Conversion of 2-Chloroallylamines into Heterocyclic Compounds. Part I. 2-Methylindoles, 1,5,6,7-Tetrahydro-3-methylindol-4-ones, and Related Heterocycles

By **Brian G. McDonald** and **George R. Proctor,*** Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL

Heating several *N*-(2-chloroallyl)anilines with polyphosphoric acid at 100 °C or with boron trifluoride–methanol at at 150 °C gave 2-methylindoles. 2-Methyloxazolo[3,2-*a*]quinolin-5-one, imidazo[1,2-*a*]pyridine, and 2-methylpyrrolo[3,2-*c*]quinolines were similarly obtained from *N*-(2-chloroallyl)-4-hydroxyquinolin-2-one, 2-(2-chloroallylamino)pyridine and 4-[*N*-(2-chloroallyl)-ethylamino]- and -anilino]-quinolines, respectively. 1-Ethyl and 1-aryl-1,5,6,7-tetrahydro-3-methyl-6,6-dimethylindol-4-ones were obtained from the corresponding dimedone enamines on treatment with polyphosphoric acid. 3-Acetonyl-2,4,6-trimethylaniline was obtained in excellent yield from *N*-(2-chloroallyl)-2,4,6-trimethylaniline.

TREATMENT of *N*-(2-halogenoallyl)anilines with Lewis acids gives 2-methylindoles.[1-4] The conditions used vary in severity from anhydrous hydrogen fluoride [1] under pressure at 160 °C to boron fluoride–methanol [3] at 150 °C. Polyphosphoric acid at 175—180 °C has also been recommended.[2] We became interested in this process accidentally,[4] discovering that some *N*-(2-chloroallyl)anilines gave 2-methylindoles when heated at *ca.* 100 °C with an excess of polyphosphoric acid. We now report briefly our results with simple indoles and the extension of this process to some more complex examples.

The *N*-(2-halogenoallyl) derivatives of aniline, *N*-methylaniline, *m*-anisidine, *p*-anisidine, *p*-chloroaniline, 2-aminobiphenyl, and methyl 3-anilinopropionate all gave the corresponding 2-methylindoles after being heated and stirred with polyphosphoric acid at 95—105 °C. The yields are no improvement on those previously reported, but in the case of *m*-anisidine a separable mixture (25%) of 4- and 6-methoxy-2-methylindoles was obtained; at higher temperatures the products decomposed. 5-Methoxy-2-methylindole was never obtained completely free from starting material (longer reaction times led to decomposition) and the BF_3–MeOH reagent is therefore preferable.[3] The product (I) from ethyl 3-[*N*-(2-chloroallyl)anilino]propionate could not be further cyclised [to (II)], although treatment of the amino-acid (III) gave the azepinoindole

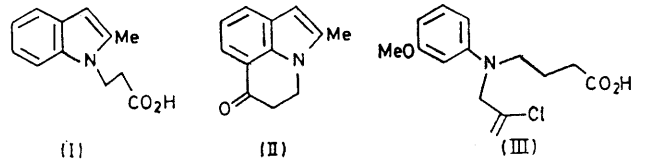
[1] E. B. Towne and H. M. Hill, U.S.P. 2,607,779/1952 (*Chem. Abs.*, 1953, **47**, 5452).

[2] Yu. A. Degutis and V. P. Barkauskas, *Khim. geterotsikl. Soedinenii*, 1969, **5**, 1003.

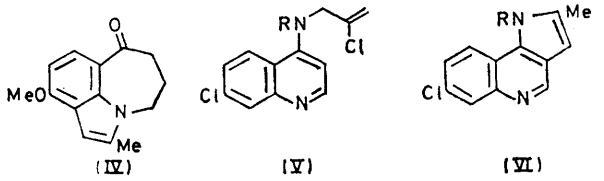
[3] C. George, E. W. Gill, and J. A. Hudson, *J. Chem. Soc.* (*C*), 1970, 74.

[4] B. McDonald, A. McLean, and G. R. Proctor, *J.C.S. Chem. Comm.*, 1973, 208.

