THE PREPARATION OF HAFNIUM-FREE ZIRCONIUM

Sir:

We have recently performed a series of experiments which indicate that silica gel strongly and preferentially adsorbs hafnium compounds from a zirconium–hafnium compound mixture in certain organic solvents, and that this fact provides a new, simple, and effective means of preparing hafnium-free zirconium.

A solution of 455 g. of zirconium tetrachloride dissolved in 2275 ml. of anhydrous methanol was allowed to stand for three hours and filtered. The filtered solution contained 106 mg. total oxide per ml. A column 30″ in length × 27 mm. in diameter was packed with 290 g. of 28 to 120 mesh silica gel which had been purified by elution with 1:1 nitric acid and activated four hours at 300°. The column was prepared by sludging silica gel and methanol, and hence initially contained approximately 200 ml. of methanol; 1800 ml. of the above solution was then fed into the column, the flow being from bottom to top at a rate of 200 ml./hr. The effluent was collected in approximately 200-ml. batches and the total oxides in 5-ml. aliquots of each batch precipitated and analyzed spectrographically. The results were as shown (weights refer to ignited oxide, analyses to per cent. hafnium in sample).

TABLE I

COMPOSITION OF SUCCESSIVE BATCHES

No.	1	2	3	4	5	6	7	8	9
Wt. g.	7	18.2	21.5	22.5	22.9	25.0	24.7	18.5	22.1
% Hf	[a]	0.00	0.03	0.15	0.38	0.66	0.80	0.93	1.10

[a] Analysis uncertain due to large Fe and Ti content. The $ZrCl_4$ used contained approximately 0.13% $FeCl_3$ and 0.53% $TiCl_4$.

The column was then stripped with one liter of methanol made 1.2 *M* in anhydrous hydrochloric acid, the eluant being collected in four fractions. Analyses over 15% Hf are rough spectrographic estimates since the method has not yet been extended to this region.

TABLE II

COMPOSITION OF FRACTIONS OF ELUANT

No.	1	2	3	4
Wt. g.	9.0	2.5	0.68	0.48
% Hf	1.8	15	60	40

Similar, but not quite so striking results have been obtained using acetone instead of methanol as solvent; the degradation of acetone by zirconium tetrachloride tends to cause tars and clogging in the column which causes some inconvenience.

To summarize: Hafnium in zirconium may be reduced to less than 0.1% by passing a 1:5 solution of the chlorides in methanol through a silica gel column; 290 g. silica gel will furnish 60 g. purified oxide; the column can be stripped with 1 *M* anhydrous hydrochloric acid in methanol and re-used. By feeding in an oxide equivalent of approximately 65 g., in this case, the purified oxide yield would be about 90%.

Work on the mechanism of this and similar processes is being continued and will be reported at a later date.

We are indebted to V. A. Fassel and C. H. Anderson for spectrographic analyses.

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THE METAL ION CATALYZED DECARBOXYLATION OF DIMETHYLOXALOACETIC ACID

Sir:

Recent investigations[1] of the metal ion catalysis of the enzymatic and non-enzymatic decarboxylation of oxaloacetic acid have prompted us to make a detailed study of the mechanism of the decarboxylation of α,α-dimethyloxaloacetic acid and of its monoethyl ester. The synthesis of these compounds is outlined below.

$$C_2H_5O_2CCO_2C_2H_5 + (CH_3)_2CHCO_2C(CH_3)_3 \xrightarrow{(C_6H_5)_3CNa}$$

$$\underset{\text{(A)}}{C_2H_5O_2CCOC(CH_3)_2CO_2C(CH_3)_3} \xrightarrow[\text{HOAc}]{\text{HBr}}$$

$$\underset{\text{(B)}}{C_2H_5O_2CCOC(CH_3)_2CO_2H} \xrightarrow[H_2O]{HCl} \underset{\text{(C)}}{HO_2CCOC(CH_3)_2CO_2H}$$

The condensation was carried out by Hauser's method,[2] the cleavage of the *t*-butyl ester, A, by a method based on the work of Tronow,[3] and the hydrolysis of the ethyl ester, B, by a method based on the work of Michael.[4]

Anal. Calcd. for diester, A, (b. p. 107–111° (7 mm.)): C, 59.0; H, 8.20. Found: C, 58.7; H, 8.21. Calcd. for monoester, B, (m. p. 38–39°): C, 51.0; H, 6.43. Found: C, 50.8; H, 6.44. Calcd. for diacid, C, (m. p. 105.5–106.5°): C, 45.0; H, 5.03. Found: C, 45.1; H, 5.18.

Both the monoester and the diacid decarboxylated smoothly at 25° in aqueous solutions of *p*H between 2 and 7 to form the expected products. (The 2,4-dinitrophenylhydrazone of α-keto-β-methylbutyric acid melted[5] at 194–194.5°; the

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(1) L. Krampitz and C. Werkman, *Biochem. J.*, **35**, 595 (1941); H. Krebs, *ibid.*, **36**, 303 (1942); A. Kornberg, S. Ochoa and A. Mehler, *J. Biol. Chem.*, **174**, 159 (1948); J. Speck, *ibid.*, **178**, 315 (1949); P. Nossal, *Australian J. Exptl. Biol. Med. Sci.*, **27**, 143 (1949).

(2) B. Hudson, Jr., and C. Hauser, THIS JOURNAL, **63**, 3156 (1941).

