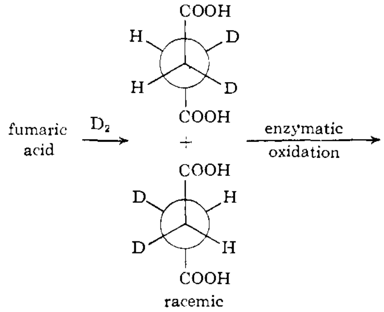
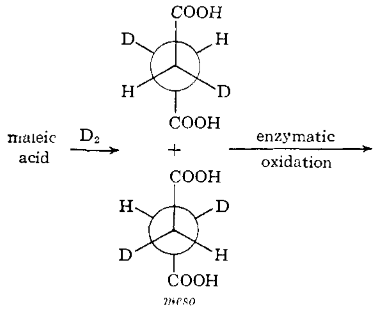
specific.[2,4] The samples of fumaric acid were isolated by ether extraction after acidification of the solution, purified by column chromatography (Dowex-1-formate), reduced catalytically to succinic acid (H_2 + Pd), and esterified with an excess of diazomethane. The dimethyl succinate samples were purified by distillation under reduced pressure and their content of dideuterated molecules analyzed with the use of an analytical mass spectrometer.

The basis of the experimental approach and the results are shown in Table I. Two *meso*-forms are drawn since, although they are identical in solution, they might be expected to be different when bound to the enzyme. The expected presence and absence of di-deuterated molecules in fumarate in excess of normal abundance are shown for the three possible mechanisms of elimination of hydrogen, namely, *cis*, random and *trans*. The value for dideuteriofumarate formed was derived from the per cent. of di-deuterated molecules in the dimethyl succinate samples as determined with the mass spectrometer. The results demonstrated conclusively that the elimination of hydrogen must be *trans*.

TABLE I

	Dideuteriofumarate expected			% of dideuterated molecules in	
	cis	Random	*trans*	Succinate used	Fumarate formed
	+	+	−	2.4	0.1
	−	+	+	2.9	1.4

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(4) H. F. Fisher, C. Frieden, J. S. M. McKee and R. A. Alberty, THIS JOURNAL, **77**, 4436 (1955).

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RECEIVED JUNE 8, 1960

THE PREPARATION OF A VOLATILE POLONIUM FLUORIDE[1]

Sir:

Polonium might be expected to form a volatile fluoride, by analogy with the sixth column elements, S, Se, Mo, Te, W and U, which form hexafluorides. However, neither heating ^{210}Po in fluorine nor treatment of it with liquid BrF_3 have succeeded in preparing a volatile compound.[2,3]

In studies with the unstable, radioactive hexafluoride of plutonium, PuF_6, it was discovered that this material could be stored successfully in the vapor phase without decomposition if a small excess of F_2 was added to the system; in sharp contrast, PuF_6 is found to decompose from the α-radiation at the rate of 1.5% per day when stored as solid.[4] It therefore seemed worth while to investigate the formation of PoF_6 with subsequent storage as vapor in the presence of excess fluorine. For these experiments we had available 0.563 curie (0.96 mg.) of ^{208}Po,[5] half-life 2.93 yr., as compared with the ^{210}Po, half-life 138 days, used by the previous workers.

Of the material used 75% was deposited on two strips of Pt gauze each approximately 3 inches long and 25% on a dozen small, approximately 1/4 inch square, Pt foils. These were loaded into the bottom of a 15.7 cm. long by 1.05 cm. radius i.d. nickel tube with the gauzes remaining upright. The nickel tube then was connected to a filling valve and a pressure gauge. Prior to starting the reaction the fast neutron yield from the F (α,n) reaction was studied as a function of F_2 pressure and the position of the Po relative to a 1.75 inch diameter scintillation counter button.[6] The total neutron yield was approximately proportional to the fluorine pressure at 335–800 mm. pressure, which corresponded to the α-range for the most part being greater than the reactor dimension. At 1600–2405 mm. pressure the total neutron yield appeared to approach a maximum value, which suggested that the α-particles were largely being stopped within the reactor.[7] As expected the maximum neutron intensity occurred when the central region of the platinum gauzes was approximately opposite to the center of the Hornyak button.

Figure 1 summarizes similar neutron yield and distribution measurements made with the intention of demonstrating the formation of a volatile Po compound. Curve A corresponds to the Po on the Pt. Curve B was measured after heating the

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(1) Based on the work performed under the auspices of the U. S. Atomic Energy Commission.

