

SYNTHESES WITH STABLE ISOTOPES: ACETYLENE- $^{13}\text{C}_2$ AND LITHIUM ACETYLIDE- $^{13}\text{C}_2$ ETHYLENEDIAMINE COMPLEX

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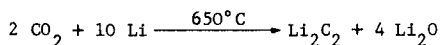
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SUMMARY

Acetylene- $^{13}\text{C}_2$ has been prepared from carbon- ^{13}C dioxide and molten lithium following hydrolysis of the resulting lithium carbide- $^{13}\text{C}_2$. The stable ethylenediamine complex of lithium acetylde- $^{13}\text{C}_2$ has been obtained from the reaction of acetylene- $^{13}\text{C}_2$ with *N*-lithioethylenediamine.

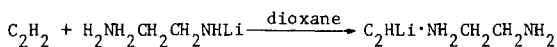
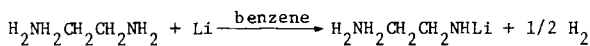
INTRODUCTION

Mole quantities of acetylene- $^{13}\text{C}_2$ (ethyne- $^{13}\text{C}_2$) and lithium acetylde- $^{13}\text{C}_2$ (ethynyllithium- $^{13}\text{C}_2$) have been required in this Laboratory as intermediates for various syntheses with stable isotopes. Acetylene- $^{14}\text{C}_2$ has been prepared by heating barium carbonate with either magnesium or barium metal and hydrolyzing the resulting barium carbide [1], but these reactions did not seem applicable to larger scale preparations. The methods developed by Noakes [2] for converting organic samples into benzene for radiocarbon dating utilize the acetylene chemistry first described by Barker [3] in which acetylene is prepared by the reactions indicated below.





Beumel and Harris [4] have reported the preparation of a stable ethylenediamine complex of lithium acetylide by the following reactions.



We have applied these reactions to the large-scale preparation of acetylene- $^{13}\text{C}_2$ and lithium acetylide- $^{13}\text{C}_2$.

DISCUSSION AND RESULTS

The acetylene synthesis apparatus used in this work (shown in Fig. 1) con-

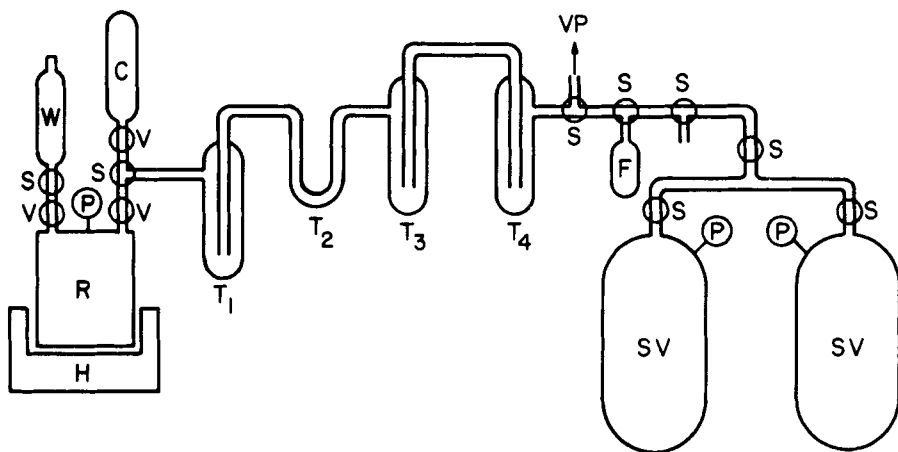


Fig. 1. Diagram of acetylene synthesis apparatus: (R) reaction chamber; (H) heater; (C) carbon dioxide cylinder; (W) water addition funnel; (T₁) Dry Ice-isopropyl alcohol trap; (T₂) Lithasorb-molecular sieve trap; (T₃ and T₄) liquid nitrogen traps; (F) freeze bulb; (SV) storage vessels; (S) stopcocks; (V) valves; (P) pressure gauges; and (VP) vacuum pump.

sists of a reaction chamber (R), a series of purification and collection traps (T_1 , T_2 , T_3 , and T_4), and two calibrated storage vessels (SV). Carbon dioxide is allowed to react with excess lithium metal at 650°C in the reaction chamber, and, after cooling, the mixture of lithium carbide, lithium oxide, and lithium is hydrolyzed with water. Water vapor is removed from the resulting gases by passing them through a Dry Ice-isopropyl alcohol trap (T_1) and a U-tube (T_2) containing molecular sieve and Lithasorb carbon dioxide absorbent. Acetylene is collected in two liquid nitrogen traps (T_3 and T_4) while hydrogen is removed through the vacuum pump. The yield of acetylene is 90-100%, and the preparation of approximately 0.5 mole of acetylene can be carried out in two days. The scale-limiting factor for the reaction is the rate of hydrolysis of the lithium carbide which Barker [3] observed to decrease markedly when the lithium hydroxide concentration in the reaction chamber exceeded 5%. With the present reaction chamber, the amount of water required to hydrolyze the carbide in a reasonable time fills the chamber and thus limits the scale to approximately 0.5 mole of acetylene.

