Site Specificity of [3,3] Sigmatropic Rearrangements of 3-Allyl- and 3-(Prop-2-ynyl)-3*H*-indoles

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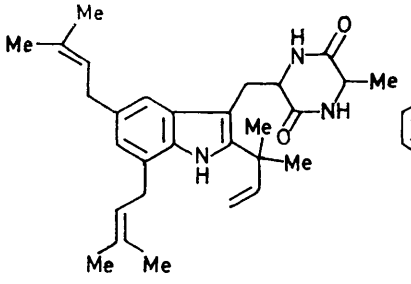
A series of 3-allyl-, 3-(prop-2-ynyl)-, and 3-(3-methylbut-2-enyl)-3*H*-indoles have been prepared by direct alkylation, and by alkylation of the appropriate indole Grignard reagent. Thermal rearrangement of these 3*H*-indoles and their *N*-methyl anhydro-bases demonstrates that the preferred migration terminus for a [3,3] sigmatropic rearrangement is, if present, a 2-alkyl group, and the rearrangement then occurs *via* the enamine tautomer of the 3*H*-indole. Allylic inversion of the migrating substituent is demonstrated by substituent labelling or deuteriation. When enamine formation is blocked the migration is diverted to nitrogen. Attempts to involve the 4-position of the indole nucleus were unsuccessful.

THERE are a number of indole alkaloids such as echinulin (1),[1] the ilamycins [*e.g.* (2)],[2] and the brevianamides [3] which contain tryptophan units with dimethylallyl substituents, and similar compounds [*e.g.* (3)] are implicated in the biosynthesis of ergot alkaloids.[4] The



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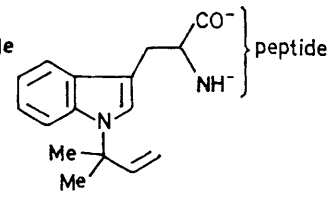

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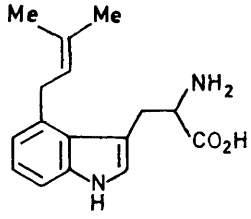

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biogenesis of these alkaloids by interaction of the ambident nucleophile tryptophan with the ambident electrophile dimethylallyl or isopentenyl pyrophosphate poses problems, especially concerning indole chemistry. Thus the intermediacy of the 4-substituted indole (3) in the biogenesis of the ergot alkaloids involves attack at the comparatively unreactive 4-position. Although these unusual substitution patterns could be explained solely by enzymic mediation, another attractive possibility is that sigmatropic processes,[5] allied in some cases to Plancher–Brunner rearrangements,[6] might be involved. Such considerations led us to study the allylation of indoles and the site specificity and ease of sigmatropic rearrangement of the resulting allyl-3*H*-indoles.[7] A biogenetic theory implicating thio-Claisen rearrangements of (dimethylallyl)indol-2-yl sulphonium salts was recently proposed [8] but did not withstand biosynthetic investigation.[9]

Allylation of 2,3-disubstituted indole Grignard reagents with both allyl and dimethylallyl bromide gave the expected 3*H*-indoles (4; R^1 = H or Me).[10] Prop-2-ynyl bromide gave the corresponding prop-2-ynyl-3*H*-indole (5; R^1 = H, R^2 = Me) although a longer reaction time was required. However, all the 3*H*-indoles could be more conveniently obtained, in the same or increased yield, by direct reaction of the allyl bromide with the substituted indole at room temperature. Reactions with prop-2-ynyl bromide sometimes required more forcing conditions. The products were obtained as hydrobromide salts from which the free bases were readily liberated, usually in very high yield. Distillation was necessary to remove small amounts of coloured impurities. While this work was in progress two reports of allylation of indoles under different conditions appeared.[11]

The n.m.r. spectra of the 2-methyl-3*H*-indoles (6a) showed no evidence of the enamine tautomers (6b). However, we observed ready exchange of the 2-methyl protons in MeOD–NaOD at room temperature, and since the 3*H*-indoles are themselves basic, the enamine tautomers must be considered as potential substrates in sigmatropic processes. Thus for the 2-methyl-3*H*-indoles (6; R = H or Me) there are three potential migration termini for a [3,3] sigmatropic process [asterisks in (6a) and (6b)].

[1] C. Cardani, G. Casnati, F. Piozzi, and A. Quilico, *Tetrahedron Letters*, 1959, 1; A. J. Birch, G. E. Blance, S. David, and H. Smith, *J. Chem. Soc.*, 1961, 3128.

[2] T. Takita, H. Naganawa, K. Maeda, and H. Umezawa, *J. Antibiotics*, 1964, **17**, 264.

[3] A. J. Birch and J. J. Wright, *Chem. Comm.*, 1969, 644.

[4] H. Plieninger, H. Immel, and A. Voelkl, *Annalen*, 1967, **706**, 223; S. Agurell and J. Lindgren, *Tetrahedron Letters*, 1968, 5127.

[5] R. Hoffmann and R. B. Woodward, *Angew. Chem., Internat. Edn.*, 1969, **8**, 781.

[6] 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1952, vol. 3, p. 80; Y. Kanaoka, K. Miyashita, and O. Yonemitsu, *Chem. Comm.*, 1969, 1365; G. Casnati and A. Pochini, *ibid.*, 1970, 1328.

[7] Preliminary communication, R. K. Bramley and R. Grigg, *Chem. Comm.*, 1969, 99.

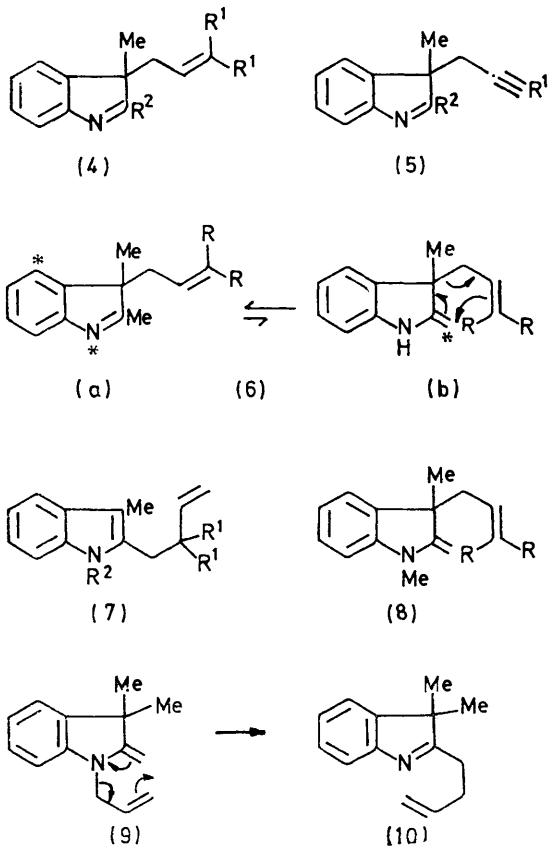
[8] B. W. Bycroft and W. Landon, *Chem. Comm.*, 1970, 967.

[9] B. W. Bycroft and G. W. Kirby, personal communication.

[10] M. Nakazaki, *Bull. Chem. Soc. Japan*, 1959, **32**, 838.

[11] K. R. Freter, *Canad. J. Chem.*, 1967, **45**, 2628; G. Casnati, M. Francioni, A. Guareschi, and A. Pochini, *Tetrahedron Letters*, 1969, 2485.

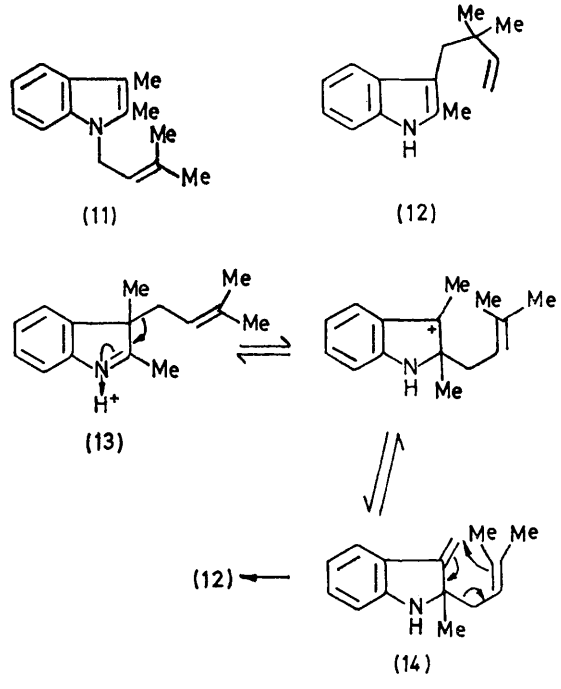
Initial experiments were carried out on (6; R = H) which, on heating in solution for 15 h at 181° or 4 h at 205° (tetralin), was quantitatively (spectra and t.l.c.) converted into an isomeric product. The product (88%)



was isolated by chromatography followed by molecular distillation, and spectral data supported the 2-(but-3-enyl)indole structure (7; $R^1 = R^2 = H$). The enamine tautomer (6b) was thus implicated and this prompted preparation and study of the anhydro-base (8; R = H). The anhydro-base (8; R = H), obtained as an air-sensitive oil from the corresponding methiodide and sodium hydroxide, rearranged in boiling benzene, or, more conveniently, toluene, to give (7; $R^1 = H$, $R^2 =$ Me) (90%). The imine–enamine tautomerism was thus the rate-determining step in the rearrangement of the 2-methyl-3*H*-indole (6a). We have investigated the rearrangement of (6; R = H) in the presence of a catalytic amount of $Rh_2(CO)_4Cl_2$, a mild Lewis acid, and found that smooth rearrangement occurred at a lower temperature (150 as opposed to 181°). The comparatively mild conditions required for the [3,3] sigmatropic rearrangement of the anhydro-base (8; R = H) owe much to the ' energy bonus ' resulting from a transition state which generates an aromatic system, as shown by the much more vigorous conditions (200°) required to effect the related rearrangement (9) ⟶ (10).[12]

