Electrophilic Substitution in Indoles. Part 12.[1] Kinetic Studies of the Rearrangement of 3,3-Disubstituted Indolenines† to 2,3-Disubstituted Indoles

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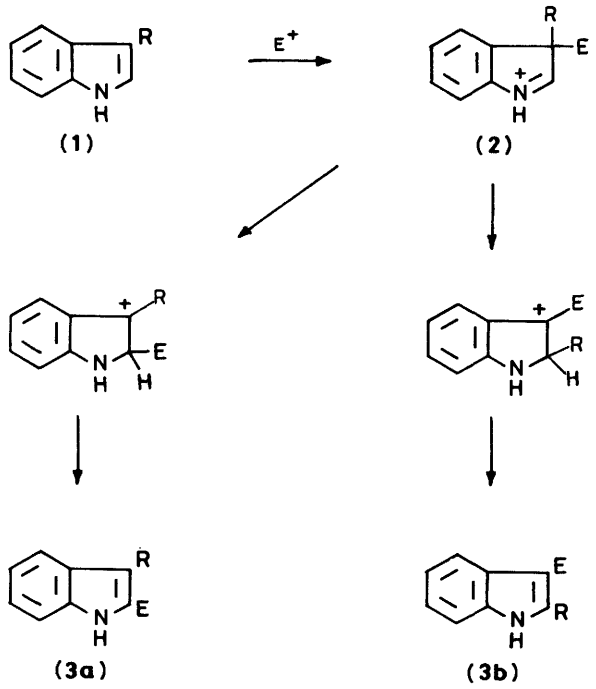
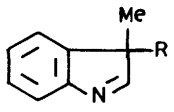
The rearrangements of 3-alkyl-3-methylindolenine salts to the corresponding 2-alkyl-3-methylindoles have been studied over a range of temperatures by u.v. methods in isopropyl alcohol containing hydrochloric acid. The relative migratory aptitudes of the various alkyl groups were as follows: Me, 1; Et, 14; Pr^i, 120; allyl, 400; *p*-nitrobenzyl, 188; benzyl, 1 520. Attempts to prepare the analogous *p*-methylbenzyl and *p*-methoxybenzyl-3-methylindolenines by alkylation of the 3-methylindole Grignard reagent gave only the 2-benzylindoles owing to the much higher migratory aptitude of the *p*-methylbenzyl and *p*-methoxybenzyl groups. Spiro[cyclopentane-3′-indolenine] hydrochloride rearranged to tetrahydrocarbazole at *ca.* 7 400 times the rate of rearrangement of 3,3-dimethylindolenine hydrochloride to 2,3-dimethylindole. Thermodynamic parameters for the various reactions were determined in view of their relevance to the mechanism of electrophilic substitution in 3-substituted indoles.

Our earlier studies[2,3] of electrophilic substitution in simple 3-alkylindoles (**1**) have shown that the initial product is the 3,3-disubstituted indolium salt (**2**) which subsequently undergoes rearrangement with formation of a 2,3-disubstituted indole (**3a**) or (**3b**) (Scheme). Either the incoming substituent, or



Scheme.

that already present, may migrate depending on their relative migratory aptitudes, but normally only one product is formed.[3] It was clear from our earlier work that it was the indolium salts which underwent rearrangement, rather than the free bases, because the latter could be prepared by electrophilic substitution of 3-alkylindole Grignard derivatives, *i.e.* essentially under basic conditions, rather than under the acidic conditions normally employed in electrophilic substitution reactions. In the previous studies[3] a range of indolenines (**4**) was prepared from 3-methylindole by alkylation of the Grignard derivative and qualitative studies of their acid-catalysed rearrangements to 2,3-disubstituted indoles (**5**) were carried out. In each case only one product was obtained, and the structures were confirmed by n.m.r. spectroscopy, and in some cases by direct comparisons with authentic materials prepared by Fischer indole syntheses. These studies showed that the migratory aptitudes of the various substituent groups were in the following order Me < Et < Pr^i < allyl < CH_2Ph, in accord with predictions based on the well known migratory aptitudes of substituents in pinacol–pinacolone, or Wagner–Meerwein-type rearrangements.[4] For example, 3,3-dimethylindolenine (**4a**) required heating for 15 min at 80 °C in 6M-hydrochloric acid to effect complete rearrangement, whereas 3-benzyl-3-methylindolenine (**4f**) rearranged in a few minutes at 20 °C on addition of trifluoroacetic acid to a deuteriochloroform solution in an n.m.r. tube. The *intra*-molecular nature of the rearrangement was also demonstrated by showing that no cross-over products were observed in the simultaneous acid-catalysed rearrangement of 3,3-dimethyl- and 3,3-diethyl-indolenine.[3]