The preparation of N-lithioethylenediamine was investigated using lithium shot, chunks of lithium metal, and a dispersion of lithium in mineral oil. Use of a lithium dispersion is preferred, since the product N-lithioethylenediamine tends to coat the larger pieces of lithium. The exchange reaction between butyllithium and ethylenediamine in benzene solution is suitable provided the butyllithium does not contain lithium bromide which precipitates with the product. In our experience, N-lithioethylenediamine was extremely air-sensitive and had to be handled in a glove box with an inert atmosphere. We also observed that the product developed a purple color in sealed containers, but this color disappeared when the container was reopened in an inert atmosphere.

The reaction between N-lithioethylenediamine and acetylene is conveniently carried out by allowing acetylene to sublime into a flask containing an N-lithioethylenediamine/dioxane slurry as opposed to bubbling acetylene through the

slurry as described by Beumel and Harris [4]. The yield of the lithium acetylide ethylenediamine complex is 80-85% from acetylene, and the complex liberates 95-100% of the theoretical amount of acetylene upon hydrolysis.

The proton nmr spectrum of acetylene- $^{13}\text{C}_2$ is shown in Fig. 2. Since the acetylene was prepared from ca. 90 atom % carbon- ^{13}C dioxide, the product contains three isotope isomers of acetylene. Thus, the spectrum consists of a superposition of three spectra: the one-line spectrum of $\text{H}^{12}\text{C}^{12}\text{CH}$ (ca. 1%), the first-order, eight-line spectrum of $\text{H}^{13}\text{C}^{12}\text{CH}$ (ca. 18%), and the ten-line

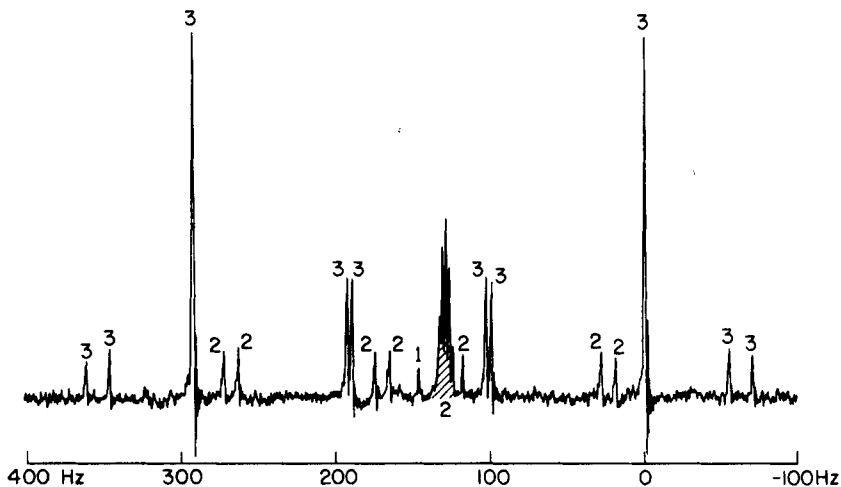


Fig. 2. Proton nmr spectrum of acetylene- $^{13}\text{C}_2$ prepared from ca. 90 atom % carbon- ^{13}C dioxide: (1) one-line spectrum of $\text{H}^{12}\text{C}^{12}\text{CH}$; (2) eight-line spectrum of $\text{H}^{13}\text{C}^{12}\text{CH}$; and (3) ten-line spectrum of $\text{H}^{13}\text{C}^{13}\text{CH}$.

spectrum of $\text{H}^{13}\text{C}^{13}\text{CH}$ (ca. 81%). Analysis of the spectrum according to the interpretation of Lynden-Bell and Sheppard [5] gives the magnitude of the J_{HH} , J_{CH} , J_{CCH} , and J_{CC} coupling constants in good agreement with their values.

EXPERIMENTAL

Materials and Methods--The stainless steel reaction chamber was purchased from the Alford Instrument Company (6017 Medlin Heights Road, Knoxville, Tenn. 37918). The heater was constructed from two 1-kW, semi-cylindrical heating elements connected in series with a 220-V variable transformer to control the temperature. Temperature measurements were made using a Chromel-Alumel thermocouple positioned between the reaction chamber and heater wall. Lithium shot for the carbide reaction was purchased from the Lithium Corporation of America (New York). Carbon- ^{13}C dioxide was produced at the Los Alamos Scientific Laboratory Isotope Separation Facility (Group CNC-4). Nmr spectra were recorded on a Perkin-Elmer R-24 spectrometer using the residual protons of acetone- d_6 as an internal standard and are reported relative to TMS. Ir spectra were recorded on a Perkin-Elmer 710 spectrophotometer and calibrated using a polystyrene film and are reported to the nearest 5 cm^{-1} with the natural abundance absorptions of peaks showing isotopic shifts given in parentheses.

