tion was filtered and the filtrate cooled and saturated with carbon dioxide. The solid material which separated was collected, washed with absolute alcohol and ether, and dried *in vacuo* to give 8.3 g. (40% yield from I) of pure title compound, m.p. 232–233°.

*Anal.* Calcd. for $C_7H_{13}ClHgN_4O_3$: C, 19.23; H, 3.00; Hg, 45.88; N, 12.81. Found: C, 19.0; H, 3.3; Hg, 45.1; N, 13.0.

*1,6-Diazabicyclo[4.4.0]-8-decene-2,5-dione* (VIII). Succinic anhydride (10 g., 0.1 mole) was added to 8.4 g. (0.1 mole) of 1,2,3,6-tetrahydropyridazine[10] with external cooling to control the reaction. The mixture was then heated at 250–260° until gas evolution ceased and cooled to give a crystalline solid. This solid was recrystallized from 95% ethanol to give 10 g. (60% yield) of massive prisms, m.p. 190–200°. Two further recrystallizations from ethanol, one from water, and one from ethanol gave 6.1 g. of material with melting point 196–200° (37% yield).

*Anal.* Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.8; H, 6.1; N, 16.8.

*8-Acetoxymercuri-9-methoxy-1,6-diazabicyclo[4.4.0]decane-2,5-dione* (IXa). To a solution of 10.6 g. (0.033 mole) of mercuric acetate in 100 ml. of hot methanol were added 4 drops of concd. nitric acid and a solution of 5.5 g. (0.033 mole) of 1,6-diazabicyclo[4.4.0]-8-decene-2,5-dione (VIII) in 110 ml. of hot methanol. The resulting solution was heated under reflux for 3 hr. and allowed to stand overnight. Crystalline solid precipitated. The mixture was chilled and filtered to give 11.1 g. A single recrystallization of this product afforded 9.2 g. (61% yield) of material which melted at 198° dec.

*Anal.* Calcd. for $C_{11}H_{16}HgN_2O_5$: Hg, 43.91; N, 6.13. Found: Hg, 43.4; N, 6.2.

*8-Chloromercuri-9-methoxy-1,6-diazabicyclo[4.4.0]decane-2,5-dione* (IXb). A mixture of 6.65 g. (0.04 mole) of 1,6-diazabicyclo[4.4.0]-8-decene-2,5-dione (VIII), 12.75 g. (0.04 mole) of mercuric acetate, 250 ml. of methanol and 4 drops of nitric acid was heated under reflux for 5 hr. The reaction mixture was filtered to remove suspended impurities and the filtrate was treated with 15 ml. of 25% aqueous sodium chloride solution. Chilling the mixture in an ice bath caused precipitation of 14.5 g. of the chloromercuri compound. Recrystallization of the product by warming it to 97° with a mixture of 200 ml. of water and 175 ml. of dimethylformamide and cooling afforded 13.77 g. (80% yield) of white prisms which softened at 240° and decomposed at 251°.

*Anal.* Calcd. for $C_9H_{13}ClHgN_2O_3$: C, 24.94; H, 3.02; Hg, 46.30. Found: C, 25.3; H, 3.2; Hg, 45.8.

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[CONTRIBUTION FROM THE ETHYL CORPORATION]

# Synthesis and Isolation of Vinyllithium. Preparation from Lithium and Heavy Metal Vinyl Compounds

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Vinyllithium was prepared by the metathetical exchange reaction between phenyllithium and tetravinyllead in ether. Vinyllithium was also prepared and isolated from the metal exchange reactions between lithium and tetravinyllead or tetravinyltin in ether solvent. Vinylation with the isolated vinyllithium from the lithium-tetravinyllead reaction was demonstrated by conversion of tributyltin chloride to tributylvinyltin.

