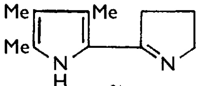
19. *Syntheses of Some 2-2′-Pyrrylpyrrolines.*

By H. Booth, A. W. Johnson, and F. Johnson.

Several synthetical approaches to 2-2′-pyrrylpyrrolines are described. The structures of certain by-products from the reactions have been determined.

In an examination of intermediates of possible use for syntheses of corrins and related compounds we have investigated the preparation of a number of 2-2′-pyrrylpyrrolines. Several methods[1] exist for the preparation of substituted 1-pyrrolines and, of these, the reaction of γ-chlorobutyronitrile with Grignard compounds was selected in the first instance. 2-2′-Pyrryl-1-pyrroline had in fact already been synthesised[2] by the reaction of γ-chlorobutyronitrile with pyrrylmagnesium bromide although the product was thought to be a derivative of 2-pyrroline. When equivalent quantities of γ-chlorobutyronitrile and the Grignard derivative of 2,3,4-trimethylpyrrole were caused to react, a crystalline base was obtained which, from its analysis and spectral properties, is formulated as the 2-2′-pyrryl-1-pyrroline (I). Its nuclear magnetic resonance spectrum, kindly determined and interpreted for us by Dr. R. J. Abraham of the National Physical Laboratory, Teddington, was also in accord with this structure. However, with an excess of γ-chlorobutyronitrile, by preferential condensation with the chlorine atom, 2,3,4-trimethylpyrrylmagnesium bromide gave the 2*H*-pyrrole (II) which was also characterised by its spectra and the formation of a picrate. This preparation of the 2*H*-pyrrole (II) is an example of substitution in an activated pyrrole at a ring-carbon atom already bearing an alkyl group, in preference to an alternative unsubstituted position. Such a reaction scheme operates in the alkylation of cryptopyrrole[3] and has been postulated[4] as part of the mechanism for the acid-catalysed self-condensation of porphobilinogen leading to uroporphyrin-III. The sole products identified from the Grignard reactions of γ-chlorobutyronitrile with 2,5-dimethyl- and 2,3,4,5-tetramethyl-pyrrole were 2*H*-pyrroles analogous to (II), but 3,4-dimethylpyrrole gave a crystalline product with spectral properties different from those of types (I) or (II), although analysis indicated that it was another isomer. The 5,6,7,8-tetrahydroindolizine structure (III; X = NH), which accords with the observed physical properties (pyrrole-type spectrum, not appreciably affected by acids; lack of carbonyl absorption), is suggested for this product. Acid hydrolysis of this product (III; X = NH) caused liberation of ammonia and the formation of the cyclic amide (III; X = O). Condensation of pyrrole α-side chains with the cyclic nitrogen atom as in the formation of (III; X = NH) can occur with surprising ease in certain cases, *e.g.*, the formation of (IV) from 2-formylpyrrole and piperidine in cold ethanol.[5]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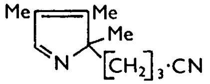
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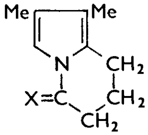
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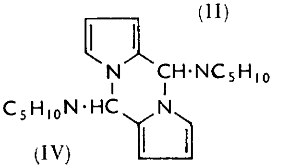
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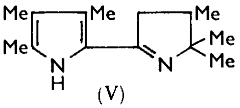
(V)

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[1] For reviews see: (*a*) Bonnett, Clark, Giddey, and Todd, *J.*, 1959, 2087; (*b*) Demoen and Janssen, *J. Amer. Chem. Soc.*, 1959, **81**, 6281; (*c*) Burckhalter and Short, *J. Org. Chem.*, 1958, **23**, 1278; Kloetzel, Pinkus, and Washburn, *J. Amer. Chem. Soc.*, 1957, **79**, 4222; (*d*) Fulhage and Vander Werf, *ibid.*, 1958, **80**, 6249.

