Reaction of Tris[(*RS*)-1-methylpropoxy]methane (IV) with CO and H_2 in the Presence of NaCo $(CO)_4$.—A solution of tris compound IV (14 g) and $NaCo(CO)_4$ (1.78 g) in butan-2-ol (19.5 ml) was introduced in a 125-ml autoclave and then CO and H_2 (1:1) were added up to 140 atm. The autoclave was heated up to 100° for 3 hr. A pressure drop of 9 atm was noted. After cooling, 29 g of liquid product was collected. The carbonyl compounds present in the reaction products were 0.011 equiv (18.3% conversion). Only traces of unreacted orthoformic ester could be detected.

Reaction of Tris[(*RS*)-1-methylpropoxy]methane (IV) with $HCo(CO)_4$.—A solution of $HCo(CO)_4$ (0.4 g, 0.0023 mol) in ethyl ether (5 ml), cooled at 0°, was slowly added, under N_2 and with stirring, to a solution of IV (5.3, g, 0.023 mol) in ethyl ether (5 ml). After standing at 0° for 1 hr, the solution was kept at room temperature for 1 hr and then $P(C_6H_5)_3$ (0.7 g, 0.0027 mol) in ethyl ether was added. After standing for 1 hr the solution was evaporated almost to dryness at 0° under reduced pressure. From the residue, by crystallization from *n*-pentane at −70°, a pale yellow crystalline precipitate was recovered which, by comparing its ir spectrum with that of an authentic sample,[8] was identified as *sec*-$C_4H_9COCo(CO)_3P(C_6H_5)_3$.

Registry No.—I, 17159-00-1; carbon monoxide, 630-08-0; $[Co(CO)_4]_2$, 14638-72-3; IV, 17159-01-2.

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Allenes by Lithium Aluminum Hydride Reduction of Propargyl Derivatives

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Although earlier reports have suggested that both allenes and acetylenes can be products of the lithium aluminum hydride reduction of propargyl or allenyl halides,[2-9] careful studies utilizing gas chromatography, reported recently by Jacobs and coworkers,[3,7] have shown that hydride reduction of either 3-chloro-3-methyl-1-butyne (**1a**) or the corresponding bromo compound **1b** yields 3-methyl-1,2-butadiene but no 3-methyl-1-butyne. Nevertheless, substantial contamination of the allene obtained from the chloro compound **1a** with over-reduced hydrocarbons such as 3-methyl-1-butene, 2-methyl-2-butene, and 2-methylbutane limited the synthetic utility of this process. Although the bromo derivative **1b** was reduced cleanly and in high yield to the desired allene, this starting material was not readily obtained in pure form.[7] The corresponding 1-halo-3-methyl-1,2-butadienes (**2**) were observed to give 3-methyl-1-butyne but no 3-methyl-1,2-butadiene, thus graphically illustrating that common intermediates are not involved in the reductions of these two related systems. Again, over-reduction was found to be a problem with both the chloro- and bromoallene.

$(CH_3)_2CXC{\equiv}CH$
1a, X = Cl
b, X = Br

$(CH_3)_2C{=}C{=}CHX$
2a, X = Cl
b, X = Br

In the present work we have demonstrated that the lithium aluminum hydride reduction of secondary and tertiary propargyl chlorides constitutes a useful synthetic method for the corresponding allenes under modified reaction conditions. Thus, hydride reduction of **1a** in diethyl carbitol cooled in an ice–salt bath, followed by hydrolysis and removal of the volatile product from the reaction mixture by distillation, gave a 47% yield of 3-methyl-1,2-butadiene. This material was homogeneous by glpc and was specifically shown not to be contaminated with the over-reduced products encountered in the earlier work.[3] Furthermore, a similar clean product can be obtained more directly in 29% over-all yield from the corresponding alcohol by hydride reduction of the *crude* product from the preparation of chloride **1a**. Since the yield of purified chloride is only *ca.* 50% and a fractional distillation is avoided, this procedure is the method of choice for preparative purposes.

Under the same conditions hydride reduction of **2b** gave 3-methyl-1-butyne. Although 7% of 3-methyl-1-butene was formed as a by-product in this case, again over-reduction was much less prevalent than found previously.

