Reduced yields of the required products could also be due to reaction of the phosphite cation-radicals with water present in the "dry" solvent when perchlorates are used as the base electrolyte $(RO) P_{+}^{*} + HO = 0$ (RO) De

$$(\mathrm{RO})_{3}\mathrm{P}^{+} + \mathrm{H}_{2}\mathrm{O} - 2e \rightarrow (\mathrm{RO})_{3}\mathrm{PO} + 2\mathrm{H}^{+}$$
(3)

A large excess of ArH suppresses reaction (3), the presence of Na_3PO_4 prevents protonation and destruction of the phosphite by perchloric acid, and the use of maximum current densities and moderate concentrations of phosphite reduces alkylation of the starting material by quasiphosphonium cations (although it does not entirely eliminate it). When the reaction is carried out under these conditions, the yields of arylphosphonates are considerably increased.

CONCLUSIONS

Electrochemical oxidation of trialkyl phosphites in the presence of aromatic hydrocarbons at glass-carbon electrodes with the addition of Na₃PO₄ gives arylphosphonates in high yields.

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SUBSTITUTION REACTIONS INVOLVING ORGANOALUMINUM

COMPOUNDS.

COMMUNICATION 2.* SYNTHESIS OF SUBSTITUTED ALLENES FROM PROPARGYL ACETATES

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UDC 542.97:547.315.1

It is known [2] that the acetylene allene rearrangement which occurs on substitution is one of the most reliable routes to substituted allenes. Much attention has recently been devoted to the substitution of acetylenic alcohols and halides by organomagnesium and organolithium compounds [3, 4]. These reactions proceed rapidly and selectively when catalyzed by transition metals, copper compounds being particularly active [5].

We have previously reported [1] the reaction of propargyl acetates with organoaluminum compounds (OAC) to give substituted allenes. A necessary condition for the reaction to occur is catalysis by Cu(I) salts. This communication describes a study of the effects of different reaction parameters (reaction temperature, solvent, structure of the substrate and the reagent) on the yields of allenes. A variety of transition metals were tried as catalysts.

The reactions of substituted propargyl acetates with a variety of OAC (R_3Al , R_2AlR' , R_2AlCl , $RAlCl_2$, R_2AlOR , $LiAlR_4$) have been examined. The best results in terms of the selectivity of the reaction were obtained with the trialkylalanes R_3Al and R_2AlR' , yields of allenes of 45-86% being obtained, whereas with R_2AlOR' , R_2AlCl , and $RAlCl_2$ the yields were much lower. The reaction goes well in ethereal solvents (diethyl ether, dipropyl ether, and THF). In CH₂Cl₂ the reaction is more vigorous, but without selectivity, and in addition to allenes considerable amounts of by-products are formed. In hydrocarbons (hexane or heptane), the rate of reaction is much slower, and complete conversion of the acetate does not occur.

*For Communication 1, see [1].

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 629-636, March, 1983. Original article submitted June 18, 1982. TABLE 1. Catalytic Activity of Transition Metals in the Reaction of 5-Acetoxy-5-methyl-1-hexene-3-yne with Triethylaluminum

Cotolyet	Reaction condition	on ions	Yield of	Catalyst	Reactio conditi	on .ons	Yield of
Catalyse	T., °C	τ, h	(VIII), %	Catalyst	Т., °С	τ, h	(VIII,%)
FeCl ₃ Fe(acac) ₂ FeBr ₂ PdCl ₂ Pd(acac) ₂ CuBr	20 20 20 20 20 20 20	$\left \begin{array}{c}2\\2\\7\\2\\2\\10\end{array}\right $	72 48 50 60 56 15 *	CuBr ₂ Cu (acac) ₂ NiCl ₂ TiCl ₄	20 40 20 20 20	48 16 48 4 3	8* 10† -†

*Low conversion.

[†]Reaction complicated by polymerization.

TABLE 2. Reaction of Trialkylalanes with Substituted Propargyl Acetates in the Presence of FeCl₃

Ac	etylene	;	Organoaluminum compound	Reaction conditions		. Yield of
R ¹	R ²	\mathbb{R}^3	R4	т., ℃	τ, h	allene, %
$(CH_2 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3$) 5 CH ₃ C ₂ H ₅ C ₆ H ₅ H CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	H H H H H H $C_{6}H_{5}$ $CH=CH_{2}$ $CH=CH_{2}$ $CH=CH_{2}$ $CH=CH_{2}$ $CH=CH_{2}$	$\begin{array}{c} C_{2}H_{5} \\ i\text{-}C_{4}H_{9} \\ C_{2}H_{5} \\ n\text{-}C_{6}H_{13} \\ C_{2}H_{5} \\ C_{2}H_{5} \\ C_{2}H_{5} \\ C_{2}H_{5} \\ c_{2}H_{5} \\ i\text{-}C_{4}H_{9} \\ n\text{-}C_{6}H_{13} \\ CH_{2}CH_{2} \\ \end{array}$	60 60 40 25 40 20 20 20 20 20 20 20	2 3 3 5 6 2 2 2 2 5 2 2 2 2 2 2 2	70 (III) 55 (IV) 74 (V) 86 (VI) 60 (VII) 45 (VIII) 62 (IX) 72 (X) 59 (XI) 62 (XII) 63 (XIII) 33 (XIV)

In the absence of a catalyst the reaction proceeds only when a substantial excess of the OAC is used. Thus, the reaction of triethylaluminum (TEA) with 3-acetoxy-3-methyl-1-pentyne (I) in a ratio of 3:1 to give the allene (V) in hexane is complete after 1 day at 25°C. No reaction occurs in ether. In the presence of a catalyst, the reaction occurs with an OAC: propargyl acetate ratio of 1:1. Only the catalyzed reaction was studied further.