[2] Craig, *J. Amer. Chem. Soc.*, 1934, **56**, 1144.

[3] Booth, Johnson, Markham, and Price, *J.*, 1959, 1587.

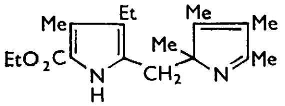
[4] Bullock, Johnson, Markham, and Shaw, *J.*, 1958, 1430; *Nature*, 1960, **185**, 607.

[5] Herz and Brasch, *J. Org. Chem.*, 1958, **23**, 711.

Condensation of γ-chlorobutyronitrile with the Grignard derivatives of pyrroles can thus give rise to a variety of products and in considering routes to 2-2′-pyrrylpyrrolines of more general applicability, we examined the reaction of pyrryl Grignard derivatives with 2-methoxy-1-pyrroline. This compound, an enol ether of 2-pyrrolidone, was prepared from pyrrolidone by the action of dimethyl sulphate, and its general reactions were similar to those of the six-[6] and seven-membered[7] ring homologues. Condensation of 2-methoxy-1-pyrroline with the Grignard derivatives of 2,3,4-trimethyl- and 3,4-dimethyl-pyrrole occurred smoothly, to give the corresponding 2-2′-pyrryl-1-pyrroline (*e.g.*, I), albeit in small yield, but the condensation product with 2,3,4,5-tetramethylpyrrole could not be isolated.

A number of other routes to particular pyrrylpyrrolines were discovered in the course of this work. Reaction of 4,5,5-trimethyl-1-pyrroline[1a] itself, or the corresponding hydrochloride, with 2,3,4-trimethylpyrrole (but not the Grignard derivative) unexpectedly gave the pyrryl-1-pyrroline (V), the spectra of which correspond exactly with those of the analogue (I). This reaction involves an unexpected dehydrogenation, possibly by disproportionation, and other somewhat similar dehydrogenations in the pyrroline series have been reported,[1b,8] although the addition of pyrrole to 1-pyrroline gives 2,2′-pyrrylpyrrolidine.[1d] In another approach it was found that, although the Grignard derivative of 2,3,4,5-tetramethylpyrrole reacted with ethyl 5-bromomethyl-4-ethyl-3-methylpyrrole-2-carboxylate to give the base (VI), attempts to obtain 2-2′-pyrryl-2*H*-pyrroles by reaction of 2-halogenopyrroles with 2,3,4,5-tetramethylpyrrylmagnesium bromide were unsuccessful. No reaction occurred with 4-acetyl-2-bromo-3,5-dimethylpyrrole, and 2-iodo-3,4,5-trimethylpyrrole[9] proved to be too unstable to be employed in the reaction. Attempts to prepare 2-bromo-3,4,5-trimethylpyrrole resulted in the formation of the dipyrromethene (VII) even under very mild conditions.

Two other methods for the synthesis of pyrrylpyrrolines were investigated. The action of Grignard compounds on *N*-substituted 2-pyrrolidones is known[10] to yield 2-pyrrolines, but no identifiable products other than unchanged starting materials were isolated on reaction of 2-pyrrolidone itself with 2,3,4-trimethylpyrrylmagnesium bromide.[11] The other approach involved the acid dimerisation of certain pyrroles. Fischer[12] reported the dimerisation of cryptopyrrole when an ethyl acetate solution of the picrate of the monomer was heated under reflux, but we have been unable to isolate any pure dimeric base from such a reaction. Allen, Gilbert, and Young[13] found that the action of ethereal hydrogen chloride on 2-phenylpyrrole gave a product which they formulated as the pyrrylpyrroline (VIII; R = Ph) and that the similarly prepared 2-methylpyrrole dimer, first reported by Dennstedt *et al.*,[14] probably had the structure (VIII; R = Me). This



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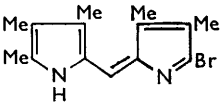

