Protonation, Alkylation, and Acetylation of Corroles and 21,24-Dioxacorroles

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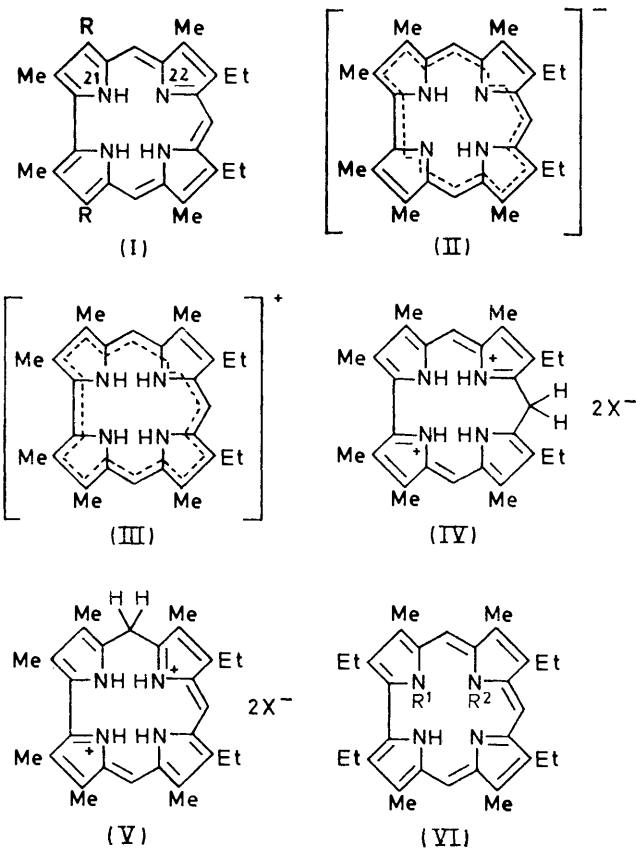
Formation of corrole dications is shown to involve protonation at C-5 rather than at C-10. A series of *N*(21)- and *N*(22)-alkylcorroles (alkyl = methyl, ethyl, allyl, or 3,3-dimethylallyl) has been prepared and although the *N*(21)-isomers and the *N*(22)-methyl and -ethyl derivatives are thermally stable, the *N*(22)-allyl and -(3,3-dimethylallyl) derivatives were transformed into mixtures of the *N*(21)-isomers and the unsubstituted corrole when they were heated in refluxing toluene. Further methylation of the *N*(21)- or *N*(22)-methylcorrole with methyl iodide yielded an *NN'*-dimethylcorrole iodide which gave the *N*(21)-methylcorrole when heated at 180°. Acetylation of corroles yielded the *N*(21)-acetyl derivatives. Alkylation of 21,24-dioxacorrole gave mixtures of mono- and di-*N*-alkylated products, the 22,23-dimethyl derivative having *trans*-22- and 23-methyl substituents, as shown by the resolution of the D-camphorsulphonate. Acetylation of 21,24-dioxacorrole gave a mixture of the 5-monoacetyl and 2,18-(3,17?-) diacetyl derivatives.

LITTLE has been published on the chemical reactivity of corroles since it was established [1] that the corrole ring system [*e.g.* (I; R = Me)], like porphin, contains an aromatic 18 π-electron chromophore, in agreement with the observed electronic, n.m.r., and mass spectra.[1,2] Unlike the porphins, which require fairly vigorous conditions for proton abstraction,[3] corroles readily form stable aromatic anions (II), which also exhibit typically aromatic spectra. The enhanced acidity of corroles over porphins might reflect the relief of the greater steric crowding of the three imino-protons of the corrole system. In this paper we describe the behaviour of corroles and 21,24-dioxacorroles towards protonation, alkylation, and acetylation.

Protonation of Corroles.—Monoprotonation of corroles occurs readily, and the ambident cations (III) so obtained show aromatic spectra. However the green solutions of corroles in concentrated sulphuric acid do not show a Soret band in the electronic spectra, indicative of ' blocked ' structures. In the earlier paper this was accommodated in structure (IV). However, the n.m.r. spectrum of a solution of compound (I; R = Me) in fluorosulphonic acid clearly indicates that structure (IV) should be amended to (V), with the additional protonation at C-5. The n.m.r. spectrum showed an unsymmetrical structure containing sharp singlet resonances at τ 2·1 and 2·23 ascribed to the two non-equivalent *meso*-protons at C-10 and C-15, a less sharp singlet at τ 5·3 corresponding to the C-5 methylene group, and broadened signals between τ 1·1 and 3·7 associated with the imino-protons. N.m.r. spectroscopy of solutions of the corrole in sulphuric acid was of little value because of broadening of the signals due to viscosity.[4] The n.m.r. spectra of the dications of *N*(21)- and *N*(22)-methylcorroles (see later) are also consistent with a C-5 blocked structure. The very large shift of the imino-proton signals from their positions (near τ 13·5) in the n.m.r. spectra of neutral corroles is ascribed to the general deshielding effect of the non-aromatic dication. The positions of the n.m.r. signals of central protons or substituents is a better probe for ring current, *i.e.* aromaticity, than those of the outer protons, *e.g.* corrole and porphin *meso*-protons, as they undergo the largest shifts from normal (*cf.* ref. 5).



In structures (II) and (III), the ambident corrole anion and cation, respectively, as aromatic structures, are each represented by 18 π-electron delocalised systems.

The ready diprotonation of corroles suggested that a rapid exchange of the *meso*-protons for deuterium should

[1] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.
[2] A. H. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, 1965, **21**, 2913.
[3] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1963, **85**, 818.
[4] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry,' Pergamon, Oxford, 1969.
[5] A. J. Jones, *Rev. Pure Appl. Chem.*, 1968, **18**, 253.

occur when the corrole was treated with deuteriotrifluoroacetic acid (DTFA), and an n.m.r. study of this process was reported.[1] However, the spectra obtained then, and later using mixtures of TFA and deuteriochloroform as solvent, showed very broad signals, the degree of broadening being dependent on the distance of the proton from the π-electron system of the corrole, *e.g.* the β-CH_2·CH_3 signals were observed as a sharp triplet, the β-CH_2·CH_3 groups and β-methyl groups gave signals which were just recognisable, and the *meso*-proton signals were not observed at all. It is known that solutions of some aromatic compounds in TFA are readily oxidised to cation radicals (*e.g.* ref. 6). Solutions of alkylcorroles in TFA also give broad n.m.r. signals and the electronic spectra of the solutions showed that both mono- and di-cationic species were present; the determination of the rate of exchange of the *meso*-protons of alkylcorroles by this method is therefore unsatisfactory. However an examination of compound (I; R = CO_2Et) [7] showed that it gave broad n.m.r. signals in deuteriochloroform solution, but TFA solutions showed sharp signals. Exchange of the *meso*-protons of (I; R = CO_2Et) is rapid (complete in <10 min) and it is probable that the rate of exchange of the *meso*-protons of the octa-alkylcorroles will be of a similar order.

Monoalkylation of Ambident Corrole Anions.—Methylation of corrole anions with methyl iodide in refluxing acetone solution was shown [1] to produce a mixture of the *N*(21)- and *N*(22)-methyl derivatives. In order to study the possibility of thermal isomerisation of these compounds we have now prepared [8] a series of *N*-alkyl derivatives (VI; R^1 or R^2 = Me, Et, allyl, or 3,3-dimethylallyl) of 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole.[9] The alkylations were carried out by the method described earlier,[1] with anhydrous potassium carbonate as the base; no reaction occurred in the absence of a base. The mixture of *N*-alkyl derivatives was separated by chromatography on Kieselgel G, and the *N*(21)-alkylcorroles were always eluted first. The product distribution favoured the *N*(21)-alkyl isomer, which is the more stable (see later) but both isomers were stable under the alkylation conditions, showing the reaction to be kinetically controlled.