(IV), albeit in low yield. There are precedents [5] for retro-Michael reactions in molecules such as (I); this side reaction, causing loss of the side chain, is not possible in compound (III).



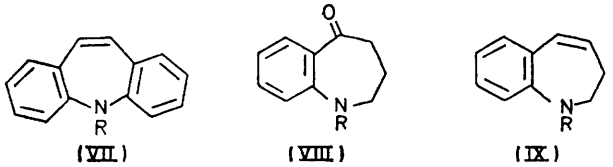
(I) (II) (III)



(IV) (V) (VI)

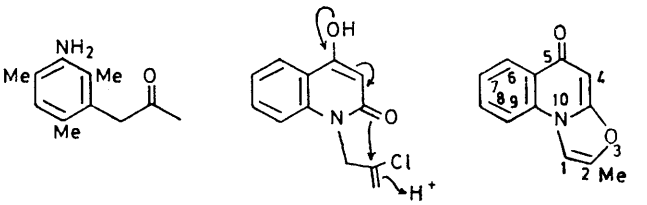
The yield (41%) of 2-methyl-7-phenylindole obtained with polyphosphoric acid is inferior to that (60%) obtained by using BF_3–MeOH and in both the cases of methyl anthranilate and ethyl *p*-aminobenzoate, polyphosphoric acid fails whereas the BF_3–MeOH treatment gives acceptable yields of the corresponding 7-methoxycarbonyl- and 5-methoxycarbonyl-2-methylindole, respectively. 2-Methyl-5-nitroindole could not be obtained by use of either reagent, although it was said [1] to be produced by using hydrogen fluoride under pressure.

The accessibility of the *N*-(2-chloroallyl) compounds from commercially available 2,3-dichloropropene and the simplicity of the cyclisation operations made it attractive to extend this work to more complex amines. Thus the quinolines (V; R = Et or Ph) gave the pyrroloquinolines (VI; R = Et or Ph) in moderate yields but the azepine derivatives [(VII)—(IX); R = 2-chloroallyl] gave no cyclisation products.



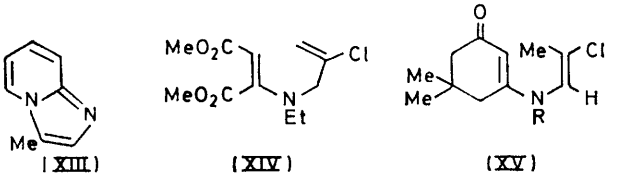
(VII) (VIII) (IX)

N-(2-Chloroallyl)-2,4,6-trimethylaniline was converted in very high yield into 3-acetonyl-2,4,6-trimethylaniline (X) on heating with polyphosphoric acid. This rearrangement [4] was unexpected but the product is potentially useful for the synthesis of bridged-ring compounds. Although *N*-(2-chloroallyl)anthranilic acid reacted in BF_3–MeOH to give, not a lactone, but the corresponding indole (as methyl ester) in 75% yield; the product from the quinolone (XI) proved to be the oxazoloquinolone (XII). Presumably the mechanism is as shown and this suggests several other heterocyclic synthetic possibilities; for example the chloroallyl



(X) (XI) (XII)

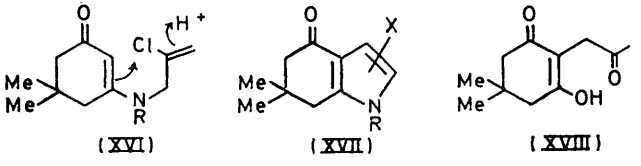
group acts also as an *electrophile* in the case of 2-(2-chloroallylamino)pyridine, which reacts with polyphosphoric acid yielding 3-methylimidazo[1,2-*a*]pyridine (XIII). This mode of reaction is common in alkenes [6]



(XIII) (XIV) (XV)

and is the converse of the principle developed by Lansbury [7,8] whereby an electrophilic centre attacks a chloroallyl group in the same molecule leading to a cyclisation.