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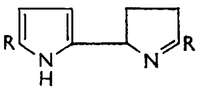

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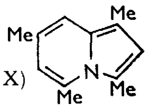

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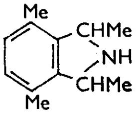

(X)

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[6] Cervinka, *Chem. listy*, 1959, **52**, 1145.
[7] Benson and Cairns, *J. Amer. Chem. Soc.*, 1948, **70**, 2115.
[8] Knott, *J.*, 1948, 186.
[9] Treibs and Kolm, *Annalen*, 1958, **614**, 176.
[10] Craig, *J. Amer. Chem. Soc.*, 1933, **55**, 295; Lukeš *et al.*, *Coll. Czech. Chem. Comm.*, 1930, **2**, 531; 1959, **24**, 1117.
[11] Cf. Lukeš, Šorm, and Arnold, *Coll. Czech. Chem. Comm.*, 1947, **12**, 641.
[12] Fischer, *Ber.*, 1915, **48**, 401.
[13] Allen, Gilbert, and Young, *J. Org. Chem.*, 1938, **2**, 227, 235.
[14] Dennstedt *et al.*, *Ber.*, 1888, **21**, 1478, 3429.

2-methylpyrrole dimer has now been obtained crystalline and its properties are in agreement with structure (VIII; R = Me). As reported by Allen *et al.*,[13] the dimer is very easily converted by dilute sulphuric acid into 2,4-dimethylindole. The infrared spectrum of compound (VIII; R = Me) shows a maximum at 1647 cm.$^{-1}$, the expected value for a non-conjugated C=N group (lit.[1b-d] values for 2-methyl-1-pyrroline are in the range 1637—1650 cm.$^{-1}$ and for 2-phenyl-1-pyrroline in the range 1613—1618 cm.$^{-1}$). Under the conditions used for 2-methylpyrrole, 2,3,4-trimethylpyrrole and cryptopyrrole were converted into crystalline hydrochlorides. Similar behaviour has been recorded[15] for 2,3,4,5-tetramethylpyrrole, whereas pyrrole itself is converted by ethereal hydrogen chloride[14] (and also by 5·5N-aqueous hydrochloric acid[16]) into a trimer. The hydrochloride of pyrrole has been prepared, however, by using 8N-aqueous hydrochloric acid in the absence of light and oxygen.[9] 2,4-Dimethylpyrrole gives a non-crystalline hydrochloride with anhydrous hydrogen chloride[17] but it is known that aqueous acetic acid causes self-condensation to 1,3,5,7-tetramethylindolizine (IX).[18] In a somewhat similar manner, the reductive self-condensation of 2,5-dimethylpyrrole yields 1,3,4,7-tetramethylisoindoline[19] (X), and it is possible that both of these condensations proceed with the intermediate formation of 2-2′-pyrrylpyrrolines or equivalent structures.

EXPERIMENTAL

Ultraviolet absorption spectra were determined for ethanolic solutions except where otherwise stated.

