[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

ACETYLENES. II. A CONVENIENT ONE-STEP SYNTHESIS OF ALLENES[1]

WILLIAM J. BAILEY AND CHARLES R. PFEIFER[2]

Received September 27, 1954

Allenes, which contain a highly reactive unsaturated system, are of interest because they are monomers for polymerization as well as unique chemical intermediates. However, many of their obvious reactions have not been investigated because the allenes are not easily accessible. The general method of synthesis of allenes, involving dehydrohalogenation of a 1,2,3-tribromo derivative, followed by removal of the bromine from the dibromo olefin with zinc (1), is long and tedious. The thermal rearrangement of acetylenes to allenes gives poor yields. Favorski (2) obtained a low yield of dimethylallene (I) by heating isopropylacetylene. More recently, Ginzburg (3) obtained dimethylallene (I) in a 63% yield by reducing 3-chloro-2-methyl-1-butyne (II) with a zinc-copper couple. Hennion and Sheehan (4) applied this same method to the synthesis of *n*-propylallene. Reduction of 3-chloro-1-hexyne with a zinc-copper couple produced the allene in a 71% yield.

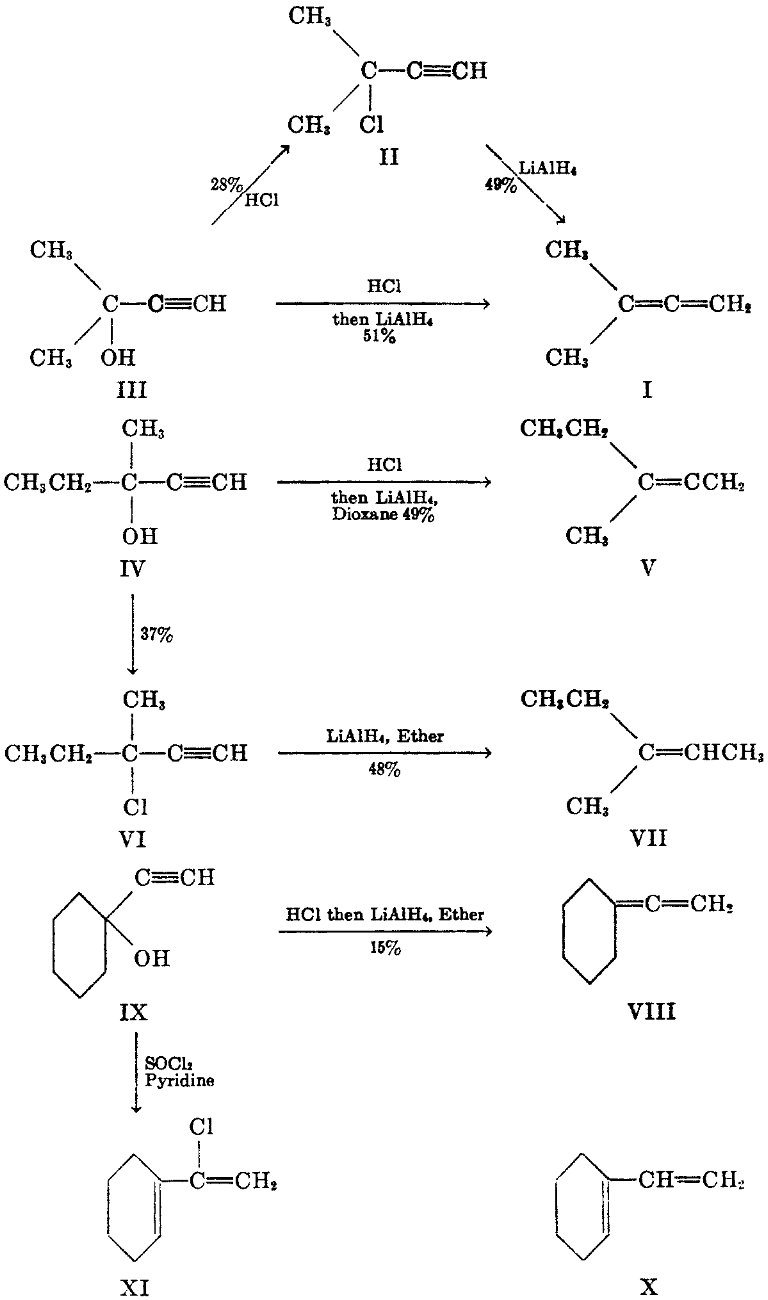
Since a series of acetylenic alcohols, such as 3-methyl-1-butyne-3-ol (III), 3-methyl-1-pentyne-3-ol (IV), and 1-ethynylcyclohexanol (IX), are now commercially available, an investigation was initiated to find a convenient route from these alcohols to the corresponding allenes. The general method of Ginzberg (3) and Hennion and Sheehan (4) appeared to be of interest, but the experimental procedures have many disadvantages. The yields of the acetylenic tertiary halides are often not high because during the distillation some hydrogen chloride is eliminated and some rearrangement to the allenic chloride occurs. The final product from the reduction always contains the isomeric acetylene that must be removed by a separate step or a careful fractionation. In addition, the alcohol used in the reduction very often forms an azeotrope with the allene, necessitating additional purification steps, and the zinc-copper couple is very tedious to prepare. Even though Wotiz (5) showed that lithium aluminum hydride reduction of 1-bromo-2-heptyne produced a mixture consisting of 94% of the corresponding acetylene and only 6% of the allene and reduction of 1-bromo-2-heneicosyne gave only the acetylene derivative, he did show that reduction of 3-bromo-1-heptyne produced a 48% yield of a mixture consisting of 90% of the allene and 10% of the acetylene. For this reason the use of lithium aluminum hydride for the preparation of allenes was investigated.