1,5,6,7-Tetrahydroindol-4-ones, which have been made by electrophilic cyclisation of enamines of cyclohexane-1,3-diones [9] and by other methods,[10] are useful precursors of 4-substituted indoles.[11] It was of interest to find out whether *N*-(2-chloroallyl)enamines (XVI) underwent cyclisation to 1,5,6,7-tetrahydroindol-4-ones and, if so, whether they gave the 2- or the 3-methyl isomers. In the event, the *N*-ethyl compound (XVI;



(XVI) (XVII) (XVIII)

R = Et), when heated with polyphosphoric acid, gave a substance, $C_{13}H_{19}NO$, which was deduced from spectral data (see Experimental section) to be the 3-methyl isomer (XVII; R = Et, X = 3-Me) and differed from the 2-methyl isomer (XVII; R = Et, X = 2-Me), made by a literature method [12] [from (XVIII)]. Thus in this case, the mechanism of cyclisation involves the chloroallyl group acting as an electrophile as shown (XVI), and this method complements those already reported.[9–12]

We next examined the case (XVI; R = Ph) where the starting material was both an enamine and an arylamine, to find out whether a 1,5,6,7-tetrahydroindol-4-one or an *N*-substituted indole was obtained.

[5] J. A. C. Allison, J. T. Braunholtz, and F. G. Mann, *J. Chem. Soc.*, 1954, 403.
[6] M. F. Ansell and M. H. Palmer, *Quart. Rev.*, 1964, 211.
[7] P. T. Lansbury and E. J. Nienhouse, *J. Amer. Chem. Soc.*, 1966, **88**, 4290.
[8] P. T. Lansbury, *Accounts Chem. Res.*, 1972, **5**, 311.
[9] J. M. Bobbitt and C. P. Dutta, *Chem. Comm.*, 1968, 1429.
[10] H. Stetter and R. Lauterbach, *Annalen*, 1962, **655**, 20.
[11] W. A. Remers, R. H. Roth, G. J. Gibbs, and M. J. Weiss, *J. Org. Chem.*, 1971, **36**, 1232.
[12] H. J. Schaeffer and R. Vince, *J. Org. Chem.*, 1962, **27**, 4503.

The former was in fact produced (XVII; R = Ph, X = 3-Me) and shown to be different from the 2-methyl isomer made by the reaction of aniline with 2-acetonyl-5,5-dimethylcyclohexane-1,3-dione [12] (XVIII). The *p*-chlorophenyl compound (XVII; R = *p*-ClC_6H_4, X = 3-Me) was also made. Probably the reduced basicity of the nitrogen atom in (XVI) inhibits cyclisation (with rearrangement) onto the benzene ring; in these cases there is no question of an aza-Claisen rearrangement [13] taking place since the 2-isomer was never found. Similar results were obtained by using BF_3–MeOH but neither polyphosphoric acid nor BF_3–MeOH caused compound (XIV) to cyclise to a pyrrole.

None of our results allow a decision to be made amongst the various mechanisms possible for the conversion of *N*-(2-chloroallyl)anilines to 2-methylindoles,[2-4] but we confirm that this is a versatile and convenient method.

EXPERIMENTAL

2-Methylindoles: General Methods (see Table).—(*A*) The *N*-(2-chloroallyl)arylamine (5 g) was stirred and heated at *ca.* 100 °C for the time shown. The cooled mixture was poured into ice (excess) and extracted with chloroform. The products were purified in the usual way by chromatography on silica gel unless stated otherwise.

