

This method of production of pregnadienolone appears to be superior to the hitherto published methods^{3,4} where some by-product¹⁰ formation is involved. The successful degradation of these steroidal alkaloids in high yields, particularly solasodine to pregnadienolone, a biologically important hormone intermediate, may be of considerable industrial importance.

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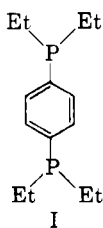
(10) The structure and the various chemical manifestations of this substance will be published in the full report.

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P,P,P',P'-Tetraethyl-*p*-phenylenediphosphine

Sir:

A recent preliminary report by Clifford and Olsen¹ prompts us to record at this time our preparation of *P,P,P',P'*-tetraethyl-*p*-phenylenediphosphine (I). This substance is the phosphorus analog of the tetraalkyl-*p*-phenylenediamines, which are the precursors of the highly colored Wurster radical ions. Our studies on the behavior toward oxidizing agents of the diphosphine I and of the



corresponding N-P system, will be published elsewhere.

The diphosphine I was obtained in *ca.* 20% yield from the reaction of diethylchlorophosphine² with *p*-phenylenedilithium³ in petroleum ether at temperatures below 30°, in a nitrogen atmosphere. I was isolated by extraction into hydrochloric acid followed by the usual alkaline treatment and frac-

(1) A. F. Clifford and R. R. Olsen, Abstracts of Papers, Division of Inorganic Chemistry, A.C.S. Meeting, Boston, Mass., April 1959, page 16M.

(2) (a) M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 411 (1951); (b) M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *J. Org. Chem.*, **14**, 429 (1949).

(3) H. Gilman, W. Langham and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1949).

tional distillation. The diphosphine I had b.p. 172–174° (9 mm.), n_D^{25} 1.5666, bands at 6.85, 7.00, 7.22, 8.1, and 8.90 μ . Calcd. for C₁₄H₂₄P₂: C, 66.2; H, 9.5; P, 24.4. Found: C, 66.2; H, 9.4; P, 23.9.

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A New Synthesis of Serotonin

Sir:

The nitroethylation of indoles and substituted indoles, yielding 3-(2-nitroethyl)indoles has been previously described.¹⁻³ Catalytic hydrogenation of the 3-(2-nitroethyl)indoles provides a general synthetic route to tryptamine and substituted tryptamines. We wish to record the successful application of this procedure to the synthesis of serotonin.

Dropwise addition of a 1*M* excess of nitroethylene^{4,5} to molten 5-benzyloxyindole at steam-bath temperature (total time 1.83 hr.) gave 3-(2-nitroethyl)-5-benzyloxyindole (I, hygroscopic white crystals from methylene chloride-light petroleum (b.p. 60–68°), m.p. 93.5–95°, calcd. for C₁₇H₁₆N₂O₃ (296.31): C, 68.90; H, 5.44; N, 9.45; found: C, 68.62; H, 5.58; N, 9.13) in 45% yield. Use of excess nitroethylene is desirable since unreacted 5-benzyloxyindole (36% by wt.) and I (64%) form a eutectic mixture, m.p. 81–81.5°. Similar reactions of 5-benzyloxyindole with equimolar portions of β -nitrostyrene (6 hr., 72% yield) and β -methyl- β -nitrostyrene (22 hr., 37% yield), both at steam bath temperature, gave 3-(1-phenyl-2-nitroethyl)-5-benzyloxyindole (II, white platelets from ethanol, m.p. 117–118° calcd. for C₂₃H₂₀N₂O₃ (372.41): C, 74.17; H, 5.41; N, 7.52; found: C, 74.36; H, 5.40; N, 7.36) and 3-(1-phenyl-2-nitropropyl)-5-benzyloxyindole (III, white rod-like crystals from ethanol, m.p. 152–152.5°, calcd. for C₂₄H₂₂N₂O₃ (386.43): C, 74.59; H, 5.74; N, 7.25; found: C, 74.80; H, 5.61; N, 7.26).

Hydrogenation at 2 atm. over platinum oxide catalyst of the adducts I–III gave in high yields the corresponding tryptamines, isolated as the picrates: Ia (84% yield from I), very hygroscopic reddish orange crystals from ethanol, m.p. 231.5–

(1) W. E. Noland and P. J. Hartman, *J. Am. Chem. Soc.*, **76**, 3227 (1954).

(2) W. E. Noland, G. M. Christensen, G. L. Sauer, and G. G. S. Dutton, *J. Am. Chem. Soc.*, **77**, 456 (1955).

(3) W. E. Noland and R. F. Lange, *J. Am. Chem. Soc.*, **81**, 1203 (1959).

(4) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(5) W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956).