2-(3,4,5-*Trimethyl*-2-*pyrryl*)-1-*pyrroline* (I).—(i) A solution of 2,3,4-trimethylpyrrole[20] (11·5 g.) in dry ether (50 c.c.) was added to one of methylmagnesium iodide (from 15·2 g. methyl iodide) in ether (200 c.c.) in 10 min. A solution of γ-chlorobutyronitrile (11·1 g.) in ether (20 c.c.) was then added and the mixture heated under reflux overnight. The Grignard derivative was decomposed with water and made alkaline with 40% aqueous potassium hydroxide. The ethereal layer was separated and the aqueous solution washed with ether (2 × 50 c.c.). The basic fraction was extracted from the combined ether extracts with saturated aqueous potassium dihydrogen phosphate (3 × 100 c.c.) and re-extracted into ether (3 × 100 c.c.) after addition of a slight excess of 40% aqueous potassium hydroxide. Evaporation of the solvent from the dried ethereal extract gave a dark brown syrup (7 g.) from which a colourless crystalline solid (2·5 g.), though still impure, was obtained by sublimation at 90°/0·2 mm. The *product* was purified by repeated sublimation, then having m. p. 126—128° [Found: C, 75·3; H, 9·45; N, 15·9%; *M* (Rast), 168. $C_{11}H_{16}N_2$ requires C, 74·95; H, 9·15; N, 15·9%; *M*, 176·2], $\lambda_{max.}$ 302 mμ (log ε 4·23), inflection 262 mμ (log ε 3·65) and in ethanolic hydrogen chloride $\lambda_{max.}$ 341 mμ (log ε 4·48), inflection 292 mμ (log ε 3·78), $\nu_{max.}$ (in CCl_4) 973, 1047, 1086, 1093, 1142, 1188, 1290, 1333, 1366, 1431, 1541, 1560, 1597, 2825, 2899, and 3425 cm.$^{-1}$.

The corresponding *picrate* formed yellow needles, m. p. 177—178° (from methanol) (Found: C, 50·9; H, 5·1; N, 17·4. $C_{17}H_{19}N_5O_7$ requires C, 50·4; H, 4·7; N, 17·3%).

(ii) A solution of 2-methoxy-1-pyrroline (see below; 3 g.) in dry ether (20 c.c.) was added to a solution of the Grignard derivative prepared from 2,3,4-trimethylpyrrole (3·2 g.) in ether (70 c.c.). The ether was then removed and replaced by dry xylene (100 c.c.), and the mixture heated under reflux for 6 hr. and then worked up by the method described for the previous experiment. A viscous brown oil (1 g.) was obtained which yielded colourless prisms, m. p. 126—128°, after sublimation at 90°/0·2 mm. This product was identical with that described above.

2-*Methoxy*-1-*pyrroline*.—Methyl sulphate (31·5 g.) was added dropwise during 2 hr. to a boiling solution of 2-pyrrolidone (21·75 g.) in dry benzene (50 c.c.), and the mixture heated under reflux for 24 hr. After cooling, the solution was treated with an excess of saturated aqueous potassium carbonate, and the aqueous layer extracted with benzene (2 × 50 c.c.). The

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[15] Abraham, Bullock, and Mitra, *Canad. J. Chem.*, 1959, **37**, 1859.

[16] Smith and Potts, *J.*, 1957, 4018.

[17] Bullock, *Canad. J. Chem.*, 1958, **36**, 1686.

[18] Saxton, *J.*, 1951, 3239.

[19] Bonnett and White, *Proc. Chem. Soc.*, 1961, 119.

[20] Johnson, Markham, Price, and Shaw, *J.*, 1958, 4254.

combined benzene extracts were dried and after removal of the solvent the residue was distilled under reduced pressure. 2-*Methoxy*-1-*pyrroline* (14 g.) had b. p. 45°/10 mm. and was further purified by conversion into the hydrochloride and subsequent regeneration and distillation (Found: N, 13·9. C_5H_9NO requires N, 14·1%). The infrared spectrum (liquid film) showed main max. at 961, 989, 1003, 1190, 1242, 1285, 1342, 1437, 1449, 1653, 2857, and 2941 cm.$^{-1}$. The corresponding *picrate* had m. p. 87—89° (from ethanol) (Found: N, 16·8. $C_{11}H_{12}N_4O_8$ requires N, 16·6%). Satisfactory analyses were not obtained for the picrolonate, which had m. p. 162—163° (from ethanol) (Found: N, 18·5. Calc. for $C_{15}H_{17}N_5O_6$: N, 19·25%).