Conversion of 2-chloroallylanilines into 2-methylindoles

2-Methylindole	Method	Temp. (°C)	Time (h)	M.p. (°C)	Yield (%)
Parent [a,b]	A	105	54	56—58	39
1-Me [c]	A	110	33	54—55	74
4-Me [c]	A	100	12	98 [d]	5
6-Me [e]	A	100	12	102	20
5-Me [a]	A	100—110	9		25 [f]
7-Ph [g]	A	105	23	103—104	41
7-Ph [g]	B	134—138	14	103—104	60
5-Cl [h]	A	100—105	24	115—116	50
5-MeO_2C [i]	B	149—152	9	139	51
7-MeO_2C [j]	B	152	7	(b.p. 110 at 0.05 mmHg)	75
1-MeO_2C·$[CH_2]_2$ [k]	A	99—101	10	(b.p. 110 at 0.01 mmHg)	33

[a] Ref. 2. [b] Identical with commercial sample. [c] Found: C, 74.2; H, 6.9; N, 8.3. $C_{10}H_{11}NO$ requires C, 74.6; H, 6.9; N, 8.7%, τ 2.25br (1H, s, NH), 2.9—3.6 (3H, m, aryl), 3.72 (1H, s. 3-H), 6.1 (3H, s, OMe), and 7.65 (3H, s, Me). [d] From light petroleum (b.p. 60—80°). [e] T. Wieland and K. Ruehl, *Chem. Ber.*, 1963, **96**, 260; R. A. Heacock and O. Hutzinger, *J. Chem. Soc.*, 1965, 3902. [f] Contaminated with starting material. [g] A. N. Kost, I. P. Rudakova, and A. P. Yakubov, *Zhur. org. Khim.*, 1965, **1**, 124 (*Chem. Abs.*, 62, 14,610h). [h] Ref. 3. [i] Found: C, 69.95; H, 6.0; N, 7.1. $C_{11}H_{11}NO_2$ requires C, 69.85; H, 5.8; N, 7.4%, τ 1.78—2.84 (4H, m, aromatic and NH), 3.75 (1H, s), 6.12 (3H, s, CO_2Me), and 7.62 (3H, s, CH_3); sublimed *in vacuo*. [j] Found M^+, 189.0795. $C_{11}H_{11}NO_2$ requires *M*, 189.0790. Hydrolysis yielded the corresponding *acid*, m.p. 183—184° [from benzene–light petroleum (b.p. 40—60°)] (Found: C, 69.0; H, 5.3; N, 7.9. $C_{10}H_9NO_2$ requires C, 68.6; H, 5.15; N, 8.0%), τ −0.8br (1H, s, exch., CO_2H), 0.5br (1H, s, exch., NH), 2.07—3.0 (3H, m, aryl), 3.74 (1H, s, 3-H), and 7.52 (3H, s, CH_3). [k] Obtained as acid and re-esterified (Found: C, 72.0; H, 7.1; N, 6.65. $C_{13}H_{15}NO_2$ requires C, 71.9; H, 6.9; N, 6.45%), τ 2.4—3.03 (4H, m, aryl), 3.80 (1H, s, 3-H), 5.67 (2H, t, CH_2), 6.38 (3H, s, CO_2Me), 7.32 (2H, t, CH_2), and 7.6 (3H, s, Me).

(*B*) The *N*-(2-chloroallyl)arylamine (3—5 g) and boron trifluoride–methanol complex (Aldrich) (50 ml) were stirred and heated for the time and at the temperature shown. After cooling, the mixture was poured into cold water and extracted with chloroform, and the product was obtained as before.

N-(*2-Chloroallyl*)*anilines*.—These were in general made by heating and stirring the corresponding anilines with 2,3-dichloro- or 2-chloro-3-iodopropene [14] and anhydrous potassium carbonate and distilling the products *in vacuo*. Many were unstable; some gave satisfactory elemental analyses and all were used as obtained provided that n.m.r. analysis indicated no gross impurities.

