The Oxidation of Carboxylic Acids to Esters by Tetravalent Lead[1]

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Lead tetrasalts of aliphatic acids are oxidized by halogens to the corresponding esters and carbon dioxide in fair to good yields under anhydrous conditions. With larger amounts of halogen the chief products are alkyl halides. These methods offer advantages in cost and simplicity of procedure over the Simonini and Hunsdiecker methods in which the starting materials are silver salts. The effects of a number of variables on yields are discussed and mechanistic possibilities are considered.

The formation of esters from carboxylic acids and their derivatives under oxidative conditions has often been observed to occur. The over-all process may be represented as follows.

$$2RCOOH + (O) \longrightarrow RCOOR + CO_2 + H_2O \qquad (1)$$

The acids themselves,[3] their metal salts,[4] and the corresponding peracids and peranhydrides[5] have served as starting materials, while the anodic current (electrolysis),[6] halogens,[7] metal oxides,[8] and even aromatic ketones[9] have been used as oxidizing agents. In most cases esters were merely observed as byproducts, and their yields were not determined. In only a few cases is the process proposed as a preparative method. The most successful of these methods is the Simonini reaction.[7,10]

$$2RCOOAg + I_2 \xrightarrow{CCl_4} RCOOR + CO_2 + 2AgI \qquad (2)$$

This reaction produces yields of esters from aliphatic acids of 20–70%. It suffers from several disadvantages, however, especially in the cost and inconvenience of preparing and drying the silver salts required.

We have studied the effects of a number of different chemical oxidizing agents on carboxylic acids and their salts and have found that the reaction of halogens with lead tetrasalts provides an ester synthesis with yields comparable to those of the Simonini synthesis and with a considerably simplified procedure.

Lead tetrasalts are readily prepared from the corresponding acids by warming them with lead tetraacetate and distilling the acetic acid liberated, preferably under reduced pressure.

$$4RCOOH + Pb(CH_3COO)_4 \xrightarrow[10\text{ mm.}]{70°} 4CH_3COOH + Pb(RCOO)_4 \qquad (3)$$

A suitable inert solvent may be present during this reaction and is especially useful when the lead salt formed is high melting. Care must be taken to avoid decomposition of the lead tetrasalts by contact with moisture or by overheating (> 100°). However, for ester synthesis, they need not be isolated or further purified, and may, in fact, be used *in situ*.

The reaction between lead tetrasalts and iodine proceeds vigorously at about 100° with evolution of carbon dioxide and formation of the considerably less soluble lead disalts. It is therefore desirable to employ a solvent to moderate the reaction and to prevent caking or gelling of the reaction mixture. This solvent should boil at or above 140°, since optimum yields of ester require a further period of heating at elevated temperatures after the gas evolution has ceased. Other necessary properties of the solvent include chemical inertness to the lead salts and iodine, and physical characteristics (especially boiling point) which permit easy separation and purification of the product ester. No one solvent meets all of these qualifications in all cases. We have found *sym*-tetrachloroethane, *o*-dichlorobenzene, and mineral oil suitable at various times. Alternatively, the reaction may be run in an autoclave with or without solvents.

Yields of ester by the lead tetrasalt–iodine method depend markedly on the structure of the acid. Straight-chained aliphatic acids react quite satisfactorily, and the yields increase with the molecular weight of the acid. An acid in which the carboxyl group was attached to a secondary carbon atom (isobutyric acid) gave diminished yields, and one in which it was attached to a tertiary carbon atom (pivalic acid) gave no ester. Glutaric acid yielded the corresponding lactone in modest yield. The introduction of unsaturation in the acid has a drastic effect. Oleic acid and picolinic acid gave tars, and benzoic acid gave iodobenzene but no phenyl benzoate. An equimolar mixture of benzoic and palmitic acids gave pentadecyl ester but no phenyl ester. Table I summarizes the results obtained with a number of acids.

