maintained while the methyllithium solution was added dropwise. There was no discernible increase in the bubble rate during the addition of the methyllithium solution and a white solid precipitated. No yellow-tan colored precipitate or yellow solution indicative of triphenyltin-lithium formed. The system was swept with nitrogen for 0.5 hour after the addition was completed. The absorption tubes were then reweighed and, within limits of allowable error, there was no change in weight for either tube. A Color Test I,[11] made one hour after the addition was completed, was negative.

The ethereal solution was filtered from the white solid, extracted with 50 ml. of water, and dried over sodium sulfate. This white solid was analyzed as lithium hydride by the method outlined previously.[3] The ether layer yielded an oil which was digested with 50 ml. of methanol, and the mixture was allowed to cool slowly. On cooling, 0.4 g. of solid melting over the range 170–225° was recovered. This solid was recrystallized from 25 ml. of petroleum ether (b.p. 77–120°) to yield 0.35 g. (25.0% calculated on the number of phenyl groups available) of tetraphenyltin melting at 222–225°. A mixed melting point with an authentic specimen showed no depression. The methanol was removed by distillation leaving an oil. Thorough cooling in a Dry Ice-bath yielded an oily solid. This mass was extracted twice with 5-ml. portions of cold ethanol to yield 0.5 g. of crude triphenylmethyltin melting over the range 48–54°. This crude solid was recrystallized from 5 ml. of ethanol to yield 0.3 g. (18.1%) of triphenylmethyltin melting at 59–61°.[12] A mixed melting point determination with an authentic specimen prepared in essential accordance with the procedure of Bullard and Robinson[12] showed no depression.

Run 2.—This run was carried out precisely as was the first. Once again no gas evolution was noted, the characteristic yellow-tan color of triphenyltin-lithium was not observed and the weight of the gas absorption tubes remained constant. In this experiment 0.35 g. (25%) of tetraphenyltin melting at 224–225° and 0.25 g. (15.0%) of triphenylmethyltin melting at 60–61° was obtained. Both compounds were identified by the method of mixed melting points.

A Method for the Quantitative Analysis for Tin in Organotin Compounds.—Tin in organotin compounds usually is determined as stannic oxide. Pfeiffer[13] introduced a method which involves decomposition of the sample by the use of fuming nitric acid in a sealed tube, followed by evaporation of the product with concd. sulfuric acid and ignition to stannic oxide. A more convenient method[14] uses fuming nitric plus fuming sulfuric acid in a covered porcelain crucible to decompose the sample, followed by ignition to stannic oxide. Concentrated sulfuric acid plus 30% hydrogen peroxide has been used in place of fuming nitric plus fuming sulfuric acid.[15] Volatile organotin compounds usually give low results by the fuming acid procedure. A method has been introduced whereby the volatile organotin compound is first decomposed with bromine in carbon tetrachloride, followed by treatment with concd. nitric plus sulfuric acid and finally ignition to stannic oxide.[16]

It has been found that organotin compounds can be completely decomposed simply by treatment with concd. sulfuric acid followed by ignition to stannic oxide. This method can be applied to volatile as well as non-volatile compounds. Vycor crucibles have been used in place of porcelain crucibles because of the greater visibility afforded by the former.

In a 30-ml. Vycor crucible (Corning Glass Works, Corning, N. Y., code word GIKYN) was weighed approximately 0.2 g. of the organotin compound to be analyzed. To this was added, with caution, 20 drops (1.0 ml.) of concd. sulfuric acid (sp. gr. 1.84), and the crucible was placed on a Rogers ring burner. The sample usually turned jet black almost immediately. The excess acid was then cautiously removed by heating the uncovered crucible at its top. The ring was then raised at intervals, thereby gradually lowering the position of the flame on the sides of the crucible until the flame was directed to the bottom, and the carbonaceous material formed by the action of the acid was completely ignited leaving a white solid. The uncovered crucible was then ignited on a Bunsen burner for 0.5 hour to insure complete conversion to stannic oxide, cooled and weighed in the usual manner. A complete analysis requires about two hours to run. Some representative results follow.

(1) Triphenyl-*o*-methoxyphenyltin, a solid; calcd. for $C_{25}H_{22}OSn$: Sn, 25.97. Found: Sn, 26.10, 26.21.

(2) Tri-*n*-butylphenyltin, a liquid; calcd. for $C_{16}H_{32}Sn$: Sn, 32.33. Found: Sn, 32.37, 32.47.[17]

(3) Triphenyl-*m*-dimethylaminophenyltin, a solid; calcd. for $C_{26}H_{25}NSn$: Sn, 25.24. Found: Sn, 25.28, 25.41.

(4) Triphenyl-3-dimethylamino-6-(4′-bromophenylazo)-phenyltin, a solid; calcd. for $C_{32}H_{28}N_3BrSn$: Sn, 18.01. Found: Sn, 18.10, 18.17.

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[11] H. Gilman and F. Schulze, This Journal, **47**, 2002 (1925).

[12] R. H. Bullard and W. R. Robinson, *ibid.*, **49**, 1369 (1927).