The electronic spectra of the products were indicative of their aromaticity: both types contained an intense Soret band. The spectra of the *N*(21)-alkylcorroles closely resembled that of the parent corrole, but the Soret band of the *N*(22)-alkylcorroles was shifted to longer wavelength with an increased intensity suggesting a greater degree of aromaticity of these isomers. Although there is no direct relationship between n.m.r. chemical shift and degree of aromaticity,[10] the close similarity in structure of the *N*(21)- and *N*(22)-alkylcorroles and the observation of mutually consistent shifts in the *meso*- (τ <1·5) and imino- (τ >12) regions suggests that the *N*(22)-isomers are more aromatic. Thus the *meso*-protons of the *N*(21)-alkylcorroles showed resonances at τ 0·8—1·2, the unsubstituted corroles at τ 0·9—1·05, and the *N*(22)-alkylcorroles at τ 0·6—0·75. Similarly the imino-protons of the *N*(21)-alkylcorroles corresponded to a singlet at 12·5—13·0, the unsubstituted corroles at τ 13·5, and the *N*(22)-alkylcorroles at τ 13·25—14·3. *X*-Ray evidence [11] suggests that the direct linkage between rings A and D of the corrole system is effectively a single bond, and thus it would be expected that the twisting of ring A, leading to loss of aromaticity, would be energetically less disfavoured than the twisting of ring B.

The n.m.r. spectra of *N*-allylcorroles showed that all the protons of the allyl group group were considerably shielded and, as with the *N*-ethylcorroles, the maximum shielding occurred at the α-carbon atom. The olefinic protons of the allyl groups absorbed in the range τ 6·9—7·7 and the α-methylene protons at τ 12·9—14·5, with *N*(22)-allyl isomers showing the maximum shielding. Slight non-equivalence of the α-methylene protons of the *N*-ethyl, -allyl, and -3,3-dimethylallyl derivatives was observed, which was ascribed either to steric hindrance around the C–N bond (*cf.* refs. 12 and 13) or to the presence of a chiral nitrogen atom. The effect varied from the observation of a broadened quartet for compound (VI; R^1 = Et, R^2 = H) to a clear eight-line ABX pattern for (VI; R^1 = H, R^2 = CH_2·CH:-CMe_2); it was greater in the *N*(22)-alkyl series and it increased with the size of the *N*-alkyl group (this again may reflect the relative ease of ring twisting from the main plane of the molecule). A large difference (1·4 p.p.m.) was observed for the chemical shifts of the terminal methyl groups within both isomers of the *N*-3,3-dimethylallyl derivatives.

Although the ethyl iodide used for the preparation of the *N*-ethylcorroles was pure (g.l.c.), the products obtained initially were contaminated with some (*ca.* 10%) of the corresponding *N*-methyl derivatives (n.m.r. evidence), although these were removed by fractional crystallisation. It therefore appeared that partial exchange of β-alkyl groups had occurred to provide a competing methylating agent, presumably with the intervention of an intermediate such as (VII) (*cf.* ref. 9).

The *N*-alkylcorroles are more basic than the parent corroles and they do not form anions when treated with bases. Protonation to give mono-salts occurs readily, and the products show typically aromatic electronic spectra. Dissolution of the *N*-alkylcorroles in TFA resulted largely in formation of green dicationic species, which were formed exclusively in sulphuric or fluoro-

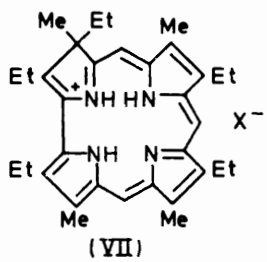
[6] W. Ij. Aalbersberg, J. Gaaf, and E. L. Mackor, *J. Chem. Soc.*, 1961, 905.
[7] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1970, 807.
[8] Preliminary communication, M. J. Broadhurst, R. Grigg, G. Shelton, and A. W. Johnson, *Chem. Comm.*, 1970, 231.
[9] R. Grigg, A. W. Johnson, and G. Shelton, *Annalen*, 1971, **746**, 32.
[10] R. J. Abraham and W. A. Thomas, *J. Chem. Soc.* (*B*), 1966, 127.
[11] Professor D. M. Hodgkin, personal communication.
[12] Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, 1967, **89**, 4910.
[13] S. K. Khetan and M. V. George, *Tetrahedron*, 1969, **25**, 527.

sulphonic acid solutions; n.m.r. spectra of the latter accorded with the second protonation at C-5 (VIII).

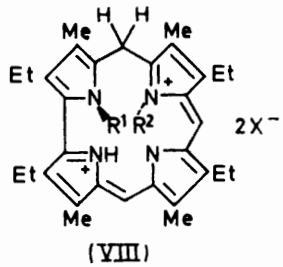
Thermolyses of N-*Alkylcorroles*.—Thermal rearrangements of the metal complexes of *N*(21)-alkylcorroles have already been described;[9,14] it was shown that, in the case of the nickel and palladium complexes, the *N*-alkyl group migrated to C-3, *i.e.* to give the appropriate metal complex of compound (VII). These considerations led to a study of the thermal properties of *N*-alkylcorroles. Apart from isomerisations similar to those of the metal complexes, an allowed pericyclic mechanism may be written whereby the *N*-alkyl group migrates from one type of nitrogen atom to the other. In other words isomerisation between *N*(21)-alkyl and *N*(22)-alkylcorroles could occur, provided that the substituted nitrogen atom approaches a state of sp^3 hybridisation or can attain such a state in the transition state for the rearrangement, which is also geometrically favourable. *N*-Alkylcorroles (VI; R^1 = Me or Et, R^2 = H) and (VI; R^1 = H, R^2 = Me or Et) were heated under reflux in an atmosphere of nitrogen in chlorobenzene, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, or 1-chloronaphthalene solution, but no change was observed even after periods of up to 15 h. At higher temperatures, *e.g.* in decalin in sealed tubes at 300—350°, gross decomposition occurred. In the case of the *N*-allyl compounds, a further symmetry-allowed process can be envisaged, *i.e.* a [3,11]-sigmatropic shift [(IX) ⇌ (X)], provided as before that the nitrogen atom involved approaches sp^3-hybridisation. Other [3,*j*]-processes leading to *meso*-allyl derivatives are symmetry-allowed but they involve loss of aromaticity and consequent higher activation energy. Thermolysis of the *N*(22)-allylcorrole (VI; R^1 = H, R^2 = CH_2·CH:CH_2) in refluxing toluene for 8 h caused isomerisation to the *N*(21)-allylcorrole (VI; R^1 = CH_2·CH:CH_2, R^2 = H) (24%) together with cleavage to the parent corrole (29%) (VI; R^1 = R^2 = H).[8] The *N*(21)-allylcorrole was stable under these conditions. It is interesting that it is the less thermally stable isomer which appears to be the more aromatic (see before).

The allowed sigmatropic process requires the allyl group to migrate with inversion, but the thermal isomerisation of the corresponding *N*(22)-(3,3-dimethylallyl) derivative in refluxing toluene proceeded without inversion to give the *N*(21)-isomer (15·5%) together with cleavage to the parent corrole (41%). These results, especially the high proportion of the cleavage product formed, suggested a free-radical mechanism for these thermolytic rearrangements. When the *N*(22)-allylcorrole was rearranged as before but in cumene as solvent, the yield of the *N*(21)-allyl isomer was only 10%, together with only 16% of unsubstituted corrole, suggesting that allyl free radicals had been produced and had reacted with cumene.[15]

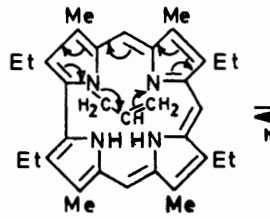
Dialkylation of Corroles and 21,24-*Dioxacorroles*.—In the light of results in the porphin series,[16] we have studied the further methylation of the *N*-methylcorroles. Treatment of either compound (VI; R^1 = H, R^2 = Me) or (VI; R^1 = Me, R^2 = H) with methyl iodide in a sealed tube for 15 h at 100° gave rise to the



(VII)

