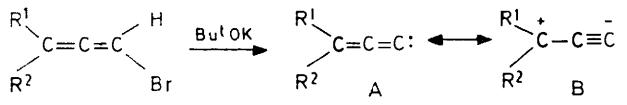
Allenes. Part 34.[1] Reactions of Methylindoles and 2,5-Dimethylpyrrole with Allenic Carbenes

By **Stephen R. Landor,*** Department of Chemistry, Exeter University, Exeter EX4 4QD
Vernon Rogers and **Hem R. Sood,** School of Chemistry, Thames Polytechnic, London SE18 6PF

1-Bromoallenes give allenic carbenes under basic conditions, which react with methylindoles to give alkenylquinolines by ring expansion and alkynyl- and allenyl-3*H*-indoles. Under the same conditions 2,5-dimethylpyrrole is converted into a 3-alkenyl-2,6-dimethylpyridine.

THE formation of allenic carbenes on treatment of 1-bromoallenes with potassium t-butoxide has been demonstrated by trapping these intermediates with styrene and cyclohexene;[2] high yields of cyclopropane derivatives were obtained with styrene but only moderate yields with cyclohexene.[3] We have now investigated the reaction of allenic carbenes with a variety of nitrogen and oxygen heterocyclic compounds and here report our results with several methylindoles and with 2,3-dimethylpyrrole.†

Equimolar quantities of 1-bromo-3-methylbuta-1,2-diene (1) and potassium t-butoxide at −10 °C, with 3-methylindole gave two isomeric liquid basic products, $C_{14}H_{15}N$ which were separated by g.l.c. The minor



(1) $R^1 = R^2 = Me$
(2) $R^1 = H, R^2 = Pr$
(3) $R^1 = R^2 = Me$
(4) $R^1 = H, R^2 = Pr$

product (*ca.* 2% yield), which readily formed a picrate, was obtained as a colourless liquid. Its i.r. spectrum showed characteristic terminal acetylenic absorption at 3 285 (≡C–H) and 2 100 cm^{-1} (C≡C) as well as bands at 1 610 and 1 590 cm^{-1} which have been attributed to the 2*H*-indole system,[4] and its identification as 3-(1,1-dimethylprop-2-ynyl)-3-methyl-3*H*-indole (8) was consistent with the n.m.r. spectrum. The major basic product (*ca.* 30% estimated by g.l.c. of crude basic fraction; 51% taking into account recovered indole) showed $\lambda_{max.}$ 227, 280, and 318 nm, a strongly deshielded one-proton singlet at τ 1.39 (–CH=N–) and three separate CMe signals at τ 7.46, 8.05, and 8.35. These and other physical data were consistent with the basic product being 4-methyl-3-(2-methylprop-1-enyl)quinoline (10). During the early stages of this work Bycroft *et al.*[5] briefly reported a quinoline from 3-chloro-3-methylbutyne, 3-methylindole, and anhydrous potassium carbonate in acetone which had similar spectral properties and was assigned the same structure (10) on the basis of the results of ozonolysis and hydrogenation. We found that at room temperature the chloroacetylene and 3-methylindole gave no reaction with potassium carbonate, but on heating under reflux for 12 h a 7.2% yield of a quinoline was obtained which was identical with our product (10). Under similar conditions the bromoallene did not react with potassium carbonate. The non-basic fraction from the reaction afforded only traces of two unidentified unsaturated compounds in addition to 3-methylindole (34% recovery). The yield of basic material was not improved by using either an excess of potassium t-butoxide or an excess of bromoallene.

Formation of the alkenylquinoline (10) may be rationalised in terms of addition of the allenic carbene (3A) to the nucleophilic 2,3-bond of 3-methylindole followed by ring opening of the alkylidenecyclopropane (Scheme). This mechanism is similar to that accepted for the formation of 3-halogenoquinolines from dihalogenocarbenes and indoles.[6,7] However the alkynyl-3*H*-indole (8) can be derived formally by electrophilic attack of the carbene [in canonical form (3B)] on 3-methylindole. Under the mild basic conditions used to generate the carbene from 3-chloro-3-methylbutyne, formation of the 3-methylindolide anion would not be expected, and we found no evidence (g.l.c.) for the presence of (8) in the product from this reaction. This suggests that the alkynyl-3*H*-indole (8) is formed by attack of the carbene (3A) on the 3-methylindolide anion which is produced under the strongly basic conditions used to generate the carbene from the bromoallene. Rees and Smithen [6] similarly found that the proportion of 3-dichloromethyl-2,3-dimethyl-3*H*-indole to 3-chloro-2,4-dimethylquinoline from the reaction of dichlorocarbene with 2,3-dimethylindole depended on the mode of carbene formation. The more basic the conditions the higher was the proportion of 3*H*-indole found in the product, showing that the indolide anion rather than the indole itself was attacked by the electrophile.