A [3,3] sigmatropic rearrangement proceeds *via* a cyclic six-membered transition state and results in allylic inversion. In order to demonstrate this inversion, the thermal rearrangement of (6; R = Me) was studied and proved to be concentration dependent. Thus a 50% (w/v) solution of (6; R = Me) in boiling tetralin gave a mixture of the *N*-(dimethylallyl)indole (11) (19%), 2,3-dimethylindole (65%), and *o*-acetamidoacetophenone (6%). The reaction was carried out under nitrogen, and isoprene could be condensed from the issuing nitrogen stream. This range of products indicated a radical process, and the concentration dependence (see below) is consistent with a short chain-length radical mechanism. The products were identified by comparisons with authentic samples, compound (11) being prepared by the reaction of the sodium salt of 2,3-dimethylindole with 3-methylbut-2-enyl bromide in liquid ammonia.

Thermal rearrangement of (6; R = Me) in a 10% (w/v) solution in boiling tetralin was complete (t.l.c.) after 3 h and gave three products. Column chromatography gave *o*-acetamidoacetophenone (6%) and a mixture (60%; 11 : 2) of two isomeric substances which were partially separated by chromatography. These two products showed similar i.r. and u.v. spectra. Their n.m.r. spectra demonstrated the presence of terminal vinyl groups and each product contained only one indolic methyl group. These observations support structures (7; R^1 = Me, R^2 = H) and (12). However, the close



correspondence of the chemical shifts of the indolic methyl groups [τ ($CDCl_3$) 7·85 and 7·95] precluded definite assignment of either structure to a particular product. Thermal rearrangement of the 2-trideuteriomethyl-3*H*-indole (4; R^1 = Me, $R^2 = CD_3$), prepared by deuteriation with MeOD–NaOD, allowed assignment of

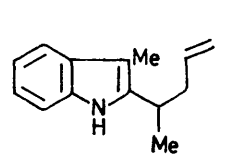
[12] R. K. Hill and G. R. Newkome, *Tetrahedron Letters*, 1968, 5059.

structure (7; R^1 = Me, R^2 = H) to the major isomer (indolic methyl at τ 7·85) and (12) (indolic methyl at τ 7·95) to the minor isomer. Whilst the major isomer could thus arise by a [3,3] sigmatropic rearrangement, the formation of (12) required a more complex pathway. One possibility is an acid-catalysed Plancher–Brunner rearrangement [6] [(13); arrows], then deprotonation to (14), and finally a [3,3] sigmatropic shift generating (12).

Conversion of the 3*H*-indole (6; R = Me) into the anhydro-base (8; R = Me) prior to thermolysis was undertaken to discourage this side reaction. The anhydro-base (8; R = Me) rearranged slowly in boiling toluene to give (7; R^1 = R^2 = Me; 74%) as the sole product. The steric problems associated with the terminal *gem*-dimethyl group in these [3,3] sigmatropic rearrangements are reflected in the reaction times required for the conversions at 110° of (8; R = H) and (8; R = Me) into the corresponding products (10 h and 6 day, respectively). Similar differences in rate were observed in the tetrahydrocarbazole series and again evidence suggesting competing radical processes was obtained.

The influence, on the rearrangement, of substitution at the migration terminus was also studied. The 2-ethyl-3*H*-indole (4; R^1 = H, R^2 = Et) rearranged cleanly in tetralin to a single product (15) (82%) with the expected structure. The tetrahydro-1*H*-carbazole (16; R = H) rearranged (8 h at 205°) less cleanly. Two products were isolated and the minor product (8%) was shown to be the *N*-allyltetrahydrocarbazole (17; R = H) whereas the major product (76%) was assigned structure (18; R^1 = R^2 = H) on the basis of n.m.r. spectral comparisons with the corresponding product from the *N*-methyl-anhydro-base (19; R = H). The tetrahydrocarbazole (18; R^1 = R^2 = H) was difficult to purify and was always contaminated with a minor unidentified impurity, possibly an oxidation product of (18; R^1 = R^2 = H). The anhydro-base (19; R = H) rearranged completely at 110° to a single product (18; R^1 = H, R^2 = Me) whose spectral characteristics closely resembled those of (18; R^1 = R^2 = H). Analogous reactions were then undertaken with (16; R = Me) and (19; R = Me) to provide evidence for allylic inversion of the migrating group. The 3*H*-indole (16; R = Me) was thermally stable at 205°, but reacted at 260° (in 1-chloronaphthalene) to give a mixture of products. Five products were isolated by chromatography and four of these were identified as carbazole, tetrahydrocarbazole, *N*-(3-methylbut-2-enyl)tetrahydrocarbazole (17; R = Me), and compound (18; R^1 = Me, R^2 = H). The fifth product was a 3-methylbut-2-enylcarbazole but was air sensitive and obtained in low yield, making characterisation difficult. The nature of the products from this thermolysis again indicates competing intramolecular and radical processes. In contrast the anhydro-base (19; R = Me) rearranged slowly but cleanly in refluxing toluene to (18; R^1 = R^2 = Me).

The related [3,3] sigmatropic rearrangement of acetylenic 3*H*-indoles has also been studied. The prop-2-ynyl-3*H*-indole (5; R^1 = H, R^2 = Me) could not be stored without deterioration, even under nitrogen in a refrigerator, but underwent thermal rearrangement at 205° to give the allenic indole (20; R^1 = R^2 = H) as expected for a [3,3] sigmatropic shift. The tetradeuterio-3*H*-indole (5; R^1 = D, R^2 = CD_3) gave (20; R^1 = D, R^2 = H) thus ruling out [1,3] migration of the prop-2-ynyl group intact, followed by acetylene–allene prototropy. The thermal instability of the allene (20; R^1 = R^2 = H) precluded a long reaction time and best yields were obtained at *ca.* 50% conversion (205° for 2 h). Once again the anhydro-base [(21); arrows] rearranged quantitatively at 110° to (20; R^1 = H; R^2 = Me). Thus the preferred path for concerted thermal rearrangement of 3-allyl- and 3-(prop-2-ynyl)-2-methyl-3*H*-indoles proceeds *via* an initial imine–enamine tautomerism followed by a [3,3] sigmatropic shift onto the terminal carbon atom of the enamine system.



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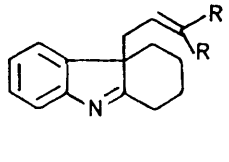

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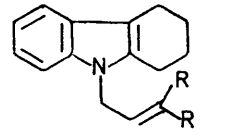

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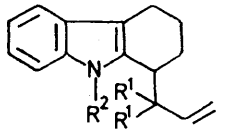

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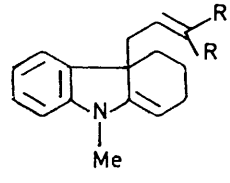

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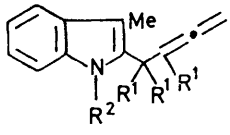

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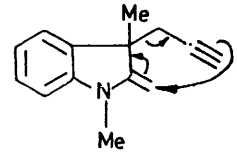

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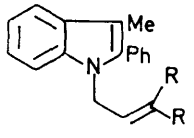
Several 3-allyl-2-phenyl-3*H*-indoles were next prepared and their thermal rearrangements studied. The 2-phenyl substituent precluded enamine formation and thus thermal (205° for 28 h) rearrangement of (4; R^1 = H, R^2 = Ph) cleanly diverted the [3,3] sigmatropic rearrangement to the nitrogen atom giving (22; R = H) (78%) and some unchanged (4; R^1 = H, R^2 = Ph). The lack of by-products from the reaction suggested that radical processes were not important and evidence for

allylic inversion of the migrating allyl group was sought. Compound (4; R^1 = Me, R^2 = Ph) was stable in refluxing tetralin, but in boiling 1-chloronaphthalene (260°) a mixture of products was obtained. The major product was 3-methyl-2-phenylindole together with a small amount (6%) of the non-inverted *N*-allylindole (22; R = Me) and a polymeric residue. The high temperature required for the reaction resulted in radical processes being dominant. Similarly attempts to rearrange thermally the (prop-2-ynyl)-3*H*-indole (5; R^1 = H, R^2 = Ph) led to cleavage products and no *N*-allenylindole.

