Dibromothymoltetrachlorophthalein.—A mixture of 5 g. of pure thymoltetrachlorophthalein and 1.6 g. of bromine in 100 cc. of glacial acetic acid was stirred mechanically for three hours. A colorless, crystalline substance separated which was filtered off and recrystallized from glacial acetic acid. After drying at 130° it melted at 223–225°.

Anal.[9] Subs., 0.2950, 0.1687: Ag halide, 0.3856, 0.2205; 24.35, 13.95 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{28}H_{24}O_4Br_2Cl_4$: Br, 22.02; Cl, 19.54. Found: Br, 22.18, 21.83; Cl, 19.43, 19.60.

The dibromothymoltetrachlorophthalein is very soluble in acetone, benzene and ether, easily soluble in ethanol, soluble in glacial acetic acid and insoluble in water. It acts as an indicator and it was found by means of buffer solutions[8] that the change from colorless to blue takes place at *P*H 8.4–8.8.

Summary

1. Thymoltetrachlorophthalein has been made. It is *colorless* and therefore has the *lactoid* structure.

2. Like other phthaleins it is *tautomeric*, and *colored* derivatives of the *quinoid* form were obtained as well as *colorless* derivatives of the *lactoid* form.

3. Thymoltetrachlorophthalein and dibromothymoltetrachlorophthalein act as indicators, changing from colorless to blue at *P*H 9.2–10.0 and *P*H 8.4–8.8, respectively.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

SOME REACTIONS OF LEAD TETRA-ETHYL

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The recent discovery by Midgley and Boyd[2] of the "anti-knock" property of lead tetra-ethyl, and the subsequent manufacture on a commercial scale of this formerly little-known substance, have centered attention on it and also made it available in unlimited quantity for experimentation. This compound, although prepared by Löwig in 1853[3] has been but little studied. Its present importance seemed to justify a further investigation of its reactions.

Historical Part

Reference is made to an excellent summary of the chemistry of the organic derivatives of lead by Calingaert.[4] The first derivatives of lead tetra-ethyl were made by Löwig,[3] who obtained some of the carbonate, $[Pb(C_2H_5)_3]_2CO_3$, as a by-product. This was transformed into triethyl-

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[9] Ref. 6, p. 380.

[1] From a dissertation of O. H. Browne, June, 1926.

[2] Midgley and Boyd, *J. Ind. Eng. Chem.*, **14**, 896 (1922).

[3] Löwig, *Ann.*, **88**, 318 (1853).

[4] Calingaert, *Chem. Rev.*, **2**, 43 (1925).

lead hydroxide. On treating the base or carbonate with acids the sulfate, nitrate, chloride, bromide and iodide were obtained. The work was continued by Klippel[5] who prepared triethyl-lead formate, acetate, butyrate, benzoate, tartrate, oxalate, cyanide and cyanate.

Triethyl-lead chloride and bromide were prepared by Grüttner and Krause[6] by adding a halogen to lead tetra-ethyl in an indifferent solvent. At —65° one ethyl group is replaced, while at —20° two are replaced.

Pfeiffer and others[7] prepared halogen derivatives by passing dry hydrogen chloride or bromide into an ether solution of the lead compound.

Krause and Pohland[8] prepared triethyl-lead hydroxide by shaking an ether solution of the bromide with aqueous potassium hydroxide, and from this prepared the fluoride.

Results

The present investigation is chiefly concerned with the salts of triethyl-lead, $(C_2H_5)_3Pb$—. The methods of preparing the chloride, hydroxide and acetate have been improved. The hydrochloride is best obtained by the action of concd. hydrochloric acid on lead tetra-ethyl kept between 30° and 33°. The hydroxide is readily made in quantity, but is difficult to obtain free from chlorine. The ease with which it takes up carbon dioxide from the air makes it inconvenient to handle. It was originally intended to prepare the salts of triethyl-lead by neutralizing the hydroxide with the desired acids, as Löwig and others have done, but the difficulties of purifying and keeping the hydroxide made other methods desirable. The less soluble salts, particularly those of inorganic acids, are best obtained by double decomposition from triethyl-lead acetate, which is sufficiently soluble in water (7.5 g. per 100 cc.) for that purpose. A water solution of the sodium or potassium salt of the desired acid or the dry salt is added to an equivalent amount of the acetate in water solution. The cyanide, benzoate and butyrate were readily obtained in this way. The ferrocyanide and ferricyanide were obtained as precipitates which are insoluble in all solvents and could not be completely purified. Both sodium chromate and dichromate gave precipitates which were intermediate in composition between the chromate and dichromate. Precipitates were obtained with alkali cyanate, sulfite, arsenite, arsenate, molybdate and nitroprusside but these were not proved to be the desired compounds. Sodium bromate, chlorate and perchlorate gave no precipitates.