Treatment of 2,3-dimethylindole (6) with 1-bromo-3-methylbuta-1,2-diene under similar conditions gave a mixture of three basic products, two of which, including the quinoline (11), were obtained pure by preparative g.l.c. The main product (*ca.* 32% estimated by g.l.c. of crude basic fraction) was 2,3-dimethyl-3-(3-methylbuta-1,2-dienyl)-3*H*-indole (13), apparently the first

† For the reactions of heterocyclic compounds with various carbenes see C. W. Rees and C. E. Smithen, *Adv. Heterocyclic Chem.*, 1964, **3**, 57; R. Gompper, *ibid.*, 1963, **2**, 245.

[1] Part XXXIII, P. M. Greaves, S. R. Landor, and M. M. Lwanga, *Tetrahedron*, 1975, **31**, 3073.

[2] S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 1965, 5625.

[3] It has recently been shown that improved yields may be obtained by phase transfer catalysis: T. B. Patrick, *Tetrahedron Letters*, 1974, 1407; P. D. Landor, S. R. Landor, and R. Liddell, unpublished work.

[4] F. J. Evans, G. G. Lyle, J. Watkins, and R. E. Lyle, *J. Org. Chem.*, 1962, **27**, 1553; B. Witkop and T. B. Patrick, *J. Amer. Chem. Soc.*, 1951, **73**, 713, 1558, 2188.

[5] B. W. Bycroft, A. P. Johnson, and W. Landon, *Chem. Comm.*, 1969, 463.

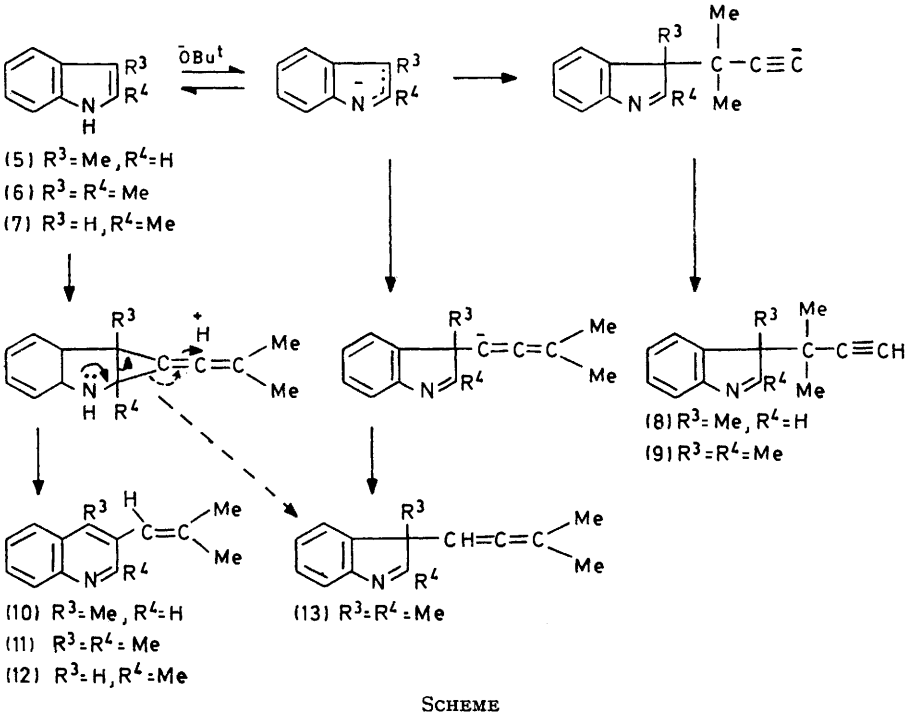
[6] C. W. Rees and C. E. Smithen, *Chem. and Ind.*, 1962, 1022; *J. Chem. Soc.*, 1964, 928.

[7] B. Robinson, *Tetrahedron Letters*, 1962, **4**, 139.

allenylindole to be described. The typical allene C=C=C stretching band at 1 965 cm^{-1} together with a one-proton septet at τ 5.25 ($HC{=}C{=}CMe_2$) confirmed the allenyl structure. Electrophilic attack on the 2,3-dimethylindole (as compared with the 3-methylindole) would be expected at the sterically least congested end of the carbene owing to steric hindrance by the extra 2-methyl group. The third base could not be completely separated from traces of allenic 3*H*-indole (13) but the presence of i.r. bands at 3 295 (≡C–H) and 2 100 cm^{-1} (C≡C) and the n.m.r. signal at τ 7.68 suggested that it was 3-(1,1-dimethylprop-2-ynyl)-2,3-dimethyl-3*H*-indole (9). Only unchanged 2,3-dimethylindole was isolated from the acid-insoluble fraction.

in 3-methyl- or 2,3-dimethyl-indole,[8] and the absence of any 3*H*-indole in its reaction with the carbene (3) is consistent with the proposal that the 3*H*-indoles arise *via* the indolide anions.

