[Contribution from the Chemistry Department of Boston University]

Hexynylmetals and 1-Bromoheptyne-2

WALTER J. GENSLER and A. P. MAHADEVAN[1]

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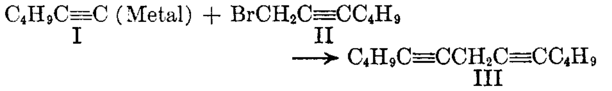
The reaction of 1-bromoheptyne-2 with hexynyllithium, sodium, silver, copper, and mercury was examined. The lithium derivative with 1-bromoheptyne-2 gave tridecadiyne-5,8. The lithium derivative with methylene bromide, as well as the sodium derivative with the propargyl bromide gave different products. The heavy metal derivatives did not react in inert solvents. The silver derivative with 1-bromoheptyne in alcohol gave 1-ethoxyheptyne-2.

The reaction of 1-bromoheptyne-2 (II) with hexynylmagnesium bromide (I, Metal = MgBr) in the presence of various catalysts has been studied.[2]



$$\underset{\text{I}}{C_4H_9C{\equiv}C}\,(\text{Metal}) + \underset{\text{II}}{BrCH_2C{\equiv}CC_4H_9} \longrightarrow \underset{\text{III}}{C_4H_9C{\equiv}CCH_2C{\equiv}CC_4H_9}$$

The reaction of 1-bromoheptyne-2 with hexynylmetals (I) other than the hexynyl Grignard is the subject of the present paper.

Hexynyllithium, formed smoothly from hexynylmercury and lithium in boiling dioxane-ether, reacted with the propargyl bromide to give tridecadiyne-5,8 (III) in 31% yield. However, comparison of the absorption spectra of this product and of the product obtained before[2] showed that impurities were present. Hexynyllithium with one-half mole of methylene bromide gave a product different from III.

Sodium acetylides have been employed before in the preparation of skipped diynes, but with limited success.[3] We found that the reaction of hexynylsodium in liquid ammonia with 1-bromoheptyne-2 did not give compound III. Hennion and Bell showed earlier that hexynylsodium with methylene bromide gave only tars.[4]

Three heavy metal derivatives, *i.e.*, hexynylsilver,[5,6] hexynylcopper, and hexynylmercury,[7,8] were prepared and tried. Hexynylsilver did not react with 1-bromoheptyne-2 in ether. Reaction did occur in absolute alcohol, but the product instead of tridecadiyne-5,8 was 1-ethoxyheptyne-2.[4,9] Evidently the propargyl bromide underwent solvolysis[10] with ethanol faster than coupling with hexynylsilver.[11] Very little if any reaction occurred between hexynylmercury and 1-bromoheptyne-2 in boiling benzene, or between hexynylcopper and 1-bromoheptyne-2 in toluene at 100°.

These results serve to emphasize the specificity demanded of the metal in I for successful reaction with II. Thus far the copper-catalyzed Grignard coupling[2] remains the method of choice.

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EXPERIMENTAL[12]

Hexynyllithium and 1-bromoheptyne-2. Hexynyllithium was formed by boiling a mixture of 9.0 g. (0.0248 mole) of hexynylmercury, 0.60 g. (0.10 g.-atom) of lithium cut into small pieces, and 50 ml. of dioxane that had been distilled over calcium hydride and stored over sodium. The condenser was provided with a calcium chloride tube connected to a line of dry nitrogen under slight pressure. The vigorous reaction at the beginning of the heating period kept the mixture boiling for ten minutes without application of heat. When the reaction had subsided the mixture was boiled for 30 minutes, and after cooling to room temperature was forced through a plug of glass wool into a dropping-funnel with the help of nitrogen under pressure. The dropping-funnel was part of an apparatus consisting of a 250-ml. three-necked flask, fitted with a stirrer, and carrying a condenser topped by a calcium chloride tube connected to a line of dry nitrogen. The dioxane solution of hexynyllithium was added with stirring over a period of two hours to a boiling solution of 9.0 g. (0.0514 mole) of 1-bromoheptyne-2[13] in 40 ml. of sodium-dry ether. After a further reflux period of three hours the mixture was allowed to stand overnight.

