SUBSTITUTION REACTIONS INVOLVING ORGANOALUMINUM COMPOUNDS. NO. 6.* SYNTHESIS OF CONJUGATED DIALLENES AND ALLENYNES FROM PROPARGYL DIACETATES

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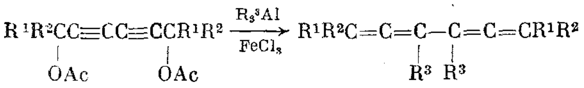
Acetates of propargylic alcohols react with organoaluminum compounds (OAC) to give substituted allenes [2]. Catalysis by salts and transition metal complexes (Cu, Pd, Fe) is necessary for these reactions. The present paper deals with a study of the reactions of diacetates of monoacetylenic and both symmetrical and unsymmetrical diacetylenic glycols with trialkylalanes, which lead to the formation of substituted allenes, and conjugated diallenes and allenynes, respectively. The latter compounds are of interest in connection with known examples of the introduction of allenyl fragments to the structures of a series of natural products, and also because of their potential use as synthons [3].

Reactions of propargyl diacetates with trialkylalanes were carried out in refluxing ether in the presence of $FeCl_3$, which is known to be an effective catalyst of acetylene–allene isomerization [2].

The reaction of tertiary propargyl diacetates of symmetrical diacetylenic glycols with trialkylalanes leads to the formation of conjugated diallenes. For example, treatment of 3,8-diacetoxy-3,8-dimethyl-4,6-decadiyne (I) with triethylaluminum (TEA) over a 4 h period yields the symmetrical diallene (II) in 56% yield. The analogous reaction of diacetate (I) with triisobutylaluminum (TIBA) occurs much more slowly (10 h) and results in the formation of greater amounts of side products. The yield of diallene (III) in this reaction is only 43%. Similar results are obtained in the reaction of 1,4-di-(1-acetoxy-1-cyclohexyl)-1,3-butadiyne (IV) with TEA: after 6 h, the crystalline diallene (V) is formed in 86% yield.



$$R^1R^2\underset{\displaystyle OAc}{\underset{|}{C}}C\equiv CC\equiv C\underset{\displaystyle OAc}{\underset{|}{C}}R^1R^2 \xrightarrow[FeCl_3]{R_3^3Al} R^1R^2C=C=\underset{\displaystyle R^3}{\underset{|}{C}}-\underset{\displaystyle R^3}{\underset{|}{C}}=C=CR^1R^2$$

(I), (IV) (II), (III), (V)

$R^1 = Me$, $R^2 = Et$ (I); $R^1R^2 = (CH_2)_5$ (IV); $R^1 = Me$, $R^2 = R^3 = Et$ (II); $R^1 = Me$, $R^2 = Et$, $R^3 = i\text{-}Bu$ (III); $R^1R^2 = (CH_2)_5$, $R^3 = Et$ (V).

Structures (II), (III), and (V) were confirmed by the presence of characteristic bands of the allenyl groups in the 1955-1970 cm^{-1} region of their IR spectra. The presence of the conjugated diallene system was verified by their UV spectra, which exhibited four bands with similar frequencies and intensities in all of the compounds. The ^1H- and ^{13}C-NMR spectra of these compounds were also consistent with the proposed structures. The properties of the diallenes are summarized in Table 1.

The formation of a diallene can be logically assumed to occur from 3,8-diacetoxy-3,8-dimethyl-1,9-decadien-4,6-diyne (VI), which is the Glaser condensation product of 3-methyl-3-acetoxy-1-penten-4-yne (VII).

Acetate (VII) can react with trialkylalanes in two different directions, to give either an enyne or vinylallene.

Thus, in the reaction of acetate (VII) with TIBA, the vinylallene (VIII) and enyne (IX) are obtained in an 88:12 ratio (GLC), with a 53% yield of (VIII).

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*For Communication No. 5, see [1].