Finally the indoline (23) was prepared, as a mixture of *cis*- and *trans*-isomers, by reduction of the corresponding 3*H*-indole methiodide with sodium borohydride. In this case the two previously observed preferred rearrangement pathways are not available. Thermal reaction of this indoline mixture occurred only slowly even at 260° and gave a complex mixture of products, none of which was identified as the desired Cope rearrangement product involving the 4-position of the benzene ring. Thus these indoles demonstrate the difficulty in achieving a Cope rearrangement when one of the participating double bonds is located in a benzene ring. It had been shown previously that Cope rearrangement involving a benzene ring required vigorous conditions and the presence of a strong base to deprotonate the



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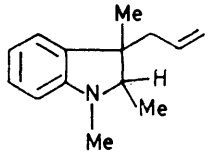

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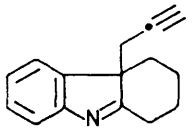

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cyclohexadiene intermediate.[13] However, the incorporation, in our case, of the weakly basic internal amine function was clearly not sufficient to promote the process at 260°.

Thus the order of preference of migration terminus for [3,3] sigmatropic processes in 3*H*-indoles is C(2)-methyl > N ≫ C(4).

EXPERIMENTAL

M.p.s were determined on a Kofler micro heating stage. U.v. spectra were recorded on a Unicam SP 700 spectrometer, and i.r. spectra on a Unicam SP 100 instrument. N.m.r. spectra were measured either on a Perkin-Elmer RS 10 instrument (60 MHz) or on a Varian HA 100 instrument (100 MHz), with tetramethylsilane as internal reference. Mass spectral data were obtained from an A.E.I. MS 902c instrument. For column chromatography, alumina refers to Spence type H, and silica to silica gel M.F.C. (Hopkin and Williams). T.l.c. plates were made up with either silica gel (May and Baker) or alumina G (Merck). Petrol refers to the fraction with b.p. 60—80°, and ligroin to the fraction with b.p. 100—120°.

2,3-*Dimethyl*-3-(3-*methylbut*-2-*enyl*)-3H-*indole* (4; R^1 = R^2 = Me).—A solution of methylmagnesium iodide [from methyl iodide (32 g) and magnesium (5·6 g) in ether (70 ml)] was added dropwise with stirring under dry nitrogen to a solution of 2,3-dimethylindole (20·5 g, 0·142 mol) in anhydrous ether (100 ml). After the vigorous evolution of methane had ceased, 3-methylbut-2-enyl bromide [14] (38·0 g, 0·195 mol) was introduced dropwise, and stirring under nitrogen was continued for a further 1 h. Glacial acetic acid (12·4 ml) in water (44 ml) was then slowly added, and the ether layer was separated and combined with ether washings of the aqueous layer. The combined extracts (400 ml) were washed with ice-cold 2N-hydrochloric acid (3 × 300 ml), and the aqueous phase was made alkaline with ice-cold 4N-sodium hydroxide (500 ml). The precipitated oil was extracted with ether (2 × 250 ml); the extract was dried (K_2CO_3) and evaporated under reduced pressure, and the residue was fractionated to give the 3H-*indole* (4; R^1 = R^2 = Me) as a pale yellow liquid (15·6 g, 33%), b.p. 109—119° at 1 mmHg. A sample for analysis was redistilled on a short-path apparatus (Found: C, 84·1; H, 9·3; N, 6·2. $C_{15}H_{19}N$ requires C, 84·5; H, 9·0; N, 6·6%); $\lambda_{max.}$ (EtOH) 212, 217, 223sh, and 256 nm (ε 19,870, 18,510, 13,010, and 5450); $\nu_{max.}$ (CCl_4) 934, 1308, 1379, 1433, 1443, 1454, 1470, 1585, 1613, 2846, 2870, 2918, 2929, 2973, 3027, 3054, and 3065 cm^{-1}; τ (CCl_4) 2·3—3·2 (4H, m, aromatic), 5·5br (1H, t, $-CH_2 \cdot CH=$), 7·65br (2H, d, $-CH_2 \cdot CH=$), 7·9 (3H, s, 2-Me), 8·5br (6H, s, $Me_2C=$), and 8·8 (3H, s, 3-Me). The *methiodide* was obtained as needles, m.p. 135—137° (from acetone) (Found: C, 54·1; H, 6·3; N, 4·0. $C_{16}H_{22}IN$ requires C, 54·1; H, 6·2; N, 3·9%); $\lambda_{max.}$ (EtOH) 219, 238sh, and 278 nm (ε 18,080, 7260, and 6940); $\nu_{max.}$ ($CHCl_3$) 1388, 1459, 1465, 1477, 1609, 1633, and 1672 cm^{-1}; τ ($CDCl_3$) 2·2—2·5 (4H, m, aromatic), 5·3br (1H, t, $-CH_2 \cdot CH=$), 5·7 (3H, s, *N*-Me), 6·9 (3H, s, 2-Me), 7·2 (2H, d, $-CH_2 \cdot CH=$), 8·3 (3H, s, 3-Me), and 8·4 and 8·5 (each 3H, s, $Me_2C=$).

4a-*Allyl*-2,3,4,4a-*tetrahydro*-1H-*carbazole* (16; R = H).—The product (16; R = H) (64%) was obtained similarly as a very viscous oil, b.p. 121—133° at 1 mmHg, which rapidly crystallised as *chunky rhombs*, m.p. 52—56° (Found: C, 85·2; H, 8·0; N, 6·6. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1; N, 6·6); $\lambda_{max.}$ (EtOH) 210sh, 213, 219, 223sh, and 262 nm (ε 17,100, 18,280, 17,610, 12,950, and 6040); $\nu_{max.}$ (CCl_4) 921, 1455, 1467, 1591, 1614, and 1641 cm^{-1}; τ (CCl_4) 2·4—3·1 (4H, m, aromatic), 4·7—5·4 (3H, m, $-CH_2 \cdot CH=CH_2$), and 6·9—9·2 (10H, m, methylene protons). The *methiodide* gave needles, m.p. 167—171° (slight decomp.) (from acetone–benzene) (Found: C, 54·3; H, 5·5; N, 4·1. $C_{16}H_{20}IN$ requires C, 54·4; H, 5·7; N, 4·0%); $\lambda_{max.}$ (EtOH) 207sh, 211, 219, 238sh, and 277 nm (ε 20,120, 19,400, 17,850, 7520 and 7100); $\nu_{max.}$ ($CHCl_3$) 1465, 1477, 1614, and 1633 cm^{-1}; τ ($CDCl_3$) 2·0—2·5 (4H, m, aromatic), 4·6—5·2 (3H, m, $-CH_2 \cdot CH=CH_2$), 5·7 (3H, s, *N*-Me), and 6·2—8·4 (10H, m, methylene protons).

4a-(3-*Methylbut*-2-*enyl*)-2,3,4,4a-*tetrahydro*-1H-*carbazole* (16; R = Me).—Reaction of the Grignard reagent from

[13] W. von E. Doering and R. A. Bragole, *Tetrahedron*, 1966, **22**, 385.

[14] H. Staudinger, W. Kreis, and W. Schilt, *Helv. Chim. Acta*, 1922, **5**, 750.

1,2,3,4-tetrahydrocarbazole (22·3 g, 0·130 mol) with 3-methylbut-2-enyl bromide (28·3 g, 0·190 mol) and work-up in the normal way yielded the 1H-*carbazole* (16; R = Me) (14·6 g, 47%) as a viscous yellow oil, b.p. 136—163° at 1 mmHg, which formed a wax at 0° overnight. Crystallisation gave plates (10·7 g, 32%), m.p. 37—42° (from petrol). A sample for analysis had m.p. 40—43° (Found: C, 85·2; H, 8·8; N, 6·0. $C_{17}H_{21}N$ requires C, 85·4; H, 8·8; N, 5·9%); $\lambda_{max.}$ (EtOH) 213, 217, 223sh, and 256 nm (ε 18,770, 17,670, 13,050, and 5890); $\nu_{max.}$ ($CHCl_3$) 1457, 1467, 1583, 1612, 2867, and 2955 cm^{-1}; τ (CCl_4) 2·4—3·1 (4H, m, aromatic), 5·5br (1H, t, $-CH_2\cdot CH=$), and 6·9—9·2 (16H, m, methylene protons and $Me_2C=$ as a split singlet at 8·5). The *methiodide* gave yellow prisms, m.p. 138—141° (from acetone) (Found: C, 56·4; H, 6·3; I, 33·4; N, 4·0. $C_{18}H_{24}IN$ requires C, 56·7; H, 6·3; I, 33·3; N, 3·7%); $\lambda_{max.}$ (EtOH) 218, 237sh, and 276 nm (ε 17,920, 7440, and 6620); $\nu_{max.}$ ($CHCl_3$) 1615 and 1633 cm^{-1}; τ ($CDCl_3$) 1·9—2·6 (4H, m, aromatic), 5·3 (1H, t, $-CH_2\cdot CH=$), 5·8 (3H, s, *N*-Me), 6·1—8·3 (10H, m, methylene protons), and 8·4 and 8·55 (6H, 2 s, $Me_2C=$).

