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A NEW METHOD FOR THE SYNTHESIS OF VINYL- AND DI-ALLENES ASSISTED BY ORGANOALUMINIUM COMPOUNDS

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Summary

The interactions of organoaluminium reagents with the acetates of substituted propargyl alcohols have been considered as the most appropriate method to synthesize allenes. Studies have been carried out on the synthesis of vinyl- and di-allenes, employing both unsaturated and saturated trialkylalanes of different structures in the presence of $FeCl_3$ and CuCl. The structures of the compounds obtained have been determined by ^1H and ^{13}C NMR assignments.

Introduction

During recent years, the substitution of acetylenic alcohols and halogenides, as well as that of the derivatives thereof, under the influence of organomagnesium and organolithium compounds has been extensively studied [1,2]. When catalyzed by transition metals or involving previously obtained [3] organocuprate reagents, the selectivity and the rate of reactions of this type are high. The nucleophilic substitution is accompanied by rearrangement of the acetylene structure to an allene one; this affords one of the most rational approaches to substituted allenes [4].

Concerning the formation of substituted allenes, we have reported earlier [5,6] on the interaction of propargyl acetates with organoaluminium compounds (OAC). The reaction can be carried out only in the presence of a catalyst based on salts or complexes of Cu, Fe, or Pd. The present paper concerns a method of synthesizing conjugated vinylallenes and diallenes, these products being of practical value as they may constitute polyenic fragments of some highly active antibiotics. Besides, vinylallenes can be easily converted into cyclopentenone derivatives, which represent important synthons for a number of natural products.

Results and discussion

According to the acetylene → allene rearrangement, the synthesis of vinylallenes can be effected, as is seen from Scheme 1, either by the introduction of a radical

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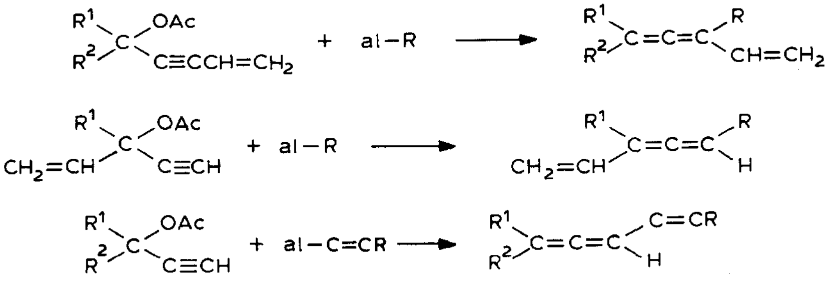


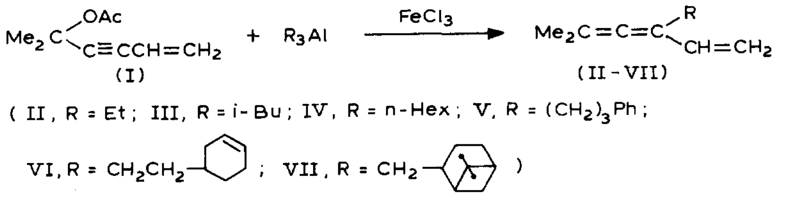
(1)

(2)

SCHEME 1

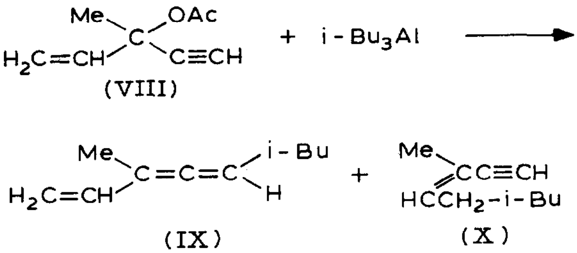
from an organoaluminium reagent into the vinylpropargyl system (reaction 1), or by introducing the vinyl radical into the propargyl moiety (reaction 2).

Both approaches have been examined and proved to be effective. Thus, the interaction between 5-acetoxy-5-methyl-1-hexene-3-yne (I) and six various trialkylalanes led to the corresponding vinylallenes II–VII in good yield. The reaction was carried out in ether at 20°C in the presence of 3–5% mol of $FeCl_3$, the most potent catalyst *. The complete conversion of the starting acetate (TLC control) was achieved in 2 h (eq. 3).



(3)

As observed earlier [7], the conditions of the substitution involving an OAC and an allyl system differ slightly from those in the case of a propargyl one. Hence, two different directions are inherent to the interaction between 3-acetoxy-3-methyl-1-penten-4-yne (VIII) and OAC, the composition of the products depending on the reactivity ratio of both the allyl and propargyl electrophilic centres. The reaction of acetate VIII and $i\text{-}Bu_3Al$ was found to lead to a mixture of allene IX and vinylacetylene X in a 88/12 ratio, hence the contribution of the propargyl moiety was predominant (eq. 4).