The salts of organic acids are generally more soluble in water and it

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[5] Klippel, *J. prakt. Chem.*, [1] **81,** 287 (1881).

[6] Grüttner and Krause, *Ber.*, **49,** 1415 (1916).

[7] Möller and Pfeiffer, *Ber.*, **49,** 2441 (1916). Pfeiffer, Truskier and Disselkamp, *Ber.*, **49,** 2445 (1916).

[8] Krause and Pohland, *Ber.*, **55,** 1282 (1922).

was found preferable to prepare them directly from lead tetra-ethyl and the acids by the aid of silica gel as a catalyst.

Silica gel was found to have quite a marked effect on the reaction between lead tetra-ethyl and an acid. At room temperature concd. nitric acid reacts very slowly, the evolution of ethane being hardly noticeable. After some time a third layer may be observed under the tetra-ethyl and finally, after about one day, a few small needle crystals, perhaps lead nitrate, will be found on the bottom of the vessel. If, however, equal volumes of the two substances are placed in a test-tube and a small piece of silica gel is added, this will settle to the interface between the two liquids and immediately begin to give off a steady stream of ethane. There is a barely perceptible rise in temperature. After about ten minutes, depending on the temperature of the room and the amount of gel used, the material suddenly foams out of the tube, ignites spontaneously and burns for several seconds, somewhat in the manner of a gunpowder flare. Broken glass does not cause the same phenomenon.

This catalytic effect of silica gel was found very useful in the preparation of salts of weak organic acids. Equimolar portions of the lead tetra-ethyl and the acid are placed in a flask provided with a reflux condenser and heated on the water-bath. When the reagents are hot a small portion of crushed silica gel is added. Instantly a vigorous generation of ethane begins. The reaction takes from about 30 minutes in the case of acetic acid to 75 for stearic. The generation of ethane never stops entirely. The heating is stopped when the evolution of gas dies down. On cooling, a cake of the crystalline salt is obtained. It is better, however, to add benzene to the hot material which crystallizes out on cooling, as decomposition, when once started, is very rapid. On allowing the filtrate to stand overnight away from air and light, a second and even a third crop of crystals may be obtained.

According to the stoichiometric equation of the reaction between lead tetra-ethyl and an acid to give the triethyl-lead salt, one mole of the compound gives one of ethane. Several attempts were made to study this reaction by measuring the ethane evolved but the volumes obtained could not be reconciled with the quantities used. The data obtained on heating 10 g. of stearic acid with 11.4 g. (one equivalent) of lead tetra-ethyl, are plotted in the curve. No sharp break is apparent at 860 cc., the volume for 1 equivalent of ethane.

By this method were prepared the following salts of triethyl-lead: acetate, m. p. 160.4°; propionate, m. p. 141–142°; butyrate, m. p. 107.9–108.5°; *iso*butyrate, m. p. 119.4–121.8°; valerate, m. p. 115.6–115.7°; *iso*valerate, m. p. 119.4–119.8°; caproate, m. p. 94.7–95.8°; heptoate, m. p. 90.0–90.8°; caprylate, m. p. 85°; pelargonate, m. p. 88–90°. These salts crystallize well, usually in long needles. A single crystal of the heptoate was 54 × 3 × 0.8 mm. Reactions took place with capric, stearic and phenylacetic acids but the products could not be obtained in sufficient purity.