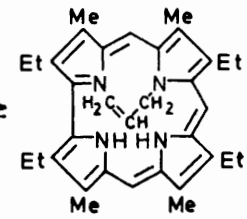


(VIII)



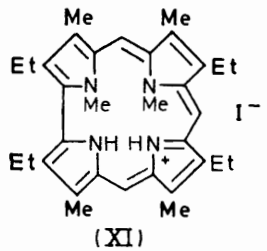
(IX)

heat

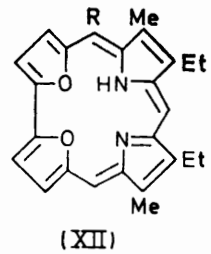


(X)

same *NN'*-dimethylcorrole salt (isolated as the iodide; 81 and 75%, respectively) with only very small recoveries of starting material. Under identical conditions, the parent corrole (VI; R^1 = R^2 = H) gave this product (71%) together with starting material (14%), but no mono-*N*-alkyl corroles were isolated. Thus the rate of introduction of the second methyl group was greater than that of the first, *i.e.* the nucleophilicity as well as the basicity of *N*-methylcorroles was greater than that of the parent corrole. The method of synthesis limits the possible structures for the *NN'*-dimethylcorrole salt to the 21,22- or 21,23-dimethyl systems. The n.m.r. spectrum contained signals at τ 0·3, 0·35, and 0·65 for the *meso*-protons, and at τ 12·32 and 12·9 for the two *N*-methyl groups. The electronic spectrum contained an intense double Soret band [$\lambda_{max.}$ 412 and 426 nm (ε 99,500 and 101,500)] which supported an aromatic formulation. By analogy with the structure of the *NN'*-dimethylporphin salts,[16] the 21,22-dimethylcorrole structure (XI) is favoured.



(XI)



(XII)

It proved impossible to obtain the free base corresponding to this salt, as was the case with the analogous

[14] R. Grigg, A. W. Johnson, and G. Shelton, *J. Chem. Soc.* (*C*), 1971, 2287.

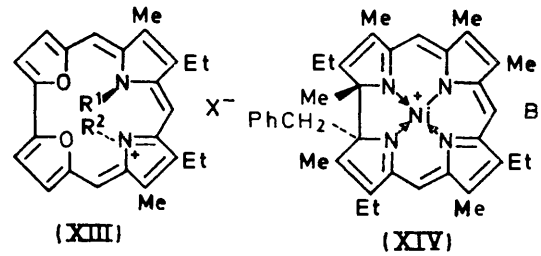
[15] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

[16] R. Grigg, A. W. Johnson, G. Shelton, and A. Sweeney, in preparation.

porphin salts. Chromatography of compound (XI) in pyridine–piperidine solution on alumina caused no change. The 21,22-dimethylcorrole iodide (XI) was thermally unstable. When it was heated in refluxing *o*-dichlorobenzene for a short time it produced the corresponding *N*(21)-methylcorrole (86%) and none of the *N*(22)-methyl isomer, which again reflected their relative stabilities.

We have extended the foregoing studies to the 21,24-dioxacorrole ring system (XII; R = H),[17] which has previously been shown to be more reluctant than corroles to form anions. In fact no reaction of compound (XII; R = H) with methyl iodide in the presence of potassium carbonate was detected after several hours in refluxing acetone. However, when (XII; R = H) was heated with methyl iodide in a sealed tube at 100° in the presence of *NN*-di-isopropylethylamine,[18] a rapid reaction occurred to give a mixture of two compounds (*cf.* the *N*-methylation of porphins [16]). These were separated and shown to be the *N*-methyl (XIII; R^1 = Me, R^2 = H) and the *NN'*-dimethyl (XIII; $R^1 = R^2$ = Me) salts, by the electronic and n.m.r. spectra. The analogous *N*-ethyl compounds were also prepared, and both of the monoalkylated derivatives could be readily converted into the dialkylated compounds by further treatment with the appropriate alkyl iodide. In common with the *N*(22)-alkyl corroles and the *N*-alkylporphins,[16] the Soret band in the electronic spectrum showed a bathochromic shift of *ca.* 11 nm after the addition of each *N*-alkyl group. The n.m.r. spectra gave clear evidence of the aromatic nature of the salts, showing highly shielded *N*-methyl groups (τ 14·73 for the mono-*N*-methyl and τ 15·5 for the di-*N*-methyl derivative) and deshielded *meso*-protons (τ −0·69 to +0·05 for the mono-*N*-derivative and τ −0·3 to +0·5 for the di-*N*-methyl derivative). In common with the *N*-alkylporphins,[19] the signals of the β-substituents on the pyrrole rings containing the *N*-alkyl groups move to higher field. These data indicate that even two alkyl groups can be accommodated in the centre of the macrocyclic ring without a significant alteration in the ring current, especially if the hybridisation at the nitrogen atoms tends towards sp^3 rather than sp^2. An *X*-ray structure determination of a copper *N*-methylcorrole [20] showed that the *N*-alkyl group is accommodated by distortion of the *N*-alkyl ring out of the general plane of the molecule, but that the angles at the nitrogen atom carrying the alkyl group are close to those expected for sp^3 hybridisation.

Evidence for the *trans* disposition of the *N*-alkyl ring in (XIII; $R^1 = R^2$ = Me or Et) was obtained by the partial resolution of the *NN'*-diethyl derivative as its D-camphorsulphonate (*cf.* refs. 16 and 21), which had a specific rotation of *ca.* +200° after two recrystallisations from acetone. The *cis*-isomer should not show optical activity. A complete resolution was not possible because of lack of material, and the highly



(XIII) (XIV)

coloured nature of the salt precluded accurate measurements although an increase in specific rotation of *ca.* 100° occurred after each crystallisation.

The monoalkyl salts (XIII; R^1 = Me or Et, R^2 = H) showed greatly enhanced basicity compared with the parent system, and like the *NN'*-dialkyl-corrole or -porphin [16] salts, they were eluted unchanged from alumina columns by methanol, and attempts to prepare the free bases were unsuccessful. The mass spectrum of the *NN'*-diethyl bromide (XIII; $R^1 = R^2$ = Et) was unusual in that the parent peak (*m/e* 442) appeared 2 mass units higher than the expected ion *M* − HBr, an effect related to the enhanced basicity of these compounds.[16] The parent ion was also the base peak; other significant fragmentations corresponded to the loss of successive ethyl groups, to give ions at *m/e* 413 and 384. In the spectrum of the *NN'*-dimethyl compound (XIII; $R^1 = R^2$ = Me), the base peak corresponded to the loss of two methyl groups.

The n.m.r. spectrum of the *NN'*-diethyl salt (XIII; $R^1 = R^2$ = Et) was also interesting because the signals of the methylene groups of the *N*-ethyl systems appeared as an ABX_3 system. Two six-line multiplets of equal spacing (*ca.* 8 Hz) were observed, centred at τ 15·63 and 16·57. The occurrence of twelve lines would be expected if $J_{AX} = J_{BX} \simeq \frac{1}{2} J_{AB}$; the non-equivalence of the methylene protons is due either to restricted rotation about the C–N bond or to the asymmetry of the macrocyclic system. The spectrum of the mono-*N*-ethyl derivative did not show this splitting. The effect of restricted rotation was also observed in the n.m.r. spectrum of nickel 19-benzyl-2,12,17-triethyl-1,3,7,8,13,18-hexamethyltetradehydrocorrin bromide (XIV),[22] where the benzylic protons appeared as an AB system [two doublets (*J* 13 Hz) at 6·98 and 8·42], each signal corresponding to one proton. The related 19-ethyl analogue did not show the effect. The maximum effect of the ring current is felt by the protons on the α-carbon atoms of the *N*-alkyl groups in (XIII), as these are the most strongly shielded. A similar effect was observed for the N-alkylporphins,[16] but this contrasts with the alkylcobalt(III) aetioporphyrin I