The scope of these ring expansion reactions was further investigated by treating 3-methyl- and 2,3-dimethyl-indole with the propyl-substituted allenic carbene (4) derived from 1-bromohex-1,2-diene (2). With 3-methylindole, *cis*- and *trans*-4-methyl-3-(pent-1-enyl)quinolines, (14) and (16), were the only basic products isolated; their formation may be explained by attack of a proton on either side of the anion formed from the intermediate cyclopropane derivative (Scheme). The isomers were readily differentiated by their i.r.



SCHEME

The formation of the allenyl compound (13), also characterised as its picrate and methiodide, may be explained by electrophilic attack of the carbene (3) at C-3 of the indolide anion followed by proton transfer (Scheme). An alternative mechanism involving ring opening of the cyclopropane intermediate would also give the allene (13) and cannot be discounted.

In contrast to the foregoing reactions, treatment of 2-methylindole (7) with the allene (1) and potassium t-butoxide gave 2-methyl-3-(2-methylprop-1-enyl)-quinoline (12) as the only isolable basic product. The non-basic fraction afforded a large amount (44%) of 2-methylindole together with a black gum.

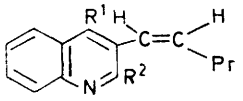
If the amount of basic material isolated from these reactions is taken as a crude estimate of the reactivity of the indoles towards carbene (3) they may be placed in the following order: 2,3-dimethylindole (62%) > 3-methylindole (33%) > 2-methylindole (20%). 2-Methylindole is more basic and the proton less acidic than that

spectra and also their n.m.r. spectra, which showed *J* 11 and 16 Hz for the olefinic protons of (14) and (16), respectively, as expected for *cis*- and *trans*-coupling. The absence of any 3*H*-indole derivative contrasts with the reaction of this indole with the 3,3-disubstituted carbene (3) and cannot readily be explained.

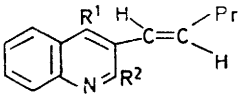
However four basic compounds were formed on reaction of the carbene (4) and potassium t-butoxide with 2,3-dimethylindole: 2,3-dimethyl-3-(1-propylprop-2-ynyl)-3*H*-indole (18) and 3-(hexa-1,2-dienyl)-2,3-dimethyl-3*H*-indole (19) formed by attack of the resonance-stabilised carbene (4) on the 2,3-dimethylindolide anion as in the corresponding reaction with 3-methylbuta-1,2-diene, and the *cis*- and *trans*-alkenylquinolines (15) and (17). There was insufficient material to allow full characterisation of (17) but the n.m.r. spectrum fully supported the assignment; in particular, the large value

[8] R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796.

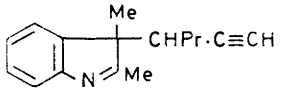
of the coupling constant for the olefinic protons (J 16 Hz) indicated the *trans*-nature of the double bond and may be contrasted with the low value (J 11 Hz) observed with the *cis*-compound (15).



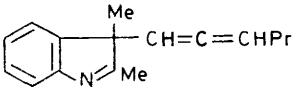
(14) R^1 = Me, R^2 = H
(15) R^1 = R^2 = Me



(16) R^1 = Me, R^2 = H
(17) R^1 = R^2 = Me



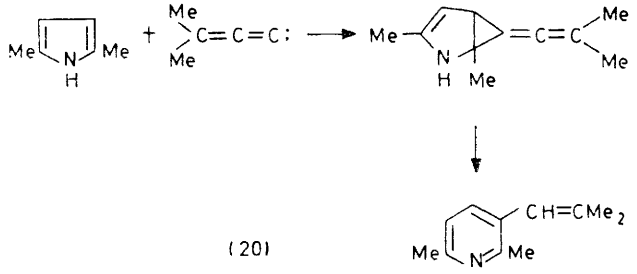
(18)



(19)

The non-basic fractions from all the reactions contained a considerable quantity of unchanged indole. Hence, although the amounts of isolated basic material were not large, the overall conversions based on material consumed were reasonable from the synthetic aspect. The main problem from the preparative point of view is that of the separation and isolation of the individual bases where mixtures were obtained.

Pyrroles undergo ring expansion with dichlorocarbene to give pyridines [8] in an analogous manner to that of the indole–quinoline interconversion; hence the reaction of pyrroles with allenic carbenes would be expected to afford alkenylpyridines. When 2,5-dimethylpyrrole was



(20)

treated with the allene (1) and potassium t-butoxide, the expected ring expansion occurred to give 2,6-dimethyl-3-(2-methylprop-1-enyl)pyridine (20); no 3*H*-pyrroles were detected.

EXPERIMENTAL

G.l.c. (analytical and preparative) was carried out on Pye 104 and 105 gas chromatographs fitted with flame ionisation detectors, with nitrogen as carrier gas (flow rate 2 l h^{-1}) and glass columns (5 ft analytical or 7 ft preparative) containing silicone oil (SE30; 10%) on Chromosorb W. I.r. spectra were determined for liquid films with Perkin-Elmer 237 and 337 spectrophotometers. U.v. spectra were obtained for ethanolic solutions with a Bausch and Lomb spectronic 505 spectrometer. N.m.r. spectra were determined with a Varian A60 spectrometer for *ca.* 20% solutions in deuteriochloroform except where otherwise stated, with tetramethylsilane as internal standard.