(2) F. Leitz, Jr., and L. Coulter reported by H. V. Moyer, editor, "Polonium," TID-5221 (1956), Office of Technical Services Department of Commerce, Washington 25, D. C.

(3) Emeleus, Maddock, Miles and Sharpe, *J. Chem. Soc.*, 1991 (1948).

(4) B. Weinstock and J. G. Malm, *J. Inorg. Nucl. Chem.*, **2**, 380 (1956).

(5) We are indebted to Dr. D. T. Vier of the Los Alamos Scientific Laboratory for the use of this material.

(6) We are indebted to Jerome L. Lerner for the use of his Hornyak button scintillation fast neutron counter. In order to use this equipment for our experiment an unfavorable geometric arrangement was used in which the nickel tube was about 1 inch from the edge of the button rather than directly in front of it.

(7) James H. Roberts, "Neutron Yields of Several Light Elements Bombarded with Polonium Alpha Particles," MDDC-731 declassified Jan. 7, 1947.

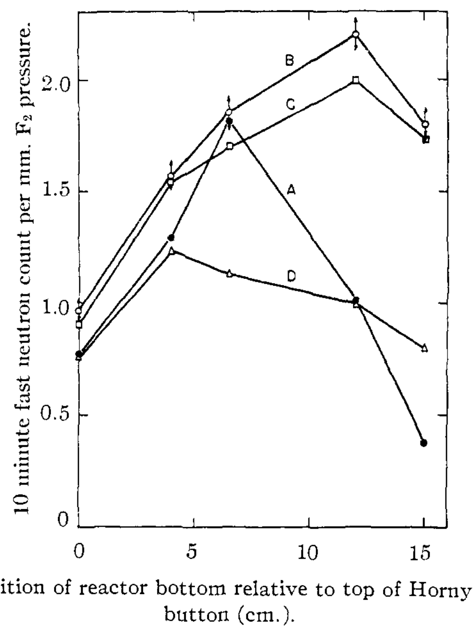

Fig. 1.—The change of fast neutron distributions resulting from the formation and decomposition of a volatile Po fluoride. The total fast neutron count in ten minutes divided by the F_2 pressure (330–350 mm.) is plotted against the position (cm.) of the reactor bottom below the top of the Hornyak button.

Ni tube for about 5 hours at temperatures up to 393°. The maximum neutron intensity, now observed at 12.5 cm. on the graph, indicates movement of the polonium away from the bottom of the tube. Our resolution did not permit differentiation between this observed maximum and the expected maximum at 10.1 cm. that would correspond to uniform distribution of the polonium in the tube. A further point of importance is that the total neutron yield in curve B is substantially higher than in curve A. This is a necessary result if the Po is present in the vapor rather than as a solid. In the latter case, at least half of the α-particles do not produce neutrons due to self-absorption or absorption by the walls. With the Po uniformly distributed in the vapor a much larger fraction of the α-particles produces neutrons. An estimate of the increased neutron yield was made by numerical integration of curves A and B. The value for curve B was increased by 23% to allow for the presence of Po vapor in the gauge and connectors. The ratio of this corrected area under curve B to the area under curve A was 1.9. Curve C was measured after first removing 7.7% of the polonium fluoride–fluorine vapor mixture from the reactor at room temperature and subsequently replenishing the fluorine pressure with tank F_2 for the neutron counting. The integrated neutron yield for curve C was 6.4% less than curve B, in reasonable agreement with the removal of 7.7% of the Po as vapor.

After the measurements of curve C the tip of the reactor was kept cold overnight with a solid CO_2 bath, after which curve D was measured. The peak neutron yield was now near the bottom of the reactor but the total neutron yield was much less than curve A. Investigation of the Po distribution in the gauge and connectors showed it to be most concentrated at a silver solder connection and also substantially present in the Bourdon tube. Although some of the vapor appears to have decomposed upon condensation a more substantial fraction has deposited due to its reactivity. These latter observations are perhaps an explanation of the previous unsuccessful attempts to form a volatile Po compound.

In conclusion, the results presented here indicate the formation of a volatile Po compound that subsequently decomposes due to chemical or radioactive decomposition. Further studies are in progress.