(4)

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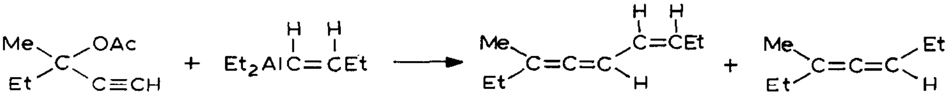
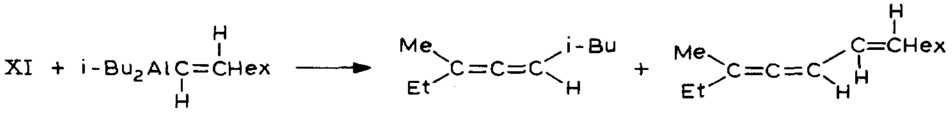
* Pd or Cu compounds were found to be less active in this reaction [6].

The high reactivity of dialkylalkenylalanes and their availability as demonstrated by Zweifel and Ashby [8] in their work concerning the hydroalumination of acetylenes, as well as the discussion of acetylene carboalumination by Negishi [9], prove that the vinyl OAC is promising for organometallic synthesis.

We investigated the interaction between 3-acetoxy-3-methyl-1-pentyne (XI) and two vinyl-OAC XII,XIII containing alkenyl radicals of different double-bond geometry. A rather exothermic reaction with OAC XII took place in the presence of 5% mol of $FeCl_3$ at 20°C. The reaction was over in 1 h. It should be stated that the reactivity of the unsaturated radical surpasses that of alkyl, since the allenes comprising butenyl (XIV) and ethyl (XV) were formed in equal amounts although stoichiometry considerations predict the ratio 2/1. The reaction between diisobutyloctenylaluminium (XIII) and acetate XI requires more rigid conditions to be applied: reflux in ether over 5 h led to a mixture of allenes containing isobutyl (XVI) and octenyl (XVII) radicals in a total yield of 45%, the ratio being 13/87.



(XI) (XII) (XIV) (XV)

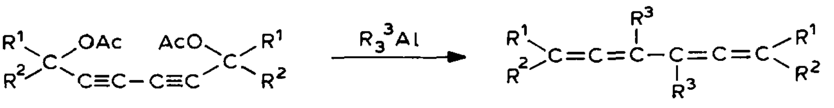


(XIII) (XVI) (XVII)

The structures of the allenes isolated were reliably proved by mass spectrometry, as well as IR, UV, and ^1H and ^{13}C NMR spectral data. The IR spectra of all these compounds showed a characteristic absorption band in the region of 1940–1970 cm^{-1}. The UV spectra of the conjugated vinylallenes demonstrated a π–π^* transfer band in the region of 224–227 nm, the molar extinction ε amounting to $(10–15) \times 10^3$. The NMR spectral data correlate well with the structures indicated and are given in the Experimental.

We used diacetylene glycols prepared by the methods of Glaser or Chodkiewicz–Cadiot [10] for investigating the comparative reactivities of propargyl systems with primary, secondary, and tertiary acetoxy groups, and for the synthesis of conjugated diallenes.

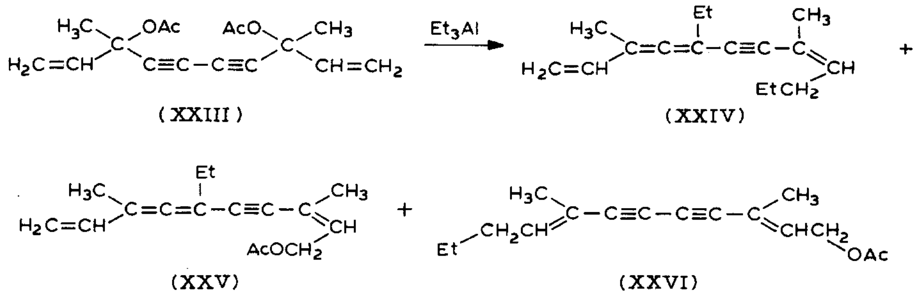
The reaction between 3,8-dimethyl-3,8-diacetoxy-4,6-decadiyne (XVIII) and Et_3Al was carried out for 4 h in refluxing ether to give a symmetrical diallene (XIX) in a 56% yield. A similar reaction of the diacetate XVIII may involve i-Bu_3Al, though it is considerably slower and gives more undesirable products. The yield of the target diallene XX did not exceed 43%. The reaction between 1,4-bis(1-acetoxy-1-cyclohexyl)-1,3-butadiyne (XXI) and Et_3Al follows the same direction. A crystalline diallene (XXII) was formed in a 86% yield during 6 h of reflux in ether.