Reaction of 3-*Methylindole with* 1-*Bromo*-3-*methylbuta*-1,2-*diene and Potassium t-Butoxide.*—1-Bromo-3-methylbuta-1,2-diene (14.7 g, 0.1 mol) was added in portions over 1 h to a vigorously stirred slurry of potassium t-butoxide (12.32 g, 0.11 mol) and 3-methylindole (13.1 g, 0.1 mol) in dry hexane (150 ml) under nitrogen while the temperature was maintained at −5 to −10 °C. The mixture was stirred at −5 °C for 2 h and at room temperature for 12 h. Volatile material was removed at 40 °C and 20 mmHg and the oily residue dissolved in ether (150 ml) and extracted with ice-cold 10% hydrochloric acid (5 × 50 ml). The extract was washed with water, dried ($MgSO_4$), and evaporated to give a non-basic fraction (12 g). The acidic extract was made alkaline with aqueous 10N-potassium hydroxide, with the temperature kept below 10 °C, and extracted with ether (6 × 60 ml). The extract was washed with water, dried ($MgSO_4$), and evaporated to give a basic fraction (6.6 g).

Distillation of the basic fraction gave a pale yellow liquid (4.5 g), b.p. 108—118° at 0.3 mmHg. G.l.c. on silicone oil at 150 °C showed three components with t_R 6.7 (1%), 9.6 (10%), and 35.0 min (89%). These were separated by preparative g.l.c. (160 °C) to give (i) the trace component, t_R 6.7, 3-methylindole, identified by i.r. and g.l.c.; (ii) 3-(1,1-*dimethylprop*-2-*ynyl*)-3-*methyl*-3H-*indole* (8) as a liquid (Found: C, 84.9; H, 7.85; N, 7.2. $C_{14}H_{15}N$ requires C, 85.25; H, 7.6; N, 7.1%), $\nu_{max.}$ 3 285 (≡C–H), 3 040, 3 020, 2 100 (C≡C), 1 610, 1 590 (ArN=C), 1 565, 770, and 750 cm^{-1} (*o*-disubstituted benzene), τ 8.85 (6 H, s, CMe_2), 8.50 (3 H, s, Me-3), 7.68 (1 H, s, C=CH), 2.34—2.85 (4 H, m, aromatic), and 1.87 (1 H, s, CH=N); [4] and (iii) 4-*methyl*-3-(2-*methylprop*-1-*enyl*)*quinoline* (10), b.p. 115—116° at 0.3 mmHg [lit.,[5] b.p. 110—120° (air bath temp.) at 0.1 mmHg] (Found: C, 85.05; H, 7.65; N, 6.95. $C_{14}H_{15}N$ requires C, 85.25; H, 7.6; N, 7.1%), $\nu_{max.}$ 3 060, 1 655 (C=C), 1 615, 1 570, and 750 cm^{-1}, $\lambda_{max.}$ 227 (ε 39 400), 280 (6 840), and 318 nm (3 283), τ 8.35 (3 H, d, J 1 Hz, CH=C*Me*), 8.05 (3 H, d, J 1 Hz, CH=C*Me*), 7.46 (3 H, s, Me-4), 3.70br (1 H, s, C*H*=CMe_2), 1.85—2.80 (4 H, m, aromatic), and 1.39 (1 H, s, C*H*=N); the *picrate* crystallised from aqueous ethanol as yellow needles, m.p. 157—158° (decomp.) (Found: C, 56.25; H, 4.4; N, 13.05. $C_{20}H_{18}N_4O_7$ requires C, 56.3; H, 4.2; N, 13.15%). The yields of the 3*H*-indole and the quinoline, estimated by direct g.l.c. analysis of the distilled basic fraction, were *ca.* 0.45 g (2%) and 4.0 g (20%), respectively.

The non-basic fraction was chromatographed on alumina (360 g). Elution with ether–hexane (10.90) gave an unidentified pale yellow liquid (0.080 g), $\nu_{max.}$ 2 015 and 1 610 cm^{-1} (C=C). Ether–hexane (20 : 80 to 40 : 60) eluted a yellow oil (0.78 g), $\nu_{max.}$ 3 300 (≡C–H), 3 040, 2 100 (C≡C), 1 640, and 1 610 cm^{-1} (C=C), unidentified, and ether–hexane (40 : 60 to 60 : 40) eluted 3-methylindole (4.5 g, 34% recovery) as white plates (from hexane), m.p. and mixed m.p. 94—95°.

No substantial difference in the yield of isolated basic material was observed when the reaction was carried out with 2 mol. equiv. of potassium t-butoxide or 2 mol. equiv. of the bromoallene. When the reaction was carried out at 30 °C the yield was approximately halved.

