

## PREPARATION OF [ $^{14}\text{C}$ ] TRIETHYLALUMINIUM

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### SUMMARY

*A method for the preparation of [ $^{14}\text{C}$ ] triethylaluminium by catalysed exchange of [ $^{14}\text{C}$ ] ethylene with inactive triethylaluminium is described. Novel methods for handling this spontaneously inflammable substance were developed and used for hydrolytic and radiochemical analyses.*

Triethylaluminium is an important constituent of many Ziegler-Natta catalysts for stereoregular polymerizations. It is spontaneously inflammable and poses interesting experimental problems associated with this property.

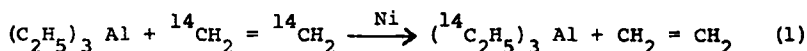
[ $^{14}\text{C}$ ] Triethylaluminium has been prepared by addition of lithium aluminium hydride (1) or diethylaluminium hydride (2) to [ $^{14}\text{C}$ ] ethylene and by displacement of isobutyl groups from tri-isobutylaluminium using [ $^{14}\text{C}$ ] ethylene (1). These methods required use of fairly large volumes of [ $^{14}\text{C}$ ] ethylene in pressure vessels and the products had rather low specific activities.

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In this paper we describe an alternative method for the preparation of [ $^{14}\text{C}$ ] triethylaluminium based on the original observation that colloidal nickel is an excellent catalyst for the displacement of alkyl groups on aluminium by olefinic compounds (3). Pure triethylaluminium in benzene solution was treated with colloidal nickel and an extremely small quantity of high specific activity [ $^{14}\text{C}$ ] ethylene in a sealed glass tube (reaction 1).



As the concentration of aluminium alkyl was approximately 300 times greater than that of the ethylene, the exchange was expected to lie almost completely to the right of equation 1. Experimentally, however, it was observed that only about 80% exchange had occurred under the reaction conditions used. However, the method avoided use of high pressure equipment and yielded a product of high specific activity which was purified by distillation and analysed by hydrolysis and by reverse isotope dilution.

### EXPERIMENTAL

#### 1. Technique for manipulation of aluminium alkyls.

Several attempts to handle triethylaluminium in a nitrogen filled glove box or by various other techniques described in the literature led to the conclusion that a

simpler approach was required. When small quantities (0-100g) were involved it was found that quite complicated transfer operations could be carried out inside nitrogen filled polyethylene bags. Thus, all the necessary containers (flasks, beakers, reaction tubes, counting vials etc.) together with stoppers, reagents, forceps, tissues and grease were placed in a large enamel tray (45 x 55 cm). The tray was then placed inside a large polyethylene bag (80 x 120 cm) on the laboratory bench. The neck of the bag was constricted round a piece of rubber tubing by means of a piece of string. Dry oxygen free nitrogen was passed through the tube into the bag. If the string was tightened, the bag inflated like a balloon. By slackening the string and applying gentle pressure on top of the bag, deflation was readily accomplished. Repeated cycles of inflation and deflation ensured that all the air was rapidly removed from inside the bag. The nitrogen flow was then adjusted so that the bag was maintained slightly inflated. All simple operations such as removing stoppers, pouring liquids, wiping and greasing stoppers etc. could readily be performed by hand from outside the bag. The polyethylene walls were sufficiently thin to permit quite intricate manipulations.

For precise volumetric transfer operations "Cornwall" hypodermic syringes (4) or "Agla" micrometer syringes (5) fitted with 200 mm x 21 gauge Luer-lock needles or canulae were used from outside the bag (Fig.1). Typically, a syringe was lightly



Fig. 1                      Technique for handling small quantities  
of aluminium alkyls in an inert atmosphere.

oiled (dry Apiezon oil 'A') to prevent entry of air around the plunger. Then the needle was inserted through the wall of the bag and the syringe pumped several times to replace residual air with nitrogen. In this way volumes of triethylaluminium or solvents from 0.1 to 50 ml were easily transferred quantitatively from vessel to vessel within the bag. To effect transfers to reaction vessels remote from the bag, a small amount of nitrogen gas was drawn into the long needle to protect the contents of the syringe during transfer. Used syringes and other containers with residual triethylaluminium were rinsed with hexane into a beaker where the residues were subsequently decomposed by slow addition of iso-propyl alcohol.