The strong acids, such as the halogen-acetic acids, react with lead tetra-ethyl even at room temperature. In some cases, cooling and dilution of the acid had to be resorted to in order to control the reaction. The following salts were obtained: chloro-acetate, m. p. 146.0–146.5°; dichloro-acetate, m. p. 113.5–114.5°; trichloro-acetate, m. p. 135.5–138.6°; bromo-acetate, m. p. 121°; dibromo-acetate, m. p. 98.6–101.8°. Reactions were observed with tribromo-acetic and bromopropionic acids but the products could not be purified. The salts of these halogen-substituted acids are strongly sternutatory. It is almost impossible to handle them without suffering considerable inconvenience.

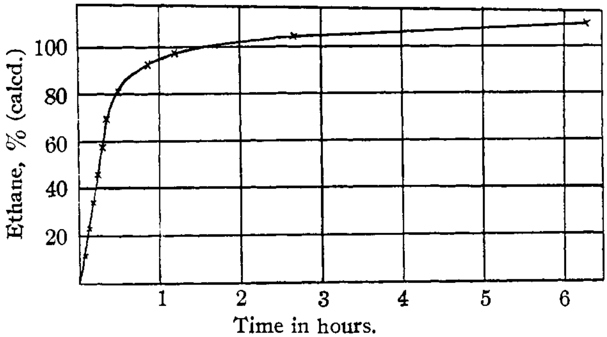

Fig. 1.—Rate of evolution of ethane from stearic acid and lead tetra-ethyl.

Calingaert reports reactions of the following type when triethyl-lead salts are heated with water: $(C_2H_5)_3PbBr \longrightarrow Pb(C_2H_5)_4 + (C_2H_5)_2PbBr_2$. In the case of the hydroxide and the acetate this was found to be true at room temperature. Freshly filtered solutions of these compounds would become cloudy in the course of an hour. This necessitated making fresh solutions of the acetate as needed.

Attempts to prepare diethyl-lead acetate and lead tetra-acetate were unsuccessful, lead acetate being obtained.

Lead tetra-ethyl reacts readily with acetyl chloride at room temperature on the addition of silica gel. A mixture of equivalent amounts of the two gave prisms on standing overnight. These proved to be triethyl-lead chloride. Benzoyl chloride reacted also; the only products that could be isolated were lead chloride and benzoic acid.

Lead tetra-ethyl and phosphorus pentachloride were mixed in carbon disulfide. A sirupy liquid was obtained from which triethyl-lead chloride was obtained by treating it with petroleum ether.

A carbon disulfide solution of lead tetra-ethyl turns dark red and later gives a black, flocculent precipitate which is insoluble in ether, alcohol or petroleum ether. It does not melt at 300°, but burns readily.

When aluminum chloride is allowed to fall on lead tetra-ethyl a violent reaction takes place with the formation of a cloud of finely divided lead. The reaction may be controlled by diluting the lead tetra-ethyl with a solvent. Benzene, chloroform and petroleum ether were used. A gas is given off during the reaction. Triethyl-lead chloride was the only compound that could be isolated.

It was hoped that the lead tetra-ethyl, or the chloride formed in the reaction, would react further with the benzene in the presence of an excess of aluminum chloride to give ethylbenzene or triethylphenyl lead. A portion of the reaction mixture was distilled. Numerous harmless explosions with the formation of clouds of finely divided lead took place, as on heating or cooling of the flask the hot vapors mixed with air. No new compounds could be isolated.

Silicon tetrachloride reacts with lead tetra-ethyl to give triethyl-lead chloride. Titanium tetrachloride is reduced by lead tetra-ethyl. When the two are mixed they react readily to give a brown, tarry substance, tinted purple by the titanium trichloride. This reaction takes place, also, in benzene solution.

Attempts were made to prepare ethers according to the supposed reaction $(C_2H_5)_3PbCl + NaOR \longrightarrow (C_2H_5)_3PbOR + NaCl$. In each case, except one, there was obtained a small quantity of an oily liquid that could not be distilled or frozen.

Solutions in absolute alcohol of triethyl-lead chloride and sodium phenylate were mixed. After a few seconds a white crystalline precipitate formed and settled. This was filtered off and found to be sodium chloride. On dilution of the alcohol with water an oily substance was thrown out.

On adding sodium *p*-nitrophenylate to an aqueous solution of triethyl-lead acetate an oil was obtained.