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TABLE 1. Properties of Diallenes

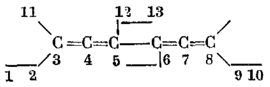
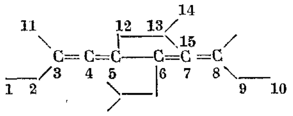
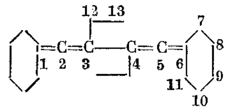
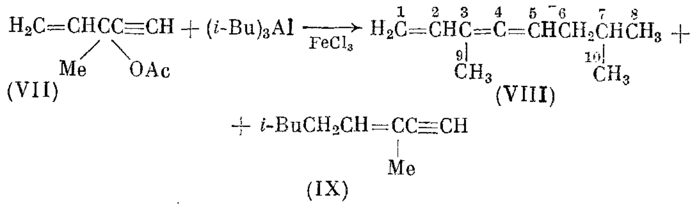
Compound	bp, °C (p, mm Hg)	n_D^{20}	IR spectrum ν, cm^{-1}	^{1}H- and ^{13}C-NMR spectra, δ, ppm	UV spectrum λ, nm (ε)	Mass spectrum, m/z
3,8-Dimethyl-5,6-diethyl-3,4,6,7-decatetraene (II)  	56—57 (0,5)	1,5022	1970, 1460, 900, 800, 740	^{1}H: 0,95 t (6H, CH_3, $J = 7$ Hz), 1,00 t (6H, CH_3, $J = 7$ Hz), 1,73 s (6H, CH_3), 1,95 q (4H, CH_2, $J = 7$ Hz), 1,98 q (4H, CH_2, $J = 7$ Hz) ^{13}C: 12,53 q (C^{1}, C^{10}), 12,99 q (C^{13}), 19,26 q (C^{11}), 24,61 t (C^{12}), 27,74 t (C^{2}, C^{9}), 104,57 s (C^{5}, C^{6}), 106,53 s (C^{3}, C^{8}), 199,75 s (C^{4}, C^{7})	204(27 415), 223(23 286), 242(12 221), 303(813)	218
3,8-Dimethyl-5,6-diisobutyl-3,4,6,7-decatetraene (III)  		1,4930	1955, 1700, 1470, 790, 735	^{1}H: 0,87 d (6H, CH_3, $J = 6{,}5$ Hz), 1,00 t (6H, CH_3, $J = 7$ Hz), 1,70 s (6H, CH_3), 1,91 m (10H, CH_2 and CH) ^{13}C: 12,50 q (C^{1}, C^{10}), 18,83 q (C^{11}), 22,78 q (C^{14}, C^{15}), 27,38 d (C^{13}), 27,84 t (C^{2}, C^{9}), 41,48 t (C^{12}), 102,45 t (C^{5}, C^{6}), 103,23 s (C^{3}, C^{8}), 200,98 s (C^{4}, C^{7})	203(24 289), 225(20 241), 243(12 357), 298(492)	247
1,1,6,6-Dipentamethylene-3,4-diethyl-1,2,4,5-hexatetraene (V)  	mp 56—57° (hexane)		1960, 1690, 1452, 975, 900, 790, 740	^{1}H: 0,92 t (6H, CH_3, $J = 7$ Hz), 1,70 m (12H, CH_2), 2,06 m (12H, CH_2) ^{13}C: 13,22 q (C^{13}), 24,54 t (C^{9}), 26,40 t (C^{12}), 27,87 t (C^{8}, C^{10}), 32,11 t (C^{7}, C^{11}), 104,21 s (C^{3}, C^{4}), 105,88 s (C^{1}, C^{6}), 196,94 s (C^{2}, C^{5})	215(32 869), 228(27 527), 245(24 642), 299(192)	270
1-Phenyl-3,4-diethyl-6-methyl-1,2,4,5-octatetraene (XXII)		1,5708	1920, 1945, 3040, 3070, 1700, 1600, 830, 750, 700	^{1}H: 0,95 t (3H, CH_3, $J = 7$ Hz), 1,05 t (6H, CH_3, $J = 7$ Hz), 1,76 d (3H, CH_3, $J = 2$ Hz), 2,02 q and 2,09 q (8H, CH_2, $J = 7$ Hz), 6,33 t (CH=C=C, $J = 3$ Hz), 7,20 s (5H, Ph) ^{13}C: 12,45 q (C^{8}), 12,82 q (C^{17}, C^{19}), 19,19 q (C^{15}), 24,51 t (C^{16}, C^{18}), 27,51 t (C^{7}), 98,14 d (C^{1}), 105,16 s (C^{4}), 105,52 s (C^{6}), 111,16 s (C^{3}), 126,51 d (C^{10}), 127,29 d (C^{12}), 128,53 d (C^{11}), 200,17 s (C^{5}), 204,90 s (C^{2})	211(48 234), 250(56 213), 281(3 173), 290(1 088)	272