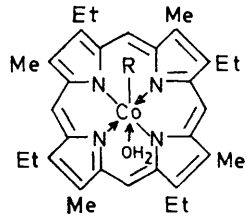
[17] M. Broadhurst, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1969, 1480.
[18] S. Hünig and M. Kiessel, *Chem. Ber.*, 1958, **91**, 380.
[19] W. S. Caughey and P. K. Iber, *J. Org. Chem.*, 1963, **28**, 269.
[20] R. Grigg, T. J. King, and G. Shelton, *Chem. Comm.*, 1970, 56.
[21] R. Grigg, A. P. Johnson, A. W. Johnson, and M. J. Smith, *J. Chem. Soc.* (*C*), 1971, 2457.
[22] R. Grigg, A. W. Johnson, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1968, 1291.

complexes (XV), in which the β-protons of the alkyl group are the most strongly shielded.[23]

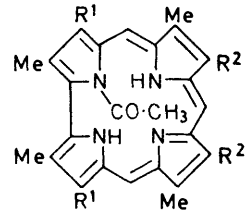
Acetylation of Corroles and 21,24-Dioxacorroles.—When 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole [1] (I) was heated under reflux in acetic anhydride solution, a neutral product (11%) could be separated from unchanged starting materials by chromatography. The n.m.r. spectrum of the product [τ 11·65 (*N*-Ac)] favoured an *N*(21)-acetyl structure (XVI; R^1 = Me, R^2 = Et) as the C-8 and C-12 ethyl groups were magnetically equivalent, and the spectrum as a whole resembled that of the *N*(21)-methyl derivative.[1] However, the electronic spectrum was closer in its form to those of the *N*(22)-alkylcorroles, but the nature of the product was established by an examination of the acetylation product (14·5%) of 3,17-diethyl-2,7,8,12,13,18-hexamethylcorrole.[9] In this case the n.m.r. signals corresponding to the C-3 and C-17 ethyl groups were non-equivalent (methyl triplets at τ 8·18 and 8·54), thus establishing the structure as (XVI; R^1 = Et, R^2 = Me). An attempt was made to obtain the *N*(22)-acetyl derivative of (I) by treatment with acetyl chloride in refluxing acetone solution in presence of *NN*-di-isopropylethylamine,[14] but the product again was the *N*(21)-acetyl isomer (24%).

The change in electronic spectra of the *N*(21)-acetylcorroles compared with those of the *N*(21)-alkylcorroles is due to a bathochromic effect of the *N*-acetyl group, although the i.r. absorption of this group (1709 cm^{-1}) indicates no extension of conjugation in the ground state of the molecule. The *N*(21)-acetylcorroles were hydrolysed to the parent corroles on alumina columns, which accounts for the low yields obtained in their preparation. Treatment of compound (XVI; R^1 = Me, R^2 = Et) with 1 equiv. of aqueous sodium hydroxide for 1 min at room temperature gave the parent corrole (66%). Other attempts to effect electrophilic acetylation of the corrole ring were unsuccessful, *e.g.* treatment in dichloromethane with acetyl chloride in the presence of aluminium chloride or bromide or tin(IV) chloride apparently caused fission of the macrocycle, and treatment of the corrole in sulphuric acid with acetyl chloride for 3 weeks caused no reaction.

Treatment of the 21,24-dioxacorrole (XII; R = H) with excess of acetyl chloride and aluminium chloride at 80° for 1 h gave a mixture of two products which were readily separated. One of these (31%) was identified as the 5-acetyl derivative (XII; R = Ac) by its n.m.r. spectrum, which contained only two *meso*-proton signals, at τ 0·4 and 1·21; the signals of the four furan β-protons were still present. No evidence was obtained for the presence of the corresponding 10-acetyl isomer. The n.m.r. spectrum ($CDCl_3$–TFA) of the second product contained sharp signals at τ −0·8 (2H), −0·41 (2H), and +0·07 (1H) corresponding to three *meso*-protons and two of the four furan β-protons (*i.e.* a two-proton singlet instead of the usual four-proton AB quartet). The 2,18- or 3,17-orientation of the two β-acetyl substituents has not yet been assigned. Attempts to prepare *meso*-acetylcorroles by the foregoing method failed, because the use of catalysts such as aluminium chloride or tin(IV) chloride caused decomposition of the corrole.



(XV)



(XVI)

EXPERIMENTAL

N.m.r. spectra were determined for solutions in deuteriochloroform [system (i)] (except where otherwise stated) with a Perkin-Elmer RS 10 instrument operating at 60 MHz or with a Varian HA 100 instrument operating at 100 MHz, with tetramethylsilane as internal reference (except where otherwise stated). U.v. and visible spectra were measured for solutions in chloroform (except where otherwise stated) with a Unicam SP 700 spectrophotometer. I.r. spectra were measured for solutions in carbon tetrachloride (except where otherwise stated) with a Unicam SP 100 spectrophotometer. Mass spectra were obtained by direct insertion into the ion source of an A.E.I. MS 902 instrument. M.p.s were recorded with a Kofler hot-stage apparatus. Light petroleum was the fraction b.p. 60—80°. Alumina for chromatography was Spence type H.

(A) *Dication of 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole.*—The corrole [1] was dissolved in fluorosulphonic acid; the n.m.r. spectrum of the green solution contained signals at τ 0·93, 1·75, and 3·53 (3 × NH, all s), 1·94 and 2·04 (2 *meso*-H, both s), 5·3 (2H,s,5-H_2), 7·3 (2 × MeCH_2, m), 7·65, 7·75, 7·8, 7·85 (6H), and 8·05 (18H, all s, 6 × Me), and 8·9 and 9·0 (each 3H, t, 2 × CH_3·CH_2).

(B) *Alkylation and Acylation of Corroles.*—*2,8,12,18-Tetraethyl-3,7,13,17,21-pentamethylcorrole and 2,8,12,18-tetraethyl-3,7,13,17,22-pentamethylcorrole.* 2,8,12,18-Tetraethyl-3,7,13,17-tetramethylcorrole [9] (250 mg) in acetone (75 ml) was treated with anhydrous potassium carbonate (4 g) followed by methyl iodide (5 ml) and the mixture was heated under reflux for 30 min. The potassium carbonate was separated and washed with acetone, and the combined filtrates were evaporated to dryness. The residue was chromatographed on a dry packed column of Kieselgel G with benzene for elution. The first, red band yielded purple plates of *2,8,12,18-tetraethyl-3,7,13,17,21-pentamethylcorrole* (73 mg, 28%), m.p. 222—223° (from acetone–methanol) (Found: C, 79·5; H, 8·45; N, 11·3. $C_{32}H_{40}N_4$ requires C, 79·9; H, 8·4; N, 11·65%), $\lambda_{max.}$ 399, 542, 557, and 600 nm (ε 88,400, 11,590, 12,200, and 11,420), $\lambda_{infl.}$ 409, 491, and 524 nm (ε 65,690, 4990, and 7150), $\lambda_{max.}$ (1% TFA–$CHCl_3$) 417 and 599 nm (ε 118,000 and 31,590), $\lambda_{infl.}$ 563 nm (ε 10,600), $\lambda_{max.}$ (conc. H_2SO_4) 295, 360, 421, and 681 nm (ε 17,440, 45,400, 9860, and 32,670); τ (i) 0·84, 1·04, and 1·21 (3 *meso*-H, all s), 6·2 (8H, four overlapping q, 4 × MeCH_2), 6·63, 6·66, 6·74, and 7·12 (all s, 4 × Me), 8·19, 8·26, 8·29, and 8·61 (all t, 4 × CH_3·CH_2), 12·55br (imino-protons, s), and 12·96 (s, NMe),

[23] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc.* (*C*), 1968, 881.