As a mechanistic probe the above reductions were also performed using lithium aluminum deuteride. Nmr analysis of the 3-methyl-1,2-butadiene thus obtained from **1a** indicated selective and complete deuterium incorporation at one olefinic hydrogen. The mass spectrum confirmed this result by demonstrating the incorporation of a minimum of 94% of one deuterium. Nmr analysis of the 3-methyl-1-butyne obtained by similar reduction of **2b** showed that one deuterium was specifically incorporated at the methine position, as indeed Jacobs and Wilcox had previously demonstrated under their conditions. These reductions imply not only that hydride attack is specific at the terminal acetylene and the disubstituted methylene, respectively, but also that related conversions will provide a useful synthetic method for the preparation of specifically labeled acetylenes and allenes.

The successful reduction of **1a** prompted comparison with a similar sequence utilizing the secondary propargyl alcohol **3a**. Unfortunately no entirely satisfactory method for the clean conversion of **3a** into the corresponding chloride (**3b**) has been developed.[5,10] Phosphorous oxychloride gave a moderate yield of chloride, but this material was an 85:15 mixture of the desired acetylenic compound and the isomeric allene **4**. Redistillation afforded **3b** contaminated by only 7% of **4**, and this material was used for the reduction studies. A variety of other reagents and conditions for preparing the chloride were even less effective in our hands. The standard hydride reduction procedure gave a good yield of 1,2-hexadiene containing about 7%

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[1] National Institutes of Health Predoctoral Fellow, 1966–1968.

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[3] T. L. Jacobs and R. D. Wilcox, *J. Amer. Chem. Soc.*, **86**, 2240 (1964).

[4] O. R. Sammul, C. A. Hollingsworth, and J. H. Wotiz, *ibid.*, **75**, 4856 (1953).

[5] T. L. Jacobs, E. G. Teach, and D. Weiss, *ibid.*, **77**, 6254 (1955).

[6] J. H. Wotiz, *ibid.*, **73**, 693 (1951).

[7] T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963).

[8] H. W. Thompson, *ibid.*, **32**, 3712 (1967). See also G. Stork, Abstracts, Nineteenth National Organic Symposium, Tempe, Arizona, June 13–17, 1965, p 37.

[9] P. D. Landor, S. R. Landor, and E. S. Pepper, *J. Chem. Soc., C*, 185 (1967).

[10] G. F. Hennion and J. J. Sheehan, *J. Amer. Chem. Soc.*, **71**, 196 (1949).

of an unidentified impurity, which was neither 1-hexyne or 1-hexene. This result reaffirms that secondary propargyl chlorides are also useful precursors of allenes; however, better preparative methods for the pure chlorides are desirable.

$CH_3(CH_2)_2CHXC\equiv CH$
3a, X = OH
b, X = Cl
c, X = OSO_2CH_2

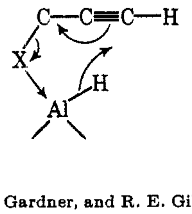
$CH_3(CH_2)_2CH{=}C{=}CHCl$
4

In an attempt to circumvent the latter problem, methanesulfonate (**3c**) was prepared and subjected to hydride reduction.[3] This ester was reduced in excellent yield to a hydrocarbon mixture which consisted of an 89:11 ratio of 1,2-hexadiene and 1-hexyne. Consequently, advantage cannot be taken of this high-yield sequence to produce pure allene without a purification step.

The mechanistic features of the lithium aluminum hydride reduction of propargyl halides have been considered in detail by Jacobs and coworkers,[3] and the present results only serve to substantiate their conclusions. The over-reduced products appear to result from direct reaction of hydride with the halogen compounds,[3] but these contaminants can be minimized by careful control of the reaction conditions.

The available information suggests that the steric environment markedly influences the competition between SN2 and SN2′ types of hydride attack on propargyl halides, since reduction apparently can occur by both processes. Primary propargyl halides undergo specific reduction to methylacetylenes by direct SN2 displacement,[4] except for the parent compound which gives some of the SN2′ product when the halogen atom is chloride.[3] Tertiary derivatives with a terminal alkyne group give a clean SN2′ reaction. The secondary chloride with a terminal alkyne examined in this work also reacted only by the SN2′ pathway. Some direct displacement may have been observed in the earlier studies[5,6] on this system, but the minor amount of acetylene found could have resulted from isomeric allenyl halide in the starting material. Versions of the propargyl system with other substitution patterns, but without directing neighboring functions,[9] have not been reported.