2,3-*Dimethyl*-3-(*prop*-2-*ynyl*)-3H-*indole* (5; R^1 = H, R^2 = Me).—Prop-2-ynyl bromide (10·7 g, 0·09 mol) in dry ether (15 ml) was added slowly to the Grignard reagent obtained from 2,3-dimethylindole (13·05 g, 0·09 mol) in dry ether (100 ml) under nitrogen. After boiling under reflux for 20 h, the mixture was allowed to cool, and crushed ice was added followed by ice-cold 5% sulphuric acid (75 ml). The ether layer was separated and extracted with 5% sulphuric acid (4 × 25 ml), and the combined acid extracts were neutralised (pH 7) with ice-cold 4N-sodium hydroxide at 0° in a CO_2–acetone bath. The neutral mixture was extracted with ether (3 × 100 ml); the extracts were washed with water (2 × 150 ml), dried (K_2CO_3), and evaporated to give a brown viscous residue at room temperature. Distillation then afforded the 3H-*indole* (5; R^1 = H, R^2 = Me) (10·6 g, 64%), as a viscous oil, b.p. 106—111° at 1·5 mmHg (Found: 84·9; H, 7·0; N, 7·4. $C_{13}H_{13}N$ requires C, 85·2; H, 7·2; N, 7·6%); $\lambda_{max.}$ (EtOH) 209sh, 212, 218, 224sh, and 258 nm (ε 16,330, 18,040, 18,000, 12,600, and 5410); $\nu_{max.}$ (CCl_4) 1297, 1314, 1380, 1432, 1458, 1470, 1594, 1614, and 3320 cm^{-1}; τ (CCl_4) 2·4—3·2 (4H, m, aromatic), 7·65 (2H, t, $-CH_2\cdot C\equiv$), 7·85 (3H, s, 2-Me), 8·0 (1H, t, $HC\equiv$), and 8·75 (3H, s, 3-Me). The *methiodide* gave fine, pale yellow needles, m.p. 175—190° (from acetone) (Found: C, 51·5; H, 5·0; N, 4·4. $C_{14}H_{16}IN$ requires C, 51·7; H, 4·9; N, 4·3%); $\lambda_{max.}$ (EtOH) 206sh, 210, 221, 238sh, and 278 nm (ε 17,150, 16,250, 17,100, 7280, and 6460); $\nu_{max.}$ ($CHCl_3$) 1614, 1637, and 3314 cm^{-1}. The 3*H*-indole became dark brown after 4 weeks at 0° under nitrogen. N.m.r. analysis of the methiodide was precluded by its insolubility in chloroform, but examination of the n.m.r. spectrum of a melt of this compound indicated that its wide m.p. range was due to thermal rearrangement of the 3*H*-indole anhydro-base formed by elimination of hydrogen iodide.

3-*Allyl*-3-*methyl*-2-*phenyl*-3H-*indole* (4; R^1 = H, R^2 = Ph).—Grignard synthesis in a similar manner to that previously described but using 3-methyl-2-phenylindole (29·4 g, 0·142 mol) and allyl bromide (23·1 g, 0·191 mol) and stirring the reaction mixture for 24 h at room temperature before work-up in the usual way gave the 3H-*indole* (4; R^1 = H, R^2 = Ph) (16·0 g, 45%), b.p. 134—136° at 0·5 mmHg. On storing at 0° crystallisation occurred giving chunky rhombs, m.p. 43—48° (Found: C, 87·5; H, 6·6; N, 5·5. $C_{18}H_{17}N$ requires C, 87·4; H, 6·9; N, 5·7%); $\lambda_{max.}$ (EtOH) 201, 228, 233, 236sh, 244sh, and 306 nm (ε 30,180, 12,380, 12,350, 12,190, 9980, and 14,090); $\nu_{max.}$ (CCl_4) 1455, 1468, 1497, 1531, 1538, 1556, and 1644 cm^{-1}; τ ($CDCl_3$) 1·7—3·1 (9H, m, aromatic), 4·5—5·6 (3H, m, $-CH_2\cdot CH=CH_2$), 7·2 (2H, d, $-CH_2\cdot CH=$), and 8·5 (3H, s, 3-Me).

3-*Methyl*-3-(3-*methylbut*-2-*enyl*)-2-*phenyl*-3H-*indole* (4; R^1 = Me, R^2 = Ph).—The usual Grignard synthesis with 3-methyl-2-phenylindole (29·4 g, 0·142 mol) and 3-methylbut-2-enyl bromide (28·4 g, 0·191 mol) was carried out for 18 h, with the mixture under reflux. The product, a viscous oil, was distilled on a short-path apparatus (65° at 0·1 mmHg) to give the 3H-*indole* (4; R^1 = Me, R^2 = Ph) (8·3 g, 21%) n_D^{24} 1·6193 (Found: C, 87·6; H, 7·7; N, 5·3. $C_{20}H_{21}N$ requires C, 87·2; H, 7·7; N, 5·1%); $\lambda_{max.}$ (EtOH) 228, 234, 242sh, and 307 nm (ε 13,550, 13,490, 10,940, and 14,080); $\nu_{max.}$ (CCl_4) 1381, 1453, 1467, 1495, and 1528 cm^{-1}; τ (CCl_4) 1·7—3·1 (9H, m, aromatic), 5·6br (1H, t, $-CH_2\cdot CH=$), 7·3br (2H, d, $-CH_2\cdot CH=$), 8·45 (3H, s, 3-Me), and 8·6 and 8·7 (6H, 2 s, $Me_2C=$).

General Method for the Direct Allylation and Propynylation of Indoles.—The alkyl indole (1 mol. equiv.) was dissolved in excess of the allyl or propynyl bromide (2 mol. equiv.) and set aside until t.l.c. showed complete disappearance of the indole. Chloroform was added and the mixture was washed with aqueous sodium hydrogen carbonate and then water. After drying (K_2CO_3), the solvent was evaporated off to afford the crude 3*H*-indole, which was purified by distillation. The yields and reaction times are summarised in the Table.

Compound	Time	Yield (%)
(4; R^1 = H, R^2 = Me)	7 day	62·7
(4; R^1 = R^2 = Me)	24 h	68·0
(5; R^1 = H, R^2 = Me)	11 day	60·5
(4; R^1 = H, R^2 = Et)	14 day	75·0
(4; R^1 = Me, R^2 = Et)	2 day	56·0
(5; R^1 = H, R^2 = Et)	28 day	87·0
(4; R^1 = H, R^2 = Ph)	14 day	63·0
(4; R^1 = Me, R^2 = Ph)	24 h	61·0
(5; R^1 = H, R^2 = Ph)	12 h *	18·0
(16; R = H)	3 day	81·0
(16; R = Me)	3 day	61·0
(24)	12 h *	25·2

* Boiled under reflux.

3-*Allyl*-2-*ethyl*-3-*methyl*-3H-*indole* (4; R^1 = H, R^2 = Et) was obtained as an oil, b.p. 60—62° at 0·05 mmHg; n_D^{24} 1·5446 (Found: N, 7·39. $C_{14}H_{17}N$ requires N, 7·03%); $\lambda_{max.}$ (EtOH) 210infl, 212, 218, 224infl, and 257 nm (ε 16,930, 18,030, 17,380, 12,700, and 5970); τ ($CDCl_3$) 2·3—2·9 (4H, m, aromatic), 4·6—5·1 (3H, m, $-CH_2\cdot CH=CH_2$), 7·55 (4H, m, $MeCH_2$ and $=CH\cdot CH_2$), and 8·6 (6H, m, 2 × Me).

2-*Ethyl*-3-*methyl*-3-(3-*methylbut*-2-*enyl*)-3H-*indole* (4; R^1 = Me, R^2 = Et) was a yellow oil, b.p. 84—86° at 0·05 mmHg; *methiodide*, prisms from acetone–petrol, m.p. 131—132° (Found: C, 54·8; H, 6·8; N, 3·8. $C_{17}H_{24}IN$ requires C, 55·3; H, 6·5; N, 3·8%); $\lambda_{max.}$ (EtOH) 210sh, 212, 216·5sh, 223infl, 256, and 304infl (ε 18,000, 18,370, 16,800, 12,430, 5740, and 590); τ ($CDCl_3$) 2·4—3·0 (4H, m, aromatic), 5·4br (1H, t, $-CH_2\cdot CH=$), 7·6 (4H, m, $MeCH_2$ and $=CH\cdot CH_2$), and 8·5—8·8 (12H, m, 4 × Me).