τ (ii) (FSO_3H with Me_4Si as external reference) 0·8br (1H, s, NH), 1·55 and 1·82 (2 *meso*-H, both s), 2·25br and 3·42br (both s, 2 × NH), 5·18 [2H, d, *J* 5 Hz, C(5)H_2], 6·7 (3H, s, Me), 7·14 (8H, q, 4 × MeCH_2), 7·4, 7·55, 7·67, and 7·93 (all s, 4 × Me), and 8·7 (12H, m, 4 × CH_3·CH_2). Elution of the column was continued with benzene until the second, purple eluate became spectroscopically pure; the eluant was then changed to chloroform. The eluate yielded purple plates of 2,8,12,18-*tetraethyl*-3,7,13,13,17,22-*pentamethylcorrole* (63 mg, 24%), m.p. 150—152° (from acetone–methanol) (Found: C, 80·1; H, 8·4; N, 11·65. $C_{32}H_{40}N_4$ requires C, 79·9; H, 8·4; N, 11·65%), $\lambda_{max.}$ 413, 510, 547, 575, and 624 nm (ε 152,700, 7370, 15,540, 10,480, and 9640), $\lambda_{max.}$ (1% TFA–$CHCl_3$) 421, 595, and 620 nm (ε 153,500, 21,840, and 18,300) $\lambda_{max.}$ (conc. H_2SO_4) 296, 364, 400, and 671 nm (ε 16,320, 35,780, 11,910, and 25,100), $\lambda_{infl.}$ 246 and 422 nm (ε 9600 and 10,910); τ (i) 0·6, 0·7, and 0·73 (3 *meso*-H, all s), 6·04 (6H) and 6·17 (2H) (both q, 4 × MeCH_2), 6·54, 6·56, 6·6, and 6·76 (all 3H, t, 4 × Me), 8·21 (6H), 8·23 (3H), and 8·52 (3H) (all t, 4 × CH_3·CH_2), 13·25br (s, imino-protons), and 14·25 (3H, s, NMe), τ (ii) (FSO_3H with Me_4Si as external reference) 0·8br and 1·35br (both s, 2 × NH), 1·73 and 1·97 (2 *meso*-H, both s), 3·35br (s, NH), 5·2br [2H, s, C(5)H_2], 7·2 (8H, m, 4 × MeCH_2), 7·48, 7·6, 7·68, 7·76, and 7·95 (15H, all s, 5 × Me), and 8·85 (12H, m, 4 × CH_3·CH_2).

2,8,12,18,21-*Pentaethyl*-3,7,13,17-*tetramethylcorrole and* 2,8,12,18,22-*pentaethyl*-3,7,13,17-*tetramethylcorrole*. 2,8,12,18-Tetraethyl-3,7,13,17-tetramethylcorrole (750 mg) was dissolved in acetone (500 ml) and treated with anhydrous potassium carbonate (10 g) followed by ethyl iodide (10 ml), and the mixture was heated under reflux for 45 min. The potassium carbonate was separated and washed with acetone, and the combined filtrates were evaporated under reduced pressure. The residue was chromatographed on a dry packed column of Kieselgel G with benzene as eluant. The first, red band yielded purple plates (340 mg) (from acetone–methanol). Two further crystallisations, from ether–methanol gave 2,8,12,18,21-*pentaethyl*-3,7,13,17-*tetramethylcorrole* (190 mg. 24%), m.p. 209—210° (Found: C, 79·95; H, 8·45; N, 11·25. $C_{33}H_{42}N_4$ requires C, 80·15; H, 8·55; N, 11·3%), $\lambda_{max.}$ 403, 546, 553, and 605 nm (ε 109,000, 17,500, 18,800, and 15,700), $\lambda_{infl.}$ 414, 490, 512, and 526 nm (ε 68,400, 4640, 7770, and 9700); τ (i) 0·8, 1·0, and 1·2 (3 *meso*-H, all s), 6·2 (8H, four overlapping q, 4 × MeCH_2), 6·65, 6·7, 6·75, and 7·15 (all 3H, s, 4 × Me), 8·2 (3H) and 8·3 (6H) (both t, 3 × CH_3·CH_2), 8·7 (3H, m, CH_3·CH_2), 11·35 (3H, t, N·CH_2·CH_3), 12·4br (imino-protons, s), and 13·4 (2H, m, N·CH_2Me). The second, purple band yielded purple plates (from acetone–methanol) (174 mg). Two further crystallisations, from ether–methanol, gave 2,8,12,18,22-*pentaethyl*-3,7,13,17-*tetramethylcorrole* (130 mg, 17%), softens >170° (Found: C, 80·2; H, 9·05; N, 10·95. $C_{33}H_{42}N_4$ requires C, 80·15; H, 8·55; N, 11·3%), $\lambda_{max.}$ (i) 416, 514, 551, 580, and 633 nm (ε 155,500, 6780, 15,200, 8030, and 7910), τ (i) 0·55, 0·6, and 0·65 (3 *meso*-H, all s), 6·1 (6H) and 6·4 (2H) (both q, 3 × MeCH_2), 6·6 (6H), 6·65 (3H), and 6·85 (3H) (all s, 4 × Me), 8·25 (9H) and 8·6 (3H) (both t, 3 × CH_3·CH_2), 11·95 (3H, t, N·CH_2·CH_3), 13·3br (imino-protons, s), and 14·68 and 14·7 (two overlapping q, N·CH_2Me).

21-*Allyl*-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole and* 22-*allyl*-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole*. 2,8,12,18-Tetraethyl-3,7,13,17-tetramethylcorrole (280 mg) was dissolved in acetone (100 ml) containing anhydrous potassium carbonate (5 g) and treated with allyl bromide (5 ml). The mixture was heated under reflux for 10 min. in an atmosphere of nitrogen. The potassium carbonate was separated and washed with acetone, and the combined filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed on a dry packed column of Kieselgel G with benzene for elution. The first, red band yielded purple, hexagonal plates of 21-*allyl*-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole* (119 mg, 39%), m.p. 188—189° (from chloroform–methanol) (Found: C, 80·75; H, 8·2; N, 11·05. $C_{34}H_{42}N_4$ requires C, 80·6; H, 8·35; N, 11·05%), $\lambda_{max.}$ 400, 542, 559, and 600 nm (ε 112,500, 19,020, 20,820, and 17,920) $\lambda_{infl.}$ 411 and 523 nm (ε 79,760 and 9750), τ (i) (CH_2Cl_2 as internal reference) 0·8, 0·96, and 1·18 (3 *meso*-H, all s), 6·2 (8H, four overlapping q, 4 × MeCH_2), 6·6, 6·63, 6·71, and 7·09 (all 3H, s, 4 × Me), 6·9br and 7·2br (both s, CH_2=CH), 8·09, 8·13, 8·15, and 8·65 (12H, all t, 4 × CH_3·CH_2), 12·45br (imino-protons, s), and 13·0 (m, N·CH_2). The second, purple band yielded purple plates of 22-*allyl*-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole* (64 mg, 21%), m.p. 177—179° (decomp.) (from chloroform–methanol) (Found: C, 80·4; H, 8·4; N, 10·95. $C_{34}H_{42}N_4$ requires C, 80·6; H, 8·35; N, 11·05%), $\lambda_{max.}$ 414, 511, 548, 577, and 627 nm (ε 154,500, 6670, 15,560, 8310, and 8620), τ (i) (CH_2Cl_2 as internal reference) 0·56, 0·59, and 0·61 (3 *meso*-H, all s), 6·0 (6H) and 6·25 (2H) (both q, 3 × CH_2·CH_3), 6·51, 6·52, 6·57, and 6·75 (all s, 4 × Me), 7·1 (m, CH=CH_2) 7·63br and 7·7br (both s, CH_2=CH), 8·18 (3H), 8·2 (6H), and 8·51 (3H) (all t, 4 × CH_3·CH_2), 13·2br (imino-protons, s), and 14·3 (m, N·CH_2).