The liquid above the white solid deposited in the bottom of the flask was poured into 300 ml. of water. The solids

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[1] Present address: Nutrition Research Laboratories (Indian Council of Medical Research), Coonoor, South India.

[2] Gensler and Mahadevan, *J. Am. Chem. Soc.*, **77**, 3076 (1955).

[3] Tchao Yin Lai, *Bull. soc. chim.*, [4], **53**, 1537 (1933); Schlubach and Wolf, *Ann.*, **568**, 141 (1950).

[4] Hennion and Bell, *J. Am. Chem. Soc.*, **65**, 1847 (1943).

[5] Danehy and Nieuwland, *J. Am. Chem. Soc.*, **58**, 1609 (1936).

[6] Van Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (*cf.* p. 356) (1926).

[7] Vaughn, *J. Am. Chem. Soc.*, **55**, 3453 (1933).

[8] Hall and Bachman, *Ind. Eng. Chem.*, **28**, 57 (1936).

[9] Kranzfelder and Vogt, *J. Am. Chem. Soc.*, **60**, 1714 (1938).

[10] Lappin, *J. Org. Chem.*, **17**, 897 (1952).

[11] Insofar as our product showed no allenic absorption in the 5.1–5.2 μ region and did show absorption at 4.55 μ, the conclusions reached by Lappin[10] concerning the absence of allenic linkages and the presence of the triple bond are substantiated. The presence of absorption peaks close to 3 μ and to 6 μ remains to be explained, however.

[12] Temperatures are uncorrected. Analyses were performed by Dr. Stephen M. Nagy and his assistants at Massachusetts Institute of Technology Microchemical Laboratory, and by Dr. Carol K. Fitz, 115 Lexington Avenue, Needham Heights 94, Massachusetts.

[13] Newman and Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

were rinsed with 30 ml. of petroleum ether, which was also added to the water. The aqueous mixture was extracted with 150 ml. of petroleum ether. Solids, presumably hexynylmercury, present in small amounts at the interface were discarded. The petroleum ether solution was first dried over calcium chloride, and then distilled first at 760 mm. and then at 20 mm. to remove solvent. The residue (10.1 g.) deposited crystals of hexynylmercury which, after crystallization from petroleum ether, weighed 2.5 g. and melted at 94–95°.

The remaining liquid was fractionated through an 8-cm. Vigreux column. Two main fractions were taken: (a) 2.31 g. of 1-bromoheptyne-2 with b.p. 50–52° (1.5 mm.) and n_D^{25} 1.4876, and (b) 2.2 g. of material (31.5% based on 1-bromoheptyne-2 not recovered) with b.p. 92–95° (mainly at 94–95°) (1.5 mm.) and n_D^{25} 1.4634.

Judging from the weight of free mercury recovered from the above-mentioned white solid, the yield of hexynyllithium from hexynylmercury was 74%. In another experiment in which the metal interchange was prolonged to two hours the yield of free mercury and accordingly of hexynyllithium was increased to 93%, but the coupling gave poorer results, a smaller amount of less pure product (n_D^{25} 1.4655) being obtained.

The boiling point of the material in fraction b was close to the boiling point of tridecadiyne-5,8, which is 95° (1 mm.), 98–100° (1.5 mm.), or 96–98° (1.5 mm.). The index of refraction, n_D^{25} 1.4634, was close to that of pure tridecadiyne, *i.e.*, n_D^{25} 1.4615.[2] All the features of the infrared absorption curve for pure tridecadiyne-5,8[2] were evident in the infrared curve for the material in fraction b. However there were bands in the latter curve, notably in the region close to 6 μ, that were not present in the former. Also the transmittance at the allenic absorption region (5.15 μ) was slightly less for tridecadiyne-5,8 from hexynyllithium than for pure tridecadiyne-5,8 (83% *vs.* 94%). The ultraviolet absorption curve for the hexynyllithium product ($\lambda_{\max}$ 272, ϵ 474) had the same appearance as that for pure tridecadiyne[2] but the entire curve was shifted upwards.