There does appear to be a definite leaving-group effect in these reactions, however, since secondary mesylate **3c** produced both acetylene and allene in contrast to chloride **3b**. A tentative explanation is that the specificity of the halide reductions is attributable to preliminary coordination of the aluminum hydride reagent with the halogen atom, followed by a cyclic hydride transfer process as depicted below. A similar mechanism has been suggested for the SN2′ reduction of allylic halides.[11] The sulfonate ester is probably not so amenable to complexation with aluminum, and therefore simple bimolecular displacement by both SN2 and SN2′ mechanisms takes place.[12]



Experimental Section

General.—Infrared and nmr spectra were obtained as solutions in carbon tetrachloride. Gas chromatographic (glpc) analysis was carried out on a Varian Aerograph Series 1200 unit with a flame ionization detector utilizing an analytical column of Carbowax 20M on Chromosorb W. Product composition was approximated by peak area. Preparative glpc was performed using a preparative column of the same material. An AEI MS-9 mass spectrometer was used for mass spectral analysis. Compound identification was made by correlation of spectra with those published or on the basis of the data given. Anhydrous magnesium sulfate was used as the drying agent.

Materials.—3-Chloro-3-methyl-1-butyne (**1a**) was prepared by reaction of 2-methyl-3-butyn-2-ol with concentrated hydrochloric acid and calcium chloride.[13] Distillation through a 5-in. Vigreux column gave glpc pure **1a** in 48–55% yield: bp 35–40° (160 mm); ir, 3.05 ($C\equiv CH$), 10.6, and 11.7 μ; nmr, τ 7.42 (s, 1, $C\equiv CH$) and 8.18 (s, 6, CH_3).

1-Bromo-3-methyl-1,2-butadiene (**2b**) was prepared by the reaction of 2-methyl-3-butyn-2-ol with 48% hydrobromic acid, copper, cuprous bromide, and ammonium bromide.[14] Distillation through a 5-in. Vigreux column gave glpc pure **2b** in 70% yield: bp 55–56° (60 mm); nmr, τ 6.28 (septet, 1, J = 2 Hz, $C{=}C{=}CH$) and 8.23 (d, 6, J = 2 Hz, CH_3).

3-Chloro-1-hexyne (3b).—To 10 g of **3a** at −5° was added dropwise 6 g of freshly distilled phosphorus oxychloride. When addition was complete, the mixture was stirred in the cold for 1 hr and then heated at 40–45° for an additional hour. The cooled mixture was poured on ice and extracted with ether. The extracts were washed with 5% sodium bicarbonate solution and water before drying. Removal of the solvent and distillation gave 12 g (49%) of a product mixture, bp 63–64° (100 mm), which consisted of 15% of **4** and 85% of **3b**. Redistillation at atmospheric pressure gave 3-chloro-1-hexyne (**3b**) which contained only 7% of the allenic isomer by glpc analysis: bp 123–124°; ir, 3.1 ($C\equiv CH$), 4.75 ($C\equiv C$), and 13.7 μ; nmr, τ 5.58 (triplet of doublets, 1, J = 7 and 2 Hz, $C\equiv CCHCl$), 7.55 (d, 1, J = 2 Hz, $C\equiv CH$), 8.32 (m, 4), and 9.03 (t, 3, J = 7 Hz, CH_3).

1-Hexyn-3-yl Mesylate (3c).—To a solution of 33 ml of **3a** and 29 ml of pyridine at −10° was added dropwise 25 ml of methanesulfonyl chloride. When addition was complete, the resulting slurry was stirred for 4 hr and was allowed to warm gradually to room temperature. The mixture was poured over ice and 29 ml of concentrated hydrochloric acid and extracted with ether. The extracts were washed with 5% sodium bicarbonate solution and water before drying. Removal of the solvent gave 52 g (98%) of crude **3c** with an ir spectrum identical with that of material further purified by distillation.

Crude **3c** (18 g) was purified by distillation to give 15 g (85%) of product: bp 88–90° (0.5 mm); ir, 3.13 ($C\equiv CH$), 4.75 ($C\equiv C$), 8.45 (sulfonate ester), and 10.9 μ; nmr, τ 4.9 (triplet of doublets, 1, J = 6 and 2 Hz, $CHOSO_2$), 6.95 (s, 3, OSO_2CH_3) 7.21 (d, 1, J = 2 Hz, $C\equiv CH$), 8.32 (m, 4), and 9.02 (t, 3, J = 7 Hz, CH_3).