## 2. Triethylaluminium.

A commercial sample was fractionally distilled in vacuo through a 60 cm Vigreux column and a pure fraction had b.p. 58-62°/0.001 mm (Found by hydrolysis (see section 4c): ethane >99%).

## 3. Nickel acetylacetonate.

Acetylacetonone (5g) in methanol (10 ml) was added to a solution of nickel chloride (5.94g,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) in water (25 ml). The solutions were mixed thoroughly and then added to a solution of sodium acetate (4.1g) in water (15 ml). The mixture was heated briefly, cooled to room temperature and then placed in a refrigerator overnight. Blue crystals of nickel acetylacetonate dihydrate settled out, were isolated, washed and then heated to 130° in vacuo to yield the green anhydrous compound.

## 4. $^{14}\text{C}$ Triethylaluminium.

(a). Preparation. Nickel acetylacetonate (23.2 mg; 0.146 m mole) was washed into reaction vessel A (fig.2) with pure dry benzene (2 ml) the vessel was flushed with nitrogen and then triethylaluminium (15 ml; 0.11 mole) added as described in section 1. The nickel compound was immediately decomposed to give a black precipitate and a brown suspension of colloidal nickel. Vessel A was then connected to the manifold as shown. Tube B contained  $^{14}\text{C}$  ethylene (8.70 mg· 0.348 m mole; 5 mCi) and tube C contained benzene (20 ml). The contents of tubes A and C were frozen in liquid nitrogen and then evacuated to  $<10^{-3}$  mm. Thorough degassing was achieved by three cycles of

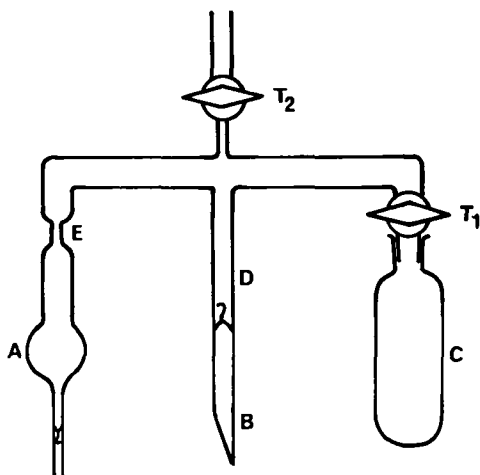


Fig. 2 Apparatus for transfer and enclosure of reactants.

freezing, pumping and thawing to room temperature. Then with taps  $T_1$  and  $T_2$  closed the seal at D was broken and [ $^{14}\text{C}$ ] ethylene transferred to A. B was rinsed several times with benzene from C and the washings transferred to A. Finally, A was flame sealed at E, immersed in an oil bath and heated to  $50^\circ$  for 19 hours.

(b). Isolation and purification. The product was purified by fractional distillation. Vessel A was attached to an apparatus as shown in fig.3 which was evacuated and then tap  $T_3$  closed. Seal F was broken and benzene and ethylene transferred to tube G cooled in liquid nitrogen. G was then flame sealed at H. A heated oil bath was placed round A and the contents distilled into a Vigreux distillation unit K (30 cm column). Nitrogen was

admitted to the manifold, K was removed and set up for conventional fractional distillation under vacuum. Distillation gave fraction (i) bp  $54-58^\circ/0.001$  mm (1.176g); fraction (ii) bp  $58-62^\circ/0.001$  mm (6.889g); fraction (iii) bp  $62-65^\circ/0.001$  mm (2.436g) plus an undistilled residue.

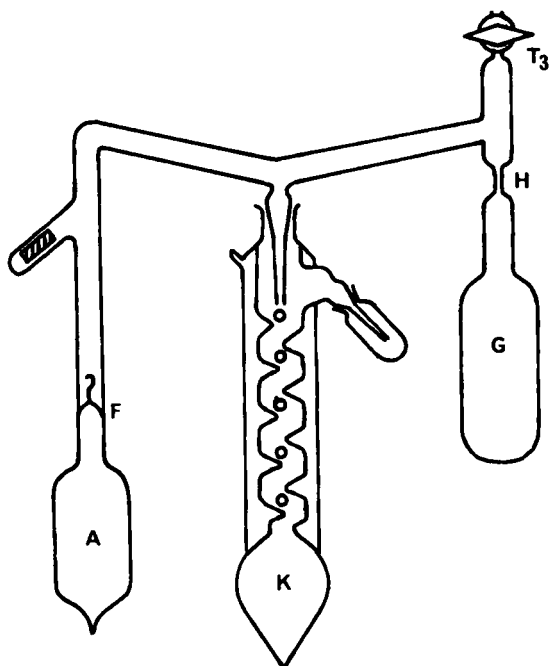


Fig. 3 Apparatus for transfer and isolation of reaction products.