2-*Ethyl*-3-*methyl*-3-(*prop*-2-*ynyl*)-3H-*indole* (5; R^1 = H, R^2 = Et) was purified by molecular distillation (80° at 0·02 mmHg) to give a yellow oil (Found: C, 84·6; H, 7·52; N, 7·3. $C_{14}H_{15}N$ requires C, 85·25; H, 7·65; N, 7·1%); $\lambda_{max.}$ (EtOH) 210infl, 212, 218, 224, and 260 nm (ε 13,990,

15,500, 15,500, 11,070, and 4810); τ ($CDCl_3$) 2·3—2·9 (4H, m, aromatic), 7·3—7·0 (4H, m, $MeCH_2$ and ≡C–CH_2), 8·6 (3H, t, $MeCH_2$), and 8·6 (3H, s, Me).

4a-(*Prop*-2-*ynyl*)-2,3,4,4a-*tetrahydro*-1H-*carbazole* (24) was a viscous oil, τ ($CDCl_3$) 2·4—3·1 (4H, m, aromatic), 7·0—9·1 (10H, m, 5 × $-CH_2-$), and 8·05 (1H, t, ≡CH); *hydrobromide*, m.p. 196—198°, as needles from acetone (Found: C, 61·75; H, 5·65; N, 4·8. $C_{15}H_{16}BrN$ requires C, 62·1; H, 5·5; N, 4·85%); $\lambda_{max.}$ (EtOH) 206, 212, 219, 225, 239, and 261 nm (ε 13,740, 13,560, 13,210, 10,040, 4490, and 5070).

3-*Methyl*-2-*phenyl*-3-(*prop*-2-*ynyl*)-3H-*indole* (5; R^1 = H, R^2 = Ph) formed prisms from ligroin, m.p. 107—110° (Found: C, 88·0; H, 6·3; N, 5·7. $C_{18}H_{15}N$ requires C, 88·15; H, 6·15; N, 5·7%); $\lambda_{max.}$ (EtOH) 222infl, 228, 233, 243·5, and 306 nm (ε 11,560, 12,790, 12,480, 9870, and 13,131); τ ($CDCl_3$) 1·8—2·8 (9H, m, aromatic), 7·2 (2H, q of d, CH_2·C≡), 8·1, (1H, t, ≡CH), and 8·35 (3H, s, Me).

[2-C^2H_3]-2,3-*Dimethyl*-3-(3-*methylbut*-2-*enyl*)-3H-*indole* (4; R^1 = Me; R^2 = CD_3). The 3*H*-indole (4; R^1 = R^2 = Me) (2·3 g) was dissolved in MeOD (4 g) containing sodium methoxide [from sodium (0·25 g)] and set aside at room temperature for 19 h; the solution was then evaporated to dryness in the cold. The residue was extracted with dry ether; the extract was filtered, evaporated, and distilled on a short-path apparatus to give an oil (1·15 g); deuterium content in 2-Me, 58% (n.m.r.).

[2-C^2H_3]-2,3-*Dimethyl*-3-([3-^{2}H]*prop*-2-*ynyl*)-3H-*indole* (5; R^1 = D, R^2 = CD_3). This was prepared as in the previous example and was estimated to be 90% tetradeuteriated (n.m.r.).

Thermal Rearrangements.—3-*Allyl*-2,3-*dimethyl*-3H-*indole* (4; R^1 = H, R^2 = Me). Under an atmosphere of dry nitrogen and in dilute solution, the 3*H*-indole was stable under reflux in xylene, but was quantitatively converted into a single product after 15 h in boiling *o*-dichlorobenzene or after 4 h in tetralin. A solution of the 3*H*-indole (4; R^1 = H, R^2 = Me) (1·30 g; R_F 0·5) in dry distilled tetralin (20 ml) was refluxed for 6·25 h under dry nitrogen; monitoring by t.l.c. (benzene; alumina) then indicated a single product (R_F 0·9) to be present. No appreciable change was observed after reflux for a further 3·5 h, so solvent was removed under reduced pressure at *ca.* 40° and the residue was distilled on a short-path apparatus to give 2-(*but*-3-*enyl*)-3-*methylindole* (7; R^1 = R^2 = H) (1·15 g, 88%) (Found: C, 84·2; H, 8·1; N, 7·5. $C_{13}H_{15}N$ requires C, 84·3; H, 8·2; N, 7·6%); $\lambda_{max.}$ (EtOH) 228, 277sh, 284, and 292 nm (ε 32,700, 6600, 7250, and 6550); $\nu_{max.}$ (CCl_4) 918, 1000, 1011, 1243, 1299, 1309, 1329, 1419, 1440, 1464, 1487, 1641, 2864, 2982, 3037, 3065, 3084, 3425, and 3490 cm^{-1}; τ (CCl_4) 2·5—3·3 (5H, m, aromatic and NH), 3·9—5·3 (3H, AB_2 m, $-CH=CH_2$), 7·2—8·2 (4H, m, $-CH_2·CH_2-$), and 7·9 (3H, s, 3-Me); *m/e* 185 (M^+, 22%), 144 (100).

2,3-*Dimethyl*-3-(3-*methylbut*-2-*enyl*)-3H-*indole* (4; R^1 = R^2 = Me). (*a*) A solution of the 3*H*-indole (4; R^1 = R^2 = Me) (4·60 g, 0·0216 mol) in dry distilled tetralin (10·0 ml) was refluxed under dry nitrogen for 1 h; t.l.c. (benzene; alumina) then showed complete disappearance of starting material (R_F 0·4) and the presence of two major components (R_F 0·8 and 0·9); in addition, a volatile material was escaping through the air condenser. This volatile product (0·30 g) was condensed out of the nitrogen stream and identified as isoprene (i.r. and n.m.r.). The involatile mixture was chromatographed on alumina. Elution with petrol removed the tetralin. Benzene eluted traces of tetralin and then 2,3-*dimethyl*-1-(3-*methylbut*-2-*enyl*)*indole* (11) (0·65 g, 19%), R_F 0·9, identical with an authentic sample (see below). Chloroform first eluted 2,3-dimethylindole (2·15 g, 65%), R_F 0·8, identified by spectral comparisons with an authentic sample. Further elution with chloroform gave *o*-acetamidoacetophenone (0·30 g, 6%), R_F 0·5, m.p. 72—74° (lit.,[15] 76—77°) (from petrol), τ (CCl_4) —1·5br (1H, s, NH), 1·3, 2·25, 2·6, 3·05 (each 1H, d, d, t, t, aromatic), 7·5 (3H, s, $CH_3CO·NH$), and 7·95 (3H, s, $CH_3CO·Ar$).

A sample of the 2,3-dimethyl-1-(3-methylbut-2-enyl)indole (0·713 g, 0·00336 mol) was hydrogenated at atmospheric pressure over platinum oxide (0·005 g) in methanol (10 ml) for 24 h [uptake of hydrogen 70·1 ml (S.T.P.) (0·00313 mol)]. Work-up gave an oily residue which was chromatographed on alumina with petrol to give a mobile oil characterised as 2,3-*dimethyl*-1-(3-*methylbutyl*)*indole* (Found: C, 83·6; H, 9·7; N, 6·4. $C_{15}H_{21}N$ requires C, 83·7; H, 9·8; N, 6·5%); $\lambda_{max.}$ (EtOH) 231, 282sh, 288, and 294sh nm (ε 29,640, 5420, 5960, and 5830); $\nu_{max.}$ (CCl_4) 1187, 1336, 1360, 1388, 1418, 1472, 2875, 2932, and 2966 cm^{-1}; τ (CCl_4) 2·5—3·3 (4H, m, aromatic), 6·1—6·4 (2H, m, NCH_2), 7·2—9·0 (3H, m, $-CH_2CHMe_2$), 7·9 (6H, s, 2- and 3-Me), and 9·15 (6H, d, $CHMe_2$).