TABLE 1 (continued

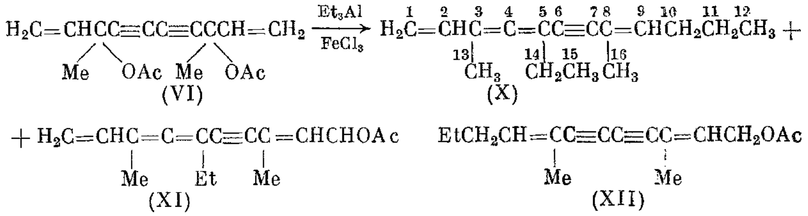
Compound	bp, °C (p, mm Hg)	n_D^{20}	IR spectrum ν, cm⁻¹	¹H- and ¹³C-NMR spectra, δ, ppm	UV spectrum λ, nm (ε)	Mass spectrum, m/z
3,8-Dimethyl-5-ethyl-1,3,4,8-dodecatetraene (X)			3095, 3020, 2200, 1935, 1680, 1615, 995, 900	¹H: 0,93 t (3H, CH_3, $J = 7$ Hz), 0,98 t (3H, CH_3, $J = 7$ Hz), 1,40 m (2H, CH_2), 1,85 s (3H, CH_3), 1,89 s (3H, CH_3), 2,11 m (4H, CH_2), 5,80 t (1H, CH=C), 5,05 m (2H, $CH=CH_2$), 6,30 m (1H, $CH=CH_2$) ¹³C: 12,73 q (C^{15}), 13,77 q (C^{12}), 14,95 q (C^{13}, C^{16}), 22,39 t (C^{14}), 24,67 t (C^{11}), 33,03 t (C^{10}), 65,86 s (C^6), 81,47 s (C^7), 104,25 s (C^3), 105,55 s (C^5), 117,11 s (C^8), 136,17 d (C^2), 141,71 d (C^9), 207,06 s (C^4)		214
1-Acetoxy-2-ethyl-4-methyl-2,3-hexadiene (XX)	40—42 (2)	1,4558	1970, 1750, 1235	¹H: 0,95 t (6H, CH_3, $J = 7$ Hz), 1,66 s (3H, CH_3), 1,95 s (3H, CH_3 in Ac), 1,99 m (4H, CH_2), 4,20 s (2H, CH_2OAc) ¹³C: 12,27 q (C^6, C^9), 19,09 q (C^7), 20,86 q (C^{11}), 23,04 t (C^8), 27,16 t (C^5), 65,77 t (C^1), 101,86 s (C^4), 104,18 s (C^2), 170,41 s (C^{10}), 198,74 s (C^3)		182
1-Acetoxy-2-ethyl-6-methyl-4,5-octadien-2-yne (XXIV)	83—84 (0,5)	1,4965	2230, 1960, 1750, 1230, 970	¹H: 0,97 t (6H, CH_3, $J = 7$ Hz), 1,70 s (3H, CH_3), 1,97 m (4H, CH_2), 2,00 s (3H, CH_3 in Ac), 4,70 s (2H, CH_2OAc) ¹³C: 12,17 q (C^{13}), 12,63 q (C^8), 18,83 q (C^{11}), 20,76 q (C^{10}), 27,22 t (C^{12}), 27,42 t (C^7), 53,14 t (C^1), 82,61 s (C^2), 83,82 s (C^3), 90,51 s (C^4), 104,54 s (C^6), 170,21 s (C^9), 205,82 s (C^5)	220 (10 204)	206


