were determined with an isoteniscope. The normal boiling points, the molar heats of vaporization calculated by the Clausius-Clapeyron equation, and Trouton constants were determined from these values and are given in Table II.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, ETHYL CORP.]

Bimetallic Ethyl Compounds as Reagents for the Synthesis of Tetraethyllead from Lead Metal

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Received October 10, 1960

The ethylation of lead metal by reaction with bimetallic ethyl compounds such as sodium tetraethylaluminum and an ethyl halide to produce tetraethyllead has been investigated. Tetraethyllead was obtained using sodium tetraethylaluminum, sodium tetraethylboron, sodium triethylzinc, sodium triethylaluminum fluoride, sodium triethylaluminum methoxide, and sodium ethylaluminum triethoxide as the bimetallic ethyl compounds. Optimum conditions for the reaction of lead metal with sodium tetraethylaluminum and ethyl chloride were explored.

The synthesis of tetraalkyllead by the reaction of lead metal and an alkyl halide with the alkyl derivative of a reactive metal, such as lithium, magnesium, or zinc, has been reported.[1,2] Calingaert and Shapiro also found in unpublished work that the yields of tetraalkyllead are very low when an alkylsodium compound is used. They attributed the poor yields from the alkylsodium compounds to their insolubility in the reaction media and to the tendency of the alkyl halide to alkylate the alkylsodium compound.

$$\mathrm{RNa} + \mathrm{R'Cl} \longrightarrow \mathrm{RR'} + \mathrm{NaCl}$$

More recently, it has been discovered in these laboratories that bimetallic alkyl compounds containing sodium, such as sodium tetraethylaluminum, will react with lead metal and alkyl halides to produce tetraalkyllead in high yield. The superiority of these compounds is attributed primarily metal to a reduction in the reactivity of the alkyl compounds with the alkyl halide and also to their increased solubilities.

A characteristic of the reactions of these bimetallic alkyl compounds is the reaction of one alkyl group to produce tetraalkyllead, sodium halide, and the alkyl, alkoxy, or halide compound of the second metal in the bimetallic alkyl compound. For example, sodium tetraethylaluminum reacts with lead metal and ethyl chloride to produce sodium chloride, tetraethyllead, and triethylaluminum, while sodium triethylaluminum fluoride reacts to produce sodium chloride, tetraethyllead, and diethylaluminum fluoride.

$$2\mathrm{NaAl(C_2H_5)_4} + \mathrm{Pb} + 2\mathrm{C_2H_5Cl} \longrightarrow (\mathrm{C_2H_5})_4\mathrm{Pb} + 2\mathrm{NaCl} + 2(\mathrm{C_2H_5})_3\mathrm{Al}$$

$$2\mathrm{Na(C_2H_5)_3AlF} + \mathrm{Pb} + 2\mathrm{C_2H_5Cl} \longrightarrow (\mathrm{C_2H_5})_4\mathrm{Pb} + 2\mathrm{NaCl} + 2(\mathrm{C_2H_5})_2\mathrm{AlF}$$

This paper reports the results of an investigation of the synthesis of tetraethyllead by the reaction of lead metal and ethyl halides with bimetallic ethyl compounds. Sodium tetraethylaluminum was investigated the most extensively. Sodium tetraethylboron, sodium triethylaluminum fluoride, sodium triethylaluminum methoxide, sodium ethylaluminum triethoxide, and sodium triethylzinc also were found to be reactive but the yields of tetraethyllead were not so high as those obtained with sodium tetraethylaluminum. However, no effort was made with these last materials to define the conditions required for maximum yields. The fact that all these materials react attests to the general reactivity of such bimetallic alkyl compounds. The results are summarized in Table I.