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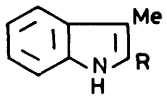
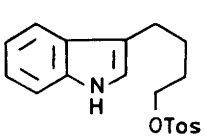


(5)

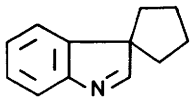
a; R = Me
b; R = Et
c; R = Pr^i
d; R = allyl
e; R = $CH_2C_6H_4$-*p*-NO_2
f; R = CH_2Ph
g; R = $CH_2C_6H_4$-*p*-Me
h; R = $CH_2C_6H_4$-*p*-OMe
i; R = $CH_2C{\equiv}CH$
j; R = COC_6H_4-*p*-OMe
k; R = $CH_2C_6H_4$-*p*-CN

† Indolenine refers to 3*H*-indole.

In this paper we describe kinetic studies of these rearrangements in order to quantify the earlier data and to obtain thermodynamic parameters relevant to the later stages of the overall processes outlined in the Scheme. Most of the required disubstituted indolenines (**4**) were synthesized by alkylation of the Grignard derivative of 3-methylindole, and their synthesis and characterisation has been described previously;[3] the spirocyclic indolenine (**7**) was prepared by potassium t-butoxide-catalysed cyclisation[5] of the indolylbutyl toluene-*p*-sulphonate (**6**). Attempts to extend the earlier observations to a wider range of 3,3-disubstituted indolenines were only partially successful; 3-methyl-3-*p*-nitrobenzyl- and 3-methyl-3-prop-2-ynyl-indolenine (**4e** and **i**) were prepared *via* the Grignard derivative of 3-methylindole but in rather low yield. An attempt to prepare 3-*p*-methoxybenzyl-3-methylindolenine (**4h**) in the same manner afforded 2-*p*-methoxybenzyl-3-methylindole (**5h**) in good yield together with a small amount of 2-*p*-methoxybenzoyl-3-methylindole (**5j**); the latter was presumably formed by autoxidation of the *p*-methoxybenzyl derivative. Attempts were also made to prepare 3-methyl-3-*p*-methylbenzylindolenine (**4g**) in the same manner but the products were entirely indolic (as shown by their u.v. spectra) and although we were unable to purify them satisfactorily by chromatography, the mass and n.m.r. spectra of the main fraction corresponded to a product assumed to be 3-methyl-2-*p*-methylbenzylindole (**5g**) (by analogy with the *p*-methoxybenzyl analogue). We interpreted our inability to prepare the 3-*p*-methoxybenzyl and -3-*p*-methylbenzyl derivatives (**4h** and **g**) to the relatively high migratory aptitudes of both the *p*-methoxy- and *p*-methylbenzyl groups, and this accords with our earlier observations of the benzylation of indoles.[6] Attempts to prepare 3-*p*-cyanobenzyl-3-methylindolenine (**4k**) were completely unsuccessful and the only product was a polymeric tar.



(6) OTos = toluene-*p*-sulphonate



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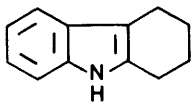

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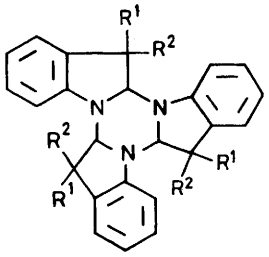

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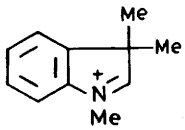