[13] P. Pfeiffer, *Z. anorg. allgem. Chem.*, **68**, 102 (1910).

[14] E. Krause and R. Becker, *Ber.*, **53**, 173 (1920).

[15] N. Strafford, *Mikrochim. Acta*, **2**, 306 (1937).

[16] H. Gilman and W. B. King, This Journal, **51**, 1213 (1929).

[17] For extremely volatile organotin compounds it may be advisable to wet the sample with acetic acid before adding the sulfuric acid; H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, *ibid.*, **72**, 5767 (1950).

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Some Glyoxylic Steroids

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The acid-catalyzed rearrangement of cortisone acetate has been shown to lead to a glyoxal side chain.[1] Some related results on glyoxylic steroids stem from our attempt to hydrolyze cortisone acetate by the Freudenberg[2] conditions. This reaction failed to give cortisone, but instead gave the product of Mattox and Kendall,[3] 21,21-dimethoxy-4-pregnene-3,11,20-trione (I). We obtained the same product from free cortisone, using the same procedure. These hydrolytic conditions were then applied to pregnane-17α,21-diol-3,11,20-trione 21-acetate which, according to infrared analysis, also gave a product with a saturated ether bond but without acetate or hydroxyl groups. This is presumably 21,21-dimethoxypregnane-3,11,20-trione (II), in analogy with the structure of the product obtained from cortisone acetate.

These structures were not then known, and we felt that possible formulations of I and II were those also considered by Mattox to be 16,21-dimethoxypregnantriones.[1] Since we had successfully cleaved methanol from 16α-methoxy-5-pregnen-3β-ol-20-one to give 5,16-pregnadien-3β-ol-20-one acetate,[4] we similarly treated the dimethoxy trione I obtained from cortisone, with acetic anhydride and *p*-toluenesulfonic acid, expecting to obtain the corresponding Δ^{16}-20-ketone. The isolated product, however, did not contain hydroxyl, methoxyl or conjugated carbonyl, according to infrared spectra. It did show infrared bands corresponding to acetate and enol acetate, conjugated diene, carbonyl (*e.g.*, at C_{11}), and interacting 21-acetate and 20-carbonyl. This evidence applied to the correct formulation of I[1] and combined with the negative rotatory shift and the analysis, indicates that the material is 3,5-pregnadiene-3,21,21-triol-11,20-dione triacetate (III).

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[1] V. R. Mattox, This Journal, **74**, 4340 (1952).

[2] K. Freudenberg and W. Jakob, *Ber.*, **74**, 1001 (1941).

[3] V. R. Mattox and E. C. Kendall, *J. Biol. Chem.*, **188**, 287 (1951).

[4] D. Gould, F. Gruen and E. B. Hershberg, This Journal, **75**, 2510 (1953).

Thus the 3-ketone has been enol-acetylated as expected, while the dimethylacetal at C-21 has been cleaved and replaced by a diacetate,[5] under the strongly acidic acetylating conditions.

Experimental[6]

21,21-Dimethoxy-4-pregnen-3,11,20-trione (I) from Cortisone.—One hundred milligrams of cortisone was dissolved in 10 ml. of methanol and treated with 0.25 ml. of acetyl chloride (equiv. to 1% HCl in the solution). The mixture was allowed to stand at room temperature for 18 hours and then was neutralized by the addition of aqueous potassium acetate solution. The mixture was concentrated to give a precipitate which was collected and dried *in vacuo*, weight 0.07 g., m.p. 145–150°. Recrystallization from isopropyl alcohol gave 30 mg. of 21,21-dimethoxy-4-pregnen-3,11,20-trione, m.p. 160–162°, ϵ_{max} 15,600 at 236 mμ (EtOH), $[\alpha]_D$ +211.4° (acetone). The infrared spectrum (Nujol mull) showed peaks at 5.85 μ (C_{11} and C_{20} carbonyl), 5.96 μ (C_3 carbonyl), 6.16 μ (Δ^4) and 9.04 μ (C–O–C), and was identical with that of material obtained by the same procedure from cortisone acetate.

21,21-Dimethoxypregnan-3,11,20-trione (II).—Two grams of pregnan-17α,21-diol-3,11,20-trione 21-acetate was suspended in 100 ml. of absolute methanol. To this was cautiously added 2.5 ml. of acetyl chloride. The mixture was warmed to dissolve the solid and allowed to stand 20 hours. Thereupon the clear solution was treated with 4 g. of potassium acetate in water and evaporated to dryness *in vacuo*. Upon crystallization from isopropyl alcohol and heptane, the residue gave 21,21-dimethoxy-pregnan-3,11,20-trione, m.p. 131–132.4°, $[\alpha]_D$ +107.8° (dioxane). *Anal.* Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78. Found: C, 70.90; H, 8.84. The infrared absorption spectrum (Nujol mull) showed carbonyl peaks at 5.78 and 5.88 μ and a strong C–O–C peak at 9.15 μ.