TABLE I

LEAD TETRASALT–IODINE SYNTHESIS OF ESTERS

Acid	Conversion, mole ester/2 moles acid
Acetic	0.20
Caproic	.34
Caprylic	.50
Lauric	.50
Palmitic	.54
Behenic	.52
Isobutyric	.18
Pivalic	.00
Glutaric	.19
Picolinic	.00
Benzoic	.00[a]
Benzoic–palmitic	.24[b]

[a] Iodobenzene, 61.5% yield based on iodine, was obtained.
[b] Product consisted of pentadecyl ester and no phenyl ester.

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[3] R. Bacon and R. Batt, *Chem. Ind.* (London), 1287 (1953).

[4] F. Fichter and E. Brunner, *Helv. Chim. Acta*, **12**, 573 (1929).

[5] D. Swern, *Chem. Rev.*, **45**, 1 (1949); C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., Chapman and Hall, Ltd., 1957, p. 491; H. Lau and H. Hart, *J. Am. Chem. Soc.*, **81**, 4897 (1959).

[6] H. Kolbe, *Ann.*, **69**, 257 (1849); and B. Weedon, *Quart. Rev.*, **6**, 380 (1952).

[7] C. Wilson, *Org. Reaction*, **IX**, 332 (1956); and R. Johnson and R. Ingham, *Chem. Rev.*, **56**, 219 (1956).

[8] O. Veiel, *Ann.*, **148**, 164 (1868).

[9] F. Paterno, *Atti accad. Lincei*, **24**, I, 675–675 (1915); *Gazz. chim. ital.*, **45**, I, 389–390 (1915); *Chem. Abstr.*, **9**, 3064 (1915).

[10] A. Simonini, *Monatsh.*, **13**, 337 (1892); **14**, 59 (1893).

The lead tetrasalt–iodine synthesis of esters proceeds in several steps, as is evident from the temperature effects observed. At 60–70° two moles of lead tetrasalt decolorize one mole of iodine without any other noticeable change—*i.e.*, no gas evolution or precipitation of lead disalt or lead iodide. At 85–105° the reaction mixture evolves carbon dioxide vigorously, and if worked up at this (second) stage yields approximately one mole of ester, two moles of alkyl iodide, two moles of lead disalt, and three moles of carbon dioxide, as illustrated in equation 4. The figures in parenthesis below each product represent the actual yields in the case of palmitic acid. A small amount of palmitic acid (9%) was regenerated. The over-all material balance was 89%.

$$2Pb(RCOO)_4 + I_2 \xrightarrow{85\text{–}105°} \underset{(92\%)}{RCOOR} + \underset{(72\%)}{2RI} + \underset{(80\%)}{3CO_2} + \underset{(89\%)}{2Pb(RCOO)_2} \quad (4)$$

The third stage of the reaction requires a still higher temperature and involves double decomposition between the alkyl iodide and the lead disalt, as in equation 5. In a separate run using pure lead dipalmitate and pentadecyl iodide a 77% yield of pentadecyl palmitate was obtained.

$$Pb(RCOO)_2 + 2RI \xrightarrow{150\text{–}180°} 2RCOOR + PbI_2 \quad (5)$$

Summing up equations 3, 4, and 5 we obtain equation 6 for the over-all synthesis. The figures in parentheses refer to the actual yields obtained with palmitic acid.

$$2Pb(CH_3COO)_4 + 8RCOOH + I_2 \longrightarrow \underset{(71\%)}{3RCOOR} + \underset{(80\%)}{3CO_2} + \underset{(86\%)}{Pb(RCOO)_2} + PbI_2 + 8CH_3COOH \quad (6)$$

Equation 6 indicates that two of the eight moles of starting acid are lost to ester formation through formation of the lead disalt. It seemed probable that the addition of more iodine would prevent this by reacting with the disalt to form more alkyl iodide and hence more ester. However this proved not to be the case, since iodine does not react with lead disalts. In one experiment lead dicaproate was heated with equimolar amounts of iodine in an autoclave to 260–270°. The principal organic products were caprone (35.8%) and caproic acid (17%) and no ester was obtained. Caprone is formed when lead dicaproate is heated alone to this temperature.[11] Mehta[12] has also observed that lead disalts do not react with iodine.