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The n.m.r. spectra of several of the indolenine free bases showed that they were equilibrium mixtures[7] of monomer (**4**) and cyclic trimer (**9**) in deuteriochloroform, although those with more bulky substituents (isopropyl and benzyl) existed entirely in the monomeric form at the normal n.m.r. probe temperature. However, studies of the monomer–trimer equilibrium and of the effects of acid (to be described in detail elsewhere) showed that on addition of a relatively large excess of acid the trimer and monomer were both quantitatively, and virtually instantaneously, converted into the corresponding indolenine monomer salts. This was confirmed both by n.m.r. studies, and by their u.v. spectra which corresponded closely with those of 1,3,3-trimethylindolenine salts[8] (**10**) ($\lambda_{max.}$ 229, 235, and 275 nm).

Isopropyl alcohol was selected as the solvent to study the kinetics of the rearrangements of the indolenines since 3,3-dimethylindolenine only rearranged very slowly in ethanol containing hydrochloric acid at 25 °C. Sealed tubes were used at the higher temperatures (80—100 °C) needed to study the reaction (to minimise autoxidation of the product).

Full details of the kinetic studies are given in the Experimental section but, with the exception of 3,3-dimethylindolenine, standard solutions of all the indolenines were diluted to a known and suitable concentration for u.v. studies and thermostatted at the appropriate temperatures in a quartz u.v. cell. Upon addition of a small amount of concentrated hydrochloric acid to the cell (*ca.* 1 000 mol. equiv.) the indolenine was converted immediately into the monomer salt, and the rearrangement of the latter to the corresponding 2,3-disubstituted indole was followed by measuring the intensity of the new u.v. maximum which developed at 223—226 nm. All the reactions showed good first-order behaviour over three or four

Table 1. Pseudo-first-order rate constants for the rearrangements of 3,3-disubstituted indolenines to 2,3-disubstituted indoles in isopropyl alcohol–hydrochloric acid at various temperatures

Indolenine	Method	Temp. (°C)	10^5 k/s^{-1}
3,3-Dimethyl	(*c*)	87	30
		100	320
3-Ethyl-3-methyl	(*a*)	41.5	0.31
		46.0	0.82
		51.3	1.53
		58.9	2.28
		64.4	5.06
		69.1	6.93
3-Isopropyl-3-methyl	(*a*)	35.8	1.75
		41.4	2.67
		47.1	6.73
		53.4	14.7
		58.9	24.3
3-Allyl-3-methyl	(*a*). (*b*)	24.6	1.57
		29.0	2.65
		30.1	2.81
		35.3	5.19
		40.6	9.90
		46.4	19.6
		52.2	33.2
		56.9	68.2
		62.1	110
		65.6	142
3-*p*-Nitrobenzyl-3-methyl	(*a*)	48.5	11.6
		53.1	17.7
		57.6	30.2
		61.5	40.6
3-Benzyl-3-methyl	(*a*)	22.4	4.2
		30.4	12
		35.8	24
		46.5	80
		50.4	108
Spirocyclopentan-3′-yl	(*a*)	20.0	20.6
		26.0	40.3
		30.0	75.6
		34.9	101
		38.9	179
		44.5	292

Table 2. Relative rates, activation energies, and entropies of rearrangement of 3,3-disubstituted indolenines to 2,3-disubstituted indoles *

Indolenine	Rel. rates †	ΔE_A/ kcal mol^{-1}	ΔS/ cal mol^{-1} K^{-1}
3,3-Dimethyl	1	33 ‡	−12 ‡
3-Ethyl-3-methyl	14	23.7 ± 2.0	−10 ± 0.8
3-Isopropyl-3-methyl	120	23.5 ± 1.4	−6.3 ± 0.4
3-Allyl-3-methyl	400	22.6 ± 0.4	−6.9 ± 0.1
3-Benzyl-3-methyl	1 520	22.2 ± 0.5	−5.4 ± 0.1
Spirocyclopentan-3′-yl	7 400	20.0 ± 0.9	−9.1 ± 0.3
3-*p*-Nitrobenzyl-3-methyl	188	21.1 ± 1.0	−12.9 ± 0.6