$$H_2C{=}CHC(Me)(OAc)C{\equiv}CH + (i\text{-}Bu)_3Al \xrightarrow[FeCl_3]{} H_2C{=}CHC(CH_3){=}C{=}CHCH_2CH(CH_3)CH_3 + i\text{-}BuCH_2CH{=}C(Me)C{\equiv}CH$$

(VII) (VIII) (IX)

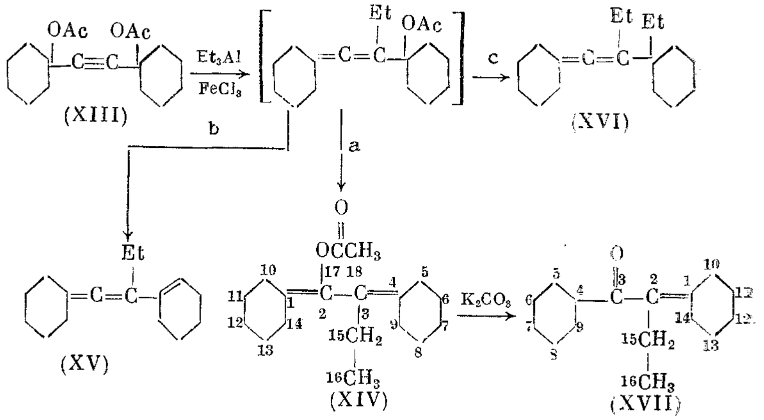
The reactions of allyl acetates with OAC have been investigated previously [4].

Diacetate (VI) reacts with TEA to a greater extent via an allylic cross-coupling scheme, with isomerization in the γ-position. As a result, a mixture of hydrocarbons and two acetates, (XI) and (XII), is formed. After chromatography on silica gel, allenyne (X) was isolated from the hydrocarbon mixture in 23% yield. It was not possible to separate the mixture of acetates, but their structures were determined by IR and PMR spectroscopy. The yield of the acetate mixture was 26%. These compounds were very unstable, and polymerized readily during the course of isolation and storage. Using a large excess of TEA does not affect the composition of the reaction mixture.


$$H_2C{=}CHC(Me)(OAc)C{\equiv}CC{\equiv}CC(Me)(OAc)CH{=}CH_2 \xrightarrow[FeCl_3]{Et_3Al} H_2C{=}CHC(CH_3){=}C{=}C(CH_2CH_3)C{\equiv}CC(CH_3){=}CHCH_2CH_2CH_3 + H_2C{=}CHC(Me){=}C{=}C(Et)C{\equiv}CC(Me){=}CHCHOAc \quad EtCH_2CH{=}C(Me)C{\equiv}CC{\equiv}CC(Me){=}CHCH_2OAc$$

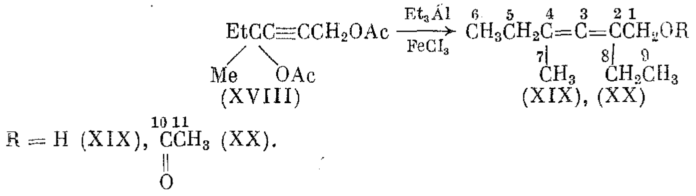
(VI) (X) (XI) (XII)

