Synthesis of 2,5-Di-t-butylpyrrole and of 2,3,5-Tri-t-butylpyrrole

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WE report two syntheses of hindered pyrrole derivatives, one of which is another[1] example of direct introduction of a t-butyl group adjacent to one already present in an aromatic system. 2,5-Di-t-butylpyrrole[2] (DBP) (m.p. 32—33°) is prepared in 93% yield by heating 2,2,7,7-tetramethyloctane-3,6-dione[3] under reflux with ammonium acetate in acetic acid.[4] 2,3,5-Tri-t-butylpyrrole[2] (TBP) (m.p. 46—47°) is formed in 72% yield (n.m.r. analysis) by alkylation of DBP with t-butyl chloride in carbon disulphide, using tin(IV) chloride as a catalyst (the yield is slightly lower with aluminium chloride). It can be separated from the di-t-butyl compound by chromatography on alumina and recrystallisation from methanol, or isolated in *ca.* 20% yield by direct recrystallisation of the reaction product from methanol.

The u.v. and i.r. spectra of the two compounds provide evidence for the substituted pyrrole structure: in cyclohexane, DBP has λ_{max} 218 mμ (ϵ 10,000), shoulder at 289 mμ (ϵ 20), and TBP has λ_{max} 218 mμ (ϵ 9600) shoulder at 283 mμ (ϵ 33). DBP (pure liquid) has ν_{max} 3500 (NH), 3000 (CH), 1380, 1360, 1260, 1200 (t-butyl groups), 1580 (ring stretching), 1045 (ring breathing), 765, and 710 cm.$^{-1}$ (out-of-plane). TBP (in nujol) has ν_{max} 3500, 1355, 1245, 1195, 1575, 1045, 795, and 690 cm^{-1}).

The n.m.r. spectra give the position of the t-butyl groups. DBP (in $CDCl_3$) has a sharp peak at τ 8·75, a doublet (J 2·7 c./sec.) at τ 4·28 [$J(^{13}C–H)$ 167 c./sec.],[5] and a broader signal at τ 2·5 (intensity ratio: 18 : 2 : 1). TBP (in CCl_4) has three peaks at τ 8·77, 8·68, 8·60, a doublet (J 3·5 c./sec.) at τ 4·37 [$J(^{13}C–H)$ 165·5 c./sec.][5] and a broader signal at τ 2·5 (Intensity ratio: 9 : 9 : 9 : 1 : 1).

Both compounds undergo spontaneous oxidation at room temperature, more rapidly in solution than in the solid state.

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[1] H. Winberg and U. E. Wiersum, *Chem. Comm.*, 1965, 1.
[2] Satisfactory microanalysis has been obtained for this compound.
[3] R. Ramasseul and A. Rassat, *Bull. Soc. chim. France*, 1963, 2214.
[4] T. Ajello and S. Cusmano, *Gazzetta*, 1939, **69**, 207.
[5] In pyrrole derivatives, α- and β-protons show τ 3·35 ± 0·3 and 4 ± 0·3 respectively,[6] and $J(^{13}C–H)$ 183 and 169 c./sec. respectively (ref. 7).
[6] *cf.* Varian N.M.R. spectra catalogue.
[7] K. Tori and T. Nakagawa, *J. Phys. Chem.*, 1964, **68**, 3163.