(3) B. Tronow and N. Ssibgatullin, *Ber.*, **62B**, 2850 (1929).

(4) A. Michael and J. Bucher, *ibid.*, **29**, 1792 (1896).

(5) G. Ramage and J. Simonsen, *J. Chem. Soc.*, 532 (1935).

2,4-dinitrophenylhydrazone of the ethyl ester (from B) melted at 171.5–172°. *Anal.* Calcd. for $C_{13}H_{16}O_6N_4$: C, 48.2; H, 4.97; N, 17.3. Found: C, 48.0; H, 4.80; N, 17.0). Some first order rates of decarboxylation, determined manometrically near *p*H 5 in the presence and absence of metal ions, are shown in the table below.

Metal ion	Monoester B Concn. of metal ion, m./l.	 k, min.$^{-1}$	Diacid C Concn. of metal ion, m./l.	 k, min.$^{-1}$
None		0.075		0.0032
Cu^{++}			0.001	.14
	0.01	.069	.01	*ca.* 1.6
Al^{+++}	.01	.070	.001	0.13
Ni^{++}	.01	.075	.01	.022
Mn^{++}	.01	.066	.01	.0046

Thus metal salts strongly catalyze the decarboxylation of the diacid, C, but do not affect the rate of decarboxylation of the monoester, B. Since no enol form of α,α-dimethyloxaloacetic acid is possible, it is clear that the *keto* acid (like dimethylacetoacetic acid[6]) undergoes decarboxylation. Further, these experiments show that the metal ion catalysis of the decarboxylation of dimethyloxaloacetic acid requires the formation of a complex between the metal ion and the carboxyl group gamma to the one lost; presumably the metal ion is also coördinated with the carbonyl oxygen atom. By analogy, these conclusions also apply to the decarboxylation of oxaloacetic acid itself.

The investigation of these reactions is continuing.

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[6] K. Pedersen, THIS JOURNAL, **51**, 2098 (1929); **58**, 240 (1936).

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DEGRADATION PRODUCTS OF PSEUDOHECOGENIN

Sir:

It has been shown that "*allo*-pregnan-3,12,20-trione" from pseudohecogenin does not agree in properties with *allo*-pregnan-3,12,20-trione prepared from 12(α)-acetoxyprogesterone.[1] We have now reinvestigated "16-*allo*-pregnen-3,12,20-trione" from pseudohecogenin. From its method of synthesis and analysis, it was assumed to be an α,β-unsaturated triketone containing a molecule of water of crystallization.[2] However, we find that this material does not show an absorption maximum in the ultraviolet typical for α,β-unsaturated ketones, that it is unchanged by conditions of hydrogenation with palladium catalyst and that *it is actually identical with the compound designated as "allo-pregnan-3,12,20-trione,"* also assumed to contain a molecule of water of crystallization. It is not changed by hot acetic anhydride and pyridine, which suggests that the "molecule of water" might be a tertiary hydroxyl group at C-17. Mild chromic acid oxidation gives impure starting material in agreement with the results of Reichstein and Gatzi[3] for this ketol system. It is noteworthy that mild oxidation of the isomeric D-homo derivative is reported to give an acidic product.[4]

Hydroxyl groups in steroids have been associated with infrared absorption maxima at 3570 to 3620 cm.$^{-1}$ along with a carbonyl harmonic band at 3300 to 3475 cm.$^{-1}$ if a ketone group is also present.[5] It was hoped that such data (Fig. 1) would support the assignment of a hydroxyl group to this substance; however, the results are inconclusive. A scarcity of material has curtailed further work.

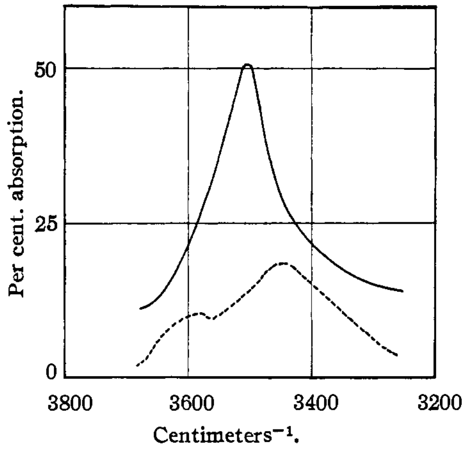

Fig. 1.—Infrared absorption spectra in carbon disulfide solution: ...., 17(α)-hydroxyprogesterone; ——, degradation product from pseudohecogenin.

Although it is not possible to state definitely the structure for this product, it becomes clear that the non-identity of it with *allo*-pregnan-3,12,20-trione is not necessarily due to an incorrect assignment of the C-12 oxygen in hecogenin and botogenin.[6]

We thank Parke, Davis and Company for their help.

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RECEIVED NOVEMBER 1, 1949

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[1] Wagner, Moore and Forker, THIS JOURNAL, **71**, 3856 (1949).

[2] Marker, Wagner and co-workers, *ibid.*, **69**, 2167 (1947).

[3] Reichstein and Gatzi, *Helv. Chim. Acta*, **21**, 1497 (1938).

[4] Ruzicka, Gatzi and Reichstein, *ibid.*, **22**, 637 (1939).

[5] Jones, *et al.*, THIS JOURNAL, **70**, 2024 (1948).

[6] At the time that this communication was in preparation, Marker, *ibid.*, **71**, 3856 (1949), presented further evidence that the degradation of pseudobotogenin diacetate can lead to a 17-hydroxy steroid.