(*b*) After 3·5 h in boiling tetralin (20 ml) under dry nitrogen, the 3*H*-indole (4; R^1 = R^2 = Me) (2·0 g, 0·0094 mol) was almost completely converted into two products (R_F 0·8), and continued reaction for a further 20·5 h produced no change. The mixture was chromatographed on alumina. Elution with petrol and then benzene gave tetralin and then a yellow oil (0·5 g) (R_F 0·8) which solidified at 0° overnight and was identified as 2-(2,2-*dimethylbut*-3-*enyl*)-3-*methylindole* (7; R^1 = Me, R^2 = H) (25%) (Found: C, 84·7; H, 9·1; N, 6·5. $C_{15}H_{19}N$ requires C, 84·5; H, 9·0; N, 6·6%); $\lambda_{max.}$ (EtOH) 229, 285, and 293 nm (ε 32,320, 8270, and 7630); $\nu_{max.}$ (CCl_4) 920, 1011, 1157, 1241, 1301, 1318, 1330, 1364, 1382, 1417, 1439, 1464, 1487, 2871, 2930, 2966, and 3485 cm^{-1}; τ (CCl_4) 2·5—3·2 (5H, m, aromatic and NH), 3·9—5·3 (3H, AB_2 m, $-CH=CH_2$), 7·6 (2H, s, $-CH_2·CMe_2-$), 7·85 (3H, s, 3-Me), and 9·0 (6H, s, $-CH_2·CMe_2-$). Further elution with benzene gave a mixture (0·5 g) of (7; R^1 = Me, R^2 = H) and (12) followed by pure 3-(2,2-*dimethylbut*-3-*enyl*)-2-*methylindole* (12) (0·2 g, 10%), as a brown oil, R_F 0·8 (Found: C, 84·0; H, 8·8; N, 6·7. $C_{15}H_{19}N$ requires C, 84·5; H, 9·0; N, 6·6%); $\lambda_{max.}$ (EtOH) 227, 284, and 291 nm (ε 31,280, 6910, and 6200); $\nu_{max.}$ (CCl_4) 910, 1242, 1297, 1337, 1359, 1430, 1462, 1486, 2870, 2918, 2965, and 3485 cm^{-1}; τ (CCl_4) 2·5—3·3 (5H, m, aromatic and NH), 3·9—5·4 (3H, AB_2 m, $-CH=CH_2$), 7·45 (2H, s, $-CH_2·CMe_2-$), 7·95 (3H, s, 2-Me), and 9·0 (6H, s, $-CH_2·CMe_2$). Chloroform then eluted a brown oil (R_F 0·4) which on trituration with petrol gave needles (0·10 g) of *o*-acetamidoacetophenone. Further elution with chloroform gave a brown polymeric residue (0·15 g). [2-(2,2-Dimethylbut-3-enyl)-3-methylindole was unchanged after treatment under thermolytic conditions for 18 h.]

[2-C^2H_3]-2,3-*Dimethyl*-3-(3-*methylbut*-2-*enyl*)-3H-*indole* (4; R^1 = Me, R^2 = CD_3). Thermolysis of the deuterio-3*H*-indole (4; R^1 = Me, R^2 = CD_3) (1·15 g) in tetralin (12·0 ml) for 24 h, and work-up in the usual way gave deuteriated forms of the yellow indole (7; R^1 = Me, R^2 = H) (0·55 g) which again solidified at 0°, and the brown indole (12) (0·10 g). The minor product (R_F 0·4) (0·20 g) and a yellow polymeric fraction (0·20 g) were also isolated. The n.m.r. spectrum of the major product (48%) showed a diminution of the (s, $-CH_2·CMe_2-$) signal at τ 7·6; deuterium content

[15] H. Gevekoht, *Ber.*, 1882, **15**, 2084.

(by n.m.r.) 36%. The n.m.r. spectrum of the minor indolic product (9%) showed a diminution of the (s, 2-Me) signal at τ 7·95; deuterium content (by n.m.r.) 54%.

3-*Allyl*-2-*ethyl*-3-*methyl*-3H-*indole* (4; R^1 = H, R^2 = Et). The 3*H*-indole (1·1 g) was boiled under reflux in dry tetralin (10 ml) under nitrogen for 4·5 h; t.l.c. then showed complete disappearance of starting material and formation of a single product. The product was freed from tetralin by chromatography on alumina and elution with benzene gave a yellow oil which was further purified by short-path distillation to give 3-methyl-2-(1-methylbut-3-enyl)indole (15) (0·9 g, 82%); $\lambda_{max.}$ (EtOH) 209, 230·5, 247·5, 286, and 292·5 nm (ε 22,920, 16,920, 11,220, 4530, and 4420); τ ($CDCl_3$) 1·9—3·1 (5H, m, aromatic and NH), 3·95—5·2 (3H, m, $-CH=CH_2$), 6·7—7·7 (3H, m), 7·8 (3H, s, 3-Me), and 7·75 (3H, d, *Me*CH); *picrate*, m.p. 104—106°, brown prisms (EtOH) (Found: N, 13·3. $C_{20}H_{20}N_4O_7$ requires: N, 13·1%).

4a-*Allyl*-2,3,4,4a-*tetrahydro*-1H-*carbazole* (16; R = H). The same products were obtained (t.l.c.) after treatment of the tetrahydro-1H-carbazole either in dilute solution in boiling tetralin under nitrogen for 8 h, or for 42 h in refluxing *o*-dichlorobenzene, but in xylene solution no reaction was observed. After 8 h in dry tetralin (25 ml), t.l.c. (benzene; alumina) indicated almost complete disappearance of starting material (2·5 g, 0·0119 mol; R_F 0·4) with formation of two products (R_F 0·9) as the major components of a complex mixture. This was chromatographed on alumina. Petrol eluted the tetralin, and then benzene eluted N-*allyl*-1,2,3,4-*tetrahydrocarbazole* (17; R = H) (0·20 g, 8%) as a viscous yellow oil, n_D^{25} 1·6048, b.p. 122—124° at 0·05 mmHg, R_F 0·9 (Found: C, 85·5; H, 8·2; N, 6·4. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1; N, 6·6%); $\lambda_{max.}$ (EtOH) 230, 279sh, 286, and 293 nm (ε 29,200, 5470, 6200, and 5760); $\nu_{max.}$ (CCl_4) 925, 1182, 1316, 1332, 1355, 1377, 1428, 1444, 1468, 1616, and 1646 cm^{-1}; τ (CCl_4) 2·2—3·4 (4H, m, aromatic), 3·9—5·5 (3H, m, $-CH=CH$), 5·55—5·75 (2H, m, $>NCH_2-$), and 7·0—8·8 (8H, m, $-[CH_2]_4-$). Further elution with benzene gave a mixture of (18; R = H) and the next component (0·05 g). This was followed by an allyltetrahydrocarbazole (1·9 g, 76%) as chunky crystals (from petrol–ether), τ (CCl_4) 2·5—3·2 (5H, m, aromatic and −NH), 4·0—5·3 (3H, AB_2 m, $-CH=CH_2$), and 7·1—8·9 (10H, m, methylene protons). This product mainly melted over 45—47°, but left a few needles in the melt which did not disappear until 110—125°. T.l.c. on numerous supports and with different solvent systems showed only a single product, and column chromatography failed to achieve any separation. Attempted sublimation gave a red oil. Continued elution with benzene gave a mixture (0·25 g) and then another allyltetrahydrocarbazole, (0·10 g) (identified by n.m.r.), which was too air-sensitive to be further characterised.

4a-(3-*Methylbut*-2-*enyl*)-2,3,4,4a-*tetrahydro*-1H-*carbazole* (16; R = Me). This tetrahydro-1*H*-carbazole was stable to reflux in tetralin under nitrogen for 9 h but in refluxing 1-chloronaphthalene (5·0 ml) conversion of a sample (3·0 g, 0·0126 mol; R_F 0·1) into three major products (R_F 0·7, 0·8, and 0·9) in a complex reaction mixture occurred (t.l.c.: 1 : 1 benzene–petrol; alumina) in 1·5 h. This mixture was chromatographed on alumina. Petrol eluted 1-chloronaphthalene and then a mixture of two components which were separated by re-chromatography on a narrow alumina column (petrol elution) and identified as N-(3-*methylbut*-2-*enyl*)-1,2,3,4-*tetrahydrocarbazole* (17; R = Me) as a yellow oil (R_F 0·9) (Found: C, 85·3; H, 8·9; N, 5·6. $C_{17}H_{21}N$ requires C, 85·4; H, 8·8; N, 5·9%); $\lambda_{max.}$ (EtOH) 232, 281sh, 287, and 294 nm (ε 30,080, 5750, 6460, and 6280); $\nu_{max.}$ (CCl_4) 1179, 1309, 1377, 1430, 1448, 1467, 2845, 2857, 2935, 2974, 3029, and 3055 cm^{-1}; τ (CCl_4) 2·5—3·3 (4H, m, aromatic), 4·85br (1H, t, $-CH_2 \cdot CH=$), 5·4 (2H, d, $>NCH_2-$), and 7·0—9·3 (14H, m, methylene protons and $Me_2C=$) and a (1,1-dimethylprop-2-enyl)-1,2,3,4-tetrahydrocarbazole (R_F 0·9) (Found: C, 85·5; H, 8·7; N, 5·8. Calc. for $C_{17}H_{21}N$: C, 85·3; H, 8·8; N, 5·9%); $\lambda_{max.}$ (EtOH) 229, 278sh, 284, and 292 nm (ε 30,810, 7090, 7680, and 6660); $\nu_{max.}$ (CCl_4) 922, 1012, 1152, 1302, 1322, 1356, 1363, 1381, 1415, 1448, 1466, 1486, 1523, 2848, 2858, 2933, 2968, 3035, 3062, 3081, and 3462 cm^{-1}; τ (CCl_4) 1·8br (1H, s, −NH), 2·5—3·3 (4H, m, aromatic), 3·55—4·95 (3H, AB_2 m, $-CH=CH_2$), 6·9—8·8 (7H, m, ring methylene protons), and 8·95 and 9·1 (6H, 2 × s, $Me_2C<$). Benzene eluted a mixture of products which was re-chromatographed on alumina to give a (3-methylbut-2-enyl)-1,2,3,4-tetrahydrocarbazole (R_F 0·8), $\lambda_{max.}$ (EtOH) 240, 278sh, and 291 nm (ε not recorded); τ (CCl_4 with a trace of benzene) 2·2—3·2 (m, aromatic), 4·75br (1H, t, $-CH_2 \cdot CH=$), 6·9—9·2 (m, allyl and ring methylene protons), and 8·25 and 8·4 (2 × s, $Me_2C=$). Further characterisation was precluded by the air-sensitivity of the product and lack of material. Further elution with benzene gave other mixtures which were re-chromatographed to give 1,2,3,4-tetrahydrocarbazole (R_F 0·7), m.p. 112—115°, and carbazole, m.p. 237—238°. The u.v. and n.m.r. spectra of these two substances were identical with those of authentic specimens.

