bromic acid, which effectively prevented hydrolysis. The first crop of crystals was obtained by allowing the solution to crystallize at 70°, filtering while hot, washing the product once by stirring with acetone, and air-drying at room temperature. The purity of this crop was just equal to that of the starting material, indicating that the practical limit of purity had been reached. This 70° crop had a slightly stressed crystal lattice as shown by extra peaks in the X-ray diffraction pattern. Subsequent crops of crystals obtained at lower temperatures yielded products of equal purity, but having considerably increased stresses in the lattice. These stresses could be relieved by heating for a few hours in an oven at about 140° or in an evacuated sealed tube (to prevent oxidation) at temperatures up to 350°. These heat treatments produced patterns which duplicated the pattern of the starting material.

Melting points were conveniently determined on a hot stage apparatus, measuring temperatures with a 400° thermometer or a thermocouple, calibrated *in situ* at one temperature (m.p. of $K_2Cr_2O_7$). By causing samples to melt within about one second, oxidation effects were minimized. The pure samples all melted at 369–370°, and the residues produced by hydrolysis generally showed partial melting at approximately 480–490°, depending on the content of lead oxybromide. Since, according to Baroni,[4] $PbBr_2{\cdot}PbO(s)$ decomposes into $PbBr_2(l)$ and $PbBr_2{\cdot}2PbO(s)$ at 480°, the observed melting points (or solidus points) of the hydrolyzed samples may be explained on this basis. The transition which, according to Knowles,[1] occurs at 497° probably corresponds to this decomposition. It is possible that some of the earlier investigators worked with lead bromide containing $PbBr_2{\cdot}PbO$, thus obtaining "melting points" which were much too high.

The oxidation of lead bromide is predictable from thermodynamic calculations. Using the most recent data from the literature,[5–9] we have calculated the free energy equation for the reaction

$$PbBr_2(s) + {}^1/_2O_2(g) = PbO(s, \text{yel.}) + Br_2(g)$$

$$\Delta F^0, \text{ cal./mole} = 14{,}385 + 3.14T \ln T + 4.63 \times 10^{-3}T^2 + 85.64T^{1/2} - 35.69T$$

This leads to a value for the equilibrium constant $K = [Br_2]/[O_2]^{1/2} = 6.3 \times 10^{-4}$ at 327°C., indicating that with a large excess of air substantial oxidation should occur. This might be suspected from the behavior of lead iodide, which is very easily oxidized on heating in air.[10]

In deriving the equation for the free energy of sublimation of lead bromide, Kelley[11] used a m.p. of 488° in connection with the corresponding heat capacity, heat of fusion and vapor pressure data, which are probably open to question. At the present writing, no newer experimental data of this type have been located with the exception of the vapor pressure data of Niwa, Sato and Yosiyama,[12] who did not give the m.p. of their lead bromide. Due to the effusion method used by these authors their values may be inherently a little too high.

On the basis of existing information, Kelley's equation for the free energy of sublimation[11] has been rederived on the basis of a m.p. of 370°, assuming that the specific heat equation for the liquid and the heat of fusion which he used were valid at this temperature. The result

$$\Delta F^0, \text{ subl., cal./mole} = 42{,}570 + 4.13T \ln T + 1.55 \times 10^{-3}T^2 - 71.20T$$

is believed to represent the best available experimental data.

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(4) Baroni, *Atti accad. Lincei*, **20**, 384 (1935).

(5) National Bureau of Standards, "Tables of Selected Values of Chemical Thermodynamic Properties," 1949.

(6) Thompson, "The Total and Free Energies of Formation of the Oxides of Thirty-two Metals," The Electrochemical Society, New York, N. Y., 1942, p. 44.

(7) Spencer and Spicer, THIS JOURNAL, **64**, 617 (1942).

(8) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(9) Kelley, Bur. Mines Bulletin 434 (1941).

(10) Van Klooster and Stearns, THIS JOURNAL, **55**, 4121 (1933).

(11) Kelley, Bur. Mines Bulletin 383 (1935).

(12) Niwa, Sato and Yosiyama, *J. Chem. Soc. Japan*, **60**, 918 (1939).

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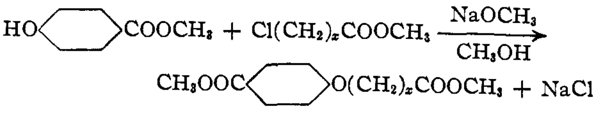
Esters of *p*-Carboxyphenoxyalkanoic Acids

BY E. F. IZARD AND STEPHANIE L. KWOLEK

In the course of research on condensation polymers, a group of dimethyl esters of quite regular structure but of varying chain length and belonging to a homologous series with the general formula, , was prepared. Included in this group are methyl *p*-carbomethoxyphenoxyacetate, methyl *p*-carbomethoxyphenoxybutyrate, methyl *p*-carbomethoxyphenoxyvalerate, methyl *p*-carbomethoxyphenoxycaproate, methyl *p*-carbomethoxyphenoxyheptanoate and methyl *p*-carbomethoxyphenoxyundecanoate.