It was also of interest to us to examine the reaction of OAC with a symmetrical monoacetylenic diacetate containing tertiary acetoxy groups. The reaction of 1,2-di-(1-acetoxy-1-cyclohexyl)ethyne (XIII) with TEA (at a molar ratio of 1:1.2) at 20°C over 20 h generates equal amounts of vinyl acetate (XIV) and a hydrocarbon mixture. Increasing the amount of OAC reagent to 4 moles per mole diacetate shortens the reaction time considerably to 3 h, but does not change the product ratio. Chromatography of the hydrocarbon fraction on silica gel resulted in the isolation of vinylallene (XV) in 35% yield. The presence of allene (XVI) in the mixture was also detected, based on the PMR spectrum and mass spectrum of its mixture with allene (XV). The yield of acetate (XIV) was 37%; after washing with K_2CO_3 in methanol at 25°C for 1.5 h, it was converted to the ketone (XVII). The structures of all of the compounds were reliably established by means of their ^1H- and ^{13}C-NMR, IR, UV, and mass spectra. These data allow us to propose that the reaction of diacetate (XIII) with TEA occurs via the formation of an unstable intermediate allenyl acetate, which can then undergo isomerization (a), elimination (b), and substitution (c) of an OAc group to give (XIV), (XV), and (XVI), respectively.

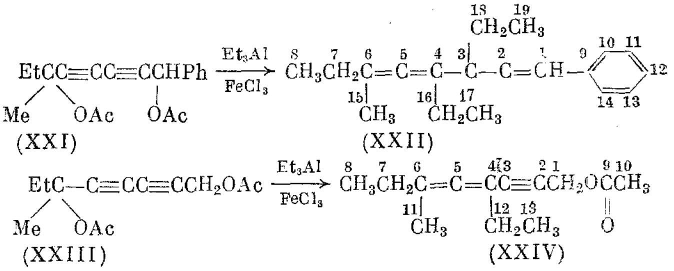


(XIII) (XVI) (XV) (XIV) (XVII)

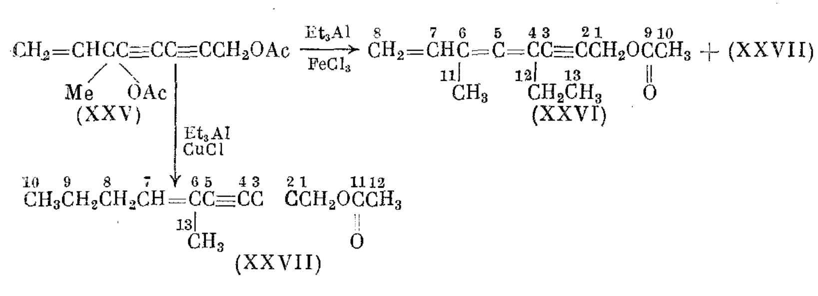
The reactivities of OAc groups attached to primary, secondary, and tertiary C atoms in propargylic systems were studied using the diacetates of monoacetylenic and unsymmetrical diacetylenic glycols, which were prepared via Khodkevich-Kad' condensation of monoacetylenic carbinols. The greater reactivity of a tertiary propargyl acetate compared to a primary one was demonstrated in the reaction of 1,4-diacetoxy-4-methyl-2-hexyne (XVIII) with TEA. At a diacetate:TEA ratio of 1:2, the reaction occurs over a 4 h period in refluxing ether to give a mixture of alcohol (XIX) (23%) and acetate (XX) (77%). Acetylation of the mixture with Ac_2O–Py gave the diacetate (XX) in 68% yield. The alcohol is apparently formed by reduction of acetate (XX) with excess TEA. At a diacetate (XVIII):TEA ratio of 1:1 the reaction proceeds significantly slower and does not proceed to completion.