Initial experiments showed that the reduction of 3-chloro-3-methyl-1-butyne (II), prepared in a 28% yield from the acetylenic alcohol III, gave a 49% yield

---

[1] Previous paper in this series, *J. Am. Chem. Soc.*, **76**, in press (1954).

[2] Office of Naval Research Fellow, 1951–1953; Union Carbide Fellow 1953–1954.



of the dimethylallene (I) plus very little acetylene. However, since the over-all yield was not high and purification steps to remove the acetylene were somewhat tedious, this method appeared to be only a slight improvement on the procedure of Ginzburg and Hennion and Sheehan. Ways to improve this method further were, therefore, explored.

Since in the reduction mixture the isopropylacetylene was in the form of its lithium or aluminum salt while the allene was free, it was reasoned that simple distillation of the mixture, omitting the hydrolysis and decomposition of the excess hydride, would permit a convenient separation of the allene and the acetylene. By use of tetrahydrofuran, which has a boiling point intermediate between that of the allene I and the chloride II, any unreacted II would also be left behind. It was also reasoned that, if this distillation was used, it was not necessary to use pure 3-chloro-3-methyl-1-butyne (II). It was hoped that any rearranged allenic chloride would also be reduced to the allene I and the unreacted alcohol III would form a nonvolatile salt. By the use of a procedure that involved shaking the acetylenic alcohol III with concentrated hydrochloric acid, adding the dried organic layer to a tetrahydrofuran solution of lithium aluminum hydride, and distilling out the allene without hydrolysis, a 51% yield of dimethylallene (I) was obtained in essentially one step. The allene (I) was characterized by infrared absorption which showed strong peaks at 850, 1007, 1075, 1190, 1285, 1389, 1445, 1700, 1980, and 2960 cm^{-1} and indicated the absence of any acetylene. A negative test with alcoholic silver nitrate also confirmed the absence of a terminal acetylenic group. It is of interest that the acetylenic chloride II used to prepare the allene I showed strong peaks in its infrared spectrum at 670, 773, 952, 1123, 1170, 1228, 1383, 1460, 3040, and 3245 $cm.^{-1}$ and showed no evidence of the presence of any allenic chloride.

Initial attempts to prepare methylethylallene (V) by reducing the acetylenic chloride VI with lithium aluminum hydride in ether produced very little of the allene V. The main product of the reaction was 3-methyl-2-pentene (VII), in a 48% yield. The olefin VII was identified by its physical properties and conversion to 3-chloro-3-methylpentane by addition of hydrogen chloride. The presence of the isomeric 3-methyl-1-pentene was not detected.