Hexynyllithium and methylene bromide. Hexynyllithium was prepared from 1.03 g. of lithium, 13.5 g. (0.0375 mole) of hexynylmercury, and 50 ml. of dry dioxane as described above. The reaction, which was not as rapid as before (total time seven hours), afforded 5.17 g. (69%) of free mercury. The filtered dioxane solution of hexynyllithium was added to a solution of 6.6 g. (0.038 mole) of methylene bromide in 50 ml. of sodium dry ether. The mixture was boiled and stirred for 18 hours. The reaction mixture containing a white precipitate was poured over crushed ice (*ca.* 300 g.) and 10 ml. of concentrated hydrochloric acid was added. The mixture was treated in the usual way for isolation of product, which was a liquid (0.85 g.) with b.p. 55–56° (0.08–0.1 mm.) and n_D^{25} 1.4670. Prominent peaks at 5.15 μ and 5.64 μ and a *single* peak at 4.55 μ were present in the infrared spectrum, which clearly was not the same as that of tridecadiyne-5,8.

Hexynylsodium and 1-bromoheptyne-2. Hexyne-1 (25 ml. or 0.20 mole) in 50 ml. of sodium dry ether was added dropwise over a period of 45 minutes to a stirred mixture of clean sodium (4.6 g.; 0.20 g.-atom) cut into small pieces and 300 ml. of liquid ammonia. After stirring further for 2¹/₄ hours under an acetone-solid carbon dioxide condenser, the volume of the mixture was brought to *ca.* 650 ml. with liquid ammonia, and more hexyne-1 (12.5 ml. or 0.10 mole) was added. Then 35 g. (0.20 mole) of 1-bromoheptyne-2 in 25 ml. of sodium dry ether was introduced over a one-half hour period, and the solution was stirred for four hours. The condenser was replaced with a water-cooled condenser and the ammonia was allowed to evaporate overnight.

Hydrolysis of the white residual solid followed by the usual treatment led to a dark orange liquid (22 g.), which did not distill through a 10-cm. Vigreux column at bath temperatures up to 180° (2 mm.). Two distillations through a short path still gave 6.2 g. of liquid, b.p. 130–155° (1 mm.) and n_D^{25} 1.4826, which although water white at first became green-yellow in the receiver.

Hexynylsilver and 1-bromoheptyne-2. To a stirred solution of 17 g. (0.10 mole) of silver nitrate in 300 ml. of 95% alcohol was slowly added a solution of 4.1 g. (0.05 mole) of hexyne-1 in 50 ml. of 95% alcohol. After stirring the mixture for two hours, it was filtered, and the white precipitate was washed in the funnel with ether, and air-dried. The product (17 g.) crystallized from ethanol in beautiful plates melting indefinitely at 150–160° after shrinking at 80°. Color developed in the crystals on exposure to light. A sample crystallized twice from ethanol away from light as much as possible was dried at 55° *in vacuo* for four hours.

Anal. Calc'd for $(C_6H_9Ag)_4 \cdot (AgNO_3)_3 \cdot C_2H_5OH$: C, 23.79; H, 3.23; N, 3.2; Ag, 57.54. Calc'd for $C_6H_9Ag \cdot AgNO_3 \cdot C_2H_5OH$: C, 23.7; H, 3.7; N, 3.46; Ag, 53.3. Found: C, 24.0; H, 3.4; N, 3.1; Ag (as ash), 59.7.

Hexynylsilver was prepared before by the action of silver bromide and hexynylmagnesium bromide[5] as well as by the method used here,[6] but no analyses were recorded.

A. Reaction in ether solvent. A mixture of 10 g. (*ca.* 0.008 mole) of powdered silver derivative of hexyne-1, 10 g. (0.057 mole) of 1-bromoheptyne-2, and 100 ml. of sodium dry ether was stirred and boiled under dry nitrogen for 12 hours, and then allowed to stand overnight. Practically all of the silver derivative was recovered, together with 9 g. (90%) of 1-bromoheptyne-2, b.p. 77–78° (15 mm.) and n_D^{23} 1.4860.