(XVIII, R^1 = Me, R^2 = Et ;
XXI, $R^1R^2 = (CH_2)_5$)

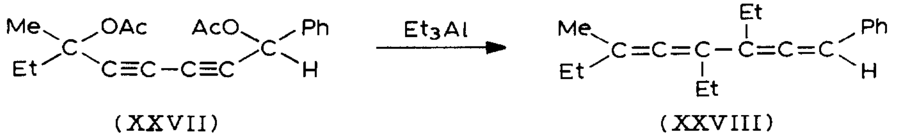
(XIX, R^1 = Me, $R^2 = R^3$ = Et ;
XX, R^1 = Me, R^2 = Et, R^3 = i-Bu ;
XXII, $R^1R^2 = (CH_2)_5$, R^3 = Et)

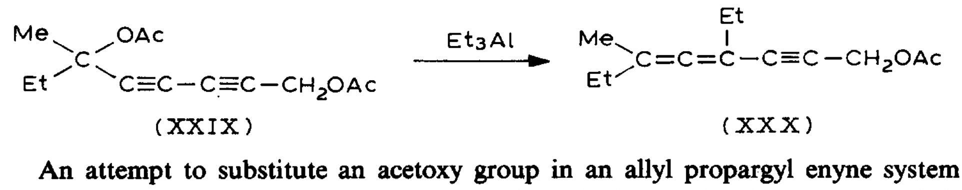
3,8-Diacetoxy-3,8-dimethyl-1,9-decadien-4,6-diyne (XXIII) is a dimer of VIII according to Glaser. A comparison of the structures of VIII and XXIII makes it reasonable to assume the course of the reaction between either of these two structures and Et_3Al to be the same. However, the dimer readily underwent an allyl cross-coupling, being alkylated by Et_3Al and suffering allyl isomerization at the γ-position. As a result, a mixture consisting of allene XXIV (which had been isolated by means of column chromatography on SiO_2), a number of minor unidentified hydrocarbons, and the acetates XXV and XXVI were obtained. The trisubstituted double bond *Z*/*E* isomeric ratio in the main hydrocarbon and in both acetates was found to be ca. 1/1.


(XXIII)
(XXIV)
(XXV)
(XXVI)

Our reactivity studies of variously substituted propargyl systems in the same structure involved some acetates of an unsymmetrical diacetylene glycols obtained by Chodkiewicz-Cadiot condensation. The interaction between 3-methyl-8-phenyl-3,8-diacetoxy-4,6-octadiyne (XXVII) and Et_3Al in ether affords the conjugated diallene XXVIII in good yield. The IR spectrum of the latter contains two characteristic absorption bands for allenes at 1920 and 1945 cm^{-1}.

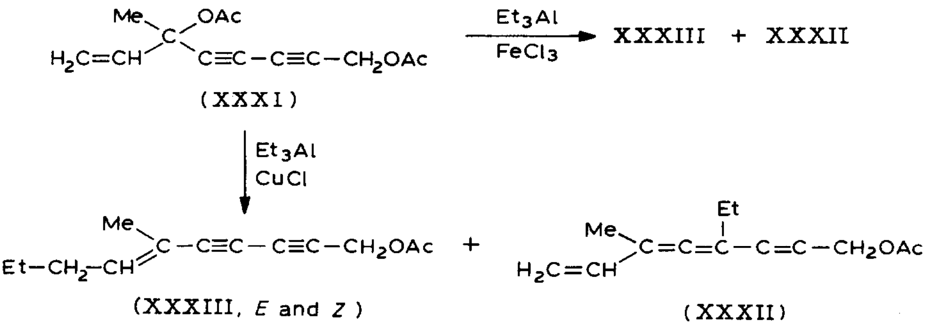
A less reactive propargyl system in 3-methyl-3,8-diacetoxy-4,6-octadiyne (XXIX) containing a primary acetoxy group fails to react with Et_3Al. The reaction terminates after 3 h of refluxing in ether with the formation of individual 3-methyl-5-ethyl-8-acetoxy-3,4-octadien-6-yne (XXX). This acetate was isolated by column chromatography; no hydrocarbons were detected.