Sodium tetraethylaluminum was found to react readily with lead metal and all the ethyl halides investigated, although the yield of tetraethyllead was less than quantitative. The limitation on yields is attributable to a deactivation of the lead metal surfaces by agglomeration of the finely divided lead metal into larger particles. A highly reactive lead metal surface is advantageous for higher yields, as shown by the relatively low yields which were obtained when lead shot (1%) and commercial lead powder (17%) were used. For this reason, the lead metal employed in the remaining experiments was synthesized by the reaction of sodium-lead alloy with ethyl chloride.

$$4\mathrm{NaPb} + 4\mathrm{C_2H_5Cl} \longrightarrow (\mathrm{C_2H_5})_4\mathrm{Pb} + 3\mathrm{Pb} + 4\mathrm{NaCl}$$

The lead metal produced in this manner is highly reactive and is pyrophoric under certain conditions. Higher yields of tetraethyllead could be obtained by using an excess of sodium tetraethylaluminum, since the excess promoted complete reaction before the lead metal could become deactivated by agglomeration.

Diethyl sulfate was found to react readily with sodium tetraethylaluminum and lead metal but

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(1) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **72**, 1760 (1950).

(2) G. Calingaert and H. Shapiro, U. S. Patents **2,535,193** (1950), **2,558,207** (1951), and **2,562,856** (1951).

TABLE I

YIELDS OF TETRAETHYLLEAD FROM REACTION OF BIMETALLIC ALKYLS WITH LEAD METAL AND ETHYL HALIDES[a]

Alkyl Metal Compound	Alkyl Halide	Solvent[b]	Reaction Temp.	TEL Yield,[c] %	Remarks
A. EFFECT OF PHYSICAL STATE OF LEAD, EXCESS ALKYLMETAL COMPOUND, AND ALKYL HALIDE					
$NaAl(C_2H_5)_4$	C_2H_5Cl	None	80–85	1.3	Used $^1/_{16}$″ lead shot
$NaAl(C_2H_5)_4$	C_2H_5Cl	None	80–85	17.3	Used commercial lead powder
$NaAl(C_2H_5)_4$	C_2H_5Cl	None	80–85	52.8, 42.8	
$NaAl(C_2H_5)_4$	C_2H_5Cl	None	80–85	67.2	Used 50% excess $NaAl(C_2H_5)_4$
$NaAl(C_2H_5)_4$	C_2H_5Cl	None	80–85	72.5	Used 100% excess $NaAl(C_2H_5)_4$
$NaAl(C_2H_5)_4$	C_2H_5Br	None	70–75	64.1	
$NaAl(C_2H_5)_4$	$(C_2H_5)_2SO_4$	Diethyl ether	75–110	21.7[d]	
B. EFFECT OF TEMPERATURE					
$NaAl(C_2H_5)_4$	C_2H_5Cl	Hexane	50–55	34.3, 41.9	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Hexane	60–65	44.0	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Hexane	70–75	54.5, 57.8	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Hexane	90–95	49.1, 55.3	
C. EFFECT OF SOLVENTS					
$NaAl(C_2H_5)_4$	C_2H_5Cl	Benzene	70–75	36.0	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Mesitylene	70–75	34.4	
$NaAl(C_2H_5)_4$	C_2H_5Cl	DME	70–75	36.7	
$NaAl(C_2H_5)_4$	C_2H_5Cl	ETHFE	70–75	52.2	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Anisole	70–75	56.8	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Diphenyl ether	70–75	34.9	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Methylal	70–75	61.5	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Pyridine	70–75	76.4	
$NaAl(C_2H_5)_4$	C_2H_5Cl	THF	70–75	73.8	
$NaAl(C_2H_5)_4$	C_2H_5Cl	THP	70–80	73.8	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Diisopropyl ether	75–80	65.9, 64.5	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Di-*n*-propyl ether	75–80	86.6	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Diethyl ether	70–75	80.0, 72.8	
$NaAl(C_2H_5)_4$	C_2H_5Cl	Diethyl ether	90–95	84.7	
$NaAl(C_2H_5)_4$	C_2H_5Br	Diethyl ether	70–75	87.2	
$NaAl(C_2H_5)_4$	C_2H_5I	Diethyl ether	70–75	79.2	Used 8% excess lead metal
D. YIELDS WITH OTHER BIMETALLIC ALKYL COMPOUNDS					
$NaB(C_2H_5)_4$	C_2H_5Cl	Diethyl ether	65–75	58.2	
$NaB(C_2H_5)_4$	C_2H_5Cl	Hexane	70–75	51.6	
$Na(C_2H_5)_3AlF$	C_2H_5Cl	Hexane	65–70	27.5	Used 5% excess lead metal
$Na(C_2H_5)_3AlOCH_3$	C_2H_5Cl	Diethyl ether	70–75	46.7	Used 15% excess lead metal
$NaC_2H_5Al(OC_2H_5)_3$	C_2H_5Cl	None	70–75	14, 26	Used 60% excess lead metal
$NaZn(C_2H_5)_3$	C_2H_5Cl	None	70–75	15	Used 60% excess lead metal
$NaAl(C_2H_5)_4 + NaOCH_2$	C_2H_5Cl	Diethyl ether	70–80	132	Used 300% excess lead metal + 3.7 moles $NaOCH_3$ per mole $NaAl(C_2H_5)_4$