21-(3,3-*Dimethylallyl*)-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole and* 22-(3,3-*dimethylallyl*)-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole*. 2,8,12,18-Tetraethyl-3,7,13,17-tetramethylcorrole (300 mg) was dissolved in acetone (150 ml) containing anhydrous potassium carbonate (5 g). 3,3-Dimethylallyl bromide (0·5 ml) was added and the mixture was heated under reflux for 20 min in an atmosphere of nitrogen. The potassium carbonate was separated and washed with acetone. The filtrates were evaporated and the residue chromatographed on a dry packed column of Kieselgel G with benzene–light petroleum (2 : 1) for elution. The first, red band yielded purple prisms of 21-(3,3-*dimethylallyl*)-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole* (122 mg; 35%), m.p. 183—184° (from acetone–methanol) (Found: C, 80·75; H, 8·5; N, 10·3. $C_{36}H_{46}N_4$ requires C, 80·85; H, 8·65; N, 10·45%), $\lambda_{max.}$ 403, 546, 562, and 601 nm (ε 104,000, 17,000, 18,800, and 15,700), $\lambda_{infl.}$ 414 and 527 nm (ε 73,100 and 9380), τ (i) (CH_2Cl_2 as internal reference) 0·82, 0·97, and 1·19 (3 *meso*-H, all s), 6·16 (8H, q, 4 × MeCH_2), 6·62, 6·64, 6·7, and 7·1 (all 3H, s, 4 × Me), 8·2, 8·24, 8·26, and 8·71 (12H, all t, 4 × CH_3·CH_2), 9·08 and 10·52 (both 3H, s, Me_2C), 12·39br (imino-protons, s), and 12·9 (2H, distorted d, N·CH_2). The second, purple band yielded purple prisms of 22-(3,3-*dimethylallyl*)-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole* (80 mg, 23%), m.p. 160—162° (decomp.) (from acetone–methanol) (Found: C, 80·65; H, 8·75; N, 10·25. $C_{36}H_{46}N_4$ requires C, 80·85; H, 8·65; N, 10·45%), $\lambda_{max.}$ 416, 515, 552, 580, and 633 nm (ε 163,400, 7170, 15,650, 9020, and 8310), τ (i) (CH_2Cl_2 as internal reference) 0·59 (1H) and 0·67 (2H) (*meso*-H, both s), 6·0 (6H) and 6·26 (2H) (both q, 3 × MeCH_2), 6·53, 6·56, 6·59, and 6·77 (all 3H, s, 4 × peripheral Me), 7·73 (distorted t, N·CH_2·CH=CMe_2), 8·21 (6H), 8·23 (3H), and 8·53 (3H) (all t, 4 × CH_3·CH_2), 9·2 and 10·64 (both

3H, s, Me_2C), 13·12br (imino-protons, s), and 14·25 (8-line ABX pattern, N·CH_2).

Attempted thermal rearrangement of N(21)-*methyl*-, N(21)-*ethyl*-, N(22)-*methyl*-, *and* N(22)-*ethyl-corroles*. Each of the *N*-alkylcorroles (10 mg) was dissolved in each of the solvents chlorobenzene, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, 1-chloronaphthalene, and 1-bromonaphthalene (100 ml) and the solutions were heated under reflux for 12 h in an atmosphere of nitrogen. The mixtures were then examined by t.l.c. and electronic spectroscopy. In every case, the only component was the starting material.

Each of the *N*-alkylcorroles was dissolved in decalin and the solutions were heated at 300—350° for 1 h in a sealed tube in an atmosphere of nitrogen. In each case gross decomposition of the macrocycles occurred, as revealed by t.l.c. and electronic spectroscopy.

Thermal rearrangement of 22-*allyl*-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole*. The macrocycle (130 mg) dissolved in toluene (130 ml) was heated under reflux for 8 h in an atmosphere of nitrogen. The solvent was removed under reduced pressure and the residue chromatographed on alumina with benzene as eluant. The first, red band yielded purple prisms of 21-allyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (31 mg, 24%), m.p. 187—189° (decomp.) (from acetone–methanol), identical (t.l.c., electronic and n.m.r. spectra) with the product already described.

The second, red band yielded purple hairs of 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (34 mg, 29%), m.p. 253—254° (from chloroform–methanol), identical with the product described earlier (t.l.c., electronic and 100 MHz n.m.r. spectra).

The foregoing reaction was repeated with cumene as the solvent, the reaction temperature being controlled by immersion of the vessel in an oil-bath at 110°. The products were isolated as before. 21-Allyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (13 mg, 10%), m.p. 186—189°, formed purple prisms (from acetone–methanol), and 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (19 mg, 16%) formed purple prisms (from chloroform–methanol). The macrocycle was also thermolysed in *o*-dichlorobenzene solution (*ca.* 5 mg in 5 ml) under reflux in an atmosphere of nitrogen; the only product detected was 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole, as revealed by t.l.c. and electronic spectroscopy.

Thermolysis of 21-*allyl*-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole*. The macrocycle (10 mg) dissolved in toluene (10 ml) was heated under reflux for 24 h in an atmosphere of nitrogen. T.l.c. and electronic spectroscopy then showed the only component to be the starting material. A similar thermolysis in refluxing *o*-dichlorobenzene gave only 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (t.l.c. and electronic spectroscopy).

Thermal rearrangement of 22-(3,3-*dimethylallyl*)-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylcorrole*. The macrocycle (150 mg) dissolved in toluene (150 ml) was heated under reflux for 3 h in an atmosphere of nitrogen. The solvent was evaporated off under reduced pressure and the residue was chromatographed on alumina with benzene as eluant. The first, red band yielded purple prisms of 21-(3,3-dimethylallyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (23 mg, 15·5%), m.p. 182—184° (from acetone–methanol), identical with the product described earlier (t.l.c., electronic and 100 MHz n.m.r. spectra).

The second, red band yielded purple hairs of 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (61 mg, 41%), m.p. 254—256° (from chloroform–methanol), identical with an authentic specimen (t.l.c. and electronic spectroscopy).

21-*Acetyl*-8,12-*diethyl*-2,3,7,13,17,18-*hexamethylcorrole*. (i) 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole [1] (400 mg) dissolved in acetic anhydride (200 ml) was heated under reflux for 1 h. The solvent was evaporated under reduced pressure and the residue was chromatographed on alumina with benzene as eluant. The first, purple band yielded blue prisms (49 mg, 11%), m.p. 217—219° (decomp.) (from acetone–methanol) (Found: C, 77·15; H, 7·6; N, 11·8. $C_{31}H_{36}N_4O$ requires C, 77·45; H, 7·55; N, 11·65%), $\lambda_{max.}$ 411, 509, 542, 570, and 630 nm (ε 136,200, 8240, 15,200, 7400, and 6300); $\nu_{max.}$ (KBr) 1709 cm^{-1} (C=O); τ (i) 0·45, 0·75, and 1·0 (3 *meso*-H, all s), 6·3 (4H, q, 2 × MeCH_2), 6·5, 6·6 (6H), 6·75, 7·05, and 7·1 (18H, all s, 6 × Me), 8·3 (6H, t, 2 × CH_3·CH_2), 11·65 (3H, s, NAc), and 13·0br (imino-protons, s).

The second, red band yielded purple prisms of the starting material (313 mg, 78%), m.p. 254—257° (from chloroform–methanol) (lit.,[1] 255—257°).

(ii) 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole (300 mg) in acetone (300 ml) was treated with *NN*-di-isopropylethylamine (1 ml) followed by acetyl chloride (0·5 ml), and the solution was heated under reflux for 30 min. The solvent was removed under reduced pressure and the residue was chromatographed on alumina with benzene as eluant. The first, red band yielded blue prisms (79 mg, 24%), m.p. 217—220° (decomp.) (from acetone–methanol), identical with the product obtained in the previous experiment (t.l.c., electronic and n.m.r. spectra). The second, red-purple band yielded purple prisms of the starting material (165 mg, 55%), m.p. 255—258° (from chloroform–methanol).