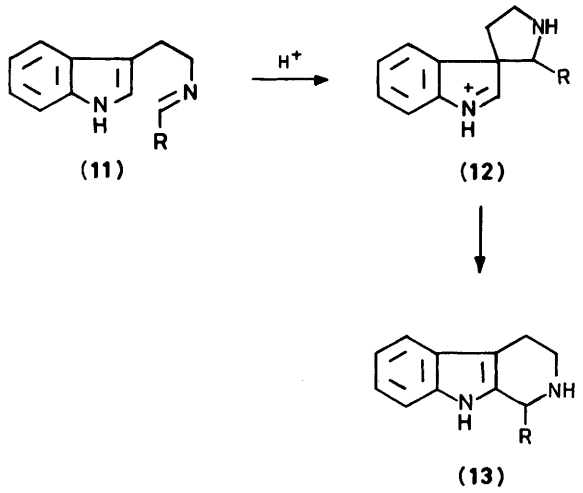
* Slopes and intercepts were obtained using least-squares regression analysis; errors were obtained from the programme and are given as one standard deviation. † Extrapolated to 46.5 °C. ‡ Estimated values (based on data at 100 and 87 °C).

half-lives, with the exception of the 3-ethyl-3-methylindolenine (**4b**). The latter only showed good first-order behaviour over the first 75% of the reaction (*i.e.* the first two half-lives) in the lower temperature runs and the observed optical densities tended to fall off towards the end of the longer reaction times giving infinity values some 10—20% lower than the theoretical. This was not a significant problem in any other case and it was attributed to side reactions such as autoxidation and polymerisation to which indoles are rather prone.[9]

Arrhenius plots of the first-order rate constants gave straight lines, and the energies and entropies of activation were calculated (see Table 2). There was an essentially inverse relationship between the relative migratory aptitudes (extrapolated to an arbitrary temperature of 46.5 °C) and the energies of activation, corresponding as expected to the ability of the migrating substituent to supply electronic charge to stabilise the carbonium ion-type transition state. The entropy of activation is negative in all cases, as is consistent with a transition state more ordered than the ground state. The entropy values also become less negative as the activation energies decrease and so the absolute rates of the reactions do not change quite as much as might have been expected from considerations of the activation energies alone. This is often observed in a related series of reactions and provides good evidence that the mechanisms are essentially similar.[10] The entropy factor for the spiro[cyclopentane-3′-indolenine] is, however, more closely comparable with that for 3-ethyl-3-methylindolenine; 3-*p*-nitrobenzyl-3-methylindolenine also has a rather higher entropy factor and so the rate of rearrangement is slower than might have been anticipated in terms of the activation energy.

We had originally also intended to study the rearrangement of a series of 3-(*para*-substituted)benzyl-3-methylindolenines, but this was frustrated by the low yields in the two successful preparations of 3-benzyl- and 3-*p*-nitrobenzyl-3-methylindolenine, and by the formation of the 2-*p*-methoxybenzyl- and 3-methyl-2-*p*-methylbenzylindole described above. An earlier attempt to prepare 3-benzyl-3-*p*-methoxybenzylindolenine had also led directly to 3-benzyl-2-*p*-methoxybenzylindole,[6] and thus it seemed clear that rearrangement was taking place during the reaction of the Grignard reagent. (Similar results were obtained even if the work-up was carried out entirely under neutral or basic conditions.) Our earlier studies had shown that alkylation of the Grignard derivative of 3-methylindole with but-2-enyl or dimethylallyl halides also gave the 2,3-disubstituted indole directly, although allylation afforded a mixture of the 3-allyl-3-methylindolenine and 2-allyl-3-methylindole.[2]

The kinetic data obtained in the rearrangements of *p*-nitrobenzyl- and benzyl-3-methylindolenine (**4e** and **f**) (and the failure to isolate the corresponding 3-*p*-methylbenzyl- and 3-*p*-methoxybenzyl-3-methylindolenines) are qualitatively in accord with expectations based on known relative migratory aptitudes of *para*-substituted aryl groups *e.g.* in pinacol–pinacolone rearrangements of tetra-aryl glycols. Bachmann *et al.*[11] found that there was a correlation between the electron-releasing capacity of the substituent and the ease of migration.