With the exception of methyl *p*-carbomethoxyphenoxyacetate, none of these esters is recorded in the literature. Christiansen[1] reported having obtained the former in a 74% yield and melting at 92–92.7° from *p*-carboxyphenoxyacetic acid. This melting point has a slightly lower value than that recorded in this paper.

The procedure employed for the preparation of this series of compounds is outlined in the general reaction



Experimental

Because of similarity in the preparation of the six dimethyl esters previously named, only the procedure for the synthesis of methyl *p*-carbomethoxyphenoxyvalerate will be given in detail.

Methyl *p*-Carbomethoxyphenoxyvalerate.—The synthesis of this compound required a preliminary preparation of methyl δ-chlorovalerate by a modified Adams and Thal procedure,[2] whereby a refluxing methyl alcohol solution of δ-chlorovaleronitrile was saturated with dry hydrogen chloride; yield 85.1%; b.p. 106–107° at 38 mm. Dry hydrogen chloride was used in place of sulfuric acid which might cause replacement of the chlorine atom.

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(1) W. G. Christiansen, THIS JOURNAL, **48**, 463 (1926).

(2) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 270.

TABLE I

	Product,[a] methyl p-carbomethoxy-	Varying component	Refluxing time (hr.)	M.p., °C.	Yield, %	Analyses: Sapon. equiv. Calcd.	Analyses: Sapon. equiv. Found	Analyses: Calcd., % C	Analyses: Calcd., % H	Analyses: Found, % C	Analyses: Found, % H
1	Phenoxyacetate	Methyl α-chloroacetate	15	93.6–94.5	63.9	112.1	112.4	58.92	5.39	58.75	5.38
2	Phenoxybutyrate	Methyl γ-chlorobutyrate	40	48.8–49.8	21.0	126.1	127.5	61.94	6.35	...	..
3	Phenoxyvalerate	Methyl δ-chlorovalerate	78	48.0–49.0	52.9	133.1	133.6	63.14	6.81	63.21	6.83
4	Phenoxycaproate	Methyl ϵ-chlorocaproate	82	44.6–45.4	52	140.2	141.0	64.27	7.19	64.35	7.10
5	Phenoxyheptanoate	Methyl ω-bromoheptanoate	39	54.2–55.3	20	147.2	147.2	65.29	7.53	65.33	7.44
6	Phenoxyundecanoate	Methyl 11-bromoundecanoate	24	69.0–70.0	91.5	175.2	175.6	68.57	8.57	...	..

[a] All products were crystallized from methyl alcohol–water; however, where unreacted methyl p-hydroxybenzoate was present, it was removed by washing a benzene solution of the product with aqueous NaOH.

Freshly cut sodium (33.1 g., 1.44 moles) was gradually introduced into 600 ml. of dry methanol in a two-liter flask equipped with a stirrer, reflux condenser with a drying tube, and dropping funnel. Upon complete solution of the sodium, first, 219.1 g. (1.44 moles) of methyl p-hydroxybenzoate in 400 ml. of methanol and later 217.6 g. (1.44 moles) of methyl δ-chlorovalerate were added rapidly. The reaction mixture was refluxed for a total of 78 hours during which time the newly formed sodium chloride was filtered away several times as a means of determining the end of reaction. Upon pouring the cooled reaction mixture into ice-water, a white lustrous precipitate settled out. The product after recrystallization from methyl alcohol–water contained a small amount of a slightly higher melting impurity (assumed to be unreacted methyl p-hydroxybenzoate) which was removed by washing a benzene solution of the precipitate with aqueous sodium hydroxide. Physical data pertaining to this compound as well as to the other dimethyl esters are found in Table I.

Intermediates necessary to the preparation of these esters were made according to methods found in literature. The following references were employed: for methyl γ-chlorobutyrate,[3] methyl ϵ-chlorocaproate,[2] methyl ω-bromoheptanoate[3] and methyl 11-bromoundecanoate.[4,5]

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(3) C. F. H. Allen, ref. 2, Coll. Vol. 1, 1941, p. 156.

(4) Conrad, *Ann.*, **188**, 218 (1877).