The reactivities of secondary and tertiary propargyl acetoxy groups are very similar, as evidenced by the reaction of 3-methyl-8-phenyl-3,8-diacetoxy-4,6-octadiyne (XXI) with TEA. The unsymmetrical diallene (XXII) was formed in 62% yield after 3 h. Its IR spectrum contained two characteristic allene bands, at 1920 cm^{-1} and 1945 cm^{-1}. In the case of 3-methyl-3,8-diacetoxy-4,6-octadiyne (XXIII), the less reactive primary acetoxy group in the propargylic system does not undergo reaction with TEA. The reaction proceeds to completion in 3 h in refluxing ether, and the yield of pure allenyne (XXIV) is 77%. This acetate was isolated by chromatography on silica gel; hydrocarbons were not detected by this process



A more complex reaction pathway was observed upon substitution of an acetoxy group in an allylic–propargylic system. For instance, treatment of 3-methyl-3,8-diacetoxy-1-octen-4,6-diyne (XXV) with TEA in the presence of $FeCl_3$ at 25°C for 3 h led to the formation of a 71% yield of a mixture of acetates (XXVI) and (XXVII) (1:1 ratio by GLC). The first acetate is formed via propargyl substitution, the second via allylic substitution, with rearrangement. The primary propargyl acetate does not participate in the reaction. An effect due to the nature of the catalyst on the direction of the reaction of diacetate (XXV) with TEA was observed upon replacement of $FeCl_3$ by CuCl. In the case of CuCl, only the allylic substitution sequence, with rearrangement, takes place, and the acetate product (XXVII) is formed in 78% yield. This enediyne acetate consists of a mixture of equal amounts of the Z- and E-isomers, according to GLC data and its PMR spectrum, in which the CH_3 groups attached to the trisubstituted double bond give rise to signals at 1.84 and 1.77, and the $AcOCH_2$ group at 4.76 and 4.78 ppm. The ^{13}C-NMR spectrum of this mixture, as well as one enriched with the Z-isomer, also confirm the formation of Z- and E-isomers of (XXVII).



EXPERIMENTAL

UV and IR spectra were recorded on Specord UV-VIS (for ethanol solutions) and UR-20 spectrophotometers (thin films); PMR spectra were obtained on Tesla spectrometers (at 60 and 100 MHz for CCl_4 solutions versus TMS), while mass spectra were taken on an MX-1306 spectrometer at 70 eV and an ionization chamber temperature of 150°C. ^{13}C-NMR spectra were obtained on a Jeol FX-90Q spectrometer using $CDCl_3$ solutions (22.63 MHz), with both broad band proton decoupling as well as in the monoresonance mode. GLC analyses were carried out on a Khrom-5 chromatograph using a 1.2 m × 3 mm or 2.4 m × 3 mm column filled with 5% SE-30 on N-AW-DMCS chromatone and helium carrier gas (50 ml/min). Preparative separations were carried out on a Khrom-31 chromatograph using a 1.5 m × 10 mm column filled with 20% SE-301 on N-AW chromatone and a He gas flow rate of 300 ml/min.

1,4-Dihydroxy-4-methyl-2-hexyne was prepared according to [5], 1,2-di(1-hydroxy-1-cyclohexyl)ethyne according to [6]. Diacetylenic glycols were prepared via Glaser or Khodkevich-Kad' [7] oxidative condensation reactions. Diacetates were obtained from the corresponding glycols via standard acetylation procedures using acetic anhydride in pyridine. Anhydrous ether was prepared via successive reflux over CaH_2 and $LiAlH_4$.

Reactions of Mono- and Diacetylenic Glycol Diacetates with Trialkylalanes (General Method). A solution of diacetate (0.01 mole) and $FeCl_3$ (0.5 mmole) or CuCl (0.8 mmole) in 25 ml dry ether was stirred under Ar at 20°C and trialkylalane (0.03 mole, 2 M solution in ether) was added. The mixture was refluxed for 3-10 h to complete conversion of diacetate (according to TLC); it was then diluted with ether, decomposed by the addition of water, followed by 10% HCl solution at 0°C, and then extracted with ether. The ether extract was washed with $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated. The reaction products were distilled or subjected to column chromatography on silica gel. Pentane was used as the eluent for hydrocarbons, and pentane—ether (3:1) for acetates.

Reaction of Acetate (VII) with TIBA. Product separation was achieved by preparative GLC.