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[a] All reactions except the first two employed a reactive lead powder synthesized as a by-product of the $NaPb-C_2H_5Cl$ reaction. Except where noted otherwise reactions were conducted for 3 hours and employed a 10% excess of bimetallic alkyl. [b] DME = 1,2-dimethoxyethane; ETHFE = ethyl tetrahydrofurfuryl ether, provided by Quaker Oats Co.; THF = tetrahydrofuran; THP = tetrahydropyran. [c] The tetraethyllead yields are based on weight of lead metal charged, except where excess lead was used, in which case yields are based on bimetallic alkyl lead compounds. The tetraethyllead yields reported include tetraethyllead actually produced in the reaction plus that realized by conversion of any hexaethyldilead to tetraethyllead and lead metal (see text). [d] A separate reaction of $NaAl(C_2H_5)_4$ and $(C_2H_5)_2SO_4$ in benzene was very exothermic and evolved 69% of the theoretical amount of butane expected from the reaction

$$NaAl(C_2H_5)_4 + (C_2H_5)_2SO_4 \longrightarrow C_4H_{10} + NaC_2H_5SO_4 + (C_2H_5)_3Al$$

the yield of tetraethyllead was lower than expected. The low yield was caused by the direct reaction of sodium tetraethylaluminum with diethyl sulfate to evolve butane, which thereby reduced the quantities of these reagents available for tetraethyllead formation.

Various solvents were tested in an effort to improve the yields. Several ethers proved to be excellent solvents, and yields of 80% or higher were obtained. Initially, the solvent activity of the ethers was attributed to their solubilization of the sodium tetraethylaluminum. This, however, is not the sole explanation, for a variation in the effectiveness of the ethers to improve the yields was found. The best yields were obtained with the low molecular weight aliphatic or cyclic ethers, such as diethyl ether, tetrahydrofuran, and tetrahydropyran. Aromatic ethers were at best only slightly effective. Spatial configuration of the solvent appears to be an important factor. This is strikingly demonstrated by a comparison of the effectiveness of di-*n*-propyl and diisopropyl ethers.

Although di-*n*-propyl ether was a very effective solvent (86.6% yield), diisopropyl ether produced only slightly higher yields (65.2%) than when no solvent or an inert solvent (hexane) was employed.

A significant increase in yield was obtained with pyridine as the solvent, but the product solution was dark red in color, suggesting that the pyridine may have participated in a side reaction.