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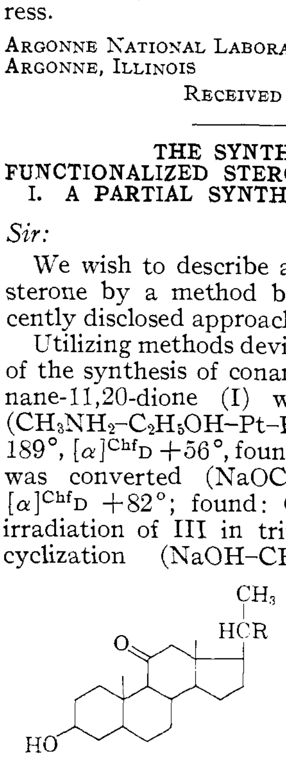
RECEIVED MAY 7, 1960

THE SYNTHESIS OF C-18 FUNCTIONALIZED STEROID HORMONE ANALOGS. I. A PARTIAL SYNTHESIS OF ALDOSTERONE

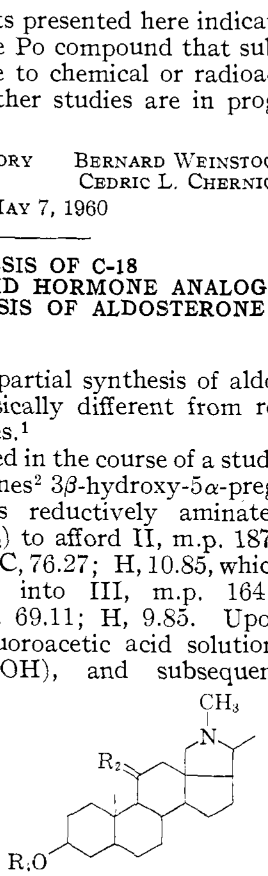
Sir:

We wish to describe a partial synthesis of aldosterone by a method basically different from recently disclosed approaches.[1]

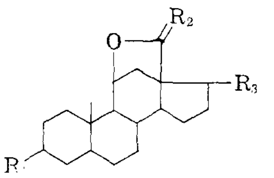
Utilizing methods devised in the course of a study of the synthesis of conanines[2] 3β-hydroxy-5α-pregnane-11,20-dione (I) was reductively aminated (CH_3NH_2–C_2H_5OH–Pt–H_2) to afford II, m.p. 187–189°, $[\alpha]^{Chf}_D$ +56°, found C, 76.27; H, 10.85, which was converted (NaOCl) into III, m.p. 164°, $[\alpha]^{Chf}_D$ +82°; found: C, 69.11; H, 9.85. Upon irradiation of III in trifluoroacetic acid solution, cyclization ($NaOH$–CH_3OH), and subsequent

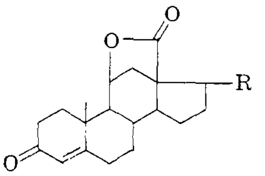


II, R = $NHCH_3$
III, R = $NClCH_3$



IV, R_1 = Ac, R_2 = O
V, R_1 = H, R_2 = OH





VII, R_1 = OH, R_2 = H_2, R_3 = $CH(N(CH_3)_2)CH_3$
VIII, R_1 = OH, R_2 = H_2, R_3 = $CH{=}CH_2$
IX, R_1 = O, R_2 = H_2, R_3 = $CH{=}CH_2$
X, R_1 = O, R_2 = H_2, R_3 = $CHOH$–CH_2OH
XI, R_1 = O, R_2 = H_2, R_3 = $CHOAcCH_2OAc$
XII, R_1 = O, R_2 = O, R_3 = $CHOAcCH_2OAc$
XIII, R = $CHOAcCH_2OAc$
XIV, R = $CHOHCH_2OH$
XV, R = $CHOH$–$CH_2OC(C_6H_5)_3$
XVI, R = $COCH_2OC(C_6H_5)_3$
XVII, R = $COCH_2OH$

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[1] K. Heusler, J. Kalvoda, Ch. Meystre, P. Wieland, G. Anner, A. Wettstein, G. Cainelli, D. Arigoni and O. Jeger, *Experientia*, **16**, 21 (1960); L. Velluz, G. Muller, R. Bardoneschi and A. Poittevin, *Compt. rend.*, **250**, 725 (1960); D. H. R. Barton and J. M. Beaton, THIS JOURNAL, **82**, 2641 (1960).

[2] J. F. Kerwin, M. E. Wolff, F. F. Owings, B. B. Lewis, B. Blank, A. Magnani and V. Georgian, in preparation.