Reaction of 2,3-*Dimethylindole with* 1-*Bromo*-3-*methylbuta*-1,2-*diene and Potassium t-Butoxide.*—1-Bromo-3-methylbuta-1,2-diene (14.7 g, 0.1 mol) was added dropwise over 45 min to a vigorously stirred slurry of potassium t-butoxide (12.32 g, 0.11 mol) and 2,3-dimethylindole (14.5 g, 0.1 mol) in dry hexane (160 ml) under nitrogen, while the temperature was maintained at −10 °C. After stirring at

−10 °C for 2 h and overnight at room temperature the mixture was worked up as above to give non-basic (4.35 g) and basic (13.2 g) fractions.

Distillation of the basic fraction gave a pale brown liquid (9.96 g), b.p. 93—99° at 0.2 mmHg. G.l.c. on silicone oil at 160 °C showed four components, t_R 9.3 (1%), 12.7 (13%), 14.6 (52%), and 31.6 min (33%), which were separated by preparative g.l.c. to give (i) 2,3-dimethylindole, m.p. and mixed m.p. 100—101°, t_R 9.3 min; (ii) a light yellow liquid, shown by g.l.c. to consist of the second component, t_R 12.7 min, contaminated with *ca.* 8% of the third component, t_R 14.6 min; the i.r. spectrum $\nu_{max.}$ 3 295s (≡C–H), 3 045w, 2 100w (C≡C), 1 960w (C=C=C), 1 610w, 1 590w, 1 575s, 770s, and 750s cm^{-1} (*o*-disubstituted benzene) suggested that the major component was 3-(1,1-dimethylprop-2-ynyl)-2,3-dimethyl-3*H*-indole (9), but it could not be obtained pure; (iii) 2,3-*dimethyl*-3-(3-*methylbuta*-1,2-*dienyl*)-3H-*indole* (13), a light yellow liquid (3.5 g, 17%), b.p. 96—97° at 0.15 mmHg, which darkened at room temperature (Found: C, 84.9; H, 8.0; N, 7.1. $C_{15}H_{17}N$ requires C, 85.3; H, 8.05; N, 6.65%), $\nu_{max.}$ 3 050, 1 965 (C=C=C), 1 610, 1 580 (Ar–N=C), 770, 755, and 740 cm^{-1} (*o*-disubstituted benzene), $\lambda_{max.}$ 212 (ε 21 100), 225sh (15 345), and 260 nm (5 755), τ 8.68 (3 H, s, Me-3), 8.25 (6 H, d, *J* 3 Hz, CH=C=C*Me*$_2$), 7.75 (3 H, s, Me-2), 5.25 (1 H, *J* 3 Hz, septet, C*H*–C–CMe$_2$), and 2.4—2.9 (4 H, m, aromatic); the *picrate* crystallised from ethanol as yellow needles, m.p. 114—116° (decomp.) (Found: C, 57.0; H, 4.65; N, 12.8. $C_{21}H_{20}N_4O_7$ requires C, 57.25; H, 4.55; N, 12.7%); the *methiodide*, prepared by refluxing with methyl iodide in dry benzene, crystallised from ethanol as yellow plates, m.p. 140—142° (decomp.) (Found: C, 54.65; H, 5.8; N, 4.1. $C_{16}H_{20}IN$ requires C, 54.4; H, 5.65; N, 3.95%); and (iv) 2,4-*dimethyl*-3-(2-*methylprop*-1-*enyl*)-*quinoline* (11) (2.5 g, 12%), a light yellow liquid, b.p. 99—100° at 0.15 mmHg (Found: C, 84.75; H, 7.95; N, 6.9. $C_{15}H_{17}N$ requires C, 85.3; H, 8.05; N, 6.65%), $\nu_{max.}$ 3 060, 1 660 (C=C), 1 615, 1 580, and 750 cm^{-1}; $\lambda_{max.}$ 228 (ε 51 129), 276 (6 826), 306 (4 033), and 319 nm (4 344), τ 8.6 (3 H, d, *J* 1 Hz, CH=C*Me*), 8.06 (3 H, d, *J* 1 Hz, CH=C*Me*), 7.51 (3 H, s, Me-4), 7.45 (3 H, s, Me-2), 3.85br (1 H, s, C*H*–CMe$_2$), and 1.95—2.84 (4 H, m, aromatic); the *picrate* crystallised from ethanol as yellow needles, m.p. 139—140° (Found: C, 57.8; H, 4.7; N, 13.05. $C_{21}H_{20}N_4O_7$ requires C, 57.25; H, 4.55; N, 12.7%).

Distillation of the non-basic fraction gave 2,3-dimethylindole (3 g, 21% recovery), b.p. 90—95° at 0.5 mmHg.