(c) Analysis by hydrolysis. Small aliquots ( $\sim 0.1$  ml) of  $^{14}\text{C}$  triethylaluminium fraction (ii) were weighed into one side arm of inverted Y tubes which were flushed with nitrogen and stoppered with serum caps. A few drops of concentrated sulphuric acid were syringed into the other side arm. The

tubes were immersed in liquid nitrogen, water carefully syringed in to freeze about 1 cm above the aluminium alkyl and then the tubes were evacuated by inserting a hypodermic needle attached to a high vacuum line. On warming slowly to room temperature, the water reacted with the  $[^{14}\text{C}]$  triethylaluminium and decomposition was completed by carefully pouring the sulphuric acid from one limb to the other. Oxygen (0.10 ml) measured from a "Hamilton" gas tight syringe (6) was then added to each tube to act as an internal standard. After thorough mixing, samples of gas were removed by gas tight syringe and injected on to a Pye Argon gas chromatograph. Analyses for hydrogen were carried out at room temperature on a 120 x 0.6 cm column packed with Union Carbide molecular sieve type 5A. Analyses for ethane and butane were conducted at room temperature on a similar column packed with 25% dinonyl phthalate on Celite (100-120 mesh). In both cases helium was used as the carrier gas and calibration curves were prepared using accurately prepared standard gas mixtures.

Determination of alkoxide groups was carried out on the dinonylphthalate column at 100°. Aqueous solutions in the analysis tubes were treated with calcium oxide to neutralise sulphuric acid. Amyl alcohol (0.5 ml) was then added to dissolve any alcohols present and also to act as internal standard. Water was removed by addition of anhydrous sodium sulphate and then small aliquots were injected on to the gas



chromatography column. Comparison with standard mixtures of all the  $\text{C}_1$  to  $\text{C}_4$  alcohols revealed that only a trace of ethanol could be detected after decomposition of  $[\text{}^{14}\text{C}]$  triethylaluminium. The results of these analyses are summarised in table I.

TABLE I

Analysis of  $[\text{}^{14}\text{C}]$  triethylaluminium fraction (ii).

Decomposition product	Mole % detected
Hydrogen	<0.3 •
Ethane	99
Butane	< 1 •
Ethanol	<0.3 •

\* minimum quantities detectable.

(d) Analysis by isotope dilution. The specific activities of  $[\text{}^{14}\text{C}]$  triethylaluminium fractions (i) and (ii) were determined. Then a portion of fraction (ii) (2.000g) was diluted with pure triethylaluminium (5.736g) and the mixture fractionally distilled as before. A middle fraction was isolated and its specific activity determined. The results are recorded in table II where the radiochemical purity is seen to be 100%  $\pm$  ( $\sim$  2% counting error).

##### 5. Radiochemical Assay.

Samples were assayed in a Packard Tricarb type 3314. The fluor solution consisted of PPO (0.6%) and dimethyl POPOP (0.06%) in redistilled "Analar" toluene to which a trace ( $\sim$  0.1%) of triethylaluminium had been added to remove water and oxygen.

TABLE II

Isotope Dilution Analysis of  $[^{14}\text{C}]$ triethylaluminiumFraction (ii)

Sample	Dilution factor	Specific activity (d sec <sup>-1</sup> mole <sup>-1</sup> x 10 <sup>-9</sup> )	
		observed	calculated
fraction (i)	-	1.426	-
fraction (ii)	-	1.342	-
diluted	3.868	0.347	0.347

All operations were conducted as described in section 1.

$[^{14}\text{C}]$ triethylaluminium samples were prepared as accurately diluted solutions in toluene or benzene and aliquots of these solutions were dispensed from an Agla micrometer syringe into standard 20 ml screw cap vials. Cork and foil lined caps provided an adequate seal when the vials were removed from the nitrogen filled bag and count rates remained constant for several days in the counter. Corrections for quenching were made by the channels ratio method and the overall reproducibility, expressed as standard deviation, was about  $\pm$  1%.

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