3,5-Pregnadiene-3,21,21-triol-11,20-dione Triacetate (III).—One gram of 21,21-dimethoxy-4-pregnene-3,11,20-trione (I) was dissolved in 4 ml. of acetic anhydride and treated with 5 mg. of *p*-toluenesulfonic acid. The mixture was refluxed for 30 minutes and chilled to give crystals which were collected and washed with cold methanol, weight 0.28 g., m.p. 170–176°, E_{max} 385 at 231 mμ (EtOH). Crystallization from isopropyl alcohol gave the triacetate, m.p. 176.5–179°, $[\alpha]_D$ +3.4° (dioxane).

The infrared spectrum (Nujol mull) showed the following bands: 5.67 and 5.75 μ (21-acetate-20-carbonyl interaction), 5.88 (11-carbonyl), 5.98 and 6.09 ($\Delta^{3,5}$-diene), 8.21 (C–O–C of acetate and enol acetate). *Anal.* Calcd. for $C_{27}H_{34}O_8$: C, 66.65; H, 7.04. Found: C, 66.89; H, 7.11.

Dilution of the mother liquor with aqueous methanol gave 0.55 g. of crude enol acetate, m.p. 160–172°, showing the same ultraviolet spectrum as above.

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[5] *Cf.* W. Schulz, *Ber.*, **85**, 249 (1952).

[6] All melting points are corrected. $E^{1\%}_{1\,\text{cm.}} = (1/cd) \log I_0/I$; $\epsilon = E \times \text{M.W.}/10$. Analyses and optical data were obtained by the Microanalytical and Physical Chemical Departments of this Laboratory.

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The Heat of Combustion of Lanthanum[1]

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Introduction.—The literature[2–6] values for the heat of formation of lanthanum oxide, like most of the rare earths, show wide variations. The discrepancies are probably due to the use of impure lanthanum metal. This paper reports the results of burning very pure lanthanum in oxygen to determine the heat of formation of the oxide.

Method.—The method involves the determination of the heat evolved from burning a weighed sample of the metal in an oxygen bomb calorimeter at 25 atmospheres pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and also was determined electrically. The completeness of combustion was determined by treating the combustion products with 6 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the corresponding standard deviations.

Results are expressed both in absolute joules and in defined calories; 1 defined calorie = 4.1840 absolute joules.

Apparatus.—Details of the construction and calibration of the calorimeter have been described.[7] The energy equivalent of the calorimeter was 10,096 ± 3.1 joules/degree.

Lanthanum Metal.—The lanthanum metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the A. E. C. This metal was analyzed with the following results: Na, 0.005%; Mg, 0.005%; Ca, 0.005%; C, 0.006%; N, 0.0075%; H, 0.001%; O, 0.061%. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. A Debye X-ray pattern showed lines only of α-lanthanum.

Combustion of Lanthanum.—The lanthanum was burned as chunks on sintered discs of 98% pure La_2O_3 supported on a platinum platform weighing 103.8 g. Two new discs were used for each run. They were formed by pressing the lanthanum oxide with an added 2.5% beeswax in a steel die. Ignition was carried out at 1200° for eight hours in air after which the discs were removed at 100° to a desiccator to prevent absorption of water. No lanthanum carbide is believed to be formed during this process since the discs when treated with 6 *N* HCl, evolve no gas and dissolution is complete. Pure magnesium fuse wire was used. The heat of combustion was taken as 24,667 joules/g.[7] The amount varied from 0.0053 to 0.0056 g. The formation of a double oxide $MgO \cdot La_2O_3$ from the two oxides is possible. The heat of formation of such an oxide is probably not great, and since only a small fraction of the total magnesium is close to the lanthanum metal and because the amount of magnesium is not large, a correction would probably be very small. Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used, taking into account the discs, the platinum, and the difference between the La_2O_3 formed and the oxygen used. The completeness of combustion of the lanthanum varied from 99.97 to 100.00%. The initial temperature was 24.6° and the average final temperature was 25.9°. The results are summarized in Table I.

TABLE I

COMBUSTION OF LANTHANUM

Mass La, g.	ΔT, °C.	Total energy, abs. joules	Energy from La, abs. joules/g.	Deviation, abs. joules/g.
2.1274	1.3626	13801.0	6414.7	2.5
2.0694	1.3247	13415.2	6413.8	1.6
2.0351	1.3035	13199.8	6413.2	1.0
1.9492_5	1.2477	12640.1	6410.0	2.2
2.0533	1.3143	13312.8	6409.5	2.7
		Av.	6412.2	2.0

2 × standard deviation = 2.1

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[1] This work was performed under the auspices of the A. E. C.

[2] W. Muthmann and L. Weiss, *Ann.*, **331**, 1 (1904).

[3] W. A. Roth, U. Wolf and O. Fritz, *Z. Elektrochem.*, **46**, 42 (1940).

[4] J. E. Moose and S. W. Parr, THIS JOURNAL, **46**, 2656 (1924).

[5] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," 1936, p. 337.

[6] L. Brewer, "The Thermodynamics of the Rare Earth Oxides," UCRL-1931, September, 1952.

[7] C. E. Holley, Jr., and E. J. Huber, Jr., THIS JOURNAL, **73**, 5577 (1951).