21-*Acetyl*-3,17-*diethyl*-2,7,8,12,13,18-*hexamethylcorrole*. Prepared by method (i) but from 3,17-diethyl-2,7,8,12,13,18-hexamethylcorrole,[9] the *product* (14·5%) formed blue-purple needles, m.p. 218—220° (from acetone–methanol) (Found: C, 77·4; H, 7·35; N, 11·6. $C_{31}H_{36}N_4O$ requires C, 77·45; H, 7·55; N, 11·65%), $\lambda_{max.}$ 410, 511, 543, 575, 596, and 626 nm (ε 118,500, 7960, 15,900, 7990, 8100, and 5430); $\nu_{max.}$ (KBr) 1712 cm^{-1} (C=O); τ (i) 0·53, 0·84, and 1·18 (3 *meso*-H, all s), 6·05 (two overlapping q, 2 × MeCH_2), 6·63, 6·7, 6·76, 6·84 (6H), and 7·12 (18H, all s, 6 × Me), 8·18 and 8·54 (6H, both t, 2 × CH_3·CH_2), 11·71 (3H, s, NAc), and 12·6br (imino-protons, s).

Starting material was also isolated during the chromatography and crystallised from chloroform–methanol as purple prisms (74%), m.p. >300°.

Hydrolysis of 21-*acetyl*-8,12-*diethyl*-2,3,7,13,17,18-*hexamethylcorrole*. The acetyl compound (30 mg) in acetone (30 ml.) was treated with methanolic 0·1M-sodium hydroxide (0·7 ml; 1·1 equiv.) and kept at room temperature for 1 min. The product was poured into water (250 ml) containing chloroform (100 ml). After shaking, the chloroform layer was separated, washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue yielded purple prisms of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (18 mg, 66%), m.p. 255—257° (from chloroform–methanol).

2,8,12,18-*Tetraethyl*-3,7,13,17,21,22(23)-*hexamethylcorrole iodide*. (i) 2,8,12,18-Tetraethyl-3,7,13,17,21-pentamethylcorrole (100 mg) dissolved in methyl iodide (25 ml) was heated at 100° for 15 h in a sealed tube. The solvent was removed and the residue chromatographed on alumina.

A trace of starting material was eluted with chloroform before the main, green band was eluted with chloroform–methanol (9 : 1). This fraction was evaporated to dryness after being shaken with aqueous sodium iodide, and the residue yielded purple needles (105 mg, 81%), softens *ca.* 200° (decomp.) (from dichloromethane–ether) (Found: C, 64·2; H, 6·75; N, 8·95. $C_{31}H_{39}IN_4$ requires C, 63·7; H, 6·95; N, 8·9%), $\lambda_{max.}$ 412, 426, 565, and 604 nm (ε 99,500, 101,500, 8890, and 21,200), $\lambda_{infl.}$ 528 nm (ε 3400); τ (i) 0·3, 0·35, and 0·65 (3 *meso*-H, all s), 6·0 and 6·5 (both m, 4 × MeCH_2), 6·45, 6·5, 6·8, and 7·15 (all 3H, s, 4 × Me), 8·08, 8·17, 8·56, and 8·63 (12H, all t, 4 × CH_3·CH_2), and 12·32 and 12·9 (both 3H, s, 2 × NMe).

(ii) A similar reaction was carried out on 2,8,12,18-tetraethyl-3,7,13,17,22-pentamethylcorrole (100 mg) and the products were isolated in the same way. After elution of a trace of starting material from the column, the product was eluted as the main, green band with chloroform–methanol (9 : 1) and isolated as its iodide, which formed purple needles (97 mg, 75%; softens *ca.* 200°) from dichloromethane–ether, identical with the product just described (t.l.c., electronic and n.m.r. spectra).

(iii) A similar reaction was carried out on 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (100 mg). A red band eluted from the column with chloroform yielded purple hairs (14 mg, 14%), m.p. 252—253° (from chloroform–methanol), identical with the starting material. The main, green band, eluted with chloroform–methanol (9 : 1), was evaporated and the residue was converted into its iodide. Evaporation and crystallisation from dichloromethane–ether gave purple needles (101 mg, 71%, softens *ca.* 200°), identical with the product already described.

Thermolysis of 2,8,12,18-*tetraethyl*-3,7,13,17,21,22(23)-*hexamethylcorrole iodide*. The salt (200 mg) dissolved in *o*-dichlorobenzene (50 ml) was heated under reflux for 10 min in an atmosphere of nitrogen. The solvent was removed under reduced pressure and the residue chromatographed on alumina with benzene–chloroform (1 : 1) as eluant. The red band yielded purple prisms of 2,8,12,18-tetraethyl-3,7,13,17,21-pentamethylcorrole (133 mg, 86%), m.p. 221—223° (from acetone–methanol), identical with an authentic sample (t.l.c., electronic and n.m.r. spectra).

(C) *Alkylation and Acylation of* 8,12-*Diethyl*-7,13-*dimethyl*-21,24-*dioxacorrole*.— 8,12-*Diethyl*-7,13,22-*trimethyl*-21,24-*dioxacorrole hydrobromide*. 8,12-Diethyl-7,13-dimethyl-21,24-dioxacorrole [17] (50 mg) was dissolved in methyl iodide (20 ml), *NN*-di-isopropylethylamine (1 ml) was added, and the solution was heated in a sealed tube at 100° for 3 h. The solvent was evaporated off and the residue dissolved in chloroform was chromatographed on alumina (acid-washed). Chloroform eluted a trace of starting material, and chloroform–methanol (1 : 1) eluted the product as a deep red-purple band. After removal of the solvent, the product was dissolved in chloroform and washed with dilute aqueous hydrobromic acid. The solution was evaporated and the product crystallised from acetone–petroleum as purple-red needles (58 mg), shown by the n.m.r. spectrum to be a mixture of the mono- and di-methyl derivatives (*ca.* 10 : 1). Two crystallisations from ethyl acetate gave 8,12-*diethyl*-7,13,22-*trimethyl*-21,24-*dioxacorrole hydrobromide* as purple-red needles (35 mg, 56%), m.p. >300° (Found: N, 5·85. $C_{26}H_{27}BrN_2O_2$ requires N, 5·8%), $\lambda_{max.}$ 283·5, 398, 473, 537·5, 548·5, and 594 nm (ε 16,200, 183,000, 7940, 12,400, 16,800, and 13,000), $\lambda_{infl.}$ 326·5 and 499·5 nm (ε 11,300 and 6610); τ (i) −0·69 (1 *meso*-H, s), −0·5 and −0·42 (2 nuclear furan H, two overlapping doublets of two AB systems), −0·38 (1 *meso*-H, s), −0·16 (1 nuclear furan proton, doublet of AB system), 0·05 (1 *meso*-H, s), 0·09 (1 nuclear furan H, doublet of AB system), 5·83 and 6·17 (each overlapping q, 2 × MeCH_2), 6·31 and 6·58 (both s, 2 × Me), 8·11 and 8·5 (6H, both t, 2 × CH_3·CH_2), 14·73 (3H, s, NMe), and 15·5br (s, NH).

8,12-*Diethyl*-7,13,22,23-*tetramethyl*-21,24-*dioxacorrole bromide*. 8,12-Diethyl-7,13-dimethyl-21,24-dioxacorrole (50 mg) was dissolved in methyl iodide (20 ml), anhydrous potassium carbonate (1 g) was added, and the mixture was heated in a sealed tube at 100° for 14 h. The solvent was evaporated off and the residue chromatographed on alumina (acid-washed). Chloroform–methanol (1 : 1) eluted a purple band as the only product. The solvent was removed; the solid residue was dissolved in chloroform and washed with dilute aqueous hydrobromic acid, and the solution was evaporated. The *product* crystallised from ethyl acetate as dark red prisms (52 mg, 81%), m.p. >300° (Found: N, 5·7. $C_{27}H_{29}BrN_2O_2$ requires N, 5·7%), $\lambda_{max.}$ 290·5, 408·5, 522·5, 559, and 605 nm, (ε 16,100, 129,300, 8100, 14,300, and 9800), $\lambda_{infl.}$ 331 nm (ε 10,400), τ (i) −0·3 (2 *meso*-H, s), −0·2 (2H) and 0·05 (4 nuclear furan protons, two doublets of AB system J_{AB} 4·5 Hz), 0·5 (1 *meso*-H, s), 6·38 (4H, q, 2 × MeCH_2), 6·77 (6H, s, 2 × Me), 8·67 (6H, t, 2 × CH_3·CH_2), and 15·5 (6H, s, 2 × NMe).