Reaction of 2-*Methylindole with* 1-*Bromo*-3-*methylbuta*-1,2-*diene and Potassium t-Butoxide.*—Addition of 1-bromo-3-methylbuta-1,2-diene (14.7 g, 0.1 mol) to potassium t-butoxide (12.32 g, 0.11 mol) and 2-methylindole (13.1 g, 0.1 mol) in dry hexane (150 ml) at −10 °C, under nitrogen, then stirring at −10 °C for 2 h and at room temperature for 45 min and work-up as above gave non-basic (10.7 g) and basic (4 g) fractions.

Distillation of the basic fraction gave 2-*methyl*-3-(2-*methylprop*-1-*enyl*)*quinoline* (12) (3 g, 15%), b.p. 116—118° at 0.4 mmHg, t_R 13.9 min on silicone oil at 170 °C (Found: C, 85.15; H, 7.75; N, 7.4. $C_{14}H_{15}N$ requires C, 85.25; H, 7.6; N, 7.1%), $\nu_{max.}$ 3 055, 1 650 (C=C), 1 620, 1 600, 1 565, 780, and 745 cm^{-1} (*o*-disubstituted benzene), $\lambda_{max.}$ 216 (ε 33 390), 230 (33 390), 250 (20 600), 278 (5 683), and 319 nm (4 262), τ 8.27 (3 H, d, *J* 1.5 Hz, CH=C*Me*), 8.05 (3 H, d, *J* 1.5 Hz, CH=C*Me*), 7.35 (3 H, s, Me-2), 3.72br (1 H, s, C*H*·CMe$_2$), and 1.95—2.75 (5 H, m, aromatic); the *picrate* crystallised from aqueous ethanol as yellow needles, m.p. 200—201° (decomp.) (Found: C, 56.45; H, 4.35; N, 13.05. $C_{20}H_{18}N_4O_7$ requires C, 56.35; H, 4.2; N, 13.15%).

Chromatography of the non-basic fraction on alumina (35 g) with hexane followed by hexane–ether, ether, and ether–methanol gave 1-bromo-3-methylbuta-1,2-diene (0.5 g) and 2-methylindole (5.8 g, 44% recovery), identified by i.r. and g.l.c. comparison, and a black gum (3.1 g) which showed several spots on t.l.c. and was not further investigated.

Reaction of 3-*Methylindole with* 1-*Bromohexa*-1,2-*diene and Potassium t-Butoxide.*—1-Bromohexa-1,2-diene (15.9 g, 0.1 mol) was added dropwise over 1 h to a vigorously stirred slurry of potassium t-butoxide (12.32 g, 0.11 mol) and 3-methylindole (13.1 g, 0.1 mol) in dry hexane (150 ml) under nitrogen while the temperature was maintained at −10 °C. The mixture was stirred at this temperature for 1 h then at room temperature overnight and worked up as in the previous experiments to give basic (4.05 g) and non-basic (13.0 g) fractions.

Distillation of the basic fraction gave a light yellow liquid (3.6 g), b.p. 123—128° at 0.2 mmHg. G.l.c. on silicone oil at 170 °C showed three components, t_R 6.7 (1%), 20.6 (62%), and 30.7 (37%) min. Preparative g.l.c. (170 °C) gave pure samples of the two main components: (i) cis-4-*methyl*-3-(*pent*-1-*enyl*)*quinoline* (14), a light yellow liquid, b.p. 126—127° at 0.2 mmHg (Found: C, 84.85; H, 8.2; N, 6.35. $C_{15}H_{17}N$ requires C, 85.3; H, 8.05; N, 6.65%), $\nu_{max.}$ 1 610, 1 570, 1 500, 1 460, 1 385, 750 (*o*-disubstituted benzene), and 730 cm^{-1} (HC=CH-*cis*), $\lambda_{max.}$ 230 (ε 40 880), 282 (6 330), and 320 nm (3 165), τ 9.13 (3 H, t, *J* 6.5 Hz, CH$_2$·CH$_2$*Me*), 7.6—8.84 (4 H, 2 m, C*H*$_2$·CH$_2$Me), 7.41 (3 H, s, Me-4), 4.10 (1 H, dt, *J* 11 Hz, CH=C*H*·CH$_2$), 3.45 (1 H, d, J_{cis} 11 Hz, C*H*=CH·CH$_2$), 1.85—2.75 (4 H, m, aromatic), and 1.34 (1 H, s, H-2); (ii) trans-4-*methyl*-3-(*pent*-1-*enyl*)*quinoline* (16), a light yellow liquid, b.p. 129—130° at 0.2 mmHg (Found: C, 84.85; H, 8.1; N, 6.8. $C_{15}H_{17}N$ requires C, 85.3; H, 8.05; N, 6.65%), $\nu_{max.}$ 1 615 (C=C), 1 570, 1 500, 1 455, 1 380, 965 (HC=CH-*trans*), and 750 cm^{-1} (*o*-disubstituted benzene), $\lambda_{max.}$ 245 (ε 35 920), 286 (9 797), and 326 nm (2 764), τ 9.01 (3 H, t, *J* 6.5 Hz, CH$_2$·CH$_2$*Me*), 7.55—8.72 (4 H, 2m, C*H*$_2$·CH$_2$Me), 7.40 (3 H, s, Me-4), 3.82 (1 H, 2 t, J_{trans} 16 Hz, CH=C*H*·CH$_2$), 3.28 (1 H, d, J_{trans} 16 Hz, C*H*=CH·CH$_2$), 1.88—2.75 (4 H, m, aromatic), and 1.12 (1 H, s, H-2).