Lithium alkyls have been isolated and the properties of these materials have long been well known,[3] but the isolation and characterization of vinyllithium has not previously been described. Isobutenyllithium has been prepared by reaction of the alkenyl halide with lithium in diethyl ether or petroleum ether[4] but analogous attempts to prepare vinyllithium were unsuccessful. Although a reaction has been reported to occur between lithium and vinyl chloride in tetrahydrofuran,[5] vinyllithium was not claimed as a product. Vinylpotassium was prepared from potassium-sodium alloy and vinyl chloride in tetrahydrofuran[5] as well as from the exchange between amylsodium with ethylene in the presence of sodium isopropoxide.[6] Vinyllithium was first prepared as an ether solution by the reaction between tetravinyltin and phenyllithium in ether.[7] The vinyllithium, however, was not isolated from this solution, which was contaminated with lithium bromide originating from the preparation of the starting material, phenyllithium.

Another approach which can be taken for the preparation of vinyllithium is that of the cleavage of a heavy metal vinyl compound with lithium. It was reported that reaction between tetraethyllead and sodium in liquid ammonia results in the cleavage of just one group from the lead alkyl, yielding triethyllead sodium.[8] An attempt was made to obtain cleavage of all the alkyl groups from tetraalkyllead compounds by reaction with sodium in gasoline to yield lead and sodium alkyls.[3] Although lead deposited in these reactions, no sodium alkyls were isolated.

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Both the exchange and displacement reactions have been used:

$$Pb(CH{=}CH_2)_4 + 4\ C_6H_5Li \longrightarrow 4\ LiCH{=}CH_2 + Pb(C_6H_5)_4$$

$$M(CH{=}CH_2)_4 + 4\ Li \longrightarrow 4\ LiCH{=}CH_2 + M$$

(M=Pb or Sn)

It has been found that the recently prepared compound, tetravinyllead,[9] like tetravinyltin, also undergoes the metathetical exchange reaction with phenyllithium in ether to yield a solution of vinyllithium. In this case, tetraphenyllead is precipitated. Isolation of vinyllithium from the solution is difficult, however, because of the presence of lithium bromide carried over from the phenyllithium preparation.

It has been found, moreover, that vinyllithium can be prepared from tetravinyllead by metal exchange reaction with lithium. In this reaction all of the vinyl groups are cleaved from the tetravinyllead. Tetravinyltin likewise will yield vinyllithium by metal exchange reaction with lithium.

The problem of isolation of vinyllithium from the metathetical reaction has been resolved by the discovery of this new metal exchange reaction which affords an easy isolation of vinyllithium. The only by-product, lead or tin, is separated by filtration. The filtrate is evaporated and vinyllithium is isolated as a fine white powder after washing with petroleum ether to remove impurities soluble in this solvent, such as tetravinyllead or tetravinyltin. In order to obtain a pure product, the isolation steps should be done quickly.

Some of the lower lithium alkyls, in contrast to the sodium compounds, are crystallizable and, except for the difficultly soluble methyllithium, are soluble in petroleum ether and benzene.[3] Vinyllithium differs from ethyllithium, which crystallizes from benzene and melts at 95°, in that it is insoluble in petroleum ether or benzene and does not melt but decomposes on heating. Ethyllithium and vinyllithium differ also in their reactivity toward ether. Vinyllithium forms fairly stable solutions in ether while ethyllithium, like the sodium alkyls, decomposes quickly in ether. On hydrolysis vinyllithium liberates ethylene and traces of ethane or butane.

When freshly prepared, vinyllithium is violently pyrophoric, but when the isolated solid is allowed to stand under nitrogen at room temperature or in a deep freeze at $-26°$, its activity decreases in a short time. On storage over longer periods it becomes slow to burn on exposure to air. This decreased reactivity is reflected by corresponding changes in the successive infrared spectra of the isolated solid. The vinyl group of vinyllithium is characterized by absorption at 6.48, 7.25, 9.35, and 10.40 $\mu$. After storage for one week, there appeared to be a decrease in the $M{-}CH{=}CH_2$ structure in the infrared so that a decrease occurred in the strength of the peaks for $CH_2$ in-plane deformation (7.25 $\mu$), CH out-of-plane deformation (9.35 $\mu$), $CH_2$ out-of-plane deformation (10.40 $\mu$), and C=C stretching of a vinyl group attached to an active metal (6.48 $\mu$). An increase occurred in the strength of the peak for C=C stretching (6.28 $\mu$), probably representing a vinyl group no longer adjacent to an active metal. This may indicate that vinyllithium was undergoing a slow polymerization.