2-(3,4-*Dimethyl*-2-*pyrryl*)-1-*pyrroline*.—A solution of 2-methoxy-1-pyrroline (5·05 g.) in dry ether (10 c.c.) was added to the Grignard derivative prepared from 3,4-dimethylpyrrole (5 g.) in ether (60 c.c.). The ether was removed and replaced by xylene, and the solution heated at 90° overnight. Removal of the solvent gave a thick brown oil which, after sublimation at 85°/0·1 mm., yielded the *product* as colourless prisms, m. p. 178—179° (Found: C, 74·1; H, 9·1; N, 16·7. $C_{10}H_{14}N_2$ requires C, 74·05; H, 8·7; N, 17·25%), $\lambda_{max.}$ 290 mμ (log ε 4·20) and in an ethanolic solution of hydrogen chloride $\lambda_{max.}$ 327 mμ (log ε 4·38), $\nu_{max.}$ (in CCl_4) 910, 963, 1053, 1081, 1183, 1295, 1339, 1395, 1408, 1449, 1600, 2857, 2933, and 3460 cm.$^{-1}$.

A similar condensation of 2-methoxy-1-pyrroline with the Grignard derivative of 2,3,4,5-tetramethylpyrrole [20] gave a low yield of an oil which decomposed on attempted distillation.

4,5,5-*Trimethyl*-(3,4,5-*trimethyl*-2-*pyrryl*)-1-*pyrroline* (V).—(i) A mixture of 2,3,4-trimethylpyrrole (2 g.) and 4,5,5-trimethyl-1-pyrroline [1a] (2 g.) was heated under reflux at 130° for 30 min. and then on the steam bath for 3 days until the penetrating odour of 4,5,5-trimethyl-1-pyrroline had disappeared. The mixture gradually changed from a light yellow mobile oil to a dark brown viscous oil which solidified on cooling. The *product* was purified by repeated sublimation at 100—120°/0·5 mm. to yield colourless prisms (0·3 g.), m. p. 84—86° (Found: C, 76·5; H, 10·35; N, 13·1. $C_{14}H_{22}N_2$ requires C, 77·0; H, 10·15; N, 12·85%), $\lambda_{max.}$ 304 mμ (log ε 4·26), inflection 260 mμ (log ε 3·68), in ethanolic hydrogen chloride: $\lambda_{max.}$ 343 mμ (log ε 4·49), inflection 292 mμ (log ε 3·80), $\nu_{max.}$ (KBr disc) 885, 949, 980, 1032, 1047, 1087, 1105, 1135, 1143, 1182, 1212, 1233, 1256, 1304, 1359, 1379, 1429, 1449, 1468, 1493, 1567, 1603, 2874, 2967, 3049, and 3125 cm.$^{-1}$. The *picrate* formed yellow prisms (from methanol), m. p. 182—184° (Found: C, 54·2; H, 5·85; N, 15·3. $C_{20}H_{25}N_5O_7$ requires C, 53·7; H, 5·65; N, 15·65%).

(ii) 4,5,5-Trimethyl-1-pyrroline (2 g.) was converted into its hydrochloride by treatment with the equivalent amount of concentrated hydrochloric acid, and to the solution was added 2,3,4-trimethylpyrrole (2 g.) in ethanol (15 c.c.); the mixture was heated under reflux for 48 hr. The solvent was removed and the residue treated with a slight excess of concentrated aqueous potassium hydroxide and then extracted with ether. The solvent was removed from the dried ethereal extract to leave a thick brown oil (3·8 g.) which was purified by repeated sublimation at 100—120°/0·5 mm., affording colourless prisms, m. p. 84—86°, identical with the product of the previous experiment.

Only negligible yields of the adduct were obtained from the reaction of the pyrroline or its salts with the Grignard derivative of the pyrrole.