Distillation of the non-basic fraction gave 1-bromohexa-1,2-diene (1.5 g, 9% recovery), b.p. 52—53° at 18 mmHg, identified by its i.r. spectrum and g.l.c. The residue (12 g) was chromatographed on alumina (360 g). Elution with hexane–ether (9 : 1) gave 3-methylindole (5 g, 42% recovery), m.p. 93—94° (from hexane). Elution with ether–ethanol (4 : 1) gave a black intractable residue (5 g).

Reaction of 2,3-*Dimethylindole with* 1-*Bromohexa*-1,2-*diene and Potassium t-Butoxide.*—2,3-Dimethylindole (14.5 g, 0.1 mol) was dissolved in a mixture of hexane (20 ml) and ether (5 ml) and added to a slurry of potassium t-butoxide (12.32 g, 0.11 mol) in dry hexane (150 ml) under nitrogen at −10 °C. 1-Bromohexa-1,2-diene (15.9 g, 0.1 mol) was then added dropwise over 45 min with vigorous stirring. Stirring was continued for 2 h at −10 °C then overnight at room temperature. Work-up as in the previous experiments gave a basic (8.1 g) and a non-basic (12 g) fraction.

Distillation of the basic fraction gave a light red liquid (5.3 g), b.p. 118—125° at 0.4 mmHg. G.l.c. on silicone oil

at 170 °C showed four components, t_R 11 (41%), 16.5 (41%), 30.7 (12%), and 42 min (6%), which were separated by preparative g.l.c. (silicone oil; 170 °C) to give (i) 2,3-*dimethyl*-3-(1-*propylprop*-2-*ynyl*)-3H-*indole* (18) as a liquid (t_R 11 min) (Found: C, 85.0; H, 8.3; N, 6.45. $C_{16}H_{19}N$ requires C, 85.35; H, 8.45; N, 6.2%), $\nu_{max.}$ 3 280 (≡C–H), 3 035, 2 090 (C≡C), 1 612, 1 580 (Ar–N=C), 760, and 740 cm^{-1} (*o*-disubstituted benzene), $\lambda_{max.}$ 214 (ε 15 750), 220 (15 975), 226sh (11 725), and 260 nm (4 612), τ 9.26 (3 H, t, unresolved, CH_2Me), 8.15—9.10 (4 H, m, $CH{\cdot}CH_2{\cdot}CH_2Me$), 8.55 (3 H, s, Me-3), 7.8 (3 H, s, Me-2), 7.62 (1 H, s, C≡CH), 7.25 (1 H, m, CH), and 2.24—2.9 (4 H, m, aromatic); (ii) 3-(*hexa*-1,2-*dienyl*)-2,3-*dimethyl*-3H-*indole* (19), a light red liquid, b.p. 122—123° at 0.3 mmHg (t_R 16.5 min) (Found: C, 85.15; H, 8.15; N, 6.5. $C_{16}H_{19}N$ requires C, 85.35; H, 8.45; N, 6.2%), $\nu_{max.}$ 3 040, 1 960 (C=C=C), 1 610, 1 580 (Ar–N=C), 765, and 745 cm^{-1} (*o*-disubstituted benzene), $\lambda_{max.}$ 215 (ε 17 300), 220 (16 600), 228sh (11 530), and 260 nm (4 780), τ 9.09 (3 H, t, unresolved, CH_2Me), 8.65 (3 H, s, Me-3), 7.80—8.56 (4 H, m, $CH_2{\cdot}CH_2Me$), 7.75 (3 H, d, *J* 1 Hz, Me-2), 5.13 (1 H, dt, $J_{3,1}$ 6.5, $J_{3,4}$ 3 Hz, $HC{=}C{=}CH{\cdot}CH_2$), 4.65 (1 H, m, $CH{=}C{=}CH{\cdot}CH_2$), and 2.34—2.87 (4 H, m, aromatic); (iii) 2,4-*dimethyl*-3-(cis-*pent*-1-*enyl*)*quinoline* (15), a light red liquid (t_R 30.7 min) (Found: C, 85.1; H, 8.0; N, 6.55. $C_{16}H_{19}N$ requires C, 85.35; H, 8.45; N, 6.2%), $\nu_{max.}$ 3 055, 1 610 (C=C), 1 580, and 750 cm^{-1} (*o*-disubstituted benzene), $\lambda_{max.}$ 212 (ε 19 500), 229 (26 060), 272 (3 560), 306 (1 875), and 319 nm (1 875), τ 9.19 (3 H, t, $CH_2{\cdot}CH_2Me$), 8.04—8.95 (4 H, m, $CH_2{\cdot}CH_2Me$), 7.45 (3 H, s, Me-4), 7.39 (3 H, s, Me-2), 4.12 (1 H, dt, J_{cis} 11, $J_{2,3}$ 7 Hz, $CH{=}CH{\cdot}CH_2$), 3.55 (1 H, d, J_{cis} 11 Hz, $CH{=}CH{\cdot}CH_2$), and 1.91—2.65 (4 H, m, aromatic); (iv) a light red liquid (t_R 42 min), τ 9.0 (3 H, t, $CH_2{\cdot}CH_2Me$), 7.65—8.66 (4 H, m, $CH_2{\cdot}CH_2Me$), 7.40 (3 H, s, Me-4), 7.37 (3 H, s, Me-2), 4.32 (1 H, dt, J_{trans} 16 Hz, $CH{=}CH{\cdot}CH_2$), 3.45 (1 H, d, J_{trans} 16 Hz, $HC{=}CH{\cdot}CH_2$), and 1.92—26.7 (4 H, m, aromatic), probably 2,4-dimethyl-3-(*trans*-pent-1-enyl)quinoline (17); there was insufficient material for elemental analysis. The yields of the acetylenic 3*H*-indole, allenic 3*H*-indole, *cis*-pentenylquinoline, and *trans*-pentenylquinoline, estimated by direct g.l.c. analysis of the distilled basic fraction were 2.1 g (10%), 2.1 g (10%), 0.6 g (3%), and 0.3 g (1%), respectively.