In further attempts to improve this ester synthesis, red lead was substituted for lead tetraacetate and bromine or chlorine for iodine. Red lead reacts with organic acids to give a mixture of lead tetrasalts and disalts. Since water is also formed and is deleterious to the subsequent reactions, it must be removed, preferably by reaction with acetic anhydride followed by vacuum distillation of the acetic acid generated. Bromine and chlorine differ from iodine in that they react with lead disalts as well as with lead tetrasalts to form alkyl halides. These bromides and chlorides react with lead salts to form esters, although considerably more slowly than do iodides. Ester synthesis may therefore be completed according to the stoichiometry of equation 8. Using lauric acid and bromine, a 50% yield of undecyl laurate was obtained. With lauric acid and chlorine, a 20% yield of undecyl laurate was obtained.

$$Pb_3O_4 + 8RCOOH + 4(CH_3CO)_2O \longrightarrow Pb(RCOO)_4 + 2Pb(RCOO)_2 + 8CH_3COOH \quad (7)$$

$$Pb(RCOO)_4 + 2Pb(RCOO)_2 + 3Br_2 \longrightarrow 4RCOOR + 3PbBr_2 + 4CO_2 \quad (8)$$

Substantial amounts of free lauric acid (*ca.* 20 and 50% respectively), we regenerated in these reactions—more than in the reactions involving iodine (10–20%). This is doubtless one of the factors which prevent the yields of ester from being higher than they are. Other investigators have explained free acid formation in the reactions of silver salts with halogens as arising from substitution reactions, which generate hydrogen halide, which in turn reacts with the silver salt to generate free carboxylic acid.[13] A similar process may operate with the lead salt. Since the amount of free carboxylic acid formed is roughly proportional to the substitutive reactivity of the halogens employed—*i.e.*, chlorine > bromine > iodine, this seems to be a reasonable assumption. However free acid formation probably occurs by other mechanisms as well, since others have observed that merely heating lead tetrasalts in the absence of halogens generates some acid.[14]

Comparisons of the lead tetrasalt–halogen and Simonini methods of ester synthesis show that the principal advantages of the first method are in convenience and cost. The lead tetrasalts are readily prepared under anhydrous conditions and may be used without isolation or purification. Furthermore, they form homogeneous solutions in the solvents employed, while silver salts are insoluble in the solvents employed in the Simonini reaction. From the standpoint of yield the two processes seem to be similar, although published yield data on the Simonini reaction are sparse and in some cases inconsistent. Since the two processes proceed by reactions with entirely different stoichiometries, cost comparisons are best made on the basis of other reagents used per mole of acid reacted or per mole of ester formed. On this basis the lead tetraacetate–iodine process is about one third as expensive and the red lead–bromine process is about one fiftieth as expensive as the silver salt–iodine process.

A number of experiments were run in attempts to oxidize caproic acid to amyl caproate using other oxidizing agents, including: PbO_2, CrO_3, MnO_2, $K_2S_2O_8$, BaO_2, H_2O_2, and various combinations of these. In no case did the yield of ester exceed 14% (using 30% hydrogen peroxide in concd. sulfuric acid), and in most cases no more than a trace of ester was detected by odor.

Although this study has been directed primarily toward the synthesis of esters, it should be noted that the lead–halogen method may also be employed for the preparation of alkyl halides. Using larger ratios of halogens to lead salts decreases the yields of esters and increases the yields of alkyl halides. This effect is smallest in the case of iodine. When the synthesis represented by equations 7 and 8 is run with seven instead of three moles of bromine, and the reaction temperature is maintained below 140°, the yield of amyl bromide increases from 0 to 0.36 mole per mole of acid

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[11] J. Kenner and F. Morton, *Ber.*, **72**, 455 (1939).