8,12,22-*Triethyl*-7,13-*dimethyl*-21,24-*dioxacorrole hydrobromide and* 8,12,22,23-*tetraethyl*-7,13-*dimethyl*-21,24-*dioxacorrole bromide*. 8,12-Diethyl-7,13-dimethyl-21,24-dioxacorrole (400 mg) was dissolved in ethyl iodide (50 ml), anhydrous potassium carbonate (2 g.) added, and the solution was heated under reflux for 1·5 h. After cooling, the crystalline product (consisting mainly of the mono-ethyl derivative) was collected; the diethyl derivative largely remained in the filtrate. The crystals were dissolved in chloroform; the solution was filtered to remove solid potassium carbonate and washed with dilute hydrobromic acid. The solvent was evaporated off, the residue was dissolved in acetone, and ether was added to precipitate the product. Crystallisation from acetone gave dark red needles (240 mg, 49%), m.p. >300°, of 8,12,22-*triethyl*-7,13-*dimethyl*-21,24-*dioxacorrole hydrobromide* (Found: C, 65·5; H, 5·8; Br, 16·4; N, 5·65. $C_{27}H_{29}BrN_2O_2$ requires C, 65·7; H, 5·9; Br, 16·25; N, 5·7%), $\lambda_{max.}$ 284, 398, 512, 546, and 589 nm (ε 14,590, 174,600, 7350, 16,120, and 11,420), $\lambda_{infl.}$ 330, 379, and 537 nm (ε 10,790, 77,120, and 11,890); τ (i) −0·71 (1 *meso*-H, s), −0·49 and −0·43 (2 nuclear furan H, two doublets of two overlapping AB systems, $J_{AB} = J_{A'B'}$ = 4·5 Hz), −0·32 (1 *meso*-H, s), −0·13 (1 nuclear furan H, doublet of AB system, J_{AB} 4·5 Hz), 0·03 (1 *meso*-H, s), 0·11 (1 nuclear furan H, doublet of AB system, $J_{A'B'}$ 4·5 Hz), 5·86 and 6·16 (4H, both q, 2 × MeCH_2), 6·33 and 6·59 (6H, both s, 2 × Me), 8·12 and 8·54 (6H, both t, 2 × CH_3·CH_2), 11·96 (3H, t CH_3·CH_2·N), and 15·25 (distorted q, N·CH_2 and NH).

The combined filtrates (above) contained a mixture of mono- and di-ethyl derivatives. The solvent was evaporated off and the residue dissolved in the minimum volume of chloroform. Ethyl iodide (50 ml) was added and the solution heated under reflux, over anhydrous potassium carbonate (2 g), for 6 h. It was filtered, washed with dilute hydrobromic acid, and evaporated. Crystallisation

from acetone–light petroleum gave 8,12,22,23-*tetraethyl*-7,13-*dimethyl*-21,24-*dioxacorrole bromide* as purple plates (250 mg, 45%), m.p. >300° (Found: C, 66·8; H, 6·4 N, 5·35. $C_{29}H_{33}BrN_2O_2$ requires C, 66·85; H, 6·15; N, 5·1%), $\lambda_{max.}$ 293, 408, 530, 565, and 603 nm (ε 15,340 112,000, 6620, 13,420, and 7990), at τ (i) −0·42 (2 *meso*-H, s), −0·35 (2H) and 0·04 (4 nuclear furan H, two doublets of AB system, J_{AB} 4·5 Hz), 0·25 (1 *meso*-H, s), 6·23 (4H, q, 2 × MeCH_2), 6·63 (6H, s, 2 × Me), 8·59 (6H, t, 2 × CH_3·CH_2), 12·53 (6H, t, 2 × N·CH_2·CH_3), and 15·63 and 1657 (4H, 2 × N·CH_2, two six-line multiplets of ABX_3 system).

The D-*camphor*-10-*sulphonate* was prepared by shaking a chloroform solution of the bromide with dilute aqueous sodium D-camphor-10-sulphonate until the aqueous washings gave a negative test for bromide. After evaporation of the solvent, the salt was crystallised from acetone to give red needles, m.p. >300°. After two recrystallisations from acetone it had a specific rotation of *ca.* +200° (Found: C, 69·6; H, 7·2; N, 4·15; S, 4·75. $C_{39}H_{48}N_2O_6S$ requires C, 69·85; H, 6·85; N, 4·2; S, 4·8%), $\lambda_{max.}$ (EtOH) 228, 293, 404, 533, 567·5, and 610 nm (ε 13,500, 17,620, 119,050, 6880, 14,820, and 8060).

5-*Acetyl*-8,12-*diethyl*-7,13-*dimethyl*-21,24-*dioxacorrole and* 2,18(3,17?)-*Diacetyl*-8,12-*diethyl*-7,13-*dimethyl*-21,24-*dioxacorrole.* 8,12-Diethyl-7,13-dimethyl-21,24-dioxacorrole (100 mg) was dissolved in 1,2-dichloroethane (50 ml) and treated with acetyl chloride (500 mg). Anhydrous aluminium chloride (500 mg.) was added and the solution was kept at room temperature for 5 min; it became blue-green. It was warmed (steam-bath) for 1 h, then poured into ice-cold water, and the product was extracted into chloroform. The extract was washed with dilute aqueous ammonia, dried ($MgSO_4$), concentrated to *ca.* 5 ml, and chromatographed on alumina (benzene as eluant). 5-*Acetyl*-8,12-*diethyl*-7,13-*dimethyl*-21,24-*dioxacorrole* was eluted first as a purple-red band, which, yielded dark red-purple prisms (34 mg, 31%), m.p. 222—224° (decomp.) (from chloroform–methanol) [Found: C, 75·65; H, 6·2; N, 6·4%; *M* (mass spec.), 426. $C_{27}H_{26}N_2O_3$ requires C, 75·8; H, 6·2; N, 6·65%; *M*, 426], $\lambda_{max.}$ (pyridine) 393·5, 535·5, 577·5, and 629 nm (ε 86,600, 19,940, 10,360, and 14,150), $\lambda_{infl.}$ 322·5 and 473 nm (ε 18,580 and 3500); $\nu_{max.}$ (KBr) 1665 (C=O) cm^{-1}; τ (i) 0·4 (1 *meso*-H, s), 0·89 (2H) and 1·17 (4 nuclear furan H, two doublets of AB system, *J* 4·5 Hz), 1·21 (1 *meso*-H, s), 6·31 (4H, q, 2 × MeCH_2), 6·78, 6·82, and 6·92 (all s, 2 × peripheral Me and Ac), 8·32 (6H, t, 2 × CH_3·CH_2), and 10·7br (s, NH).

Chloroform–benzene (1 : 1) eluted a blue-red band, which yielded dark blue hairs (33 mg, 27%), m.p. >300° (from chloroform–methanol). The n.m.r. spectrum showed that the *product* was either 2,18-diacetyl- or 3,17-diacetyl-8,12-diethyl-7,13-dimethyl-21,24-dioxacorrole [Found: C, 74·4; H, 6·1; N, 6·45%; *M* (mass spec.), 468. $C_{29}H_{28}N_2O_4$ requires C, 74·35; H, 6·0; N, 6·0%; *M*, 468], $\lambda_{max.}$ (pyridine) 404, 557, 580, and 647 nm (ε 83,000, 18,000 16,470, and 18,900), $\lambda_{infl.}$ 388, 418, and 597 nm (ε 56,970, 60,900, and 15,440), τ ($CDCl_3$–TFA) −0·8 (2H) and −0·41 (2 nuclear furan H and 2 *meso*-H, both s), 0·07 (1 *meso*-H, s), 5·93 (4H, q, 2 × MeCH_2), 6·4 (6H) and 6·5 (both s, 2 × peripheral Me and 2 × Ac), 8·17 (6H, t, 2 × CH_3·CH_2), and 13·82br (s, NH).

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