The relatively rapid rate of rearrangement of the spirocyclic indolenine (**7**) to tetrahydrocarbazole (**8**) compared with that of the other simple alkyl-substituted indolenines is of considerable interest, and presumably reflects the relief of steric effects which occurs on going through the transition state to the product. Our very early studies[12] in this field showed that the analogous intermediate (**12**; R = Ph) presumably formed in the cyclisation of *N*-benzylidenetryptamines (**11**; R = Ph) rearranged even more rapidly; in this case the migrating carbon is not only benzylic but is also attached to nitrogen, both of which features enhance the migratory aptitude. These results are also relevant to the more general case of the cyclisation of alkylidenetryptamines (**11**) to give tetrahydro-β-carbolines (**13**) which is of both synthetic and biosynthetic significance; the intermediate spirocyclic indolium salts (**12**) cannot be observed directly in the course of these cyclisations, and our work provides further circumstantial evidence that such intermediates probably rearrange much more rapidly than they are formed. Indirect evidence for their formation has however been obtained in cyclisations carried out under reductive conditions, the intermediate indolenines being reduced to indolines before rearrangement can occur.[6,13]

Intermediate indolenines have also been trapped by intramolecular cyclisation by appropriate nucleophiles in synthetic approaches to indole alkaloids.[14–16]

The rearrangement of 3,3-dialkylindolenines to 2,3-disubstituted indoles may provide a more satisfactory method of comparing migratory aptitudes of alkyl groups than the pinacol–pinacolone-type rearrangements previously studied;[4,11] rearrangement of the indolenines can only occur in one sense whereas in the pinacol case there are two alternative possibilities for formation of the initial carbonium ion.

Experimental

M.p.s were measured on a hot-stage and are uncorrected; u.v., n.m.r., and mass spectra were determined with Unicam SP800, Varian HA-100, and AEI MS902 spectrometers, respectively.

Preparation of Indolenines.—3,3-*Dimethylindolenine* (**4a**). To magnesium turnings (1.2 g, 0.05 mol) in dry ether (30 ml) excess of methyl iodide (10.8 g, 0.075 mol) was added slowly. When all the magnesium had reacted, dry benzene (30 ml) was added and the ether and excess of methyl iodide were distilled out. 3-Methylindole (6.6 g, 0.05 mol) in benzene (20 ml) was then added slowly and the resulting yellow solution was boiled under reflux for 15 min. Methyl iodide (8.6 g, 0.06 mol) in benzene (50 ml) was added and the mixture was heated gently under reflux for 2 h. The golden brown solution was then poured into hydrochloric acid (2M; 50 ml) to decompose the complex.

The acidic layer was then separated, and traces of neutral products were extracted with ether (30 ml). After basification with sodium hydroxide (2M), the product was isolated by ether extraction (3 × 50 ml) and dried ($MgSO_4$). On evaporating to dryness a yellow oil was obtained, which slowly crystallised from absolute alcohol (2 days) and gave 3,3-dimethylindolenine (**4a**) (31 g, 43%) as needles, m.p. 217—220 °C (lit.,[3] 224 °C). (Found: C, 82.55; H, 7.5; N, 9.6. Calc. for $C_{10}H_{11}N$: C, 82.8; H, 7.6; N, 9.7%). 3-Ethyl-3-methylindolenine (**4b**) (20%), m.p. 162—165 °C (lit.,[3] 163 °C), 3-isopropyl-3-methylindolenine (**4c**) (17%), m.p. 73—75 °C (lit.,[3] 75 °C), 3-allyl-3-methylindolenine (**4d**) (22%), m.p. 135—141 °C (lit.,[5] 144 °C), and 3-benzyl-3-methylindolenine (**4f**) (4%), m.p. 60—62 °C (lit.,[3] m.p. 61 °C) were all prepared in a similar manner to 3,3-dimethylindolenine.