[12] T. Mehta, W. Mehta, and T. Thosar, *J. Indian Chem. Soc., Ind. Ed.*, **3**, 166 (1940).

[13] J. Cason, M. Kahn, and R. Mills, *J. Org. Chem.*, **18**, 1670 (1953).

[14] C. Hurd and P. Austin, *J. Am. Chem. Soc.*, **53**, 1543 (1931).

$$Pb_3O_4 + 8RCO_2H + 4(CH_3CO)_2O + 7Br_2 \longrightarrow 8RBr + 8CO_2 + 3PbBr_2 + 8CH_3CO_2H \quad (9)$$

(36% yield by equation 9). A yield of 92% is reported for amyl bromide in the Hunsdiecker reaction using silver caproate. However, this yield was estimated from the results of a quantitative determination of bromine on a neutral fraction of the reaction products and not by weighing an isolated purified material. The average yield reported for primary alkyl bromides is about 60%.[7] It is difficult to judge the relative merits of the two processes from a standpoint of yield using such insufficient data, but it seems probable that the silver salt method gives somewhat higher yields. On the other hand, the lead salt method is obviously more convenient to use.

The mechanism of formation of esters and alkyl halides by the Simonini and Hunsdiecker reactions cannot be considered to be thoroughly established in all details. The same is true of the lead salt method here described, but some of the facts developed are pertinent to mechanistic considerations and will be mentioned. Ester formation between alkyl halides and lead salts, as illustrated in equation 5, may well proceed by a combination of S_N1 and S_N2 processes as proposed by Kornblum[15] for reactions of alkyl halides with silver salts. However, ester formation as well as alkyl halide formation by reactions involving decarboxylation and a change in valence of lead from four to two, as illustrated in equations 4 and 8, are apparently much more complicated. It seems to us that they cannot proceed by an ionic mechanism involving formation of carbonium ion intermediates as proposed for similar reactions by Mosher,[16] since they proceed best in nonionizing solvents, the yields of ester are not improved by addition of excess carboxylate ions (from excess acid), and no olefins are formed (through loss of protons from the intermediate carbonium ion) from unbranched acids. A free radicals process also seems unlikely, since any $R\cdot$ radical formed might be expected to dimerize to R—R hydrocarbons to some extent, especially with minimal amounts of halogen present. To test this point we made a run with four moles of lead tetrapalmitate and one mole of iodine and found that the only hydrocarbon produced in detectable amounts was pentadecane (0.19 mole/mole of acid). We conclude that any radicals formed in these decompositions cannot be very free.

This leaves for consideration concerted and cage-type mechanisms. We are of the opinion that one of the other or both of these can best be used to explain the formation of esters, alkyl halides, and free carboxylic acids directly from lead tetrasalts. Acyl peroxides are unlikely intermediates, since it has been shown that they give low yields of esters from straight-chained aliphatic acids. Thus lauroyl peroxide gives not over a 16% yield of undecyl laurate,[17] and 4-phenylvaleryl peroxide gives only a 17.5% yield of the corresponding symmetrical ester[18] on thermal decomposition. Hence a more direct means of formation of the ester molecule seems likely. Acyl hypohalites have frequently been proposed as intermediates in the formation of alkyl halides,[7] and iodine triacyls have been shown to form in the reaction of silver carboxylates with iodine and to decompose into alkyl iodide and ester on warming.[19] Such intermediates are therefore sufficient to account for the qualitative results of the lead tetrasalt–iodine reactions, but whether they are necessary intermediates in this synthesis is not certain. Further work along these lines is now under way and will be reported in a later publication.