2,3-*Dimethyl*-3-(*prop*-2-*ynyl*)-3H-*indole* (5; R^1 = H, R^2 = Me). A solution of the 3*H*-indole (2·55 g) in dry distilled tetralin (20 ml) was refluxed under dry nitrogen for 2 h. The solution was cooled and chromatographed on alumina. Petrol eluted the high boiling solvent, and benzene yielded 2-(*buta*-2,3-*dienyl*)-3-*methylindole* (20; R^1 = R^2 = H) (1·20 g, 47%), as a viscous oil which solidified overnight at 0° (Found: C, 85·3; H, 6·7; N, 7·4. $C_{13}H_{13}N$ requires C, 85·2; H, 7·2; N, 7·6%); $\lambda_{max.}$ (EtOH) 227, 278sh, 285, and 292 nm (ε 35,030, 8240, 8940, and 8130); $\nu_{max.}$ (CCl_4) 1244, 1277, 1306, 1333, 1439, 1463, 1487, 1624, 1959, 3429, and 3484 cm^{-1} τ (CCl_4) 2·3—3·1 (5H, m, aromatic and −NH), 4·6—5·4 (3H, m, $-CH{:}C{:}CH_2$), 6·6—6·9 (2H, m, $-CH_2 \cdot CH{:}C{:}CH_2$), and 7·9 (3H, s, 3-Me). Ethyl acetate eluted unchanged starting material (1·05 g, 41%).

3-*Allyl*-3-*methyl*-2-*phenyl*-3H-*indole* (4; R^1 = H, R^2 = Ph). Although stable to reflux in *o*-dichlorobenzene, the 3*H*-indole (0·55 g, 0·0028 mol) in boiling tetralin (10·0 ml) was converted into a single product in 28 h under nitrogen, and the mixture was chromatographed on alumina. Petrol eluted the tetralin, and benzene gave a clear oil which solidified at 0° in 3 days to give 1-*allyl*-3-*methyl*-2-*phenylindole* (22; R = H) (0·43 g, 78%), m.p. 53—54° (Found: C, 87·8; H, 6·8; N, 5·5. $C_{18}H_{17}N$ requires C, 87·4; H, 6·9; N, 5·7%); $\lambda_{max.}$ (EtOH) 228, 238sh, and 299 nm (ε 27,910, 20,780, and 12,770); $\nu_{max.}$ (CCl_4) 925, 1194, 1334, 1357, 1442, 1466, 1607, and 1646, cm^{-1}; τ (CCl_4) 2·4—3·3 (9H, m, aromatic), 3·9—5·4 (3H, m, $-CH=CH_2$), 5·7 (2H, m, $>NCH_2-$), and 7·8 (3H, s, 3-Me). Chloroform eluted unchanged starting material (0·04 g, 7%).

3-*Methyl*-3-(3-*methylbut*-2-*enyl*)-2-*phenyl*-3H-*indole* (4; R^1 = Me, R^2 = Ph). A solution of the 3*H*-indole (1·60 g) in redistilled 1-chloronaphthalene (16 ml) was refluxed under nitrogen for 15 h. Chromatography on alumina with petrol removed the high boiling solvent, and then

elution with benzene gave 3-*methyl*-1-(3-*methylbut*-2-*enyl*)-2-*phenylindole* (22; R = Me) (0·10 g, 6%) (R_F 0·95) (Found: C, 87·3; H, 7·6; N, 5·0. $C_{20}H_{21}N$ requires C, 87·2; H, 7·7; N, 5·1%); $\lambda_{max.}$ (EtOH) 224, 238sh, and 298 nm (ε 34,400, 22,100, and 14,610); $\nu_{max.}$ (CCl_4) 1181, 1213, 1313, 1335, 1354, 1383, 1465, and 1607 cm^{-1}, τ (CCl_4) 2·3—3·2 (9H, m, aromatic), 4·8br (1H, t, $-CH_2\cdot CH=$), 5·5 (2H, d, $>NCH_2-$), 7·8 (3H, s, 3-Me), and 8·35 and 8·5 (6H, 2 × s, $Me_2C=$). Further elution with benzene and then with chloroform gave 3-methyl-2-phenylindole (0·50 g), m.p. 86—90°, identified by comparison of its i.r., u.v., and n.m.r. spectra with those of an authentic sample.

Syntheses and Thermal Reactions of 3H-*Indole Anhydro-bases.—General conditions of preparation and thermolysis.* A solution of the 3*H*-indole methiodide (0·7—2·0 g) in ether (30 ml) was stirred vigorously under nitrogen for 15 min with aqueous sodium hydroxide (150 ml; N). The organic layer was separated, washed with water (3 × 50 ml), and dried (Mg_2SO_4). Removal of solvent gave the anhydro-base. The (usually pale pink) extremely air-sensitive crude product was then dissolved in the solvent of choice and refluxed under nitrogen until all traces of starting material had disappeared or reaction was complete (t.l.c.). The product was isolated by evaporation of solvent under reduced pressure, and then either chromatography or molecular distillation of the residue.

(b) *Thermolyses of some* 3H-*indole anhydro-bases.* (i) 3-Allyl-1,2,3-trimethyl-3*H*-indolium iodide and 3-allyl-1,3-dimethyl-2-methyleneindoline (8; R = H). The *methiodide* was prepared from the 3*H*-indole in the usual way and crystallised from acetone–benzene as fine hairs, m.p. 164—175° (Found: C, 51·4; H, 5·5; N, 4·4. $C_{14}H_{18}IN$ requires C, 51·4; H, 5·5; N, 4·3%); $\lambda_{max.}$ (EtOH) 206, 211, 219, 237sh, and 280 nm (ε 16,940, 16,540, 16,840, 7190, and 7690); $\nu_{max.}$ ($CHCl_3$) 1612 and 1636 cm^{-1}; τ ($CDCl_3$) 2·1—2·5 (4H, m, aromatic), 4·6—5·2 (3H, m, $-CH=CH_2$), 5·75 (3H, s, NMe), 6·9 (3H, s, 2-Me), 7·1—7·2 (2H, m, $-CH_2\cdot CH=$), and 8·3 (3H, s, 3-Me). The wide m.p. range of this derivative is due to loss of hydrogen iodide at or near the m.p. and thermal rearrangement of the anhydro-base thus formed (as evidenced by n.m.r. spectral analysis of a melt of the methiodide). The anhydro-base obtained from this methiodide (2·0 g) was boiled under reflux in toluene (20 ml) for 22 h, to give 2-(*but*-3-*enyl*)-1,3-*dimethylindole* (7; R^1 = H, R^2 = Me) as a mobile oil (1·1 g, 90%) (Found: C, 84·0; H, 8·5; N, 7·1. $C_{14}H_{17}N$ requires C, 84·4; H, 8·6; N, 7·0%); $\lambda_{max.}$ (EtOH) 230, 281sh, 287, and 293 nm (ε 32,800, 6520, 7270, and 6930); $\nu_{max.}$ (CCl_4) 916, 999, 1015, 1189, 1250, 1328, 1367, 1384, 1410, 1416, 1442, 1471, 1641, 2865, 2933, 2980, and 3063 cm^{-1}; τ (CCl_4) 2·55—3·2 (4H, m, aromatic), 3·8—5·2 (3H, AB_2 m, $-CH=CH_2$), 6·5 (3H, s, NMe), and 7·05—8·0 (7H, m, 3-Me at 7·85 and $-CH_2CH_2\cdot CH{:}C$).