3-p-*Nitrobenzyl*-3-*methylindolenine* (**4e**) was prepared in the same way as the foregoing compounds except that the reaction mixture was kept at 0 °C for 15 min. After work-up in the usual way the *indolenine* (**4e**) (0.5 g, 5%) was obtained as tiny pale yellow prisms, m.p. 142—145 °C (Found: C, 64.3; H, 4.55; N, 9.3. $C_{16}H_{14}N_2O_2$ requires C, 64.4; H, 4.7; N, 9.4%); $\delta_H(CDCl_3)$ 1.36 (s, Me), 3.0 (s, CH_2), 7.0—8.0 (8H), and 8.1 (s, 2-H); *m/z* (%) 266 (49), 151 (21), 150 (19), 144 (15), 131 (20), and 130 (100); $\lambda_{max.}$ (log $\varepsilon_{max.}$) (95% EtOH) 257 (3.90) nm.

Attempted preparation of 3-p-*methoxybenzyl*-3-*methylindolenine* (**4h**). This reaction was carried out in the same manner and using the same relative molar concentrations as the foregoing experiments but the mixture was stirred at 0 °C for 15 min. After work-up using Rochelle salt (instead of acid) and subsequent extraction, the crude product was shown by t.l.c. to consist of three components. Column chromatography of the crude product on silica in benzene gave three products, (i) unchanged 3-methylindole, (ii) (0.5 g) which was identified from its u.v. and i.r. spectra and comparisons with the authentic material 2-p-*methoxybenzyl*-3-*methylindole* (**5h**) (9.3 g, 74%) (Found: C, 80.3; H, 6.1; N, 5.2. $C_{17}H_{17}NO$ requires: C, 81.3; H, 6.8; N, 5.6%); $\delta_H(CDCl_3)$ 3.72 (s, OMe), 4.1 (s, 2-CH_2), and 6.8—7.8 (m, ArH); *m/z* (%) 251 (52), 250 (20), 236 (36), 163 (38), 135 (94), and 120 (100), (iii) 2-p-*methoxybenzoyl*-3-*methylindole* (**5j**) (1.1 g, 8%) (Found: C, 77.0; H, 5.7; N, 5.3. $C_{17}H_{15}NO_2$ requires C, 76.8; H, 5.8; N, 5.0%); $\nu_{max.}(CCl_4)$ 3 345s (NH) and 1 620s cm^{-1} (C=O); *m/z* (%) 265 (10), 264 (8), 236 (27), 163 (30), and 135 (100). The latter product presumably arises by oxidation of the 2-*p*-methoxybenzyl-3-methylindole (**5h**).

The reaction was repeated twice, once with acid work-up, but none of the required indolenine was obtained.

Attempts to prepare 3-*p*-methylbenzyl-3-methylindolenine were unsuccessful but the presence of 2-*p*-methylbenzyl-3-methylindole was inferred from the u.v. and mass spectra of the chromatographed product (benzene–silica).

3-*Methyl*-3-(*prop*-2-*ynyl*)*indolenine* (**4i**). In a similar manner alkylation of 3-methylindole (6.6 g) with 3-bromoprop-1-yne gave 3-*methyl*-3-(*prop*-2-*ynyl*)*indolenine* (1.4 g, 17%) as microcrystals from ethanol (Found: C, 85.0; H, 6.4; N, 8.2. $C_{12}H_{11}N$ requires C, 85.2; H, 6.5; N, 8.3%); $\delta_H(CDCl_3)$ 4.26, 4.36, and 5.19 (trimer) (2-H), 6.8—7.6 (m, ArH), and 7.95 (monomer) (2-H); *m/z* (%) 169 (48), 168 (46), 154 (43), 149 (23), and 130 (100); $\lambda_{max.}$ (log ε) (95% EtOH) 258 (3.86) nm.

Spiro[*cyclopentane*-3′-*indolenine*] (**7**).—4-(Indol-3-yl)butyl toluene-*p*-sulphonate (0.35 g) was dissolved in dry tetrahydrofuran (120 ml) and treated with powdered solid potassium t-butoxide (0.50 g). After a short time the solution turned pale yellow, and was then warmed for 2.5 min, when t.l.c. showed that none of the tosylate remained. The mixture was evaporated to *ca.* 25 ml, poured into water, and extracted with chloroform (to remove t-butyl alcohol). The solution was then dried ($MgSO_4$) and evaporated to give a red oil (0.20 g). Preparative t.l.c. (silica–benzene) was then carried out to separate the slower moving of the two components present. This second band was scraped off and eluted with chloroform to give a yellow gum (0.08 g) which crystallised from light petroleum (b.p. 60—80 °C) as prisms, m.p. 145—146 °C (lit.,[5] 146—147 °C) (Found: C, 84.2; H, 7.6; N, 8.1. Calc. for $C_{12}H_{13}N$: C, 84.2; H, 7.6; N, 8.2%).