TABLE II

LEAD TETRASALTS

Acid	Solvent	M.p.	Anal. for Pb	
			Calcd.	Found
Caproic	...	Oil	...	...
Caproic	...	Oil	...	...
Lauric	Pet. ether	61–62	20.63	20.88
Palmitic	Pet. ether	77–78	16.86	17.01
Behenic	Pet. ether	86–87	13.24	13.42
Oleic	...	Oil	...	...
Isobutyric	Pet. ether	102–103	...	...
Pivalic	Benzene	173	...	...
Benzoic	Benzene	180–181	...	...
Glutaric	Insol.	Dec.	...	...

Experimental

Preparation of Lead Tetrasalts.—Lead tetraacetate (0.25 mole) and a carboxylic acid (1.0 mole) were heated together at 60–80° and the acetic acid distilled at 10-mm. pressure as it formed. The product was pure enough for further reactions without other treatment. When the lead tetrasalt melted above 80–100° a solvent, such as 1,1,2,2-tetrachloroethane, *o*-dichlorobenzene, or mineral oil, was used to prevent caking and local superheating of the product.

In separate experiments each of the lead tetrasalts prepared was isolated, purified by recrystallization, and characterized by m.p. Those which have not previously been reported (tetralaurate and tetrabehenate) and one for which an analysis has not been reported (tetrapalmitate) were analyzed quantitatively for lead. The m.p.'s. which were above 100° occurred with decomposition and were determined fairly rapidly to avoid extensive decomposition.

Thermal Decomposition of Lead Tetracaproate.—When lead tetracaproate was heated alone in an autoclave for 1.5 hr. at 140–200°, it yielded 0.048 mole of amyl caproate per mole of starting caproic acid. Other products which formed were not identified. When heated similarly with sulfur or red phosphorus (equimolar amounts), or with barium peroxide in mineral oil to 170°, it gave no detectable amounts of amyl caproate.

Generalized Preparation of Esters. A. Lead Tetrasalts and Iodine.—To the lead tetrasalt (0.25 mole) was added solvent, about 300 ml., and iodine (0.125 mole). The stirred mixture was heated until gas evolution began and maintained at 85–105° until gas evolution ceased (about 20 min.). The temperature was then raised to 150–200° (depending on b.p.'s of solvent and alkyl iodide) for about 1 hr.

The work-up of the reaction mixture depended on the relative b.p.'s of the solvent and the ester. With higher boiling solvents the ester was distilled from the reaction mixture, washed with dilute sodium carbonate solution, dried, and fractionated through a short column. With lower boiling solvents the solvent was distilled, the residue was triturated with 300 ml. of ether, filtered to remove lead salts, the ether solution washed with sodium carbonate solution and sodium thiosulfate solution, dried, and fractionally distilled. With high boiling esters the product was not distilled but was recrystallized from a suitable solvent. Yields of esters were determined on purified materials showing correct elementary analyses, physical properties corresponding to those in the literature, and infrared spectra showing no extraneous peaks in the 4000–1600-cm.$^{-1}$ region. Only heneicosylbehenate, m.p. 72–73°, is new. It showed characteristic ester carbonyl absorption peaks at 1750–1735 cm.$^{-1}$ and no extraneous peaks.

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[15] N. Kornblum, R. Smiley, R. Blackwood, and D. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

[16] W. Mosher and C. Kehr, *ibid.*, **75**, 3172 (1953).

[17] W. Cass, *ibid.*, **72**, 4915 (1950).

[18] D. De Tar and C. Weis, *ibid.*, **78**, 4296 (1956).

[19] W. Oldham and A. Ubbelohde, *J. Chem. Soc.*, 368 (1941).

Anal. Calcd. for $C_{43}H_{86}O_2$: C, 81.31; H, 13.65. Found: C, 81.16; H, 13.60.

Recovery of free carboxylic acids was accomplished by acidifying the sodium carbonate wash solutions with mineral acid and distilling or recrystallizing the nonaqueous phase which separated.