To avoid the formation of the olefin during the preparation of the methylethylallene (V), the simple one-step procedure described above was modified by using dioxane as the solvent and removing the allene V as fast as it was formed. This was possible because the dioxane has a boiling point higher than the allene V but lower than the chloride VI. With this modified procedure a 49% yield of the allene was obtained directly from the commercially available acetylenic alcohol IV. The structure of methylethylallene (V) was indicated by its analysis, chemical reactions and infrared absorption. The infrared absorption spectrum of V showed strong peaks at 847, 1002, 1370, 1440, 1700, 1960, and 2960 $cm.^{-1}$

An effort was made to determine the course of the reaction that produced the olefin VII. It was found that the methylethylallene (V) could be recovered unchanged from an ether solution of lithium aluminum hydride that had been heated under reflux for several days. This was also true even when an excess of lithium chloride was added to the reaction mixture. In work that will be reported later it was shown that an isolated acetylenic bond was not reduced under these conditions. Even the possibility that the active hydrogen on the acetylenic chloride VI would form a more powerful reducing combination with the hydride was eliminated. The allene V was recovered unchanged from an ether solution of lithium aluminum hydride to which 1-hexyne had been added over a 2-day period. One must conclude that the hydride reduced the unsaturation in the acetylenic chloride before the chloro group was removed.

An attempt to prepare pentamethyleneallene (VIII) in one step from 1-ethynylcyclohexanol (IX) by using a high-boiling ether failed because the hydride was not stable at the elevated temperature. For this reason the reaction was carried out in ether and the reaction mixture was hydrolyzed to give a mixture consisting primarily of the allene VIII, the 1-vinyl-1-cyclohexene (X), and some unreduced chloride. The chloro compound plus any trace of the cyclohexylacetylene were removed by treatment with a silver nitrate solution and any diene was removed by reaction with maleic anhydride to give a 15% yield of pentamethyleneallene (VIII). The low yield of the allene VIII is not surprising in view of the fact that Hurd and Jones (6) could not produce the acetylenic chloride from IX with thionyl chloride and pyridine but obtained instead the chloro diene XI. The pentamethyleneallene had been previously prepared in an unreported yield from the rather inaccessible cyclohexylacetylene (7). The structure of the allene VIII was indicated by strong infrared absorption bands at 843, 895, 970, 1235, 1283, 1440, 1680, 1955, and 2960 cm.$^{-1}$

The present convenient one-step synthesis makes these simple allenes readily available. A comprehensive program to study their reactions, including polymerization, is now under way.

EXPERIMENTAL[3]

Materials. The 3-methyl-1-pentyne-3-ol (IV) and the *3-methyl-1-butyne-3-ol* (III) were obtained from the Air Reduction Corp.[4] and the *1-ethynylcyclohexanol* (IX) was obtained from the Farchan Research Laboratories. All three of these acetylenic alcohols were used without purification.

3-Chloro-3-methyl-1-butyne (II), b.p. 75°, n_D^{26} 1.4142–1.4149 [reported (8) b.p. 76–76.5°, n_D^{20} 1.4172], was prepared in a 28% yield by treating 3-methyl-1-butyne-3-ol (III) with concentrated hydrochloric acid according to the procedure of Campbell, Campbell, and Eby (9).

3-Chloro-3-methyl-1-pentyne (VI), b.p. 51–51.5° (135 mm.), n_D^{25} 1.4314–1.4323 [reported (9) b.p. 51–52° (135 mm.), n_D^{20} 1.4328–1.4333], was prepared in a 37% yield by treating 3-methyl-1-pentyne-3-ol (IV) with concentrated hydrochloric acid according to the method of Campbell, Campbell, and Eby (9).

Tetrahydrofuran (Matheson, Coleman, and Bell) was dried over sodium and fractionated through a 12-inch, helix-packed column to produce pure material, b.p. 65.0–65.4°.

Dioxane was heated under reflux with sodium for 2 days and distilled through the same column to produce pure material, b.p. 101–101.2°.