Kinetics of Indolenine Rearrangements.—Samples of each indolenine were recrystallised twice from ethanol, and shown to be free of indole impurities by t.l.c. and by the absence of the characteristic indole absorption *ca.* 225 nm in the u.v. spectra. The recrystallised samples were dried under reduced pressure at 25 °C for 1 day.

Procedures. (*a*) Standard solutions (*ca.* 4×10^{-3}M) of each of the indolenines were prepared in isopropyl alcohol (spectroscopic grade), and after dilution (× 20) were used for the kinetic experiments. The diluted isopropyl alcohol solution (2.5 ml) of each indolenine was pipetted into a quartz u.v. cell (1 cm path length) and thermostatted at the appropriate temperature for 30 min. Concentrated hydrochloric acid (50 μl) was then added with a microsyringe, and nitrogen bubbled through the solution for 30 s to achieve rapid mixing. The formation of the 2,3-disubstituted indoles was followed by measuring the increase in absorption at 225 nm over 30—60 min (*ca.* half-lives in each case). First-order rate constants for each compound were determined at a range of temperatures using the standard rate equation $\log (D_\infty - D_t) = kt + c$. Satisfactory infinity values for the optical densities could not be obtained in the kinetic runs owing to autoxidation of the indoles formed; theoretical values were therefore used, based on the previously determined extinction coefficients for the 2,3-disubstituted indoles produced. This procedure was used for all the indolenines except 3,3-dimethylindolenine.

Each experiment was run in duplicate, and the rates obtained were shown to be reproducible to ±2—3% as shown by least-squares regression analysis. The errors in the Arrhenius plots were calculated in a similar fashion and shown to be ±3% on the slopes ($\log k$ *versus* $1/T$) and ±5% on the intercepts (from which the entropy values were calculated). The results are shown in Tables 1 and 2.

(*b*) In the case of 3-allyl-3-methylindolenine we also demonstrated that the rearrangement was first order and independent of concentration over an eight-fold concentration range, using the modified technique outlined below. Standard solutions of concentrated hydrochloric acid in isopropyl alcohol and of the indolenine in isopropyl alcohol were thermostatted in two separate flasks. Appropriate portions of the two solutions were then transferred quickly to a third flask and mixed rapidly; the mixture was then transferred to a quartz u.v. cell, and the formation of 2-allyl-3-methylindole was followed by measuring the optical density at 225 nm. The reaction was followed to *ca.* 90% completion and first-order rate constants were determined as previously. The concentration of acid in each experiment was 1.37×10^{-2}M and the concentration and rates of formation of indole were as shown in Table 3.

(*c*) The rearrangement of 3,3-dimethylindolenine was studied as follows. A standard solution (50 ml) of the indolenine (2×10^{-4}M) in isopropyl alcohol containing hydrochloric acid

Table 3.

10^5 [3-Allyl-3-methylindolenine]/ mol l^{-1}	First-order rate constant for rearrangement 10^5 k/s^{-1} at 29 °C
1.72	2.67
3.45	2.64
6.89	2.69
13.8	2.61

was prepared and portions (10 ml) sealed in Pyrex tubes which were then suspended in a thermostatted oil-bath for timed intervals up to 1 h. Each tube was removed from the thermostat at a known time, cooled rapidly in ice, and washed and wiped clean externally before being opened. The optical density at 225 nm was then measured (at 30 °C). The results obtained for a series of runs at 87 °C and 100 °C are given in Table 1. The reproducibility was not as good as the studies of the rearrangements of the other indolenines and as measurements were only made at two temperatures the values given in Table 2 for the thermodynamic parameters can only be regarded as approximate.

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