Although ethers promote the formation of tetraethyllead, they also promote the formation of hexaethyldilead as a reaction by-product. Hexaethyldilead is a by-product of many reactions employed for the synthesis of tetraethyllead. Under certain conditions it is formed as a by-product in the commercial synthesis of tetraethyllead by reaction of ethyl chloride and sodium lead alloy.[3,4] Its formation generally is favored by mild reaction conditions. In the laboratory, it is synthesized conventionally by the reaction of the ethyl Griguard reagent with lead dichloride at 0–5°.[5] Therefore, its presence in this system is not surprising. Oddly, hexaethyldilead formation occurs primarily with the low molecular weight aliphatic and cyclic ethers. Its formation can be controlled by employing a minimum quantity of ether and increasing the reaction temperature. Also, any hexaethyldilead that is produced in the reaction can be readily converted to tetraethyllead by catalytic methods[3,4,6] according to the equation:

$$2(C_2H_5)_3PbPb(C_2H_5)_3 \longrightarrow 3(C_2H_5)_4Pb + Pb$$

The yields reported in Table I are based on the conversion of any hexaethyldilead to tetraethyllead by this reaction.

The other bimetallic ethyl compounds appeared to behave identically to sodium tetraethylaluminum, although the yields were somewhat lower. Sodium tetraethylboron was unique in that hexaethyldilead was obtained along with the tetraethyllead even in the absence of an ether solvent.

The reactivity of sodium triethylaluminum fluoride and methoxide suggested the possibility of a unique method of utilizing more than one ethyl group of the sodium tetraethylaluminum by conducting the reaction in the presence of sodium methoxide, which would produce sodium triethylaluminum methoxide *in situ* by reaction with the by-product triethylaluminum:

$$2NaAl(C_2H_5)_4 + Pb + 2C_2H_5Cl \longrightarrow$$
$$(C_2H_5)_4Pb + 2NaCl + 2(C_2H_5)_3\,Al \xrightarrow{2\ NaOCH_3} 2Na(C_2H_5)_3AlOCH_3$$

$$2Na(C_2H_5)_3AlOCH_3 + Pb + 2C_2H_5Cl \longrightarrow$$
$$(C_2H_5)_4Pb + 2NaCl + 2(C_2H_5)_2AlOCH_3$$

In one experiment, a 132% yield, based on the utilization of one ethyl group of the sodium tetraethylaluminum, was obtained when sodium methoxide was present.

In conclusion, this investigation has shown that bimetallic ethyl compounds containing sodium react very readily with lead metal and an ethyl halide to produce tetraethyllead. Excellent yields are obtained at reaction temperatures of 70–90° in a low molecular weight ether solvent. At temperatures below 70° the yields are lower, probably because the rate is slower. Above 90° the yields are reduced somewhat by thermal decomposition of tetraethyllead. The activity of these bimetallic ethyl compounds in this system is indicative of their high reactivity in general.

EXPERIMENTAL

Reagents. Unless otherwise specified, all reagents were Fisher Reagent Grade chemicals and were used without further purification. 1,2-Dimethoxyethane was purchased from Ansul Chemical Co. and was purified by distillation from lithium aluminum hydride. Tetrahydrofuran was purified in an identical manner. The sample of ethyl tetrahydrofurfuryl ether was provided by the Quaker Oats Co. and was used without further purification.

Sodium tetraethylaluminum was synthesized from triethylaluminum and sodium. A sodium dispersion was prepared by the method described by Whaley[7] from 27.0 g. of sodium pellets in 500 ml. of toluene. To the hot dispersion was added, dropwise, 150 ml. of triethylaluminum (Ethyl Corp.) and the mixture was heated for 2 hr. at 105–110°. The solids then were permitted to settle, after which the solution was transferred to an evacuated flask. Care was taken to assure that no solids were transferred. The colorless needles which separated from the solution on cooling were separated by filtration with suction in a dry nitrogen atmosphere, washed with toluene, and dried *in vacuo.* The product melted at 123–124° (uncorrected).[8]

Sodium tetraethylboron was prepared by J. B. Honeycutt and J. M. Riddle of this laboratory by the reaction of sodium hydride with a 5% excess of triethylboron in hexane solution at 150° and under 1000 p.s.i.g. ethylene pressure. Elemental analysis indicated a purity of 98%.[9]

Sodium triethylzinc was prepared *in situ* by dissolving diethylzinc and sodium hydride in 1,2-dimethoxyethane followed by reaction with ethylene at 80° and 500 p.s.i.g. ethylene pressure for 2 hr. The diethylzinc was prepared by reaction of zinc metal with ethyl iodide.[10] The yield of sodium triethylzinc was determined by mass spectrometric analysis of the gases evolved on hydrolysis of an aliquot of the filtered product solution. The product was allowed to react with lead metal and ethyl chloride in the ether solution.