With sodium β-naphtholate a heavy, greenish-brown liquid separated. This would not solidify in an ice-salt mixture.

Sodium methoxide and ethoxide, also, were tried. The latter gave an oil, the former nothing.

Experimental Part

Lead Tetra-ethyl.—During the early part of this work the crude lead tetra-ethyl[9] was purified by shaking with sodium bisulfite solution, to remove unsaturated compounds, and neutralizing with sodium hydroxide. However, because of the reaction between lead tetra-ethyl and sulfur dioxide, this method was abandoned for that of Calingaert[4] who recommends repeated stirring with sulfuric acid (d., 1.4), keeping the temperature below 30°, and finally neutralizing with sodium carbonate solution.

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[9] For a generous supply of this compound our thanks are due to E. I. du Pont de Nemours and Co.

The material was then steam-distilled and dried over calcium chloride. Most of it was subjected to vacuum distillation. Fresh portions were run into the distillation flask during the distillation in order to minimize the time of heating of any portion. At 3 mm. the compound distilled at about 65°. In spite of these precautions, there was some subsequent decomposition. A dark red material (lead diethyl?) formed on the side of the bottle and needle-like crystals appeared on the bottom, although it was always kept stoppered and in the dark. However, the tetra-ethyl, when poured off, was found to be as clear and colorless as when first prepared.

Derivatives

Benzene was found to be the best solvent for purifying most of the compounds prepared. Good crystals may be obtained with dil. alcohol in some cases but the water present always causes some decomposition. However, evaporation of a solution in absolute alcohol is sometimes satisfactory.

After numerous attempts at filtration of hot solutions with the hot-water funnel and suction pump the following method was tried and found to be fairly rapid and quite efficient.

An extraction thimble is suspended in a large test-tube surrounded by a vessel of hot water. The hot solvent is poured through the thimble. The thimble is then raised and by careful manipulation the solvent may be refluxed so as to extract from the thimble most of the remaining solute. This method is especially applicable to small quantities and it has the advantages that there is no chance of a clogged funnel and no necessity to use an excess of the solvent with the consequent loss of material. There is no danger of contamination and no great loss is sustained in the filter.

Most of the compounds studied begin to decompose at their melting points, if not before. For this reason the melting point is somewhat affected by the rate of heating. As an example, the melting point of triethyl-lead propionate was found to be 141° when the temperature was raised about 5° per minute. With a rise of about 2° per minute a reading of 138.5° was obtained. In making melting-point determinations, therefore, the temperature was raised as rapidly as possible, consistent with an accurate reading of the thermometer. To avoid this error in melting-point determinations for purity a portion of the recrystallized compound was heated simultaneously with some of the original material. In most cases a temperature range is reported. The lower temperature is that at which melting began and the higher that at which a meniscus was formed. As far as possible the thermometers were totally immersed.

For the determination of lead the method of Treadwell-Hall[10] was found most satisfactory. The sample was dissolved in concd. sulfuric acid and heated to fuming, nitric acid being used as an oxidizing agent if necessary. The lead was weighed as sulfate.

To get the material in aqueous solution, as for the determination of chlorine ion in triethyl-lead chloride, the sample is dissolved first in a few

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[10] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, London, 1915, 4th English ed., vol. 2, p. 175.

drops of alcohol. On the addition of a considerable volume of water it precipitates but soon redissolves. The chlorine ion may then be precipitated as usual.

Triethyl-lead Chloride.—Of all the methods that have been proposed for preparing this compound the action of aqueous hydrochloric acid on lead tetra-ethyl is the best. In this the rate and extent of replacement of ethyl groups by chlorine are greatly affected by the temperature and the concentration. After making a number of runs in which these factors were varied the following method was found to be quite satisfactory.