N-(*2-Chloroallyl*)*dibenz*[b,f]*azepine* (VII; R = CH_2·CCl·CH_2).—The *dibenzazepine* crystallised from methanol as flakes, m.p. 80—81° (Found: C, 76.45; H, 5.25; N, 5.1. $C_{17}H_{14}ClN$ requires C, 76.3; H, 5.25; N, 5.25%). Compounds (VIII) and (IX) were obtained as previously described.[15]

4-[N-(*2-Chloroallyl*)-m-*methoxyanilino*]*butyric Acid*.—*N*-(2-Chloroallyl)-*m*-anisidine (b.p. 102° at 0.5 mmHg; 34.3 g) was stirred with ethyl 4-bromobutyrate (38 g) and anhydrous potassium carbonate (20 g) at 100 °C for 3 days. Ethyl 4-bromobutyrate (30 g) and potassium carbonate (24 g) were then added and heating and stirring were continued for a further 3 days. Treatment of the crude ester with sodium hydroxide in ethanol gave the *sodium salt* of the product, m.p. 70° (from acetone) (Found: C, 54.8; H, 5.6; N, 5.0. $C_{14}H_{17}ClNNaO_3$ requires C, 55.05; H, 5.6; N, 4.6%), τ (D_2O) 2.8—3.0 (1H, m, aryl), 3.6—3.8 (3H, m, aryl), 4.8 (2H, dd, vinyl), 6.0 (2H, s, CH_2), 6.3 (3H, s, OMe), 6.6—7.82 (2H, m, CH_2), 7.7—7.9 (2H, m, CH_2), and 8.05—8.35 (2H, m, CH_2). Addition of dilute hydrochloric acid gave the *acid* (39 g), b.p. 175° at 0.05 mmHg (Found: C, 60.0; H, 6.4. $C_{14}H_{18}ClNO_3$ requires C, 59.4; H, 6.4%), which slowly darkened.

This acid (5.6 g) was stirred at 110 °C for 9 h. Chromatography then gave 5,6-*dihydro*-2-*methyl*-10-*methoxyazepino*-[3,2,1-hi]*indol*-7(4H)-*one* (IV) (620 mg), which crystallised from light petroleum (b.p. 80—100°) in yellow needles, m.p. 145—146° (Found: C, 73.3; H, 6.7; N, 6.1%; M^+, 229.11064. $C_{14}H_{15}NO_2$ requires C, 73.4; H, 6.6; N, 6.1%; *M*, 229.11027), τ 2.05 (1H, d, 8-H), 3.5 (1H, d, 9-H), 3.62 (1H, s, 1-H), 5.95 (2H, m, 6-H), 6.1 (3H, s, OMe), 7.02 (2H, m, 4-H), 7.67 (3H, s, Me), and 7.6—7.9 (2H, m, 5-H), $\nu_{max.}$ ($CHCl_3$) 1 645 cm^{-1} (C=O).

7-*Chloro*-4-[N-(*2-chloroallyl*)*ethylamino*]*quinoline* (V; R = Et).—4,7-Dichloroquinoline (6.89 g) and *N*-(2-chloroallyl)ethylamine [16] (12 g) were stirred and kept at 160 °C for 5 h. Work-up as usual followed by chromatography on silica (elution with ether) gave the *product* as a syrup (6.67 g, 68%) (Found: C, 59.7; H, 5.05; N, 9.8. $C_{14}H_{14}Cl_2N_2$ requires C, 59.8; H, 5.0; N, 9.95%); τ 1.35 (1H, d, aryl), 1.95 (1H, s, aryl), 2.0 (1H, d, aryl), 2.62 (1H, d, aryl), 3.17 (1H, d, aryl), 4.4—4.6 (2H, m, vinyl), 5.97 (2H, s, N·CH_2), 6.6 (2H, q, CH_2), and 8.82 (3H, t, CH_3).

7-*Chloro*-1-*ethyl*-2-*methylpyrrolo*[3,2-c]*quinoline* (VI; R = Et).—The preceding amine (1.23 g) and polyphosphoric acid were stirred at 90—94 °C for 5.5 h. Work-up gave the *product* (0.45 g, 42%) as needles, m.p. 107.5—109.5° (Found: C, 69.15; H, 5.45; N, 11.45. $C_{14}H_{13}ClN_2$ requires

[13] M. Schmid, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 105.

[14] I. McCall, G. R. Proctor, and L. Purdie, *J. Chem. Soc.* (*C*), 1970, 1126.

[15] M. Lennon, A. McLean, I. McWatt, and G. R. Proctor, *J.C.S. Perkin I*, 1974, 1828.