B. **Red Lead and Halogens.**—The carboxylic acid (1.0 mole), acetic anhydride (0.54 mole), and acetic acid (20 ml.) were placed in a 1-l. three-necked flask fitted with a stirrer, a thermometer, and a Y-tube, one arm of which held a condenser and drying tube and the other arm of which held a rubber addition tube and flask containing red lead (0.125 mole). The mixture was heated to 60–80°, and the red lead was added incrementally as rapidly as it was decolorized. The Y-tube was replaced by a distilling head and condenser, and the acetic acid was removed completely at 70° under vacuum. The reaction mixture was cooled, the distilling head replaced by a reflux condenser fitted with a drying tube, and the solvent (300 ml.) and halogen (0.375 mole) were added. The stirred mixture was then heated slowly through the gas evolution period to about 200°, where it was held for 2–4 hr. or until the refluxing alkyl halide had reacted. The reaction mixture was worked up as described in procedure A. When a low boiling solvent was used it was removed by distillation before the final heating period.

When alkyl halide was the desired product, more halogen (0.875 mole) was added, and the temperature was not raised above 140°.

Reaction of Lead Tetrapalmitate with Iodine. Isolation and Material Balance of All Products.—Tetrachloroethane, 250 ml., and iodine, 20.9 g. (0.0825 mole), were added to lead tetrapalmitate, 101.2 g. (0.165 mole), prepared as described above in A. The mixture was stirred and heated to about 120° for 2 hr. During this period carbon dioxide was evolved and measured through the wet test meter, 0.198 mole (80.0%). The solvent was removed under a water aspirator, and the solid residue was extracted with several samples of benzene–methanol (70:30), totalling 750 ml. The liquid solution was titrated with a 1 *N* solution of sodium methoxide in methanol using Thymol Blue as indicator to determine the free carboxylic acid, 0.057 mole (8.6%). The precipitated sodium salt was filtered off, dried, and weighed as a check on this determination, 0.057 mole (8.6%). The remaining liquid was fractionally distilled, eventually under vacuum, to obtain pentadecyl iodide, b.p. 110–120° (0.03–0.06 mm.), m.p. 20–22°, $n^{25}\text{D}$ 1.4754, 0.118 mole (71.8%). The residue was recrystallized from acetone to obtain pure pentadecyl palmitate, m.p. 53–54°, 0.077 mole (34.1%).

Anal. Calcd. for $C_{31}H_{62}O_2$: C, 79.76; H, 13.39. Found: C, 79.47; H, 13.16.

The pentadecyl iodide was converted to pentadecylpyridinium iodide,[12] m.p. 105–106°, for further identification. The residue from the ester extraction was recrystallized from benzene to obtain pure lead dipalmitate, m.p. 112–114°, 0.146 mole (88.5%).

In an identical run the reaction mixture was heated to 200° for 15 min. after removal of the solvent. The solid residue was treated as before and the carboxylic acid content determined as 0.0062 mole (15.0%). The isolated and recrystallized pentadecyl palmitate amounted to 0.175 mole (70.6%). The inorganic residue from these extractions was boiled with 1 l. of benzene, filtered hot to obtain the lead iodide, 0.149 mole (91%). The hot benzene on cooling deposited the lead dipalmitate as a nearly white amorphous solid, which was separated by filtration and dried, 0.066 mole (80.0%).

Reaction of Lead Dipalmitate and Pentadecyl Iodide.—Lead dipalmitate, 7.32 g. (0.0102 mole), and pentadecyl iodide, 5.68 g. (0.0168 mole), were heated together at 200° for 15 min., cooled, and treated as above to obtain pentadecyl palmitate, 0.0128 mole (77.0%, based on iodide).