Sodium ethylaluminum triethoxide was prepared by the addition of diethylmercury[11] to sodium sand in a diethyl ether solution of Eastman aluminum ethoxide (converted to the *alpha* form). The *alpha* modification was prepared by

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(3) T. W. Gittins and E. L. Mattison, U. S. Patent **2,763,673** (1956).

(4) T. W. McDyer and R. D. Closson, U. S. Patent **2,571,987** (1951).

(5) G. Calingaert and H. Soroos, *J. Org. Chem.*, **2**, 535 (1938).

(6) I. T. Krohn and H. Shapiro, U. S. Patent **2,555,891** (1951).

(7) T. P. Whaley in *Inorganic Syntheses*, McGraw-Hill Book Co., Inc., New York, N. Y. (1957), Vol. V, p. 6.

(8) E. B. Baker and H. H. Sisler, *J. Am. Chem. Soc.*, **75**, 5193 (1953), report m.p. 125°.

(9) J. B. Honeycutt and J. M. Riddle, *J. Am. Chem. Soc.*, **83**, 369 (1961).

(10) L. M. Dennis and F. E. Hance, *J. Am. Chem. Soc.*, **47**, 370 (1925).

(11) H. Gilman and R. E. Brown, *J. Am. Chem. Soc.*, **52**, 3314 (1930).

the method of Child and Adkins.[12] The addition of diethylmercury was made at 10–15°, after which the reaction mixture was allowed to warm to room temperature and the reaction continued for 2 hr. Excess sodium sand and diethylmercury were employed. The ether solution was filtered and the ether evaporated under reduced pressure. The product (m.p. 80-81° uncorrected) was recrystallized from cold hexane.

Anal. Calcd. for $C_8H_{20}O_3AlNa$: C, 44.86; H, 9.41 Al, 12.60. Found: C, 45.13, 45.17; H, 9.46, 9.48; Al, 12.67.

Sodium triethylaluminum fluoride was prepared by the addition of a 10% excess of triethylaluminum to a suspension of sodium fluoride (dried by azeotropic distillation of any water with toluene) in refluxing xylene.The resultant solution was heated at reflux for 2 hr. and filtered with suction in a dry nitrogen atmosphere. The xylene was evaporated at elevated temperature under reduced pressure until a viscous solution remained. Petroleum ether (b.p. 30–60°) was added to the concentrated solution to yield a homogeneous solution. Evaporation of a portion of the petroleum ether under reduced pressure produced sufficient cooling to effect crystallization of the desired product as fine white crystals. The product melted at 68–69° (uncorrected). The yield was 59%.

Anal. Calcd. for $C_6H_{15}FAlNa$: Al, 17.28. Found: Al, 16.8, 17.0.

Sodium triethylaluminum methoxide was prepared by the addition of triethylaluminum to a slurry of 5% excess sodium methoxide in xylene. The resultant mixture was heated at reflux for 1 hr. and then filtered under suction in a dry nitrogen atmosphere. A small amount of gelatinous solids was present in the mixture and made the filtration proceed very slowly. The xylene was evaporated under reduced pressure to the point of crystallization. Petroleum ether was added to the concentrated liquor to precipitate fine white crystals. The product melted at 102–103°. The yield was 36%.

Anal. Calcd. for $C_7H_{18}OAlNa$: Al, 16.05. Found: Al, 16.57, 16.58.

Reaction Procedure. The reactions were conducted in a stainless steel reactor of two inches inner diameter and 140 ml. capacity. The flanged reactor head was made of 1/2-inch mild steel and was fitted with threaded openings for an anchor-type stirrer, an alkyl halide feed tube, a vent line teed to a recording manometer, a rupture disk rated at 125 p.s.i., and a thermowell containing an iron-constantan thermocouple. A Teflon gasket was used to effect a pressure seal at the head. The reactor was heated by immersion in a constant temperature water bath. All connections were made with standard 1/4" or 1/8" copper fittings and tubing.