3,7-Dimethyl-1,3,4-octatriene (VIII), bp 69-70°C (20 mm), n_D^{20} 1.4765. IR spectrum (ν, cm^{-1}): 3095, 3030, 1950, 1620, 995, 900. PMR spectrum (δ, ppm): 0.90 d (6H, CH_3, J = 6 Hz), 1.73 d (3H, CH_3, J = 3 Hz), 1.97 m (3H, CH_2 and CH), 4.92 m (3H, CH=C=C and CH_2=C), 6.15 m (1H, C=CH). ^{13}C-NMR spectrum (δ, ppm): 14.85 q (C^9), 22.19 q (C^8, C^{10}), 28.36 d (C^7), 38.38 t (C^6), 88.91 s (C^5), 99.54 s (C^3), 111.56 t (C^1), 136.49 d (C^2), 207.58 s (C^4). m/z = 136.

3,7-Dimethyl-3-octen-1-yne (IX). IR spectrum (ν, cm^{-1}): 3300, 2105 (C≡CH), 3035, 1630, 810 (C=CH). PMR spectrum (δ, ppm): 0.87 d (6H, CH_3, J = 6.5 Hz), 1.25 m (3H, CH_2 and CH), 1.79 s (3H, CH_3), 2.10 q (2H, CH_2, J = 7.5 Hz), 2.86 s (H, C≡CH), 5.60 t (H, C=CH, J = 7 Hz).

Reaction of Acetate (VI) with TEA. Compound (X), see Table. Mixture of 1-acetoxy-3,8-dimethyl-6-ethyl-2,6,7,9-decatetraen-4-yne (XI) and 1-acetoxy-3,8-dimethyl-2,8-dodecadien-4,6-diyne (XII). IR spectrum (ν, cm^{-1}): 3100, 3020, 2210, 1935, 1750, 1640, 1620, 1230, 995, 910, 845. PMR spectrum (δ, ppm): 0.93 t (3H, CH_3, J = 7 Hz), 1.03 t (3H, CH_3, J = 7 Hz), 1.39 m (2H, CH_2), 1.83 s (6H, CH_3), 1.88 s (6H, CH_3), 1.99 s (6H, CH_3 in Ac), 2.20 m (4H, CH_2), 4.55 d (4H, CH_2OAc, J = 7 Hz), 5.10 m (2H, C=CH_2), 5.90 m (3H, —CH=C), 6.30 m (1H, CH=CH_2). m/z 224.

Reaction of Diacetate (XIII) with TEA. 1,1-Pentamethylene-3-(cyclohexen-1-yl)-1,2-pentadiene (XV). IR spectrum (ν, cm^{-1}): 3035, 1940, 1450, 845. PMR spectrum (δ, ppm): 0.95 t (3H, CH_3, J = 7 Hz), 1.57 m (10 H, CH_2), 2.07 m (10 H, CH_2—C=C), 5.56 m (H, CH=C). UV spectrum: λ_{max} 226 nm, ε 12,600, m/z 216.

1,1,4,4-Dipentamethylene-2-acetoxy-3-ethyl-1,3-butadiene (IV), mp 43-45°C (from hexane). IR spectrum (ν, cm^{-1}): 1755, 1680, 1645, 1452, 1215. PMR spectrum (δ, ppm): 0.83 t (3H, CH_3, J = 7Hz), 1.47 m (12H, CH_2), 1.96 s (3H, CH_3 in Ac), 2.05 m (10H, CH_2—C=C). ^{13}C-NMR spectrum (δ, ppm): 13.60 q (C^{16}), 20.91 q (C^{18}), 22.86 t (C^{15}), 26.49 t, 26.85 t, 26.95 t, 27.06 t, 27.55 t, 27.69 t, 28.09 t, 29.83 t (2 C), 32.34 t (C^5—C^9, C^{10}—C^{14}), 125.86 s, 127.30 s, 138.65 s, 140.14 s (C^1—C^4), 169.15 s (C^{17}). UV spectrum: λ_{max} 222 nm, ε 9813. m/z 276.