Reduction Procedure.—In general, 1 equiv of the halide was added dropwise to a slurry of 2 equiv of lithium aluminum hydride in diethyl carbitol cooled in an ice–salt bath. (It is important that the diethyl carbitol be purified by distillation from lithium aluminum hydride.) The reaction mixture was stirred for 12–15 hr, during which time the mixture was allowed to warm to 25°. The mixture was cooled, and after the dropwise addition of water, volatile material of a selected boiling range was distilled from the crude mixture, separated by glpc, and spectroscopically analyzed.

3-Methyl-1,2-butadiene.—Treatment of 30.9 g of **1a** with 5.7 g of lithium aluminum hydride in 150 ml of diethyl carbitol for

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[11] L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1949).

[12] Organometallic reagents have also been reported to react with propargyl halides in a fashion similar to lithium aluminum hydride: L. Brandsma and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **86**, 734 (1967); D. B. Miller, *J. Org. Chem.*, **31**, 908 (1966); and T. L. Jacobs and P. Prempree, *J. Amer. Chem. Soc.*, **89**, 6177 (1967).

[13] G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *ibid.*, **72**, 3542 (1950).

[14] D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *J. Chem. Soc., C*, 1223 (1966).

15 hr followed by the addition of 23 ml of water gave 10.8 g of material, bp 38–55°. Distillation through a 5-in. Vigreux column yielded 9.6 g (47%) of 3-methyl-1,2-butadiene: bp 39.5–41.0°; nmr, τ 5.55 (septet, 2, J = 2.9 Hz, $C{=}C{=}CH_2$) and 8.37 (t, 6, J = 2.9 Hz, CH_3). Glpc analysis indicated that this material was homogeneous. The absence of 3-methyl-1-butyne, 3-methyl-1-butene, and 3-methyl-2-butene was shown by glpc retention time comparison.

3-Methyl-1,2-butadiene-1-d_1.—Treatment of 2.05 g of **1a** with 0.42 g of lithium aluminum deuteride gave 0.75 g (55%) of 3-methyl-1,2-butadiene-1-d_1 of 96% purity by glpc analysis: bp 35–55°; nmr, τ 5.58 (m, 1.00 ± 0.1 H, $C{=}C{=}CH$) and 8.37 (d, 6, J = 3.1 Hz, CH_3).[15] Mass spectral analysis indicated 5% d_0, 94% d_1, 1% d_2.

One-Step Preparation of 3-Methyl-1,2-butadiene.—2-Methyl-3-butyn-2-ol (84 g) was added dropwise to a vigorously stirred slurry of 111 g of calcium chloride, 420 ml of concentrated hydrochloric acid, and 1.0 g of hydroquinone. After stirring for 45 min, the top layer was separated and dried over sodium carbonate. After filtration, 54 g of the crude filtrate (90 g total) was treated for 15 hr with 5.7 g of lithium aluminum hydride in 150 ml of diethyl carbitol. After addition of 25 ml of water, material of boiling point range 40–55° was collected. Distillation gave 12.0 g (29%) of 3-methyl-1,2-butadiene which was homogeneous by glpc.

3-Methyl-1-butyne.—Treatment of 14.7 g of **2b** with 1.9 g of lithium aluminum hydride in 60 ml of diethyl carbitol for 15 hr followed by the addition of 8 ml of water gave 4.9 g (72%) of material, bp 30–35°, which was identified as 3-methyl-1-butyne (90%) [ir, 3.05 ($C{\equiv}CH$), 4.72 ($C{\equiv}C$), 7.28 and 7.38 μ (CH_3); nmr, τ 7.55 (septet of doublets, 1, $C{\equiv}CCH$), 8.13 (d, 1, J = 2 Hz, $C{\equiv}CH$), and 8.86 (d, 3, J = 6.5 Hz, CH_3)] and 3-methyl-1-butene (10%).

3-Methyl-1-butyne-3-d_1.—Treatment of 4.3 g of 1-bromo-3-methyl-1,2-butadiene (**2b**) with 0.57 g of lithium aluminum deuteride gave 1.35 g (65%) of material, bp 25–35°, 90% of which was 3-methyl-1-butyne-3-d_1: nmr, τ 8.16 (s, 1, $C{\equiv}CH$) and 8.85 (t, 6, J = 1 Hz, CH_3). No signal was observed for the methine proton.