The active lead metal used in all but two of the experiments (Table I) was prepared as a by-product of the sodium-lead alloy-ethyl chloride reaction. In a typical experiment 15 g. of sodium-lead alloy (Ethyl Corp.) was charged to the reactor and the reactor was heated to 80°. Six times the theoretical amount (25 g.) of ethyl chloride (also from Ethyl Corp.) was added slowly to the alloy over a 45-min. period by forcing the ethyl chloride under 80 p.s.i.g. nitrogen pressure from a graduated vessel. The mixture was heated at 80–85° and stirred for an additional 2 hr. After the reactor was cooled and vented, it was opened and discharged. The residual ethyl chloride and tetraethyllead were washed from the solids with hexane and the solids dried in a stream of nitrogen. The solids, containing lead metal and by-product sodium chloride, were charged to the reactor together with the desired quantity of bimetallic alkyl compound and solvent, and the reactor was then sealed and connected to the various feed and vent lines. The reactor was heated to the desired temperature and stirring was begun. A total of 36–40 g. of ethyl chloride was fed to the reactor over a 20-min. period, after which the reactants were stirred and heated an additional 2.7 hr. The reactor was cooled, vented, and discharged into an open beaker. The excess bimetallic alkyl compound and by-product alkylmetal compound were destroyed by addition of isopropyl alcohol, and the by-product metal values were removed from the organolead product and solvent by extraction with aqueous caustic. The organic phase was transferred to a volumetric flask and the solution analyzed for tetraethyllead by the dithizone or iodometric titration procedures (see Analytical Methods).

In one experiment in which sodium tetraethylaluminum was used as the bimetallic alkyl compound the reaction mixture was filtered directly, the solvent removed under reduced pressure, and the concentrated product analyzed by infrared spectrophotometry to demonstrate the presence of triethylaluminum as a reaction by-product. The infrared spectrum of the product solution indicated the presence of both triethylaluminum and tetraethyllead.

All of the above procedures were accomplished under a nitrogen atmosphere.

Analytical methods. Yields were determined by analysis of the product solution for organolead content by the dithizone[13] and iodometric[14] methods. Both methods were used to permit determination of hexaethyldilead. When hexaethyldilead is present, the iodometric titration yields a low value for soluble lead content, since 1 mole of iodine is equivalent to 1 mole of hexaethyldilead or 2 atoms of lead, whereas 1 mole of iodine is equivalent to 1 mole of tetraethyllead or 1 atom of lead. The hexaethyldilead and tetraethyllead content can be calculated by solving simultaneous equations:

$$(C_2H_5)_4Pb + I_2 \longrightarrow (C_2H_5)_3PbI + C_2H_5I$$

$$(C_2H_5)_3Pb\text{—}Pb(C_2H_5)_3 + I_2 \longrightarrow 2(C_2H_5)_3PbI$$

The bimetallic alkyl compounds were analyzed for aluminum by slow hydrolysis of a weighed sample and titration of the aluminum content with excess ethylenediaminetetraacetic acid. The excess ethylenediaminetetraacetic acid was backtitrated with ferric chloride solution in the presence of salicylic acid indicator.

Acknowledgment. The authors are indebted to Dr. R. P. Curry for the infrared analyses, to Mr. J. B. Chidester for the mass spectrometer analyses, and to Messrs. R. Ashby and S. R. Henderson for the chemical analyses.

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[12] W. C. Child and H. Adkins, *J. Am. Chem. Soc.*, **45**, 3013 (1923).

[13] M. E. Griffing, A. Rozek, L. J. Snyder, and S. R. Henderson, *Anal. Chem.*, **29**, 190 (1957).

[14] R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, Interscience Encyclopedia, Inc., New York, N. Y. (1952), Vol. VIII, p. 279.