B. Reaction in ethanol solvent. A mixture of 10 g. (*ca.* 0.008 mole) of hexynylsilver, 10 g. (0.057 mole) of 1-bromoheptyne-2, and 150 ml. of absolute alcohol was stirred and boiled for 2¹/₂ hours. The slightly brown solid (silver bromide) was removed, alcohol was distilled from the filtrate, and the residual oil was distilled through a 10-cm. Vigreux. The distillate (3.5 g.; b.p. 53–60° at 1.5 mm.), which contained halogen, was exposed to 2 g. of zinc dust in 15 ml. of boiling ethanol for 2¹/₂ hours. After removal of solids and of solvent, the residue boiled sharply at 71° (15 mm.). The pleasant smelling product (1.5 g.) was free of bromine (by the sodium fusion test) and had n_D^{25} 1.4377. The constants recorded for heptynyl ethyl ether are b.p. 77–78° (20 mm.) and 90° (24 mm.), and n_D^{25} 1.4391 and n_D^{20} 1.4334.[4,9]

Hexynylmercury and 1-bromoheptyne-2. A solution of hexyne-1 (1.0 g. or 0.012 mole) in 20 ml. of 95% alcohol was added over a five-minute period with vigorous stirring to 20 ml. of a solution of mercuric iodide, prepared as described by Johnson and McEwen.[14] The white precipitate was quickly removed and after several washes on the filter with (*ca.*) 30% alcohol was air-dried. The yield of hexynylmercury, m.p. 93–95°, was 2.1 g. (95%). Crystallization from petroleum ether (b.p. 30–65°) afforded glistening plates, m.p. 95–95.5°.

Anal. Calc'd for $(C_6H_9)_2Hg$: C, 39.72; H, 4.96. Found: C, 39.31; H, 4.68.

Loss on crystallization from petroleum ether or from petroleum ether containing benzene was considerable. Subsequently ethyl acetate was found to be the solvent of choice.

A clear solution of 9.0 g. (0.025 mole) of hexynylmercury, 8.5 g. (0.0486 mole) of 1-bromoheptyne-2, and 50 ml. of sodium dry benzene was boiled for 24 hours. Most of the hexynylmercury as well as 5.8 g. (68%) of the 1-bromoheptyne-2, b.p. 82° (51 mm.) and n_D^{25} 1.4880, was recovered.

Hexynylcopper and 1-bromoheptyne-2. A paste of 10 g. of cuprous chloride and 50 ml. of 1 *N* sulfuric acid was poured into 800 ml. of 5% aqueous sodium bisulfite. The cuprous chloride, now pure white, was washed with water and alcohol by decantation, and was then stirred into a solution of 400 ml. of absolute alcohol and 50 ml. of liquid ammonia. Finally 350 ml. of water was added. A solution of 10 ml. of

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(14) Johnson and McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

hexyne-1 in 30 ml. of 95% alcohol was added dropwise under nitrogen to the vigorously stirred light blue ammoniacal solution. After an hour of stirring the slurry was poured into 3 liters of water. The yellow solid was collected, and washed on the filter with dilute aqueous ammonia, water, alcohol, and finally ether. This hexynylcopper, which after drying in a vacuum desiccator weighed 6 g., melted at 140–150°, set to a solid on further raising the temperature, and melted again to a clear liquid above 220°. A sample from a similar preparation in which somewhat less alcohol was used was dried *in vacuo* at 50°.

Anal. Calc'd for C_6H_9Cu: C, 49.75; H, 6.29; Cu, 43.93. Found: C, 49.8; H, 6.2; Cu (from CuO ash), 44.0.

Van Risseghem[6] mentions this compound without detail.

A mixture of 4 g. of the yellow powdery hexynylcopper, 3.5 g. of 1-bromoheptyne-2, and 75 ml. of toluene was stirred at steam temperature for eight hours, and then allowed to stand overnight at room temperature. Almost all the starting solid (3.85 g.) could be recovered by filtering, washing the solid with ether, and drying. The filtrate was distilled under a slight vacuum to remove toluene and then through a 12-cm. Vigreux column. 1-Bromoheptyne-2 (1.65 g. or 47%) was obtained with b.p. 90° (20 mm.) and n_D^{25} 1.4884.

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