3-Methyl-1,2-butadiene (I). *A. From 3-chloro-3-methyl-1-butyne* (II). To a stirred slurry of 79.7 g. (2.10 moles) of lithium aluminum hydride in 1 liter of tetrahydrofuran was added 108.0 g. (1.05 moles) of 3-chloro-3-methyl-1-butyne (II) at a rate necessary to maintain gentle reflux of the solvent. After the mixture had been heated under reflux for an additional 1.5 hours, the excess hydride was decomposed with water and enough 10% hydrochloric acid was added to lower the aqueous phase to *p*H 3. The volatile hydrocarbons plus part of the

---

[3] The authors are indebted to Kathryn Gerdeman for the analysis and to Joseph Wenograd, Franklin Byers, Kathryn Gerdeman, and Dr. Robert A. Spurr for the infrared absorption spectra. A Perkin-Elmer model 12-C infrared spectrophotometer, modified for double-pass operation, was used.

[4] The authors are indebted to the Air Reduction Corp. for a generous supply of these two acetylenic alcohols.

tetrahydrofuran were removed from the reaction mixture by distillation and dried over potassium carbonate. Careful fractionation through a 6-inch, helix-packed column produced 35.0 g. (49%) of dimethylallene (I), b.p. 40.0–40.2° (761 mm.), n_D^{25} 1.4148 [reported (3) b.p. 39.5–40.5°, n_c^{13} 1.4216, n_F^{13} 1.4329, n_G^{13} 1.4416 (which corresponds to a calculated value of n_D^{25} 1.4152)]. This sample of the 3-methyl-1,2-butadiene (I) gave a negative test with ammoniacal silver nitrate. There was also obtained 5.9 g. of a forerun, b.p. 32–40°, n_D^{20} 1.4092, that gave a slight positive test with ammoniacal silver nitrate.

B. By a one-step synthesis from 3-methyl-1-butyne-3-ol (III). In a 2-liter separatory-funnel were shaken, for 10 minutes at room temperature, 276 g. (3.28 moles) of 3-methyl-1-butyne-3-ol (III) and 1 liter of concentrated hydrochloric acid. The organic layer was dried overnight at 0° with potassium carbonate.

The drying agent was removed by filtration and the filtrate was added dropwise over a 2-hour period to a solution of 66.0 g. (1.74 moles) of lithium aluminum hydride in 800 ml. of dry tetrahydrofuran contained in a 2-liter, three-necked flask, equipped with a Hershberg stirrer, a dropping-funnel, and a bulb condenser. To prevent loss of the volatile product during reduction, a Dry Ice trap with a cold finger, protected with a calcium chloride tube, was placed at the top of the condenser. After the addition had been completed, the reaction mixture was stirred and heated under reflux for an additional 18 hours. The water was removed from the condenser and the Dry Ice trap was replaced by a 13-inch, helix-packed column. The crude allene plus about one-third of the tetrahydrofuran were removed by distillation through the column. Fractionation of this distillate through the same column produced 114 g. (51%) of 3-methyl-1,2-butadiene (I), b.p. 39–40.6°, n_D^{25} 1.4142.

This sample of the 3-methyl-1,2-butadiene (I) gave only a very slight precipitate with ammoniacal silver nitrate, indicating the almost complete absence of any acetylene derivative. As in the previous reduction, the forerun had a low refractive index. If one assumes that the only impurity was 3-methyl-2-butene, n_D^{25} 1.3854, one would calculate that a maximum of 4.2% yield of this olefin was produced.

Reduction of 3-chloro-3-methyl-1-pentyne (VI). In a 5-liter, three-necked flask, equipped with a Hershberg stirrer, a dropping-funnel and a reflux condenser protected with a drying tube, were placed 73.4 g. (1.93 moles) of lithium aluminum hydride and 500 ml. of absolute ether. Over a period of 1 hour 101 g. (0.965 mole) of 3-chloro-3-methyl-1-pentyne (VI) was added dropwise and the mixture was heated under reflux for 1 week. After the excess hydride was decomposed with water, the salts were dissolved in 20% hydrochloric acid. The ether layer was removed and the aqueous layer was exhaustively extracted for 3 days with ether. The combined ether solutions were dried over potassium carbonate and distilled through a 6-inch, helix-packed column to yield 23.2 g. of a forerun, b.p. 40–62°, n_D^{25} 1.3610–1.3891, and 38.7 g. (48%) of 3-methyl-2-pentene (VII), b.p. 62–68° (763 mm.), n_D^{25} 1.3940–1.4052 [reported (10) b.p. 68°, n_D^{20} 1.4005].