(XXVII)
(XXVIII)


(XXIX)
(XXX)

An attempt to substitute an acetoxy group in an allyl propargyl enyne system revealed a more complex reaction course. Thus, the interaction between 3-methyl-3,8-diacetoxy-1-octen-4,6-diyne (XXXI) and Et_3Al in the presence of $FeCl_3$ led to a mixture of the acetates XXXII and XXXIII in a total yield of 71%. The former acetate is formed via a reaction of propargyl substitution while the latter is formed via an allyl one and a rearrangement. Neither hydrocarbons nor propargyl substitution products involving the primary acetoxy group were found.

In the presence of CuCl, allyl substitution and the above rearrangement take place exclusively in the reaction between Et_3Al and diacetate XXXI. Refluxing in ether over 3 h results in the formation of a mixture of equal amounts of *Z*- and *E*-isomers of the acetate XXXIII in a total yield of 78%.

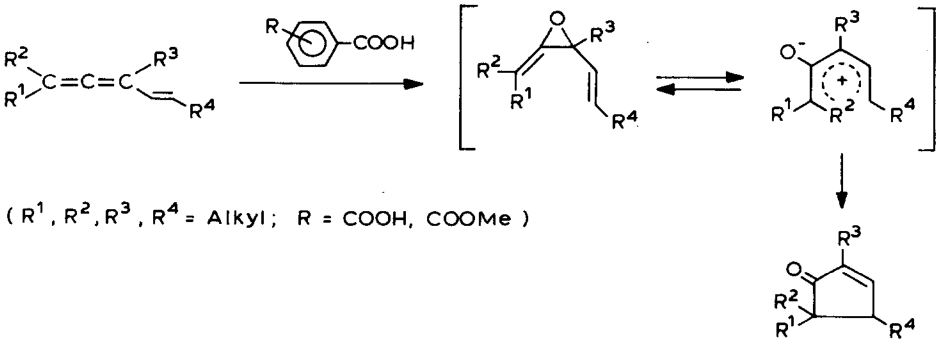


The structures of the allenes were established by spectral analysis methods, ^{13}C NMR spectroscopy proving the most reliable and informative.

The chemical shifts of the central carbon signal are represented by a low-field singlet at 196–201 ppm; those of the two terminal carbons of the allene system appear at 102–111 ppm. Complete sets of the spectral data of the greater part of the allenes are presented in Table 2 (see Experimental); they correlate closely with the structures indicated.

Hence, the novel method we have elaborated may be successfully utilized as a preparative synthetic approach to polyene and enyne structures containing allene moieties. The most important point is the possibility of obtaining products with various functional substituents.

More evidence for the value of the method under consideration is given by the oxidative conversion of vinylallenes into substituted cyclopentenones performed in our laboratory according to [11]. We altered this procedure by employing perphthalic (PPA) and *p*-carbomethoxyperbenzoic (CMPBA) acids as the oxidants [12]. The oxidation follows Scheme 2 and involves the formation of an epoxyallene, which further cyclizes into a cyclopentenone. The yields of the substituted cyclopentenones are listed in Table 1.

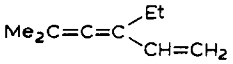
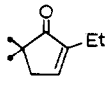
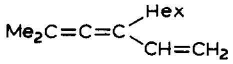
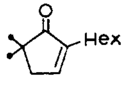
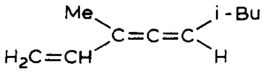
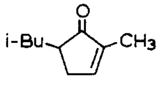
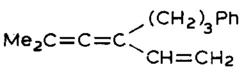
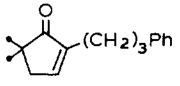


(R^1, R^2, R^3, R^4 = Alkyl ; R = COOH, COOMe)

SCHEME 2

TABLE 1

THE DEPENDENCE OF THE YIELD OF CYCLOPENTENONE DERIVATIVES IN VINYL OXIDATION ON THE PERACID USED

Vinylallene	Cyclopentenone		Yield (%) on oxidation	
			by PPA	by CMPBA
 $Me_2C=C=C<^{Et}_{CH=CH_2}$		XXXIV	58	42
 $Me_2C=C=C<^{Hex}_{CH=CH_2}$		XXXV	65	62
 $^{Me}_{H_2C=CH}>C=C=C<^{i\text{-}Bu}_{H}$		XXXVI	56	
 $Me_2C=C=C<^{(CH_2)_3Ph}_{CH=CH_2}$		XXXVII	67	53

Experimental

IR spectra were recorded in thin film on a UR-20 spectrophotometer, and UV spectra of ethanolic solutions were run on a Specord UV-Vis spectrometer. ^1H NMR spectra were obtained on a Tesla (60 and 100 MHz) instrument for solutions in CCl_4 using tetramethylsilane as the internal standard. Mass spectra were recorded on a MX-1306 spectrometer at 70 eV, the ionization chamber temperature being 150°C. ^{13}C NMR spectra were run for the solutions in $CDCl_3$ on a JEOL FX-90Q radiospectrometer (22.63 MHz).