1,2-Hexadiene.—Treatment of 5.8 g of **3b** with 0.95 g of lithium aluminum hydride in 20 ml of diethyl carbitol for 12 hr followed by the addition of 4 ml of water gave 3.3 g of material of boiling range 66–90°. Distillation through a 5-in. Vigreux column yielded 2.9 g (72%) of product which consisted of 1,2-hexadiene (93%): ir, 5.13 ($C{=}C{=}C$), 7.28 (CH_3), 11.5, and 11.9 μ; nmr, at τ 5.04 (quartet, 1, J = 6.5 Hz, $C{=}C{=}CH$), 5.4 (m, 2, $C{=}C{=}CH_2$), 8.1 and 8.6 (m, 4), and 9.05 (t, 3, J = 7 Hz, CH_3); and an unknown terminal olefin (7%) with infrared absorption at 6.1, 10.1, and 11.0 μ, which was not 1-hexene.

Reduction of 1-Hexyn-3-yl Mesylate.—A slurry of 11 g of lithium aluminum hydride in 300 ml of diethyl carbitol was maintained below 0° in an ice–methanol bath during the dropwise addition of 53 g of crude **3c**. The mixture was then stirred for 5 hr. After recooling to 0°, 46 ml of water was added dropwise. When reaction ceased, volatile material was distilled from the reaction mixture to give 19.8 g (80%) of crude product, bp range 60–90°, which was identified as 89% 1,2-hexadiene and 11% 1-hexyne.

Lithium aluminum hydride reduction of 1-hexyn-3-yl mesylate which had been purified by distillation gave a identical result.

Registry No.—Lithium aluminum hydride, 1302-30-3; **3b**, 761-79-5; **3c**, 17159-63-6; 3-methyl-1,2-butadiene, 598-25-4; 3-methyl-1,2-butadiene-1-d_1, 17159-64-7; 3-methyl-1-butyne, 598-23-2; 3-methyl-1-butyne-3-d_1, 17159-65-8; 1,2-hexadiene, 592-44-9.

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The Aluminum Alcoholate of a Hemiacetal. An Intermediate in the Tishchenko Reaction

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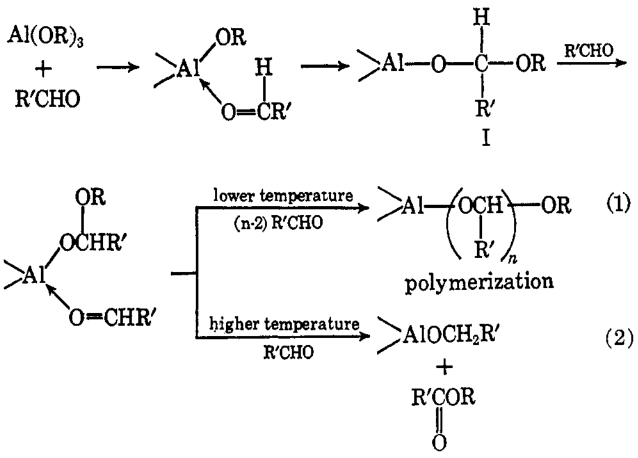
Previously,[1–4] the aluminum alcoholate of a hemiacetal (I) has been formulated as the key intermediate in the polymerization of aldehyde by aluminum alcoholate and in the Tishchenko reaction (eq 1 and 2).



Tishchenko reaction

However, other possible mechanisms of the Tishchenko reaction which do not involve the intermediate I have also been presented.[5,6]

In the present study, the aluminum alcoholate of a hemiacetal corresponding to I was isolated in a specified combination of reaction components, *i.e.*, aluminum *t*-butoxide and trichloroacetaldehyde (chloral), and the reactivity of I was examined to obtain support for the scheme shown in eq 1 and 2.

When the reaction was carried out at 30° in *n*-heptane, the aluminum alcoholate of a semiacetal (II) (R = *t*-Bu, R′ = Cl_3C in I) separated as a white crystalline solid from the yellow reaction mixture after 10 days. The amount of II increased progressively up to 30 days (yield 67%). The reaction temperature is quite important for the isolation of II. In the reaction at 0°, only the polymerization of chloral took place to produce an insoluble polymer of chloral. At 60°, only the Tishchenko ester, 2,2,2-trichloroethyl trichloroacetate, was isolated.

The success in isolation of II is also ascribed to the choice of the reaction components. The trichloromethyl group of hemiacetal alcoholate II suppressed the hydride transfer from II to chloral (eq 2) by its

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