through a short, thick column of Florisil in chloroform solution. The crystalline product, 9.8 g., had a m.p. 164–168°. Crystallization from methanol gave irregular plates subliming to needles on heating, m.p. 174°, $[\alpha]^{25}_D$ +81.6° (lit.[17] gives m.p. 168–170°, $[\alpha]^{20}_D$ +79°). Infrared spectrum shows strong band at 1705–1720 cm.$^{-1}$ (3- and 20-ketone).

16α,17α-Epoxy-11α-hydroxypregnane-3,20-dione (Va).—To a 5-gallon stainless steel fermentor equipped with an agitator was added 12 liters of a medium consisting of 240 g. of Edamine, 600 g. of dextrose and 60 ml. of corn steep liquor. The fermentor and contents were sterilized in an autoclave at 15 lb. per sq. in. pressure (121°) for one hour. The medium was allowed to cool and inoculated with a spore culture (6 days old) of *Rhizopus nigricans* ATCC 6227b. After 24 hours at 28° with rapid stirring (500 r.p.m.) and 1.2 liters of air per minute being added a vigorous growth of mycelium was noted. At this time 3.0 g. of IV in 120 ml. of a 1:1 mixture of acetone–ethanol was added and the fermentation continued for 48 hours. The mycelium was recovered by filtration and extracted three times with a total of 5 liters of acetone and three times with 5 liters of chloroform. The filtrate was extracted eleven times with a total of 24 liters of chloroform. The extracts were combined and concentrated. The foregoing procedure differs slightly in detail from, but is essentially based on, the techniques described by the Upjohn group.[9,18] The residue from the concentrated solvent extracts was resinous. It was saponified with hot methanolic potassium hydroxide solution. After addition of water and the usual ethereal extraction and work up, the product in benzene solution was passed through a Florisil column. Elution with benzene gave 1.3 g. of unreacted IV. Elution with benzene-containing 20% chloroform gave 1.4 g. of Va. The analytical sample was crystallized from ether as rods, m.p. 170–172°, $[\alpha]^{25}_D$ +57.3° (lit.[14] gives m.p. 158–160°, $[\alpha]^{21}_D$ +68°). Infrared spectrum shows bands at 3640 cm.$^{-1}$ (hydroxyl) and strong, broad band at 1705–1720 cm.$^{-1}$ (3- and 20-ketone).

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.55; H, 8.82.

11α-Acetoxy-16α,17α-oxido-pregnane-3,20-dione (Vb).—Compound Va (0.1 g.) was refluxed 0.5 hour in 1 ml. of acetic anhydride. The solvent was removed *in vacuo*. Crystallization from methanol gave plates, m.p. 222–224°, $[\alpha]^{25}_D$ +24.4° (lit.[14] gives m.p. 215–216°, $[\alpha]^{19}_D$ +25°). Infrared spectrum shows strong band at 1735 cm.$^{-1}$ (11-acetate) and strong, broad band at 1705–1720 cm.$^{-1}$ (3- and 20-ketone).

16α,17α-Oxidopregnane-3,11,20-trione (VI).—A solution of 0.7 g. of Va in 15 ml. of glacial acetic acid was oxidized with 0.3 g. of chromium trioxide in 50% aqueous acetic acid as described under the preparation of IV; yield 0.6 g., m.p. 194–196°. The analytical sample was crystallized from ether as plates, m.p. 199–201°, $[\alpha]^{25}_D$ +115° (lit.[14] gives m.p. 181°, $[\alpha]^{21}_D$ +105°). Infrared spectrum shows a strong, broad band at 1705–1720 cm.$^{-1}$ (3-, 11- and 20-ketone).

17α-Hydroxypregnane-3,11,20-trione (VIII).—A solution of 0.6 g. of compound VI in 18 ml. of acetic acid was cooled to 15° and mixed with 6 ml. of acetic acid containing 8% v./v. hydrobromic acid. The mixture was allowed to stand overnight at 15°. It was then diluted with water and given the usual ethereal extraction and work up. The ether was removed *in vacuo* at room temperature. The crystalline residue which we believe was 16β-bromo-17α-hydroxypregnane-3,11,20-trione (VII) was not further characterized. The crude VII was dissolved at once in 100 ml. of 90% methanol and hydrogenated in the presence of 0.3 g. of palladium on calcium carbonate for five hours at 4 atmospheres pressure. The solution then was filtered and concentrated. A crystalline product, weight 0.6 g., m.p. 180–188°, was obtained. Crystallization from ether gave 0.4 g. of rods, m.p. 198–201°, $[\alpha]^{25}_D$ +41° (lit.[12] gives m.p. 203–204°, $[\alpha]^{25}_D$ +41°). Infrared spectrum (chloroform) shows a strong band at 3500 cm.$^{-1}$ (bonded 17-hydroxyl), and a strong, broad band at 1700–1720 cm.$^{-1}$ (3-, 11- and 20-ketone). The infrared spectrum was identical to authentic VIII.[18]

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[17] O. Mancera, H. J. Ringold, C. Djerassi, G. Rosenkranz and F. Sondheimer, THIS JOURNAL, **75**, 1286 (1953).