A 600cc. beaker is placed in a water-bath and provided with a stirrer. In it is placed 275 cc. of concd. hydrochloric acid, to which is slowly added 75 cc. of lead tetra-ethyl from a dropping funnel. The temperature must not be allowed to go above 34°. A white, butter-like mass is formed. When all of the lead compound has been added, the temperature is maintained between 30° and 33° (no higher). After some time the mass separates into grains of the size and shape of wheat. These are bunches of minute needle crystals. The evolution of ethane is quite rapid. (If the stirrer be stopped the gas will accumulate and lift the product to the surface.) When the grains begin to break up to give a powdery precipitate the reaction is completed, although ethane will still be coming off to some extent. The chloride is filtered off, washed with water and dried on a porous plate in the dark. In one instance 109 g. was obtained; yield, 86%. Analysis of one product gave 10.74, 10.77% of chlorine; calculated, 10.75%. The compound should be prepared only as needed, for it decomposes readily even when kept dry and in the dark.

Triethyl-lead Hydroxide.—Buckton[11] prepared triethyl-lead hydroxide by heating the chloride with strong potassium hydroxide solution. The hydroxide forms a yellow oil which solidifies to a white, crystalline mass on cooling. The following is a modification of his method. Care must be taken to exclude air as far as possible because of the ease with which the carbonate is formed. The reaction is best performed in a balloon flask provided with a stirrer and closely fitting stopper.

A solution of 50 g. of triethyl-lead chloride in 35 cc. of warm benzene was stirred rapidly with an aqueous solution of 10 g. of sodium hydroxide. On cooling, the benzene layer solidified; the aqueous solution was poured off. This was followed with two additional portions of sodium hydroxide and finally water. The product was warmed with an additional 10 cc. of benzene and allowed to crystallize; yield, 35 g., or 74%.

The hydroxide recrystallized beautifully from benzene, giving slender, white needles but was never entirely free of the chloride. In one case, shaking the warm benzene solution with silver oxide was tried but the latter could not be filtered out. The product was ruined.

Triethyl-lead Acetate.—This is prepared easily and efficiently by the following method.

A mixture of 30 cc. of acetic acid and 90 cc. of lead tetra-ethyl is heated in a water-bath at 90° for about an hour, with pieces of silica gel. The solution becomes greenish at first and then sets to a white, crystalline mass of the crude acetate. The yield is practically quantitative. The product was recrystallized in small amounts from the

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[11] Buckton, *Ann.*, **112**, 226 (1859).

same portion of benzene and gave a beautiful mass of fine, white needles which kept indefinitely, in the dark; m. p., 160.4°, with decomposition. Klippel[5] reports that this compound does not melt at 100°, but at a higher temperature decomposes explosively.

Other Salts.—Several other compounds reported by Klippel were prepared in order to determine their melting points.

To the saturated solution of the acetate in water an excess of potassium cyanide was added. A heavy, white, flocculent precipitate of triethyl-lead cyanide was obtained. This was dried and recrystallized from benzene; m. p., 194°.

The benzoate prepared in the same manner melts at 127°.

With sodium tartrate no precipitate was obtained.

Triethyl-lead butyrate was prepared both by the same reaction and by heating the tetra-ethyl with the acid. It melts at 107.9–108.5° to a light brown liquid.

In an attempt to prepare diethyl-lead diacetate, 32 g. of lead tetra-ethyl was heated with 12 g. (two parts) of acetic acid. The product obtained was washed with alcohol, dissolved in water and evaporated to dryness on the water-bath. It melted to a clear liquid at 200°.

Anal. Subs., 0.7251: $PbSO_4$, 0.6706. Calcd. for $Pb(C_2H_3O_2)_2$: Pb, 63.70. Found: 63.12.

In an attempt to prepare lead tetra-acetate, 10 g. of lead tetra-ethyl, 10 g. (about five parts) of acetic acid and a small portion of silica gel were heated, first on the water-bath and finally with a free flame. Lead tetra-acetate, when added to water, gives a colloidal precipitate of lead peroxide. None was found in this product. Acetic anhydride used alone and in conjunction with potassium permanganate or a small amount of bromine failed to give the desired compound.

Salts of Inorganic Acids.—Considerable work was done in an attempt to prepare a series of triethyl-lead salts of the weak inorganic acids by double decomposition with triethyl-lead acetate as described for the cyanide. The results were disappointing. In most cases insoluble precipitates were obtained but the yields were generally very poor. Analysis usually indicated mixtures.

