s, OCH_3), 6.50—6.61 (2 H, m, 5- and 7-H), 7.14 (1 H, t, *J* 8 Hz, 6-H), and 8.10 (1 H, br s, NH).

Acknowledgements

We thank Professor Shun-ichi Yamada of this University for encouragement.

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Received 26*th September* 1983; *Paper* 3/1686