[18] D. H. Peterson, *et al.*, *ibid.*, **74**, 5933 (1952), and subsequent papers in THIS JOURNAL.

COMMUNICATIONS TO THE EDITOR

π-TROPENIUM-MOLYBDENUM-TRICARBONYL FLUOROBORATE

Sir:

Even though "sandwich" complexes of transition metals or their carbonyls with 5- or 6-membered aromatic systems, *e.g.*, $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_5H_5)Mn(CO)_3$, $(\pi\text{-}C_6H_6)Cr(\pi\text{-}C_6H_6)$, $(\pi\text{-}C_6H_6)\text{-}Cr(CO)_3$, are well-known[1] and similar complexes with the unknown 4-membered aromatic system, cyclobutadiene, have been postulated on theoretical grounds as reaction intermediates,[2] no report of the preparation of an analogous metal-π-molecular orbital complex with the 7-membered aromatic system, tropenium ion ($C_7H_7^+$), has appeared. In a recent attempt to prepare such a complex, Abel, Bennett and Wilkinson[3] found that cycloheptatriene reacted with molybdenum hexacarbonyl to give only the cycloheptatriene complex, $(\pi\text{-}C_7H_8)Mo(CO)_3$ (I). Application of our previously reported general preparative method for tropenium ions,[4] involving hydride ion abstraction from cycloheptatrienes by trityl carbonium ions, to the cycloheptatriene complex (I) has resulted in the first synthesis of a metal-tropenium ion complex, $(\pi\text{-}C_7H_7^+)Mo(CO)_3$, BF_4^- (II).

π-Cycloheptatriene-molybdenum-tricarbonyl (I), prepared in low yield by the passage of cyclohepta-

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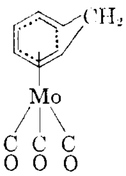
[1] (a) P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955); (b) T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955); (c) E. O. Fischer and W. Hafner, *Z. anorg. Chem.*, **286**, 146 (1956); H. H. Zeiss and W. Herwig, THIS JOURNAL, **78**, 5959 (1956); (d) E. O. Fischer and K. Öfele, *Chem. Ber.*, **90**, 2532 (1957).

[2] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956). *Cf.*, J. C. Sauer and T. L. Cairns, THIS JOURNAL, **79**, 2660 (1957), and M. Tsutsui and H. H. Zeiss, Abstracts, 134th Meeting, American Chemical Society, Chicago, Ill., Sept. 7–12, 1958, p. 59-P, for experimental evidence bearing on this postulate.

[3] E. W. Abel, M. A. Bennett and G. Wilkinson, *Proc. Chem. Soc.*, 152 (1958).

[4] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, THIS JOURNAL, **79**, 4557 (1957); K. M. Harmon, Ph.D. Thesis, University of Washington, 1958.

triene and molybdenum hexacarbonyl vapors through a hot tube at 150–250°, was identical in all respects with the previously reported material made by an unspecified method[3] (orange-red plates by sublimation or from pentane, m.p. 100.5–101.5°; ultraviolet (λ_{max}, ϵ_{max}, CH_2Cl_2): 252 (sh., 12,300), 324 (7450), 383 (4200), 482 mμ (600); infrared (KBr): 3.02 w, 5.15 s, 5.30 s, 5.36 (sh.) s, 6.90 w, 7.01 w, 10–10.75 w, 11.93 w, 12.77 w. Equivalent quantities of I and trityl fluoroborate in methylene chloride react immediately to give a crystalline precipitate of π-tropenium-molybdenum-tricarbonyl fluoroborate (II) and evaporation of the filtrate, then chromatography on alumina, furnishes tritane, both in 98–100% yields; recrystallization of the precipitate from methylene chloride yields II as light orange fine needles, m.p. >270° (gradual darkening from 140°), insoluble in water or pentane, slightly soluble in methylene chloride, very soluble in acetone, acetonitrile or 96% sulfuric acid, stable in air but slow decomposition with liberation of tropenium fluoroborate occurs in these organic solvents; *anal.* Calcd. for $C_{10}H_7O_3BF_4Mo$: C, 33.55; H, 1.97. Found: C, 33.20; H, 2.09; u. v. (λ_{max}, ϵ_{max}, CH_2Cl_2 or 96% H_2SO_4): 238 (sh., 14,700), 299 (29,000), 380 mμ (1,300); i.r. (KBr): 3.02 w, 4.93 (sh.) w, 5.03 s, 5.13 s, 7.00 w, 8.5–10.0 s (BF_4^-), 9.70 m, 12.52 m.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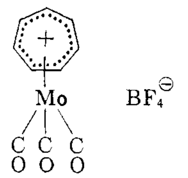
II