The 3-methyl-2-pentene (VII) was further characterized by conversion to the known 3-chloro-3-methylpentane. At 0°, 4.0 g. (0.045 mole) of the olefin VII was saturated with gaseous hydrogen chloride and allowed to stand for 24 hours at the same temperature. The solution was resaturated with hydrogen chloride and allowed to stand an additional 3 days at 0°. The reaction mixture was neutralized with anhydrous potassium carbonate and distilled through a 4-inch Vigreux column to yield 2.0 g. of unreacted olefin, b.p. 67–68°, n_D^{25} 1.3990, and 1.1 g. (20%) of 3-chloro-3-methylpentane, b.p. 115–116° (761 mm.), n_D^{25} 1.4191 [reported (11) b.p. 115–117°, n_D^{20} 1.4208]. This chloro compound gave an immediate precipitate with a silver nitrate solution, but gave no precipitate with potassium iodide in acetone.

Attempts to isolate 3-methyl-1-pentene dibromide by bromination of the hydrocarbon fractions failed.

3-Methyl-1,2-pentadiene (V). In a 2-liter separatory-funnel were shaken 85 g. (0.868 mole) of 3-methyl-1-pentyne-3-ol (IV) and 900 ml. of concentrated hydrochloric acid for 40 minutes. The organic layer was dried overnight at 0° with potassium carbonate and then added dropwise over a 2-hour period to a solution of 16.5 g. (0.434 mole) of lithium aluminum hydride in 1 liter of anhydrous dioxane contained in a 2-liter, three-necked flask and heated under reflux. The flask was equipped with a Hershberg stirrer, a dropping-funnel, and an 18-inch, helix-packed column leading to a Dry Ice trap. The crude allene plus some dioxane were removed through the distillation column as fast as the allene was formed. The crude allene was washed with an ammoniacal silver nitrate solution and with a 5% silver nitrate solution to remove any chloro compound or acetylene. After the allene had been dried over magnesium sulfate plus sodium hydride, the crude material was fractionated through a 6-inch, helix-packed column to yield 34.8 g. (49%) of 3-methyl-1,2-pentadiene (V), b.p. 70.3° (754 mm.), n_D^{25} 1.4257 [reported (12) b.p. 70–71° (760 mm.)]. V gave a negative test with a silver nitrate solution.

Anal. Calc'd for C_6H_{10}: C, 87.75; H, 12.25.

Found: C, 87.73; H, 12.28.

unsym-Pentamethyleneallene (VIII). In a 1-liter separatory-funnel were shaken 100 g. (0.805 mole) of 1-ethynylcyclohexanol (IX) and 300 ml. of concentrated hydrochloric acid for 8 minutes. The organic layer was dried overnight at 0° with potassium carbonate and added dropwise over a 1-hour period to a solution of 16.0 g. (0.421 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether contained in a 2-liter, three-necked flask. This flask was equipped with a stirrer, a dropping-funnel, and a condenser connected to a Dry Ice trap. After the mixture had been heated under reflux for 17 hours, the excess hydride was decomposed with water and the salts were dissolved in 20% hydrochloric acid. The aqueous layer was extracted with two 150-ml. portions of ether and these extracts were combined with the original ether layer. After the solution had been dried over potassium carbonate, it was distilled through a 6-inch, helix-packed column to give 24.9 g. of the crude allene, b.p. 56–61° (45 mm.). An ether solution of this crude material was heated under reflux with 2.0 g. of maleic anhydride to remove any diene X and then washed with 2.5% aqueous silver nitrate and with ammoniacal silver nitrate to remove any acetylene. The ether solution was dried over magnesium sulfate and potassium carbonate and distilled through a 6-inch, helix-packed column to yield 13.4 g. (15%) of *unsym*-pentamethyleneallene (VIII), b.p. 56.5–58.5° (45 mm.), n_D^{25} 1.4840, d_4^{25} 0.8457 [reported (7) b.p. 138–141°, n_D^{20} 1.4826, d_0^{20} 0.8508].