GLC analyses were carried out on a Chrom-5 gas chromatograph on 1200 × 3 mm stainless steel columns filled with 5% loaded liquid phase on N-AW-DMCS Chromosorb. SE-30 was used as the liquid phase for all analyses. The carrier gas (He) flow rate was 50 ml min^{-1}.

OAC of the R_3Al type, except Et_3Al and $i\text{-}Bu_3Al$, were obtained by transalkylation of the corresponding olefins according to the technique given in ref. 13. The propargyl mono- and di-ols were acetylated, using a standard procedure, by acetic anhydride in pyridine. All operations involving OAC were carried out in an argon atmosphere!

General method of vinylallene synthesis.

OAC (15 mmol) solution (2 *M*) in ether was added dropwise to a stirred solution of propargyl acetate (10 mmol) and $FeCl_3$ (0.5 mmol) in dry ether (25 ml), cooling the mixture to 20°C. The reaction terminated in 2 h (with compounds V and IX in 10 h). The reaction mass was diluted with ether and hydrolyzed, first with water, then with aqueous HCl (10% w/v) at 0°C. The mixture was extracted with ether. The organic extracts were washed with aqueous $NaHCO_3$ (10% w/v) and water, and then dried over $MgSO_4$, concentrated and distilled to give the target vinyl-allene.

Compounds V and XVI were chromatographed on a column packed with silica gel, using pentane as the eluent. Enyne XX was isolated by preparative GLC. IR: 3300, 2105 (C≡CH), 3035, 1630, and 810 cm^{-1} (C=CH); ^1H NMR: σ 0.87 (6H, d, CH_3), 1.25 (3H, m, CH_2 and CH), 1.79 (3H, s, CH_3), 2.10 (2H, q, CH_2), 2.86 (1H, s, C≡C), 5.60 ppm (1H, t, C=CH).

Reaction of the diacetates of acetylenic glycols with trialkylalanes

Trialkylalane (30 mmol) solution (2 *M*) in ether was added dropwise at 20°C to a stirred solution of diacetate (10 mmol) and $FeCl_3$ (0.5 mmol) in dry ether (25 ml). The reaction mixture was refluxed for 3 to 8 h, depending on the reagent used. Then the mixture was worked up by the above procedure to give a mixture of hydrocarbons and acetates, which was separated on a chromatographic column packed with silica gel. Hydrocarbons were eluted with pentane, acetates with a mixture of pentane and ether (3/1).

Thus, the interaction of diacetate XXIII with Et_3Al resulted in a mixture, which on separation produced a hydrocarbon and an acetate fraction. The former consisted mainly of 3,8-dimethyl-5-ethyl-1,3,4,8-dodecatetraen-6-yne (XXIV). IR: 3095, 3020, 2200, 1935, 1680, 1615, 995, and 900 cm^{-1}; ^1H NMR: σ 0.93 (3H, t, *J* 7 Hz, CH_3), 0.98 (3H, t, *J* 7.5 Hz, CH_3), 1.85 (3H, s, CH_3), 1.89 (3H, s, CH_3), 3.65 (4H, m, CH_2C=C), 5.80 (1H, t, HC=C), 5.05 (2H, m), 6.30 ppm (1H, m) CH=CH_2. The latter fraction consisted of acetates XXV and XXVI, which were identified from the spectrum without separation. IR: 3100, 3020, 2210, 1935, 1750, 1640, 1620, 1230, 995, 910, and 845 cm^{-1}. ^1H NMR: σ 0.93 (3H, t, *J* 7 Hz, CH_3), 1.03 (3H, t, *J* 7 Hz, CH_3), 1.83 (6H, s, CH_3), 1.88 (6H, s, CH_3), 1.99 (6H, s, CH_3 in acetate group), 2.20 (4H, m, CH_2C=C), 4.55 (4H, d, *J* 7 Hz, C=CCH_2OAc), 5.10 (2H, m, C=CH_2), 5.90 (3H, m, CH=C), 6.30 (1H, m, CH=C).

