

this base has been shown to be identical to the bufotenine picrate obtained from *piptadenia peregrina*.³

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RECEIVED JUNE 14, 1954

CYCLOPENTADIENYL COMPOUNDS OF Sc, Y, La, Ce AND SOME LANTHANIDE ELEMENTS

Sir:

The cyclopentadienyl ring is unusual in the number of metals with which it forms organometallic compounds. This property arises from the fact that the ring may be attached to a metal in three ways: (a) by the two electron covalent bond, which may be referred to as the "sandwich bond," to many transitional metals,^{1a,b}; (b) by a covalent bond between a metal and a single carbon atom of the ring. The silicon cyclopentadienyl compounds² may be of this type, (c) by ionic bonds.

The ability of electropositive elements to form ionic cyclopentadienyl compounds is of a more general nature than has been realized previously, although compounds such as cyclopentadienylsodium have long been known.³ The elements scandium, yttrium, lanthanum and the lanthanide elements provide an ideal test case, since no organometallic compounds of these elements have been confirmed.

The anhydrous metal chlorides were stirred with cyclopentadienyl sodium in tetrahydrofuran solution. The solvent was removed and the residues heated at 200–250° in vacuum. Tricyclopentadienyl metal compounds of the formula (C₅H₅)₃M, where M may be Sc, Y, La, Ce, Pr, Nd, Sm and Gd, were obtained as sublimates in yields of the order of 65%. Typical analyses are: *Sc*—Found: C, 73.7; H, 6.0; Sc, 18.3; required: C, 74.0; H, 6.2; Sc, 18.5; *Ce*—Found: C, 51.6; H, 4.1; Ce, 42.8; required: C, 53.7; H, 4.5; Ce, 41.8; *Nd*—C, 51.8; H, 4.6; Nd, 41.2; required: C, 53.1; H, 4.5; Nd, 42.5. *Sm*—Found: C, 51.3; H, 4.2; Sm, 43.3; required, C, 52.2; H, 4.3; Sm, 43.5.

The compounds are all crystalline solids, thermally stable to at least 400°, which sublime above 220° at 10⁻⁴ mm.: *Sc*, straw color, m.p. 240°; *Y*, pale yellow m.p. 295°; *La*, colorless, m.p. 395°; *Ce*, orange, m.p. 435°; *Pr*, pale green, m.p. 420°; *Nd*, pale blue, m.p. 380°; *Sm*, orange, m.p. 365°; *Gd*, pale yellow, m.p. 350°. The compounds decompose with water giving cyclopentadiene and the hydroxide. They are insoluble in hydrocarbon solvents but dissolve readily in tetrahydrofuran and glycol dimethyl ether. They react only slowly with air. Tricyclopentadienylcerium is an exception, in that it is blackened instantaneously by even traces of oxygen; it is also unusual in giving a blue green vapor. The ionic nature of the compounds is indicated by their instantaneous and quantitative reaction with ferrous chloride in tetra-

hydrofuran solution to give ferrocene. The absorption spectra in tetrahydrofuran show complex and very sharp bands reminiscent of those of the lanthanide ions in aqueous solutions; this resemblance is shown also in their magnetic properties.

The remaining lanthanide elements will probably form similar compounds. In the "actinide" series where similar behavior is to be expected we have prepared a brown dicyclopentadienyl chloro compound of uranium.

In the transitional series we have shown that dicyclopentadienyl manganese⁴ is ionic. It has a magnetic moment corresponding to five unpaired electrons when magnetically dilute, and forms conducting solutions in liquid ammonia. The formation of the ionic dicyclopentadienylmanganese, rather than a covalent bis-cyclopentadienylmanganese, must be attributed not to a high electropositive nature of the metal, but to the exceptional stability of the manganous ion, which has the 3d shell half filled. It may be noted, however, that since the negative charge will be distributed over the anion, the most likely packing in the crystal will have the cation between the planes of the rings in a "sandwich" configuration similar to that of ferrocene.^{1a}

(4) G. Wilkinson and F. A. Cotton, *Chemistry and Industry (London)*, **11**, 307 (1954).

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RECEIVED NOVEMBER 10, 1954

STERIODS. LXIII.¹ SYNTHESIS OF Δ⁴-19-NOR- PREGNENE-11β,17α,21-TRIOL-3,20 DIONE (19- NORHYDROCORTISONE) AND RELATED 19-NOR- ADRENAL HORMONES

Sir:

The observation that removal of the C-19 angular methyl group in the case of progesterone,^{2a} desoxycorticosterone^{2b} and 17α-ethynyltestosterone^{2c} resulted in a marked increase in hormonal activity has encouraged us to undertake the more complicated task of preparing similar derivatives of 11-oxygenated hormones. We should now like to announce the successful synthesis by a combined chemical-biochemical procedure of the 19-nor analog (III) of the most important adrenal hormone Δ⁴-pregnene-11β,17α,21-triol-3,20-dione (hydrocortisone or Compound F) and of some related substances.

Alkaline hydrogen peroxide oxidation of 3-hydroxy-17-acetyl-1,3,5,16-estratetraene³ gave the corresponding 16α,17α-epoxide [m.p. 234–236°, [α]_D²⁰ +124° (all rotations in CHCl₃); found: C, 76.72; H, 7.88] which upon conversion to the 3-methyl ether (m.p. 141–144°) followed by hydrogen bromide opening, catalytic debromination to 3-methoxy-17α-hydroxy-17-acetyl-1,3,5-estratriene

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(3) C. Djerassi, G. Rosenkranz, J. Iriarte, J. Berlin and J. Romo, *ibid.*, **73**, 1523 (1951).

(1) (a) J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953); (b) W. Moffitt, *THIS JOURNAL*, **76**, 3386 (1954).

(2) K. C. Frisch, *ibid.*, **75**, 6050 (1953).

(3) J. Thiele, *Ber.*, **34**, 68 (1901).