In order to test whether the vinyllithium had undergone any physical or chemical change during the isolation of the material in its solid state, this solid was used in a vinylation reaction. It was found that solid vinyllithium would redissolve completely in ether, if dissolved immediately after isolation, and that it converted tributyltin chloride to tributylvinyltin in 85% yield. In conclusion, the isolation of vinyllithium as a solid does not appear to change its solubility nor its reactivity as a vinylating agent but these properties are reduced on storage over several hours under an inert atmosphere.

## EXPERIMENTAL[10]

*Vinyllithium from tetravinyllead and phenyllithium.* Phenyllithium was prepared from 6 g. of lithium (0.86 g.-atom) and 62.8 g. of bromobenzene (0.4 mole) according to the procedure of Gilman.[11] A portion of this solution was titrated to determine the exact concentration of phenyllithium (1.092*N*) in the ether solution.

Phenyllithium (0.05 mole) in 45.8 ml. of ether solution was added to 3.92 g. of tetravinyllead (0.0125 mole) prepared by an established procedure.[8] There appeared to be a 2-min. induction period after which tetraphenyllead suddenly precipitated. The white solid was collected by filtration and shown to be tetraphenyllead by melting point techniques, m.p. 228–229°, mixture m.p. with an authentic sample of tetraphenyllead 229.5–230°. The tetraphenyllead weighed 5.87 g., corresponding to a 91.2% yield.

The filtrate was diluted to 100 ml. and a 20-ml. aliquot was taken for gas evolution. This aliquot was evaporated to dryness at room temperature, leaving a white solid which was hydrolyzed to give 0.41 mmole of gas. Analysis of this gas by mass spectrophotometry showed it to be ethylene with traces of some higher molecular weight compounds, possibly butanes.

Another portion of the filtrate was evaporated. The presence of the vinyl group was confirmed by infrared examination of this solid on a potassium bromide disk, giving an absorption peak at 6.4 $\mu$.

*Preparation and isolation of vinyllithium from the reaction of tetravinyllead and lithium.* Lithium (2.20 g., 100% excess) was hammered to leaf under argon, cut into small pieces, and introduced into a creased flask fitted with a condenser and a high speed dispersion stirrer. Ether (36 ml.) dried over sodium, 0.002 g. of benzophenone as catalyst, and 12.4 g. of tetravinyllead were added to the flask. The mixture was stirred for 2 hr. After 10 min. the solution turned black and began boiling vigorously. The refluxing stopped after 1 hr.

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20 min. After the reaction was complete a fine black powder containing metallic lead settled at the bottom of the flask, leaving no lithium floating. Filtration in a dry box gave a light yellow solution. The ether was removed by vacuum, leaving a solid. The solid was washed quickly with petroleum ether, and 4.8 g. of pale white vinyllithium (90% yield) was collected on a filter. This solid was violently pyrophoric in air, evolved ethylene on hydrolysis, and was shown to contain vinyl groups by infrared absorption peaks at 6.4 μ. The analytical sample was dried under vacuum for 0.5 hr. at room temperature.

*Anal.* Calcd. for $C_2H_3Li$: C, 70.69; H, 8.90. Found: C, 70.77, 70.85; H, 8.93, 8.99.

*Preparation and isolation of vinyllithium from the reaction of tetravinyltin and lithium.* The procedure used in the metal exchange reaction between tetravinyllead and lithium was repeated with 1.68 g. of lithium (200% excess), 0.008 g. of benzophenone, 4.54 g. of tetravinyltin (0.02 mole), and 10 ml. of dry diethyl ether solvent. The suspension turned black in 2 hr. The mixture was stirred overnight and then worked up as described above. The black solid was found to contain metallic tin. The product was isolated as a pure white solid which was violently pyrophoric, giving a brilliant red flash on contact with air. The product evolved ethylene on hydrolysis. The yield of vinyllithium was 1.15 g. or 42.5%.