The reaction of acetate XXXI with Et_3Al in the presence of CuCl (8% mol) proceeds chemoselectively to give a mixture of *Z*- and *E*-1-acetoxy-6-methyl-6-decen-2,4-diyne (XXXIII). IR and ^1H NMR spectra are given for the mixture. IR: 3020, 2240, 1755, 1628, 1220, 975, and 835 cm^{-1}. ^1H NMR: σ 0.91 (3H, t, *J* 7 Hz, CH_3), 1.41 (2H, m, CH_2), 1.77 and 1.84 (3H, s, CH_3), 2.09 (3H, s, CH_3 in acetate group), 2.19 (2H, m, CH_2C=C), 4.70 and 4.76 (2H, s, CH_2OAc), 5.90 ppm (1H, m, CH=C). Splitting of the singlets at 1.8 and 4.7 ppm in the ^1H NMR spectrum as well as in the ^{13}C NMR spectrum gives evidence for the presence of both *Z*- and *E*-isomers in the mixture.

In the presence of $FeCl_3$ (5% mol), acetate XXXI and Et_3Al react to form a mixture of enyne XXXIII and 1-acetoxy-4-ethyl-6-methyl-4,5,7-octatrien-2-yne (XXXII). The latter has the following spectral pattern: IR: 3095, 3020, 2235, 1940, 1750, 1690, 1595, 1230, 995, 910, and 835 cm^{-1}; ^1H NMR: σ 0.95 (3H, t, *J* 7 Hz, CH_3), 1.75 (3H, s, CH_3), 1.93 (3H, s, CH_3 in acetate group), 2.17 (2H, m, CH_2C=C), 4.64 (2H, s, CH_2OAc), 5.00 (2H, m, CH_2=C), 6.18 ppm (1H, m, CH=C).

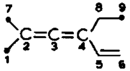
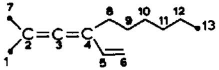
Oxidation of vinylallenes by perphthalic and p-carbomethoxyperbenzoic acids

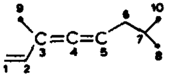
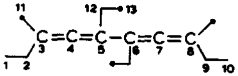
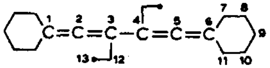
PPA (10 mmol) in ether was added to vinylallene (5 mmol) and kept at 20°C for 24 h; or *p*-CMPBA (7.5 mmol) was added to vinylallene (5 mmol) solution in CH_2Cl_2 (10 ml) and kept at 10°C over 48 h. The precipitate from the reaction mass was filtered off in both cases and washed with ether. The organic extracts were washed with aqueous NaOH (5% w/v) and water, dried over $MgSO_4$, and con-

(Continued on p. 82)

TABLE 2

PHYSICAL CONSTANTS AND SPECTRAL CHARACTERISTICS OF THE ALLENES OBTAINED

Yield (%)	B.p. (°C (mmHg))	n_D^{20}	IR (ν, cm^{-1})	^{1}H and ^{13}C NMR spectra (δ, ppm)	UV (λ, nm)	Mass spectra (m/z)
2-Methyl-4-ethyl-2,3,5-hexatriene (II)						
72  	39–40 (20)	1.4789	1950, 3095, 3020, 995, 900, 1620	^{1}H:0.90(t,3H,CH$_3$,J 7 Hz),1.63(s,6H,CH$_3$),2.00(q,2H,CH$_2$, J 6.5 Hz),4.88 and 6.10(m,3H,CH$_2$=CH); ^{13}C:12.21(q,C(9), 20.56(q,C(1)C(7)),21.48(t,C(8)),96.57(s,C(2)),105.26(s,C(4)), 110.71(t,C(6)),136.69(d,C(5)),204.19(s,C(3))	221	122
2-Methyl-4-isobutyl-2,3,5-hexatriene (III)						
59	59–60 (12)	1.4760	1950, 3095, 3020, 995, 900, 1620	^{1}H:0.83(d,6H,CH$_3$,J 7 Hz),1.66(s,6H,CH$_3$),1.85(m,3H,CH$_2$ and CH),4.86 and 6.10(m,3H,CH$_2$=CH)	227	150
2-Methyl-4-hexyl-2,3,5-hexatriene (IV)						
62  	53–55 (1)	1.4730	1945, 3095, 3020, 995, 900, 1615	^{1}H:0.82(t,3H,CH$_3$,J 7 Hz),1.25(m,8H,CH$_2$),1.66(s,6H,CH$_3$), 1.93(m,2H,CH$_2$),4.92 and 6.10(m,3H,CH$_2$=CH);^{13}C:14.17(q,C(13), 20.50(q,C(1)C(7)),22.85(t,C(12)),27.68(t,C(10)),28.26(t,C(8)),29.31(t,C(9), 32.02(t,C(11)),95.70(s,C(2)),103.20(s,C(4)),110.71(t,C(6)), 136.69(d,C(5)),204.31(s,C(3))	225	178
2-Methyl-4-vinyl-7-phenyl-2,3-heptadiene (V)						
34	–	1.5375	1940, 3090, 3070, 3030, 1610, 1585, 995, 900, 750, 705	^{1}H:1.25(s,2H,CH$_2$),1.72(s,6H,CH$_3$),1.97(m,2H,CH$_2$),2.52 (m,2H,CH$_2$C=C),4.92 and 6.15(m,3H,CH=CH$_2$),7.15(m,5H, Ph)	–	212
2-Methyl-4-vinyl-6-(3-cyclohexenyl)-2,3-hexadiene (VI)						
63	85–87 (2)	1.5150	1945, 730, 3090, 3025, 995, 900, 1650, 1615	^{1}H:1.33–2.08(m,11H,CH$_2$ and CH),1.63(s,6H,CH$_3$),5.55(s, 2H,CH=CH),4.92 and 6.12(m,3H,CH$_2$=CH)	224	202

