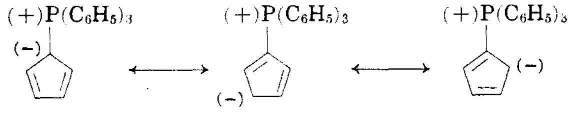
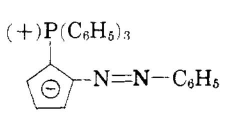
Communications TO THE EDITOR

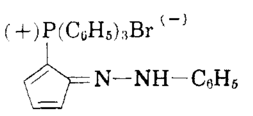
A New Type of Azo Compound by Coupling at the Cyclopentadienide Ring

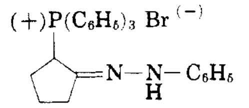
Sir:

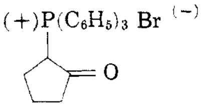
We wish to report the preparation of a new type of azo compound, triphenylphosphonium-(2-phenylazo)cyclopentadienylide [II, deep orange, m.p. 239–240°, from benzene; $\lambda_{\max.}^{\mathrm{CH_3CN}}$ 220 mμ (ϵ 49,700), 250 mμ (ϵ 17,000) and 452 mμ (ϵ 23,500); band at 7.00 μ but no bands at 3.0 or 4.0–6.6 μ; *Anal.* Calc'd for $C_{29}H_{23}N_2P$: C, 80.9; H, 5.4; N, 6.5; P, 7.2; M.W., 430. Found: C, 80.7; H, 5.8; N, 6.8; P, 7.5; M.W., 413]. II resulted, in high yield, from a coupling reaction between the phosphinemethylene[1] (I) and benzenediazonium chloride in an aqueous-methylene chloride system containing sodium acetate. II formed an orange-red *hydrobromide* best formulated as a derivative of cyclopentadienonephenylhydrazone, III [m.p. 232–233°; $\lambda_{\max.}^{\mathrm{EtOH}}$ 219 mμ (ϵ 50,800) 227 mμ (ϵ 46,200), 259 mμ (ϵ 17,100), 266 mμ (ϵ 15,700), 273 mμ (ϵ 10,100), and 446 mμ (ϵ 26,700); bands at 3.0 and 6.48 μ (strong); *Anal.* Calc'd for $C_{29}H_{24}BrN_2P$: N, 5.5. Found: N, 5.1].


Ia Ib Ic


II, etc.


III


IV


V

Catalytic hydrogenation of III in aqueous methanol afforded (2-phenylhydrazonocyclopentyl)triphenylphosphonium bromide [IV, colorless, m.p. 204–205°; $\lambda_{\max.}^{\mathrm{EtOH}}$ 217 mμ (ϵ 45,400), 225 mμ (ϵ 40,600), 269 mμ (ϵ 20,200), and 277 mμ (ϵ 20,600); bands at 2.92–3.02, 6.25, and 7.00 μ; *Anal.* Calc'd for $C_{29}H_{28}BrN_2P$: C, 67.6; H, 5.5; N, 5.4; Br, 15.5. Found: C, 67.4; H, 5.8; N, 5.8; Br, 16.0.] An authentic sample of IV was independently prepared from phenylhydrazine and (2-oxocyclopentyl)triphenylphosphonium bromide [V, colorless, m.p. 270–272°; $\lambda_{\max.}^{\mathrm{EtOH}}$ 217 mμ (ϵ 38,500), 225 mμ (ϵ 37,500), 257 mμ (ϵ 10,100), 266 mμ (ϵ 9,200), and 275 mμ (ϵ 6,700); bands at 5.80 and 7.00 μ; *Anal.*, Calc'd for $C_{23}H_{22}BrOP$: C, 65.0; H, 5.2. Found: C, 65.3; H, 5.5]. V was prepared from triphenylphosphine and 2-bromocyclopentanone.

This manifestation of aromaticity in the cyclopentadienide ring opens a route to a family of phosphorus-containing azo compounds of remarkably long wave length absorption (azobenzene: $\lambda_{\max.}^{\mathrm{CH_3CN}}$ 317 mμ (ϵ 18,100). The substitution on I occurs at a position which preserves the cyclopentadienide system and which gives rise to the longest of the possible conjugated systems terminating at a phosphorus atom. The dipole moment of II was found[2] to be 6.52 D, as compared with 6.99 D for I.

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[1] F. Ramirez and S. Levy, *J. Org. Chem.*, 21, 488 (1956).

[2] The dipole moments were measured by Prof. M. T. Rogers of Michigan State University and will be the subject of a separate communication.

Steroids. LXXXIII.[1] Synthesis of 2-Methyl and 2,2-Dimethyl Hormone Analogs

Sir:

The discovery that profound changes in biological activity may be effected by removal of the steroid *C*-10 angular methyl group[2] or by shift of the group from C-10 to C-1[3] prompted us to investigate steroid analogs with additional alkyl substituents in other parts of the molecule. This communication is concerned with the synthesis of a number of 2-methyl and 2,2-dimethyl substituted testosterone and dihydrotestosterone derivatives,[4] compounds of great interest due to the discovery that certain members of this series have been found to be mass-

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[1] Paper LXXXII. H. J. Ringold, E. Batres, O. Mancera, and G. Rosenkranz, *J. Org. Chem.*, 21, December 1956.

[2] *Cf.* (a) C. Djerassi, L. Miramontes, and G. Rosenkranz, *J. Am. Chem. Soc.*, **75**, 4440 (1953); (b) C. Djerassi, L. Miramontes, G. Rosenkranz, and F. Sondheimer, *J. Am. Chem. Soc.*, **76**, 4092 (1954); (c) C. Huggins, E. V. Jensen and A. S. Cleveland, *J. Exp. Med.*, **100**, 225 (1954); (d) A. Sandoval, G. H. Thomas, C. Djerassi, G. Rosenkranz and F. Sondheimer, *J. Am. Chem. Soc.*, **77**, 148 (1955).

[3] (a) H. J. Ringold, G. Rosenkranz, and F. Sondheimer, *J. Am. Chem. Soc.*, **78**, 2477 (1956); (b) C. Djerassi, A. E. Lippman, and J. Grossman, *J. Am. Chem. Soc.*, **78**, 2479 (1956).

[4] Presented in part at the 129th meeting of the American Chemical Society, Dallas, April 1956.