[16] A. G. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1957, **76**, 1462.

C, 68.7; H, 5.3; N, 11.45%), τ 1.02 (1H, s, 4-H), 1.86—2.75 (3H, m, aryl), 3.23 (1H, s, 3-H), 5.72 (2H, q, N·CH_2), 7.67 (3H, s, CH_3), and 8.57 (3H, t, CH_3). Neutralisation of the aqueous acidic layer, gave *7-chloro-4-ethylaminoquinoline* (0.22 g), m.p. 177—177.5° (Found: C, 63.8; H, 5.35; N, 13.3. $C_{11}H_{11}ClN_2$ requires C, 63.9; H, 5.35; N, 13.55%), τ 1.51 (1H, d), 2.08 (1H, s), 2.36 (1H, d), 2.81 (1H, d), 3.64 (1H, d), 4.75—5.05br (1H, s, exch., NH), 6.7 (2H, m, N·CH_2, q with D_2O added), and 8.65 (3H, t, CH_3).

7-Chloro-2-methyl-1-phenylpyrrolo[3,2-c]*quinoline* (VI; R = Ph).— 7-Chloro-4-[*N*-(2-chloroallyl)anilino]quinoline (2.6 g) was made by stirring 4,7-dichloroquinoline (7.67 g), *N*-(2-chloroallyl)aniline (14.6 g), and hydrochloric acid (40 ml; 2N) at 144 °C for 5.5 h. After chromatography this intermediate (2.09 g) was stirred with polyphosphoric acid (100 g) at 74—78 °C for 11 h. The *product* (0.56 g, 30%), m.p. 158—160°, crystallised from light petroleum (b.p. 60—80°) (Found: C, 74.2; H, 4.65; N, 9.3. $C_{18}H_{13}ClN_2$ requires C, 73.8; H, 4.45; N, 9.6%), τ 0.9 (1H, s, 4-H), 1.88 (1H, s, 6-H), 2.4—2.95 (7H, m, aryl), 3.07 (1H, s, 3-H), and 7.57 (3H, s, CH_3).

3-Acetonyl-2,4,6-trimethylaniline (X).—N-(2-*Chloroallyl*)-*2,4,6-trimethylaniline*, b.p. 92—95° at 0.5 mmHg (Found: M^+, 209.0903. $C_{12}H_{16}{}^{35}ClN$ requires *M*, 209.0971) (5.51 g), and polyphosphoric acid (120 g) were stirred at 104—108 °C for 18 h. The *product* (4.12 g, 96%) gave needles, m.p. 73—74° (Found: C, 75.0; H, 8.95; N, 7.35. $C_{12}H_{17}NO$ requires C, 75.4; H, 8.9; N, 7.3%), τ 3.28 (1H, s, aryl), 6.33 (2H, s, CH_2), 6.6br (2H, s, exch., NH_2), and 7.88, 7.92, 7.96, and 8.02 (12H, 4s, Me).

Methyl N-*Acetyl*-N-(*2-chloroallyl*)*anthranilate*.—This was made by treating methyl *N*-(2-chloroallyl)anthranilate [17] with acetic anhydride at 160 °C for 7 h, and crystallised in *needles*, m.p. 94—94.5° (Found: C, 58.7; H, 5.35; N, 5.0. $C_{13}H_{14}ClNO$ requires C, 58.3; H, 5.25; N, 5.25%).

N-(*2-Chloroallyl*)-*4-hydroxyquinolin-2-one* (XI).—Treatment of the preceding compound (27 g) with sodium hydride (25 g, 60%) in toluene (700 ml) gave the *product* (13 g, 54%) from ethanol as a yellow powder, m.p. 239° (Found: C, 60.95; H, 4.3; N, 6.1. $C_{12}H_{10}ClNO_2$ requires C, 61.15; H, 4.25; N, 5.95%).