2-Methyl-4-mirthanyl-2,3,5-hexatriene (VII)						
33	75–77 (0.2)	1.5083	1950, 3095, 3020, 995, 900, 1615	^{1}H:0.75(s,3H,CH_3),1.10(s,3H,CH_3),1.60(s,6H,CH_3),1.75 (m,11H,CH_2 and CH),4.83 and 6.04(m,3H,CH_2=CH)	225	230
3,7-Dimethyl-1,3,4-octatriene (IX)						
53	69–70 (20)	1.4765	1950, 3095, 3030, 995, 900, 1620	^{1}H: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:14.85(q,C(9)),22.19(q,C(8)C(10)),28.36(d,C(7)), 38.28(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))	222	136
						
3-Methyl-3,4,6-nonatriene (XIV)						
25	88–89 (25)	1.5130	1960, 3040, 1640, 740	^{1}H:0.88(t,3H,CH_3),1.00(t,3H,CH_3),1.63(d,3H,CH_3,*J* 1.5Hz),1.75(m,2H,CH_2),1.95(q,2H,CH_2,*J* 7 Hz),4.83–6.41 (m,3H,CH=CH and C=C=CH)	228	136
3-Methyl-3,4,6-tridecatriene (XVII)						
41	74–75 (0.5)	1.4885	1950, 3020, 1650, 970	^{1}H:0.83(t,3H,CH_3,*J* 7 Hz),0.90(t,(3H,CH_3,*J* 7 Hz),1.25(s, 8H,CH_2),1.62(d,3H,CH_3,*J* 1.5 Hz),1.98(m,4H,CH_2),5.50(m, 1H,CH=C=C),5.63(s,2H,CH=CH)		192
3,8-Dimethyl-5,6-diethyl-3,4,6,7-decatetraene (XIX)						
56	56–57 (0.5)	1.5022	1970, 950, 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))	205 224	218
						
1,1,6,6-Dipentamethylene-3,4-diethyl-1,2,4,5-hexatetraene (XXII)						
86	56–57 (m.p.)		1960, 1690, 975, 900, 855, 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))	219 230	270
						

continued

TABLE 2 (continued)

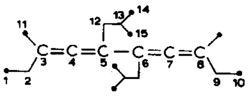
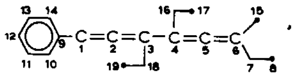
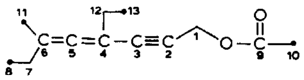
Yield (%)	B.p. (°C (mmHg))	n_D^{20}	IR (ν, cm^{-1})	^{1}H and ^{13}C NMR spectra (δ, ppm)	UV (λ, nm)	Mass spectra (m/z)
3,8-Dimethyl-5,6-diisobutyl-3,4,6,7-decatetraene (XX)						
43 		1.4930	1950, 1700	^{1}H:0.87(d,6H,CH$_3$,J 6.5 Hz),1.00(t,6H,CH$_3$,J 7 Hz),1.70 (s,6H,CH$_3$),1.91(m,10H,CH$_2$ and 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(s,C(5),C(6)),103.23(s,C(3),C(8)), 200.98(s,C(4),C(7))	205 225	274
1-Phenyl-3,4-diethyl-6-methyl-1,2,4,5-octatetraene (XXVIII)						
62 		1.5708	1920, 1945, 3040, 3070, 700, 750, 830, 1600, 1700	^{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 and 2.09(q,6H,CH$_2$,J 7 Hz),6.33(t, 1H,CH=C=C,J 3 Hz),7.20(s,5H,Ph); ^{13}C:12.47(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(q,C(11)),200.17(s,C(5)), 204.90(s,C(2))	211 250	272
1-Acetoxy-4-ethyl-6-methyl-4,5-octadien-2-yn (XXX)						
77 	83–84 (0.5)	1.4965	1960, 2230, 1750, 970	^{1}H: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$_2$OAc); ^{13}C: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	206