Attempted reduction of 3-methyl-1,2-pentadiene (V). A solution of 23.6 g. (0.289 mole) of 3-methyl-1,2-pentadiene (V) and 10.7 g. (0.290 mole) of lithium aluminum hydride in 200 ml. of absolute ether was heated under reflux for 10 days. When the reaction mixture was worked up in the usual way, 19.2 g. (81%) of the allene V was recovered unchanged. No evidence of any olefin or paraffin was observed. Similar results were obtained when 12.3 g. (0.290 mole) of lithium chloride was added to the reaction mixture. The allene was also recovered unchanged from a solution of V and an equimolar quantity of lithium aluminum hydride in dioxane that had been heated at 60° for 6 days.

Attempted reduction of 3-methyl-1,2-butadiene (I). A solution of 42.5 g. (0.625 mole) of 3-methyl-1,2-butadiene (I) and 11.9 g. (0.313 mole) of lithium aluminum hydride in 150 ml. of tetrahydrofuran was stirred at 32° for 1 week. When the reaction mixture was worked up in the usual manner, 35.1 g. (83%) of the dimethylallene was recovered unchanged with no evidence of any reduction.

A solution of 25.0 g. (0.368 mole) of allene I, 14.0 g. (0.368 mole) of lithium aluminum hydride, 44 g. (0.536 mole) of 1-hexyne, and 14.8 g. (0.350 mole) of lithium chloride in 150 ml. of dioxane was stirred at 0° for 4 days. When the reaction mixture was worked up in the usual manner, 22.8 g. (91%) of the allene I and 38.7 g. (88%) of the 1-hexyne were recovered unchanged. No evidence of any reduction to the olefin was found.

SUMMARY

Three allenes, 3-methyl-1,2-butadiene (I), 3-methyl-1,2-pentadiene (V), and *unsym*-pentamethyleneallene (VIII) were synthesized in convenient one-step syntheses from the corresponding commercially available acetylenic alcohols in yields of 51%, 49%, and 15%, respectively.

College Park, Maryland

REFERENCES

(1) GUSTAVSON AND DEMJANOFF, *J. prakt. Chem.*, [2] **386,** 202 (1888); BOUIS, *Bull. soc. chim.*, [4] **41,** 1160 (1927); *Ann. chim.*, [10] **9,** 402 (1928).

(2) FAVORSKI, *J. prakt. Chem.*, [2] **37,** 392 (1888).

(3) GINZBURG, *J. Gen. Chem.* (*U. S. S. R.*), **10,** 513 (1940).

(4) HENNION AND SHEEHAN, *J. Am. Chem. Soc.*, **71,** 1964 (1949).

(5) WOTIZ, *J. Am. Chem. Soc.*, **73,** 693 (1951); SAMMUL, HOLLINGSWORTH, AND WOTIZ, *J. Am. Chem. Soc.*, **75,** 4856 (1953).

(6) HURD AND JONES, *J. Am. Chem. Soc.*, **56,** 1924 (1934).

(7) JEGOROWA, *J. Russ. Phys.-Chem. Soc.*, **43,** 1119 (1911).

(8) BERGMANN AND HERRMAN, *J. Am. Chem. Soc.*, **73,** 4013 (1951).

(9) CAMPBELL, CAMPBELL, AND EBY, *J. Am. Chem. Soc.*, **60,** 2883 (1938).

(10) WHITMORE AND MOSHER, *J. Am. Chem. Soc.*, **63,** 1122 (1941).

(11) HUNTRESS, *Organic Chlorine Compounds*, John Wiley and Sons, New York, 1948.

(12) IPATIEFF, *J. prakt. Chem.*, [2] **61,** 526 (1899).