Acetylene- $^{13}\text{C}_2$ --The reaction chamber of the acetylene synthesis apparatus (Fig. 1) was charged with lithium shot (46.5 g, 6.7 mol), sealed, evacuated, and heated while still open to the vacuum pump. After the lithium had been degassed and heated to 620°C , the reaction chamber was isolated from the vacuum pump, and carbon- ^{13}C dioxide (42.8 g, 0.953 mol, 90.34 atom % ^{13}C , 3.37 atom % ^{18}O) was pulsed into the reaction chamber in 17-34 kPa (5-10 in Hg) increments over 1.25 hr at a rate such that the temperature remained between 640 and 670°C . After the carbon dioxide addition was completed, the apparatus was opened to the vacuum pump and heated at 760°C for 1.25 hr. After cooling, the contents of the reaction chamber were hydrolyzed by the cautious addition of carbon dioxide-free water (ca. 2.0 dm^3) while the apparatus was open to the vacuum pump. The mixture of acetylene, hydrogen, and water vapor liberated upon hydrolysis was purified by passing it through a Dry Ice-isopropyl alcohol trap, a U-tube containing molecular sieve (3A) and anhydrous lithium hydroxide (Lith-

asorb), and two liquid nitrogen traps. The acetylene, which was collected in the liquid nitrogen traps, was then sublimed into two 4.5-dm³ storage vessels. Hydrolysis of the contents of the reaction chamber and collection of the majority of the acetylene required approximately 8 hr, and after standing overnight the remainder of the acetylene was collected. From the pressure in the calibrated storage vessels, it was calculated that 0.447 mol (94%) of acetylene-¹³C₂ was produced: nmr (acetone-d₆) δ 2.35 (J_{HH} = 9.4 Hz, J_{CH} = 248.8 Hz, J_{CCH} = 49.2 Hz, J_{CC} = 170 Hz); ir (gas) 3305, 3260, 1335 (1350), 1290 (1305), 730 cm⁻¹.

Lithium Acetylde-¹³C₂ Ethylenediamine Complex--A 500-cm³, three-neck flask previously flushed with argon and equipped with a magnetic stirrer, addition funnel, and condenser fitted with a glass T-tube attached to an argon tank was charged with a lithium dispersion which had been prepared by melting lithium metal (7.0 g, 1.01 mol) in mineral oil (200 cm³) under an argon atmosphere with vigorous stirring, followed by filtration of the cooled lithium particles. The lithium dispersion was washed with anhydrous benzene (3 x 150 cm³) under an argon atmosphere to remove residual mineral oil and was finally suspended in anhydrous benzene (150 cm³). A small portion of a solution of ethylenediamine (66 g, 1.1 mol) in anhydrous benzene (70 cm³) was added to the lithium suspension, and the mixture was brought to gentle reflux. The remainder of the ethylenediamine solution was added dropwise over a 2.5-hr period while the mixture, which developed a tan precipitate, was gently refluxed under an argon atmosphere. Refluxing was continued for 6 hr, at which time all of the lithium had been consumed. After cooling, the condenser and addition funnel were removed, and the flask was quickly stoppered and transferred to a glove box (argon atmosphere) where the mixture was filtered and washed thoroughly with argon-flushed petroleum ether and dried to give N-lithioethylenediamine as a tan powder (62 g, 94%) which was air-sensitive.

Inside an argon-flushed glove box, a 500-cm³, three-neck flask was charged

with N-lithioethylenediamine (26.4 g, 0.399 mol) and anhydrous dioxane (200 cm³) and stoppered. The flask was removed from the glove box and set up with an ice bath, magnetic stirrer, thermometer, condenser with a vacuum outlet and balloon, and a gas inlet tube connected to the acetylene synthesis apparatus with an intermediate vacuum trap immersed in liquid nitrogen. After the system had been evacuated (aspirator) and the N-lithioethylenediamine/dioxane slurry had been cooled to 15°C, one-half of the acetylene- $^{13}\text{C}_2$ (0.210 mol) in the storage vessels of the synthesis apparatus was transferred into the liquid nitrogen-cooled vacuum trap. The acetylene was allowed to sublime into the reaction flask at a rate such that the temperature remained at 15°C and a slight positive pressure (as indicated by the balloon) was maintained. After this portion of the acetylene was consumed, the reaction mixture was seeded with a few crystals of lithium acetylide ethylenediamine complex. The second half of the acetylene (0.209 mol) from the storage vessels was then transferred into the vacuum trap and sublimed into the reaction flask as previously described. After the second portion of the acetylene had been consumed, the reaction mixture, which had maintained a tan precipitate throughout the reaction, was stirred at room temperature for 3 hr. After the flask was disconnected from the condenser, thermometer, and gas inlet, it was stoppered and transferred to an argon-flushed glove box where the contents were poured into petroleum ether (200 cm³). The product was filtered, washed with petroleum ether, and dried to give lithium acetylide- $^{13}\text{C}_2$ ethylenediamine (32.4 g, 83% based on acetylene) as a light tan powder which was stable in dry air. Upon hydrolysis, the product liberated 95% of the theoretical amount of acetylene.

ACKNOWLEDGMENT

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