Reaction of Lead Dicaproate with Iodine.—Lead dicaproate, 166.3 g. (0.38 mole), and iodine, 63.5 g. (0.25 mole), were ground together, placed in a 250 ml. autoclave, and heated at 260–270° for 4 hr. After cooling, the gases were bled off through Dry Ice traps to isolate any low boiling hydrocarbons or other compounds. None was found. The remaining contents of the autoclave were distilled rapidly under vacuum, the distillate washed several times with sodium carbonate solution, dried, and redistilled to obtain caprone, b.p. 90–92° (6 mm.), $n^{25}\text{D}$ 1.4270, 23.0 g. (0.135 mole), 35.8% yield based on the dicaproate, The sodium carbonate solutions were acidified, extracted with ether, the ether solution dried and distilled to obtain caproic acid, b.p. 82–83° (3.8 mm.), $n^{20}\text{D}$ 1.4165, 15.4 g. (0.132 mole), 17.4% yield.

Reaction of Lead Dipalmitate Dibenzoate with Iodine.—Lead dipalmitate dibenzoate, prepared from a mixture of lead tetraacetate (0.120 mole), palmitic acid (0.24 mole), and benzoic acid (0.24 mole), reacted with iodine, 15.23 g. (0.06 mole), in tetrachloroethane, 170 ml., at 120° for 2 hr. The solvent was distilled under a water aspirator, and the residue heated at 250° for 15 min. The cooled solid product was extracted several times with ether, filtered from the inorganic residue, the ether solution washed several times with sodium carbonate solution, dried, and distilled to obtain a mixture of pentadecyl esters from which pentadecyl palmitate separated on treatment with cold acetone, m.p. 54–55°, 0.013 mole (21% yield based on the expectation of 1 mole of ester from each 2 moles of lead tetrasalt); identity was confirmed by a mixture m.p. with an authentic sample, 54–55°, and by comparisons of the infrared spectra. The residual ester was assumed to be pentadecyl benzoate. Hydrolysis with 5% potassium hydroxide in ethyl yielded only pentadecyl alcohol, m.p. 43–44° (from acetone), 0.045 mole (37%, based on the expectation of 1 mole of ester from each mole of tetrasalt). No phenol was found among the hydrolysis products.

Ester and Alkyl Bromide Syntheses Using Red Lead.—Red lead, 27.4 g. (0.04 mole), lauric acid, 65.0 g. (0.32 mole), acetic anhydride, 20.0 g. (0.20 mole), and acetic acid, 12 ml., reacted as in B to form the mixed lead dilaurate and tetralaurate. The solvent, tetrachloroethane, 150 ml., was added, the mixture warmed to 60°, and bromine, 19.2 g. (0.12 mole), dissolved in tetrachloroethane, 50 ml., was added dropwise over a period of 1 hr. The reaction mixture was heated at 140° until gas evolution ceased, then the solvent was distilled and the temperature of the residue was raised to 210–220° for 4 hr. The mixture was distilled under diminished pressure and the product purified as in A. Undecyl laurate, b.p. 220° (0.3 mm.), m.p. 32–33°, $n^{40}\text{D}$ 1.4400, 0.081 mole (50.0% yield) was obtained.

Anal. Calcd. for $C_{23}H_{46}O_2$: C, 77.90; H, 13.08. Found: C, 77.91; H, 12.92.

Red lead, 27.5 g. (0.04 mole), caproic acid, 37.0 g. (0.32 mole), acetic anhydride, 20.4 g. (0.20 mole), and acetic acid, 11 ml., reacted as in B. Then *o*-dichlorobenzene, 150 ml., was added, the mixture warmed to 60°, and bromine, 44.6 g. (0.28 mole), dissolved in *o*-dichlorobenzene, 50 ml., was added dropwise over a period of 1 hr. After gas evolution ceased, the mixture was heated at 140° for 0.5 hr. Then the product was distilled from the mixture, purified by washing with sodium carbonate solution, dried, and fractionally distilled to obtain amyl bromide, b.p. 127–128° (760 mm.), $n^{20}\text{D}$ 1.4443, 0.115 mole (36% yield).