γ-(2,3,4-*Trimethyl*-2H-2-*pyrryl*)*butyronitrile* (II).—γ-Chlorobutyronitrile (16·7 g., 1·5 mol.) in dry ether (30 c.c.) was added to the Grignard derivative (prepared as above) of 2,3,4-trimethylpyrrole (11·5 g., 1 mol.) in ether (250 c.c.), and the mixture heated under reflux overnight. The basic fraction, obtained by extraction with aqueous potassium dihydrogen phosphate as described above, was a thick brown oil which was purified by sublimation at 120°/0·2 mm. to yield a colourless oil (1·2 g.) together with a very small quantity of the pyrrylpyrroline (above). The infrared absorption of a sample regenerated from the picrate showed max. at 844, 889, 918, 957, 1026, 1086, 1119, 1161, 1176, 1202, 1221, 1250, 1290, 1323, 1361, 1374, 1418, 1437, 1441, 1517, 1558, 1600, 1613, 1645, 2257, 2740, 2882, 2941, and 2985 cm.$^{-1}$. The *picrate* formed yellow prisms, m. p. 109—111°, from methanol (Found: C, 50·5; H, 4·45; N, 17·3. $C_{17}H_{19}N_5O_7$ requires C, 50·4; H, 4·7; N, 17·3%).

γ-(2,3,4,5-*Tetramethyl*-2H-2-*pyrryl*)*butyronitrile*.—Prepared by a similar method from γ-chlorobutyronitrile (11·5 g., 1 mol.) with the Grignard derivative of 2,3,4,5-tetramethylpyrrole (14 g., 1 mol.), the crude *product* (8 g.) was distilled at 100°/1 mm. from a bulb-tube to yield a colourless oil (3·08 g., 14·3%) (Found: C, 76·1; H, 9·85. $C_{12}H_{18}N_2$ requires C, 75·75; H, 9·55%), $\lambda_{max.}$ 242 mμ (log ε 3·54) and in ethanolic hydochloric acid $\lambda_{max.}$ 267 mμ (log ε 3·66). The infrared absorption of a sample (liquid film) regenerated from the picrate showed max, at 707, 748, 791, 912, 920, 943, 988, 1036, 1042, 1085, 1101, 1127, 1157, 1192, 1227, 1264, 1312, 1325, 1359, 1379, 1429, 1439, 1445, 1560, 1613, 1629, 1656, 2242, 2857, 2915, and 2950 cm.$^{-1}$. The corresponding *picrate* formed greenish-yellow prisms, m. p. 132—133°, from methanol (Found: C, 51·7; H, 4·85; N, 17·1. $C_{18}H_{21}N_5O_7$ requires C, 51·55; H, 5·05; N, 16·7%).

γ-(2,5-*Dimethyl*-2H-2-*pyrryl*)*butyronitrile*.—Prepared similarly from γ-chlorobutyronitrile (10·35 g., 1 mol.) and the Grignard derivative of 2,5-dimethylpyrrole (8·5 g., 1 mol.), the crude *product* (3 g.) was distilled at 100°/0·2 mm. from a bulb-tube to yield a colourless oil (1·4 g.) which was stable in air (Found: C, 74·0; H, 9·2. $C_{10}H_{14}N_2$ requires C, 74·0; H, 8·7%) and had $\lambda_{\max.}$ 225 mμ (log ε 3·35) and in ethanolic hydrochloric acid $\lambda_{\max.}$ 240 mμ (log ε 3·50). The *picrate* formed yellow prisms, m. p. 134—136°, from methanol (Found: C, 49·4; H, 4·6; N, 17·4. $C_{16}H_{17}N_5O_7$ requires C, 49·1; H, 4·4; N, 17·9%).