This experiment was checked in repeated runs which showed that yields as high as 55% of pure product can be obtained in reaction periods as short as 4 hr. when high purity tetravinyltin and clean lithium are used.

*Anal.* Calcd. for $C_2H_3Li$: C, 70.69; H, 8.90. Found: C, 70.46; H, 9.20.

*Conversion of tributyltin chloride to tributylvinyltin with isolated vinyllithium.* Vinyllithium (4.8 g. or 0.141 mole) was dissolved in 110 ml. of dry diethyl ether in a flask fitted with a condenser, stirrer, and dropping funnel, resulting in the formation of a clear solution. By means of a dropping funnel, 45.9 g. of freshly distilled tributyltin chloride (0.141 mole, $n_D^{28}$ 1.4880) was added at a sufficient rate to maintain a gentle reflux. On addition of the tributyltin chloride to the solution, a vigorously exothermic reaction occurred with deposition of a white solid. The addition was complete in 20 min. The cooled reaction mixture was hydrolyzed by addition of water followed by 10% hydrochloric acid. The ether layer was washed with water and dried overnight over anhydrous sodium sulfate. The ether was removed through a 9-inch column filled with fine helices, and the product was distilled through a regular Claisen head. The yield was 38.0 g. or 85% of colorless liquid, b.p. 60–63° at 0.2 mm., $n_D^{26.5}$ 1.4770. The literature value for tributylvinyltin is $n_D^{25}$ 1.4761.[12] The presence of the vinyl group was confirmed by absorption in the infrared at 6.31 μ. The elemental analysis as well as the refractive index indicates about 8% tributyltin chloride contaminant in the tributylvinyltin. A small (2.7 g.) final fraction of unchanged tributyltin chloride was collected at 70–73° at 0.2 mm., $n_D^{26.5}$ 1.4838.

The purification of the product and identification as tributylvinyltin was done as follows: The tributyltin chloride in the crude tributylvinyltin was converted to the nonvolatile bistributyltin oxide by treatment with aqueous sodium hydroxide. Ten grams of the crude product was treated in this fashion and after fractionation there was recovered 7.76 g. of pure tributylvinyltin, b.p. 73–74° at 0.1 mm., $n_D^{26.5}$ 1.4763.

*Anal.* Calcd. for $C_{14}H_{30}Sn$: C, 53.03; H, 9.54. Found: C, 53.10, 53.18; H, 9.61, 9.75.

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[CONTRIBUTION FROM THE PETRO-TEX DEPARTMENT, FOOD MACHINERY AND CHEMICAL CORP. CENTRAL LABORATORY]

# Metal-Salt–Catalyzed Oxidation of Methacrolein

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The kinetics and products of the metal-salt–catalyzed oxidation of methacrolein and other unsaturated aldehydes in acetic acid were investigated. Methacrolein goes to peroxide, methacrylic acid, and, on extended oxidation, soluble polymer. At high aldehyde concentrations the oxidation rate was dependent on the first power of the oxygen pressure and to a fractional power of catalyst concentration. Unsaturated aldehydes were oxidized more slowly then the corresponding saturated aldehydes. Results are explained by a conventional oxidation mechanism in which the rate is determined by the reaction of unsaturated acyl radical with oxygen. The influence of termination due to the presence of monomer was considered.

The autoxidation of aldehydes to carboxylic acid occurs readily in solution at room temperature and has been shown by a large number of investigators to be catalyzed by metal ions and peroxides and to proceed by a free radical chain mechanism.[1] The nature of the peroxide intermediates and the reaction kinetics for the oxidation of saturated aldehydes, especially acetaldehyde,[2] has been widely studied but no attention has yet been given to unsaturated aldehydes which present unique experimental difficulties.

The oxidation of acrolein in acetic acid has been cursorily described[3] as occurring readily but, contrary to what is reported in the patent literature,[4] as yielding little or no monomeric acid. Church and Lynn[5] were unable to detect any re-

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