Distillation of the non-basic fraction gave 1-bromohexa-1,2-diene (1.6 g, 10% recovery), b.p. 53—54° at 21 mmHg, and 2,3-dimethylindole (4.35 g, 30% recovery), b.p. 80—85° at 0.25 mmHg; both compounds were identified by comparison (i.r. spectra and g.l.c.) with authentic samples. An intractable residue remained in the distillation flask.

Reaction of 2,5-*Dimethylpyrrole with* 1-*Bromo*-3-*methylbuta*-1,2-*diene and t-Butoxide*.—2,5-Dimethylpyrrole (9.5 g, 0.1 mol) was added to a slurry of potassium t-butoxide (12.32 g, 0.11 mol) in dry hexane (135 ml) under nitrogen at −10 °C. 1-Bromo-3-methylbuta-1,2-diene (14.7 g, 0.1 mol) was added dropwise after 45 min. Stirring was continued for 2 h at −5 °C and then overnight at room temperature. Volatile material was removed under nitrogen at 40 °C and 15 mmHg and the residue worked up in the usual way to give a basic fraction (11 g) and a non-basic fraction (3.4 g).

The basic fraction, a dark red oil, was chromatographed on neutral alumina (300 g). Elution with hexane and then ether–hexane (1 : 9 to 1 : 1; 1.5 l) gave a pale yellow oil (2 g); distillation gave 2,6-*dimethyl*-3-(2-*methylprop*-1-*enyl*)-*pyridine* (20) (1.2 g, 9%), b.p. 53—54° at 0.2 mmHg (Found: C, 81.7; H, 9.1; N, 8.55. $C_{11}H_{15}N$ requires C, 82.0; H, 9.3; N, 8.7%), $\nu_{max.}$ 1 640 (C=C), 1 565, 1 040, and 835 cm^{-1} (2,3,6-trisubstituted pyridine), $\lambda_{max.}$ 216 (ε 5 898), 239 (7 023), and 280 nm (3 089), τ 8.35 (3 H, d, *J* 1.5 Hz, $CH{=}CMe$), 8.10 (3 H, d, *J* 1.5 Hz, $CH{=}CMe$), 7.6 (3 H, s, Me-6), 7.53 (3 H, s, Me-2), 3.86br (1 H, s, $CH{\cdot}CMe_2$), 3.12 (1 H, d, $J_{5,4}$ 8 Hz, H-5), and 2.75 (1 H, d, $J_{4,5}$ 8 Hz, H-4); g.l.c. on Carbowax 20M at 110 °C showed a single peak, t_R 10.0 min. Elution with ether (800 ml) gave a brown solid (0.5 g); attempts to crystallise the material were not successful. Further elution with ether (100 ml) and then ether–methanol (4 : 1) gave a dark brown solid (4.9 g) which did not melt below 360 °C and was not investigated further.

Distillation of the non-basic fraction gave 1-bromo-3-methylbuta-1,2-diene (1.5 g, 10% recovery), b.p. 34—36° at 18 mmHg, and 2,5-dimethylpyrrole (1.5 g, 15%), b.p. 69—70° at 18 mmHg, both identified by comparison (g.l.c. and i.r. spectra) with authentic specimens.

[6/459 *Received*, 8*th March*, 1976]