5,6,7,8-*Tetrahydro*-5-*imino*-1,2-*dimethylindolizine* (III; X = NH).—γ-Chlorobutyronitrile (4·36 g.) in dry ether (10 c.c.) was added to the Grignard derivative of 3,4-dimethylpyrrole (4 g.) in ether (35 c.c.), and the mixture heated under reflux for 3 hr. The ether was then removed and replaced by an equal volume of xylene, and the solution was heated at 90° overnight. The product was worked up in the standard manner and gave the crude product (4 g.) as a mobile brown oil. Distillation from a bulb-tube gave a colourless wax (1·6 g.) which on fractional sublimation gave the imino-compound (0·59 g.) together with a small quantity of a more volatile compound. The latter compound was obtained, together with ammonia, by hydrolysis of the imino-compound with dilute hydrochloric acid. The *imino-compound* had m. p. 58—60° (Found: C, 74·6; H, 8·6; N, 16·8. $C_{10}H_{14}N_2$ requires C, 74·05; H, 8·7; N, 17·25%), $\lambda_{\max.}$ 255 mμ (log ε 4·13) and in ethanolic hydrochloric acid $\lambda_{\max.}$ 263 mμ (log ε 4·21), $\nu_{\max.}$ (KBr disc) 866, 905, 960, 1075, 1119, 1139, 1149, 1185, 1238, 1272, 1318, 1332, 1339, 1370, 1391, 1410, 1429, 1435, 1515, 1600, 1639, 2857, and 2933 cm.$^{-1}$. The *picrate* formed yellow prisms (from methanol), m. p. 225° (Found: C, 48·6; H, 4·1. $C_{16}H_{17}N_5O_7$ requires C, 49·1; H, 4·4%).

The hydrolysis product, 5,6,7,8-*tetrahydro*-1,2-*dimethyl*-5-*oxoindolizine* (III; X = O), had m. p. 58—59° (Found: N, 8·95. $C_{10}H_{13}NO$ requires N, 8·6%), $\lambda_{\max.}$ 249 mμ (log ε 4·05), $\nu_{\max.}$ 862, 905, 912, 970, 1124, 1188, 1222, 1335, 1346, 1374, 1399, 1418, 1447, 1626, 1724, 2899, and 2976 cm.$^{-1}$.

Ethyl 4-*Ethyl*-3-*methyl*-5-(2,3,4,5-*tetramethyl*-2H-2-*pyrrylmethyl*)*pyrrole*-2-*carboxylate* (VI) (with K. B. Shaw).—2,3,4,5-Tetramethylpyrrole (3·0 g.) in ether (25 c.c.) was added to a solution of methylmagnesium iodide, prepared from magnesium (0·6 g.), methyl iodide (1·5 c.c.), and ether (10 c.c.), and the mixture was heated under reflux for 1 hr. To the cooled solution was added a slurry of ethyl 5-bromomethyl-4-ethyl-3-methylpyrrole-2-carboxylate [21] (6·6 g.) in ether (150 c.c.), and the mixture was heated under reflux for 18 hr. A saturated solution of ammonium chloride (50 c.c.) was added to the cooled mixture, and the ethereal layer separated. The aqueous solution was extracted with ether (25 c.c.) and the combined ethereal extracts were shaken with N-hydrochloric acid (2 × 25 c.c.). When the ethereal solution was dried ($MgSO_4$) and evaporated to dryness, a dark solid (0·75 g.) remained. Sublimation of the solid at 80°/20 mm. gave 2,3,4,5-tetramethylpyrrole, m. p. 109—110°. The aqueous solution was basified with sodium hydroxide solution and extracted with ether. After removal of solvent from the dried extract, there remained a brown solid (6·5 g.) which resisted attempts at crystallisation. Purification of the solid through the picrate (see below) gave an almost colourless solid, m. p. 85°, $\lambda_{\max.}$ 246 and 284 mμ (log ε 3·96 and 4·27, respectively), and in ethanolic hydrogen chloride $\lambda_{\max.}$ 270 mμ (log ε 4·30). The *picrate* formed dark yellow prisms (from ethanol), m. p. 150—152° (Found: C, 55·0; H, 5·75; N, 13·2. $C_{25}H_{31}N_5O_9$ requires C, 55·05; H, 5·75; N, 12·85%). The *picrolonate* formed dark yellow-green needles (from ethanol), m. p. 130—133° (Found: C, 60·2; H, 5·95; N, 14·4. $C_{29}H_{36}N_6O_7$ requires C, 60·0; H, 6·25; N, 14·5%).