1,1,4,4-Dipentamethylene-2-ethyl-1-buten-3-one (XVII). IR spectrum (ν, cm^{-1}): 1685, 1640, 1452. PMR spectrum (δ, ppm): 0.92 t (3H, CH_3, J = 7 Hz), 1.58 m (16H, CH_2), 2.11 m (7H, CH_2—C=C and CHC=O). ^{13}C-NMR spectrum (δ, ppm): 14.26 q (C^{16}), 22.13 t (C^{15}), 25.95 t (2C), 26.60 t, 28.49 t (2C) (C^5—C^9), 28.13 t, 28.36 t, 30.09 t, 32.67 t (2C) (C^{10}—C^{14}), 49.35 d (C^4), 135.45 s, 140.25 s (C^1—C^2), 213.13 s (C^3). m/z 234.

Reaction of Diacetate (XXV) with TEA. 1-Acetoxy-6-methyl-6-decen-2,4-diyne (XXVII), mixture of Z- and E-isomers (1:1). IR spectrum (ν, cm^{-1}): 3020, 2240, 1755, 1628, 1220, 975, 835. PMR spectrum (δ, ppm): 0.91 t (3H, CH_3, J = 7 Hz), 1.41 m (2H, CH_2), 1.84 s and 1.77 s (3H, CH_3), 2.09 s (3H, CH_3 in Ac), 2.19 m (2H, CH_2), 4.76 s and 4.78 s (2H, CH_2OAc), 5.90 m (1H, CH=C). ^{13}C-NMR spectrum (δ, ppm) (Z:E = 2:1) Z-isomer: 13.74 q (C^{10}), 20.63 q (C^{12}), 22.10 q (C^{13}), 22.29 t (C^9), 33.03 t (C^8), 52.61 t (C^1), 69.68 s (C^3), 71.48 s

(C^4), 76.05 s (C^2), 78.69 s (C^5), 116.45 s (C^6), 143.18 d (C^7), 169.98 s (C^{11}). The following signals were different for the E-isomer: 16.48 q (C^{13}), 30.78 t (C^8), 71.28 s (C^3), 74.87 s (C^4), 76.14 s (C^2), 82.28 s (C^5), 142.89 d (C^7). m/z 204.

Mixture of Acetate (XXVII) and 1-Acetoxy-4-ethyl-6-methyl-4,5,7-octatrien-2-yne (XXVI) (1:1). IR spectrum (ν, cm^{-1}): 3095, 3020, 2235, 1940, 1750, 1690, 1620, 1230, 995, 910, 835. PMR spectrum (δ, ppm): 0.95 t (6H, CH_3, J = 7 Hz), 1.36 m (2H, CH_2), 1.75 s (6H, CH_3), 1.93 s (6H, CH_3 in Ac), 2.17 m (4H, CH_2), 4.64 s and 4.66 s (4H, CH_2OAc), 5.00 m (2H, $CH{=}CH_2$), 5.75 m (1H, CH=C), 6.18 m (1H, $CH{=}CH_2$). ^{13}C-NMR spectrum (δ, ppm) for acetate (XXVI): 12.43 q (C^{13}), 14.62 q (C^{11}), 20.63 q (C^{10}), 27.25 t (C^{12}), 52.94 t (C^1), 82.25 s (C^2), 83.69 s (C^3), 90.54 s (C^4), 102.94 s (C^6), 113.94 t (C^8), 134, 43 d (C^7), 170.18 s (C^9), 212.24 s (C^5).

CONCLUSIONS

1. The reaction of tertiary and secondary propargylic diacetates derived from diacetylenic glycols with triethyl- and triisobutylaluminum, catalyzed by $FeCl_3$, is a suitable method for the preparative synthesis of conjugated diallenes.

2. We have developed a method for the synthesis of oxygen-containing allenes and allenynes from mono- and diacetylenic glycol diacetates, based on the greater reactivity of tertiary propargyl acetate groups relative to primary ones with respect to trialkylalanes.

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