2-Methyloxazolo[3,2-a]*quinolin-5-one* (XII).—*N*-(2-Chloroallyl)-4-hydroxyquinolin-2-one (1.45 g) and polyphosphoric acid (50 g) were stirred at 100—110 °C for 5 h. The *product* (1.1 g, 89%) crystallised from water in needles, m.p. 225° (Found: C, 72.25; H, 4.6; N, 7.0%; M^+, 199.0633. $C_{12}H_9NO_2$ requires C, 72.35; H, 4.5; N, 7.0%; *M*, 199.0633), τ 1.37 (1H, d, 6-H), 1.7—2.2 (4H, m, 4-, 7-, 8-, 9-H), 2.7 (1H, s, 1-H), and 7.31 (3H, s, CH_3).

2-(2-Chloroallylamino)pyridine.—2-Aminopyridine (23.7 g), dry dimethylformamide (200 ml) and sodium hydride (13 g, 50%) were stirred at 80 °C for 18 h. 2,3-Dichloropropene (28 g) was added; after 5 h stirring and heating, more 2,3-dichloropropene (11 g) was added and heating was continued for 10 h. The *product* (23.7 g, 67%) had b.p. 100—110° at 0.1 mmHg (Found: C, 56.7; H, 5.6; N, 16.2. $C_8H_9ClN_2$ requires C, 57.0; H, 5.35; N, 16.6%).

3-Methylimidazo[1,2-a]*pyridine* (XIII).—The previous compound (3.3 g) and polyphosphoric acid (100 g) were stirred at 95—100 °C for 7 h. The product (0.86 g, 39%) was purified by sublimation *in vacuo* and had m.p. 63.5° (lit.,[18] 63.5°) (Found: C, 72.7; H, 6.3; N, 20.85. Calc. for $C_8H_8N_2$: C, 72.75; H, 6.05; N, 21.2%), τ 2.24 and 2.46 (2H, 2d), 2.64 (1H, s), 2.92 and 3.26 (2H, 2t), and 7.62 (3H, s).

1-Ethyl-1,5,6,7-tetrahydro-3,6,6-trimethylindol-4-one (XVII; X = 3-Me, R = Et).—*N*-(2-Chloroallyl)-*N*-(5,5-dimethyl-3-oxocyclohex-1-enyl)ethylamine (XVI; R = Et) (2.83 g) [from dimedone and *N*-(2-chloroallyl)ethylamine] and polyphosphoric acid (100 g) were stirred at 102—105 °C for 22 h. Chromatography [elution with methylene chloride–diethyl ether (9 : 1)] gave the *product* (1.15 g, 48%), which crystallised from light petroleum (b.p. 60—80°) as plates, m.p. 73—74° (Found: C, 76.45; H, 9.45; N, 7.05%; M^+, 205.1467. $C_{13}H_{19}NO$ requires C, 76.1; H, 9.25; N, 6.85%; *M*, 205.1467), τ 3.68 (1H, s, 2-H), 6.25 (2H, q, CH_2), 7.46 (2H, s, CH_2), 7.73 (5H, s, CH_2 and Me), 8.68 (3H, t, Me), and 8.9 (6H, s, Me), $\nu_{max.}$ (Nujol) 1 645 cm^{-1} (C=O). Elution with diethyl ether–methanol (9 : 1) yielded N-(*2-chloroprop-1-enyl*)-N-(*5,5-dimethyl-3-oxocyclohex-1-enyl*)*ethylamine* (XV; R = Et) (0.69 g, 25%) as a gum (Found: C, 64.45; H, 8.55; N, 5.7. $C_{13}H_{20}ClNO$ requires C, 64.6; H, 8.3; N, 5.8%), τ 3.9 (1H, d, vinyl), 4.73 (1H, s, vinyl), 6.56 (2H, q, N·CH_2), 7.73 (2H, s, CH_2), 7.81 (5H, s, CH_2 and Me), 8.8 (3H, t, Me), and 8.9 (6H, s, Me), $\nu_{max.}$ (film) 1 623 cm^{-1} (C=O).