Ultraviolet and infrared spectra, by differing markedly from those for tropenium fluoroborate,[4] clearly establish II as a molecular complex. The presence of two intense carbonyl stretching bands in its infrared spectrum, as found in analogous aromatic complexes, (π-C_5H_5)Mn(CO)$_3$ and (π-C_6H_6)Cr(CO)$_3$, of similar symmetry but in contrast to the three carbonyl bands shown by the cycloheptatriene complex (I) with lower symmetry, and of a single proton resonance band in its high resolution nuclear magnetic resonance spectrum in D_2SO_4 are only consonant with a structural assignment of a fully aromatic structure to II in which the molybdenum atom is complexed with the cyclic π-molecular orbital encompassing all seven carbon atoms of the tropenium ion ligand.

Additional studies on this and other metal-tropenium ion complexes are in progress.

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THE B_8Cl_8 STRUCTURE: A NEW BORON POLYHEDRON IN SMALL MOLECULES

Sir:

Samples of a boron chloride hitherto known[1] only as $(BCl_{0.9})_x$ have been supplied to us through the courtesy of H. I. Schlesinger, T. Wartik and G. Urry. In a preliminary X-ray diffraction study, completed about three years ago, M. Atoji and W. N. Lipscomb obtained 1175 diffraction maxima, and showed that there were four molecules in an orthorhombic unit cell having symmetry $P2_12_12_1$ and dimensions a = 13.64, b = 7.85 and c = 12.91 Å. A density of 1.75 g. cm.$^{-3}$, measured with difficulty, agrees best with the formula B_8Cl_8, but this formula was then regarded as highly uncertain.

We have now solved the complete molecular structure with the use of point-by-point Patterson superposition techniques on the UNIVAC SCIENTIFIC 1103 Computer. Present values of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.20$ and $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4 = 0.18$ indicate that refinement is nearly complete. The resulting molecular structure is shown in Fig. 1. A polyhedron of boron atoms is surrounded by Cl atoms, each of which is joined to B by a single bond, as is true in the B_4Cl_4 structure.[2] Although no molecular symmetry is required by the space group, the isolated molecule apparently has D_{2d} symmetry.

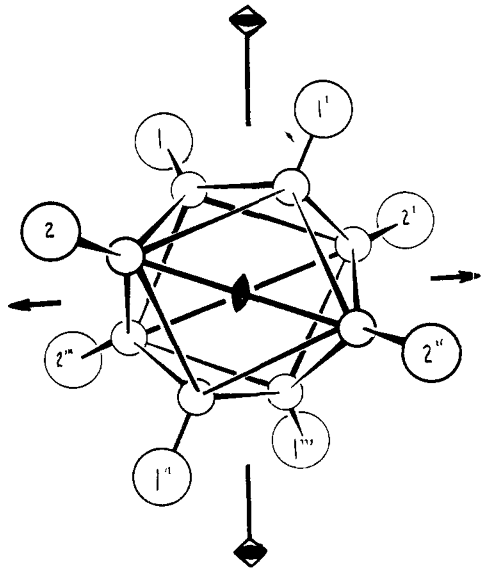

Fig. 1.—The B_8Cl_8 structure: small circles represent B and large circles represent Cl. Average Cl . . . Cl distances (±0.04 Å.) are 4.05 Å. for the 8 symmetry-equivalent distances of type 1–2, 3.51 Å. for the other 4 of type 1–2, 4.45 Å. for the 4 of type 2–2, and 3.94 Å. for the two of type 1–1. Corresponding average B–B distances (±0.05 Å.) are, respectively, 1.79, 1.85, 2.07 and 1.78 Å. The average B–Cl distance is 1.70 ± 0.04 Å.

As usual in such a compact structure, the use of three-center bonds is not a very satisfactory descrip-

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[1] G. Urry, T. Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **76**, 5293 (1954).

[2] M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 172 (1953); *Acta Crystallographica*, **6**, 547 (1953).