(ii) 1,3-*Dimethyl*-3-(3-*methylbut*-2-*enyl*)-2-*methyleneindoline* (8; R = Me). After reflux for 6 days in toluene (20 ml), traces of the anhydro-base derived from 1,2,3-trimethyl-3-(3-methylbut-2-enyl)-3*H*-indolium iodide (2·0 g) still remained, so the product was separated by chromatography on alumina with benzene and distilled on a short-path apparatus (56° at 0·02 mmHg) to give 2-(2,2-dimethylbut-3-enyl)-1,3-dimethylindole (7; R^1 = R^2 = Me) (0·95 g, 74%) as a mobile oil; n_D^{23} 1·5732 (Found: C, 85·0; H, 9·0; N, 6·4. $C_{16}H_{21}N$ requires C, 84·6; H, 9·3; N, 6·2); $\lambda_{max.}$ (EtOH) 232, 282sh, 288, and 295 nm (ε 30,780, 6240, 7000, and 6690); $\nu_{max.}$ (CCl_4) 916, 1192, 1328, 1362, 1382, 1439, 1473, 1640, 2871, 2931, 2967, and 3064 cm^{-1}; τ (CCl_4) 2·55—3·25 (4H, m, aromatic), 3·95—5·4 (3H, AB_2 m, $-CH=CH_2$), 6·65 (3H, s, NMe), 7·4 (2H, s, $-CH_2\cdot CMe_2-$), 7·8 (3H, s, 3-Me), and 9·0 (6H, s, $Me_2C<$), *m/e* 227 (M^+, 48%), 158 (100).

(iii) *N*-Methyl-4a-allyl-2,3,4,4a-tetrahydrocarbazole (19; R = H). Reflux for 15 h in toluene (20 ml) of the anhydro-base from *N*-methyl-4a-allyl-2,3,4,4a-tetrahydro-1*H*-carbazolium iodide (2·0 g) caused isomerisation to N-*methyl*-1-*allyl*-1,2,3,4-*tetrahydrocarbazole* (18; R^1 = H, R^2 = Me), which was isolated as a pale yellow viscous oil (1·05 g, 82%) (Found: C, 85·4; H, 8·4; N, 6·2. $C_{16}H_{19}N$ requires C, 85·3; H, 8·5; N, 6·2%); $\lambda_{max.}$ (EtOH) 232, 281sh, 287, and 293sh nm (ε 35,650, 6750, 7440, and 7030); $\nu_{max.}$ (CCl_4) 918, 1191, 1316, 1378, 1417, 1449, 1472, 1640, 2880, 2937, and 3063 cm^{-1}; τ (CCl_4) 2·6—3·3 (4H, m, aromatic), 3·85—5·2 (3H, m, $-CH=CH_2$), 6·55 (3H, s, NMe), and 7·0—8·5 (9H, m, ring and allyl methylene protons).

(iv) *N*-Methyl-4a-(3-methylbut-2-enyl)-2,3,4,4a-tetrahydrocarbazole (19; R = Me). After reflux for 5 days in toluene (15 ml), some of the anhydro-base derived from *N*-methyl-4a-(3-methylbut-2-enyl)-2,3,4,4a-tetrahydro-1*H*-carbazolium iodide (1·50 g) still remained, so the product was separated by chromatography on alumina with benzene and distilled on a short-path apparatus as N-*methyl*-1-(1,1-*dimethylallyl*)-1,2,3,4-*tetrahydrocarbazole* (18; R^1 = R^2 = Me) (0·60 g, 64%), a pale yellow viscous oil (Found: C, 85·6; H, 9·0; N, 5·5. $C_{18}H_{23}N$ requires C, 85·3; H, 9·2; N, 5·5%); $\lambda_{max.}$ (EtOH) 233, 281sh, 287, and 294 nm (ε 37,010, 13,590, 15,200, and 14,520); $\nu_{max.}$ (CCl_4) 913, 1181, 1308, 1333, 1349, 1372, 1415, 1470, 1637, 2877, 2945, 2965, and 3060 cm^{-1}; τ (CCl_4) 2·6—3·3 (4H, m, aromatic), 3·9—5·3 (3H, AB_2 m, $-CH=CH_2$), 6·5 (3H, s, NMe), 7·1—8·55 (7H, m, ring methylene protons), and 8·9 and 8·95 (6H, 2 × s, $Me_2C<$).

(v) 1,3-Dimethyl-2-methylene-3-(prop-2-ynyl)indoline (21). Reflux for 17 h in toluene (20 ml) of the anhydro-base from 1,2,3-trimethyl-3-(prop-2-ynyl)-3*H*-indolium iodide (0·70 g) caused quantitative isomerisation to 2-(*buta*-2,3-*dienyl*)-1,3-*dimethylindole* (20; R^1 = H, R^2 = Me), which was isolated as an oil (0·40 g, 96%) (Found: C, 85·9; H, 7·5; N, 6·9. $C_{14}H_{15}N$ requires C, 85·2; H, 7·7; N, 7·1%); $\lambda_{max.}$ (EtOH) 231, 282sh, 288, 294, and 325sh nm (ε 32,810, 6800, 7460, 7250, and 1590); $\nu_{max.}$ (CCl_4) 1191, 1279, 1329, 1368, 1384, 1409, 1438, 1474, 1617, and 1961 cm^{-1}; τ (CCl_4) 2·55—3·2 (4H, m, aromatic), 4·7—5·6 (3H, m, $-CH{:}C{:}CH_2$), 6·55 and 6·5—6·8 (5H, s and m, NMe and $-CH_2CH{:}C{:}CH_2$), and 7·85 (3H, s, 3-Me); *m/e* 197 (M^+, 12%), 105 (100).

Synthesis and Thermal Reactions of 3-*Allyl*-1,2,3-*trimethylindoline* (23).—Sodium borohydride (0·8 g, 0·022 mol) was added in portions with shaking to a cooled solution of 3-allyl-1,2,3-trimethyl-3*H*-indolium iodide (6·25 g, 0·019 mol) in methanol (30 ml) at 0°. The solution was allowed to warm, and was set aside at room temperature for 10 min. The mixture was then evaporated, and the residue was dissolved in ether (50 ml); the solution was washed with water (3 × 25 ml), and dried (K_2CO_3). Removal of solvent left an oil containing two components (t.l.c.; benzene, silica) (R_F 0·1 and 0·8). These were separated by chromatography on silica; benzene eluted the major product (R_F 0·8), identified after molecular distillation (b.p. 39° at 0·06 mmHg) as the indoline (23) (3·0 g, 78%) (mixture of *cis*- and *trans*-methyl forms); n_D^{24} 1·5448 (Found: C, 83·6; H, 9·3; N, 6·8. Calc. for $C_{14}H_{19}N$: C, 83·5; H, 9·5; N, 7·0%); $\lambda_{max.}$ (EtOH) 208, 255, and 298 nm (ε 21,350, 8360,

and 2590); $\nu_{max.}$ (CCl_4) 915, 1120, 1272, 1298, 1310, 1347, 1379, 1457, 1466, 1484, 1608, 1639, 2801, 2968, and 3079 cm^{-1}; τ (CCl_4) 2·9—3·8 (4H, m, aromatic), 4·0—5·4 (3H, AB_2 m, $-CH=CH_2$), 7·15 (1H, q, 2-H), 7·45 (3H, s, NMe), 7·6—8·3 (2H, m, $-CH_2 \cdot CH=$), and 8·7—9·0 (6H, s, and 2 × d, 2- and 3-Me, not individually assignable). Ether eluted the minor product (R_F 0·1), identical (by n.m.r. spectra) with the anhydro-base of the parent 3*H*-indole methiodide. Thermal reaction of a solution of the *cis*- and *trans*-indoline mixture (2 g) in 1-chloronaphthalene (20 ml) showed slow disappearance of the indoline over 1 week with formation of a complex mixture, from which no identifiable product could be isolated.

2,3-*Dimethyl*-1-(3-*methylbut*-2-*enyl*)*indole* (11).—To a solution of sodamide [from Na (0·5 g)] in liquid ammonia (20 ml) was added 2,3-dimethylindole (2·88 g, 0·02 mol), and the mixture was stirred for 10 min to allow complete formation of the sodium salt. 3-Methylbut-2-enyl bromide (3·0 g, 0·02 mol) was then added dropwise with stirring, the ammonia was allowed to evaporate, and the residue was extracted with ether (100 ml). The extract was washed with water (80 ml), and dried (K_2CO_3). Evaporation and distillation of the residue yielded the *indole* (11) as an oil (Found: C, 84·8; H, 9·2; N, 6·4. $C_{15}H_{19}N$ requires C, 84·5; H, 9·0; N, 6·6%); $\lambda_{max.}$ (EtOH) 231, 281sh, 287, and 293 nm (ε 31,610, 5850, 6550, and 6320); $\nu_{max.}$ (CCl_4) 1180, 1312, 1333, 1357, 1386, 1418, and 1470 cm^{-1}; τ (CCl_4) 2·5—3·2 (4H, m, aromatic), 4·95br (1H, t, $-CH_2 \cdot CH=$), 5·6 (2H, d, $>NCH_2-$), 7·8 (6H, s, 2- and 3-Me), and 8·25 and 8·3 (6H, 2 × s, $Me_2C=$).

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