

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 another¹ example of direct introduction of a *t*-butyl group adjacent to one already present in an aromatic system. 2,5-Di-*t*-butylpyrrole² (DBP) (m.p. 32–33°) is prepared in 93% yield by heating 2,2,7,7-tetramethyloctane-3,6-dione³ under reflux with ammonium acetate in acetic acid.⁴ 2,3,5-Tri-*t*-butylpyrrole² (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 μ

(ϵ 10,000), shoulder at 289 μ (ϵ 20), and TBP has λ_{\max} 218 μ (ϵ 9600) shoulder at 283 μ (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 [$J(^{13}\text{C}-\text{H})$ 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 [$J(^{13}\text{C}-\text{H})$ 165.5 c./sec.]⁶ 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 \pm 0.3 and 4 \pm 0.3 respectively,⁶ and $J(^{13}\text{C}-\text{H})$ 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.