To a saturated aqueous solution of 5 g. of triethyl-lead acetate was added an excess of potassium chromate solution. A heavy, flocculent precipitate of bright yellow color was formed. This was filtered off, washed with water, alcohol and ether and dried; yield, 4 g. No solvent was found for it. It burns much like gunpowder and when heated rapidly explodes at about 190°. It turns dark in direct sunlight. Chromium and lead interfered with each other in the analysis. Five determinations of chromium gave values from 8 to 12%; calcd. for $[(C_2H_5)_3Pb]_2CrO_4$: Cr, 7.38%. Three determinations of lead ranged from 53.3 to 55.5%; calcd. for $[(C_2H_5)_3Pb]_2CrO_4$: Pb, 58.9%. Possibly the substance is a mixture of triethyl-lead chromate and triethyl-lead dichromate.

Sodium dichromate, similarly, gave an orange precipitate resembling in properties the preceding substance, 4.6 g. from 5 g. of the acetate. Washing with alcohol was omitted as this seemed to convert it to the yellow compound. Five determinations of chromium failed to give concordant results. However, for lead the values 52.5 and 50.7% were obtained; calcd. for $[(C_2H_5)_3Pb]_2Cr_2O_7$: Pb, 51.6%.

From 5 g. of the acetate and an excess of potassium ferrocyanide, 4.5 g. of a pale buff precipitate was obtained. This, being insoluble, was washed as the previous substances. It does not melt but decomposes above 200°.

Anal. Calcd. for $[(C_2H_5)_3Pb]_4Fe(CN)_6$: Fe, 4.02; Pb, 59.66. Found: Fe, 3.04, 3.37; Pb, 58.34, 58.32.

From 5 g. of the acetate and an excess of potassium ferricyanide 3.8 g. of a brick-red precipitate resembling the previous substance was obtained.

Anal. Calcd. for $[(C_2H_5)_3Pb]_3Fe(CN)_6$: Fe, 5.10; Pb, 56.77. Found: Fe, 3.55, 3.60; Pb, 55.74, 56.45.

Salts of the Fatty Acids.—These were made by the method given above for triethyl-lead acetate. The details are given in Table I and II.

TABLE I

PREPARATION AND ANALYSES OF TRIETHYL-LEAD SALTS

	$Pb(C_2H_5)_4$, g.	Acid, g.	M. p., °C.	Yield, g.	Anal. for Pb Calcd., %	Anal. for Pb Found, %		
Propionate	24	5	141–142	...	56.40	56.98	57.10	56.11
*iso*Butyrate	21	8	119.4–121.8	...	54.32	53.95		
Valerate[a]	...	...	115.6–117.0	...	52.40	52.48		
*iso*Valerate	15.8	5	119.4–119.8	...	52.40	52.05	52.01	52.04
Caproate	20	7.2	94.7–95.8	...	50.60	49.97	50.64	
Heptoate	12.5	5	90.0–90.8	8.4	48.93	47.70	48.18	48.38
Caprylate	11.2	5	85.0–87.5	4.3	47.36	47.82	46.42	
Pelargonate	10.3	5	88.0–90.0	8	45.89	44.42	44.94	44.69

[a] By precipitation from the acetate.

TABLE II

PROPERTIES AND ANALYSES OF TRIETHYL-LEAD SALTS OF HALOGEN-ACETIC ACIDS

	M. p., °C.	Anal. for Pb Calcd., %	Anal. for Pb Found, %		Anal. for halogen Calcd., %	Anal. for halogen Found, %
Chloro-acetate	146–146.5	53.43	53.18		9.14	9.57
Dichloro-acetate	113.5–114.5	49.07	49.58		16.80	16.03
Trichloro-acetate	135.5–138.6	45.37	46.08	45.75	23.29	23.34
Bromo-acetate	121	47.93	47.62		...	...
Dibromo-acetate	98.6–101.8	40.53	40.14		31.27	30.17

Summary

The methods of preparing triethyl-lead chloride, hydroxide and acetate have been improved. A number of salts of triethyl-lead have been made by double decomposition from the acetate. A number of other salts of this base have been obtained by the action of organic acids on lead tetraethyl. Silica gel has been found to be an efficient catalyst for this reaction.

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