Action of Hydrogen Chloride on Pyrroles (with K. B. Shaw).—(i) 2-Methylpyrrole (2 g.; prepared by reduction of the semicarbazone of 2-formylpyrrole,[22] itself obtained from pyrrole with dimethylformamide and phosphorus oxychloride [23]) was dissolved in dry ether (25 c.c.), and the cooled solution was saturated with dry hydrogen chloride. The ether was decanted, leaving a sticky yellow solid, which was dissolved in dilute sodium hydroxide solution (10 c.c.).

[21] Hayes, Kenner, and Williams, *J.*, 1958, 3779.

[22] Cantor, Lancaster, and Vander Werf, *J. Org. Chem.*, 1956, **21**, 918.

[23] Silverstein, Ryskiewicz, Willard, and Koehler, *J. Org. Chem.*, 1955, **20**, 668.

This solution was extracted with ether (2 × 20 c.c.), the combined extracts were dried ($MgSO_4$) and evaporated, leaving a yellow oil (1·3 g., 65%), which distilled at 80° (bath temp.)/0·05 mm. to give 2-*methyl*-5-(5-*methyl*-2-*pyrryl*)-1-*pyrroline*, m. p. 62—64° (Found, in a sample sublimed at 50°/0·05 mm.: C, 74·1; H, 8·35; N, 17·3. $C_{10}H_{14}N_2$ requires C, 74·05; H, 8·7; N, 17·25%), $\lambda_{max.}$ 220 mμ (log ε 3·95) and in ethanolic hydrogen chloride $\lambda_{max.}$ 221 and 289 mμ (log ε 3·99 and 2·98, respectively). The dimer hydrochloride [from 2-methylpyrrole (1·0 g.)] was warmed for 2 min. on the steam-bath with dilute sulphuric acid (10 c.c.). The solution was steam-distilled and the distillate extracted with ether (2 × 50 c.c.). When the combined extracts were dried ($MgSO_4$) and evaporated, 2,4-dimethylindole (0·2 g.) remained as a pale brown oil. The picrate formed red-brown needles, m. p. 158—159° (lit.,[13] 158°).

(ii) 2,3,4-Trimethylpyrrole [20] (3 g.) was dissolved in dry ether (50 c.c.), and the cooled solution was saturated with dry hydrogen chloride. The precipitated white solid was set aside overnight in contact with the mother liquors before being separated, washed with ether, and dried *in vacuo*. The residue of 2,3,4-*trimethylpyrrole hydrochloride* (3·2 g.; m. p. 130—134°) crystallised from acetic acid–ether as grey needles, m. p. 137—138° (decomp.) (Found: C, 57·45; H, 8·25. $C_7H_{12}ClN$ requires C, 57·75; H, 8·30%). The salt became red when exposed to air. The salt (2·5 g.) was dissolved in water (20 c.c.), and the solution was basified with aqueous sodium hydroxide and extracted with ether (3 × 25 c.c.); evaporation of the dried ethereal solution gave 2,3,4-trimethylpyrrole (2·0 g.) (picrate, m. p. and mixed m. p. 136—137°). In a second experiment, a stream of dry hydrogen chloride was passed through an ethereal solution of 2,3,4-trimethylpyrrole (3·5 g.) (30 c.c.) until the precipitated solid had redissolved. The ethereal solution was left overnight and then the ether was removed, leaving a solid (4·3 g.) which crystallised from acetic acid–ether in needles, m. p. 137—138° (decomp.), identical with the hydrochloride prepared as above. Treatment of 2,3,4-trimethylpyrrole with aqueous hydrochloric acid under a variety of conditions gave no dimer, the pyrrole being in all cases recovered in yields exceeding 90%.

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