(5) R. Ashton and J. C. Smith, *J. Chem. Soc.*, 435 (1934).

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Ethyl 3β-Acetoxy-5,17(20)-pregnadiene-21-thiolate

BY ROGER W. JEANLOZ[1]

In a study of reductive desulfuration with Raney nickel, ethyl 3β-acetoxy-5,17(20)-pregnadiene-21-thiolate has been prepared directly from 3β,17β-diacetoxy-5-androstene-17α-acetic acid[2] and from 3β-acetoxy-5,17(20)-pregnadiene-21-ic acid.

3β-Acetoxy-5,17(20)-pregnadiene-21-ic Acid.—By the use of acetic acid and pyridine, 150 mg. of 3β-hydroxy-5,17(20)-pregnadiene-21-ic acid was acetylated. The product was crystallized from ether and gave 165 mg. (93%) of prisms, melting at 135–137°; $[\alpha]^{20}\text{D}$ −74° (c, 1.04 in chloroform).[3]

Anal. Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 74.10; H, 8.69.

Ethyl 3β-Acetoxy-5,17(20)-pregnadiene-21-thiolate.—Thionyl chloride (1.5 ml.) was added at 0° to 270 mg. of dry 3β,17β-diacetoxy-5-androstene-17α-acetic acid (m.p. 200°)[1] and kept at 0° for 12 hours with exclusion of moisture. The excess thionyl chloride was evaporated and the last traces removed by addition of absolute benzene and evaporation at reduced pressure. The crystalline acid chloride (not isolated) was dissolved in 2 ml. of absolute benzene and, after addition of 0.3 ml. of ethyl mercaptan and 0.1 ml. of absolute pyridine, was kept at room temperature for two days. The solution was then diluted with a small amount of water and extracted with ether. The extract was washed with dilute hydrochloric acid, sodium carbonate and water and dried over anhydrous sodium sulfate. The ethereal solution was decolorized with charcoal, evaporated to dryness and the residue, recrystallized from ether–pentane, yielded 255 mg. (95%) of colorless prismatic needles, m.p. 154–155°; $[\alpha]^{20}\text{D}$ −65° (c, 1.38 in chloroform).

Anal. Calcd. for $C_{25}H_{36}O_3S$: C, 72.07; H, 8.71; S, 7.70. Found: C, 71.57; H, 9.15; S, 7.84.

One hundred and twenty-five milligrams of 3β-acetoxy-5,17(20)-pregnadiene-21-ic acid was treated with thionyl chloride and then with ethyl mercaptan, as described above for 3β,17β-diacetoxy-5-androstene-17α-acetic acid. There was obtained 130 mg. (90%), melting at 150–152° (mixed m.p. with the specimen described above, 151–154°).

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[1] Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts.

[2] T. Reichstein, H. Müller, Ch. Meystre and M. Sutter, *Helv. Chim. Acta*, **22**, 741 (1939); Pl. A. Plattner and W. Schreck, *ibid.*, **22**, 1178 (1939).

[3] The melting points were determined on the Kofler micro melting point apparatus and the rotations observed in a 1-dm. tube of 0.8-ml. capacity.

Further Studies of the Ion-Exchange Separation of the Rare Earths[1]

BY B. H. KETELLE AND G. E. BOYD

Recently Higgins and Street[2] have called attention to the mislabelling of the Tb activity peak in our Fig. 6c which reported on the ion-exchange column separation of all fourteen of the trivalent rare earths using citrate buffers at 100°.[3] Partly reported[4a,b] further work in the Tb–Gd–Eu region conducted at this Laboratory in 1948 and 1949 has revealed not only this mistake, in agreement with Higgins and Street, but has shown also that the peak marked Y in Fig. 6c was actually Dy.

Before discussing our later ion-exchange separations, the reasons for these misidentifications, which we take this occasion to correct, may be of interest: The earlier assignment of the activity peak in Fig. 6c occurring at 2400 minutes to Y was based partly upon the argument that after such a time dysprosium activity (assumed to be 145 m Dy^{165}) would not have been detectable, and partly

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[1] This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

[2] G. H. Higgins and K. Street, THIS JOURNAL, **72**, 5321 (1950).

[3] B. H. Ketelle and G. E. Boyd, *ibid.*, **69**, 2800 (1947).

[4] (a) B. H. Ketelle, *Phys. Rev.*, **76**, 1256 (1949). (b) See private communication K(101) by B. H. Ketelle (Dec. 1948) to G. T. Seaborg concerning the decay sequence 3.6 m $Gd^{161} \rightarrow$ 7.0 d Tb^{161} reported in a Table of Isotopes by G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.*, **20**, 585 (1948).