1-Ethyl-1,5,6,7-tetrahydro-2,6,6-trimethylindol-4-one (XVII; X = 2-Me, R = Et).—2-Acetonyl-5,5-dimethylcyclohexane-1,3-dione [12] (2.5 g), methanol (30 ml), and ethanolic ethylamine (10 ml, 33%) were kept at 160 °C for 15 h in a pressure bottle. The *product* (1.66 g, 63.5%) crystallised from benzene–light petroleum (b.p. 60—80°) as plates, m.p. 106—108° (Found: C, 76.3; H, 9.35; N, 6.7. $C_{13}H_{19}NO$ requires C, 76.1; H, 9.25; N, 6.8%); τ 3.83 (1H, s, 3-H), 6.24 (2H, q, CH_2), 7.45 (2H, s, CH_2), 7.74 (2H, s, CH_2), 7.81 (3H, s, Me), 8.77 (3H, t, Me), and 8.9 (6H, s, Me), $\nu_{max.}$ (Nujol) 1 638 cm^{-1} (C=O).

1,5,6,7-Tetrahydro-3,6,6-trimethyl-1-phenylindol-4-one (XVII; R = Ph, X = 3-Me).—*N*-(2-Chloroallyl)-*N*-(5,5-dimethyl-3-oxocyclohex-1-enyl)aniline (XVI; R = Ph) (2.67 g) [from dimedone and *N*-(2-chloroallyl)aniline] and polyphosphoric acid (90 g) were stirred at 100—104 °C for 22 h. The *product* (0.91 g, 39%), sublimed *in vacuo*, had m.p. 200—201° (Found: C, 80.35; H, 7.6; N, 5.45%; M^+, 253.1436. $C_{17}H_{19}NO$ requires C, 80.65; H, 7.5; N, 5.55%; *M*, 253.1467), τ 2.4—2.9 (5H, m, aryl), 3.43 (1H, s, 2-H), 7.4 (2H, s, CH_2), 7.63 (3H, s, Me), 7.82 (2H, s, CH_2), and 8.9 (6H, s, Me), $\nu_{max.}$ (Nujol) 1 648 cm^{-1} (C=O).

1-p-Chlorophenyl-1,5,6,7-tetrahydro-3,6,6-trimethylindol-4-one (XVII; R = *p*-ClC_6H_4, X = 3-Me).—This was made in similar fashion (30%) and had m.p. 142° (Found: C, 71.2; H, 6.3; N, 4.75. $C_{17}H_{18}ClNO$ requires C, 71.1; H, 6.3; N, 4.85%).

1,5,6,7-Tetrahydro-2,6,6-trimethyl-1-phenylindol-4-one (XVII; R = Ph, X = 2-Me).—2-Acetonyl-5,5-dimethylcyclohexane-1,3-dione [12] (3.7 g), aniline (2 g), and glacial acetic acid (50 ml) were refluxed for 0.75 h. The *product* (4.23 g, 88%) crystallised from ethanol in needles, m.p. 145—146° (Found: C, 80.55; H, 7.55; N, 5.3. $C_{17}H_{19}NO$ requires C, 80.65; H, 7.5; N, 5.55%), τ 2.48—2.86 (5H, m, aryl), 3.68 (1H, s, 3-H), 7.62 (2H, s, CH_2), 7.68 (2H, s, CH_2), 7.97 (3H, s, Me), and 8.95 (6H, s, Me), $\nu_{max.}$ (Nujol) 1 653 cm^{-1} (C=O).

Dimethyl 2-[N-(*2-Chloroallyl*)*ethylamino*]*maleate* (XIV).—Dimethyl acetylenedicarboxylate (3.84 g), *N*-(2-chloroallyl)ethylamine [16] (4.2 g), and dry benzene (100 ml) were

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stirred and refluxed for 16 h. Chromatography and distillation (b.p. 100° at 0.1 mmHg) gave the *product* (6.42 g, 91%) (Found: C, 50.2; H, 6.05; N, 5.1. $C_{11}H_{16}ClNO_4$ requires C, 50.5; H, 6.1; N, 5.35%).

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