TABLE 3

PHYSICAL CONSTANTS AND SPECTRAL CHARACTERISTICS OF CYCLOPENTENONES

B.p. (°C (mmHg))	n_D^{20}	IR (ν, cm^{-1})	^{1}H NMR (δ, ppm)	UV (λ, nm)	Mass spectra (m/z)
2-Ethyl-4-dimethyl-cyclopenten-2-one (XXXIV)					
45–46(5)	1.4596	1710, 1640, 3040, 840	1.02(s,6H,CH_3),1.05(t,3H,CH_3,*J* 7 Hz),2.03 and 2.34 (m,4H,$CH_2C{=}C$),7.05(m,H,CH=C),	230	138
2-Hexyl-4-dimethyl-cyclopenten-2-one (XXXV)					
62–63(0.5)	1.4590	1715, 1640, 3050, 840	0.87(t,3H,CH_3,*J* 6 Hz),1.02(s,6H,CH_3),1.28(s,8H,CH_2), 2.03 and 2.34 (m,4H,$CH_2C{=}C$),7.06(m,H,CH=C)	230	194
2-Methyl-4-isobutylcyclopenten-2-one (XXXVI)					
74–75	1.4640	1710, 1640, 3040, 840	0.90(d,6H,CH_3,*J* 6 Hz),1.44–1.87(m,3H,CH and CH_2), 1.67(m,3H,CH_3),2.20(m,2H,$CH_2C{=}C$),2.50(m,1H,CHCO), 7.12(m,1H,CH=C)	229	152
2-(3-Phenylpropyl)-4-dimethyl-cyclopenten-2-one (XXXVII)					
	1.5228	1710, 1640, 1605, 3030, 3070, 3090, 840	1.00(s,6H,CH_3),1.14(s,2H,CH_2),1.55(m,2H,CH_2),2.26 (m,2H,$CH_2C{=}C$),2.46(t,2H,$CH_2C{=}C$,*J* 7 Hz),6.90(m,1H, CH=C),7.05(s,5H,Ph)	211 230	228

centrated. Then the residue was distilled or purified on an alumina packed column, eluting with a mixture of pentane and ether (5/1). The properties and spectral data of the allenes are listed in Table 2 and those of the cyclopentenones isolated in Table 3.

References

1 M.V. Mavrov and V.F. Kutcherov, Usp. Khim., 36 (1967) 553; S.A. Vartanyan and Sh.O. Badanyan, ibid., 36 (1967) 1563.
2 D.J. Pasto, R.H. Shults, J.A. McGrath and A. Waterhouse, J. Org. Chem., 43 (1978) 1382.
3 E.M. Kaiser, J. Organomet. Chem., 227 (1982) 89.
4 G.H. Posner, An Introduction to Synthesis Using Organocopper Reagents, Wiley-Interscience, New York, 1980, p. 11.
5 G.A. Tolstikov, T.Yu. Romanova and A.V. Kutchin, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1438.
6 G.A. Tolstikov, T.Yu. Romanova and A.V. Kutchin, Izv. Akad. Nauk SSSR, (1983) 629.
7 G.A. Tolstikov, A.Yu. Spivak, A.V. Kutchin and S.I. Lomakina, Izv. Akad. Nauk SSSR, (1983) 1146.
8 G.A. Tolstikov and V.P. Yuriev, Aluminiiorganitcheskiy sintez (Organoaluminium Synthesis), Moscow, Nauka, 1979, p. 98.
9 E. Negishi, Pure Appl. Chem., 53 (1981) 2333.
10 Advances in Organic Chemistry, Vol. 4, Interscience, New York, 1960, p. 240; I.L. Kotlyarovsky, M.S. Shvartzberg and L.B. Fisher, Reaktsii atsetilenovykh soedineniy (Reactions of Acetylenic Compounds), Novosibirsk, Nauka, 1967, p. 7.
11 T.H. Chan and B.S. Ong, Tetrahedron, 36 (1980) 2269.
12 G.S. Bylina, U.M. Dzhemilev, H.C. Vostrikov, G.A. Tolstikov, A.M. Moiseenkov, A.V. Semenovsky and S.S. Ivanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 447.
13 A.F. Zhigatch (Ed.), Aluminiyorganitcheskie soedineniya (Organoaluminium Compounds), IL (Foreign Literature Edition), Moscow, 1962, s. 27.