We have examined the catalyic activity of a variety of halides and acetylacetonates of the transition metals in the reaction of 5-acetoxy-5-methyl-1-hexene-3-yne (II) with TEA. The catalysts were used in amounts of 3-5 mole% (for copper compounds, 8-10 mole%). The results are shown in Table 1. In the reaction of the acetate (I) with TEA, the catalytic activities of $Fe(CO)_5$ and $FeCl_5$ are comparable. With either catalyst, the reaction proceeds at the boiling point of diethyl ether for 3 days, the yield of allene (V) being 45%. It will be seen from the experimental results that the presence of different counterions has little effect on the catalytic activity of the metals, which decreases in the sequence: Fe > Pd > Cu > Ni > Ti.

The reaction of trialkylalanes with propargyl acetates was carried out in the presence of anhydrous FeCl₃ (the most effective catalyst), which substantially increases the selectivity of the reaction and the yields of allenes. The reaction times and temperatures were determined by the maximum conversion of the acetate starting materials. The solvent used was diethyl or dipropyl ether. The results are given in Table 2.



					Yield of al	lene, %
Rı	R ²	R ³	R4	R ⁵	c R4	c R5
CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	CH3 CH3 CH3 C2H5 C2H5	$CH = CH_2$ $CH = CH_2$ $CH = CH_2$ H H	C_2H_5 <i>i</i> -C ₄ H ₉ C_2H_5 C_2H_5 C_2H_5	$CH_{2}CH_{2}$ $CH_{2}CH_{2}$ $CH_{2}CH_{2}$ $*$ $*$ $-CH=CHCH_{2}CH_{3}$	48 (X) 25 (XI) 43 (X) 36 (V) 26 (V)	22 (X111) 30 (X111) 11 (X1V) 13 (XV) 25 (XVI)

TABLE 3. Yields of Allenes Obtained from Mixed Organoaluminum Compounds



TABLE 4. Reaction Conditions and Yields of Allenes Obtained from ${\rm LiAlR_4}^4$

-	Acetylene		Organoaluminum	Reactio conditi	n ons	Yield of
R١	R ²	R ³	compound, R ⁴	т. , °С	τ, h	allene, %
(CH CH3 CH3	I2) 5 C2H5 CH3	H H CH=CH ₂	$\begin{array}{c} C_2H_5\\ n\text{-}C_6H_{13}\\ CH_2CH_2 \end{array}$	40 20 20	5 48 2	45 (III) 60 (VI) 30 (XIII)

It will be seen from the table that the acetates of alcohols which have a vinyl or phenyl group instead of the acetylenic proton react with OAC at lower temperatures than the unsubstituted compounds. Higher OAC react as readily as the lower members. Only in the case of trimyrtanylaluminum do steric effects apparently occur, the yield of allene being reduced. The structures of the allenes obtained were reliably confirmed by IR, PMR, and mass spectrometry. Thus, all the allenes displayed characteristic absorption at 1940-1970 cm^{-1} . The UV spectra of all the allenes containing a vinyl group conjugated with the allene group, a $\pi-\pi^*$ transition band was seen at 224-227 nm with a molar extinction coefficient $\varepsilon = (10-15) \cdot 10^3$, typical of substituted 1,3-dienes. An interesting feature of the PMR spectra of (IV)-(VII), (XV), and (XVI), which contain an allene proton, is its further interaction with the protons of the alkyl groups situated on the opposite side of the allene system, shown most characteristically by the splitting of the signal for the CH_3 group into a doublet with J = 3 Hz. Thus, the PMR spectrum of the allene (V) contains signals for the allene proton at 4.97 ppm as a multiplet, a split quartet for four CH_2 protons of the ethyl group centered at 1.80 ppm, three CH_3 protons as a doublet with J = 3 Hz at 1.58 ppm, and a six-proton signal for the two CH₃ groups as a triplet at 0.88 ppm.

Since it is often easier to obtain mixed OAC of the R_2AlR' type from dialkylaluminum hydrides and olefins, we have studied the reaction of the acetate (II) with diethyl-2-(cyclo-hexen-3-yl)ethylaluminum (XVII), diisobutyl-2-(cyclohexen-3-yl)ethylaluminum (XVII), and diethylmirtanylaluminum (XIX). As is the case with the trialkylalanes AlR_3 , the reaction proceeds within 2 h at 20°C. In (XVII), the reactivity of the substituents is the same, allenes (X) and (XIII) being formed in a 2:1 ratio in accordance with the stoichiometry. In the cases of (XVIII) and (XIX), however, steric effects become apparent, and the allenes with more highly branched radicals (XI) and (XIV) are formed in smaller amounts than would be expected from stichiometric calculation (Table 3).



To study the reactivities of saturated and unsaturated radicals at the Al atom, the reaction of the acetate (I) with diethylbutenylaluminum was examined. The reaction proceeded

			0110100			
Compound	bp (p, mm Hg)	n_d^{20}	It spectrum $(\nu, \text{ cm}^{-1})$	PMR spectrum (5, ppm)	UV spectrum λ , nm (log ε)	Mass pectrum n/z
1,1-Pentamethylene-1,2-pentadiene (III)	60-62 (5)	1,4856	1965	0,88 t (3H, CH ₃), 1,45–1,98 m (12H, CH ₂) 4,86 m (1H, C=C=CH)		136
2.6-Dimethyl-2.3-heptadiene (IV)	63-65 (100)	1,4431	1965	0.83 d (6H, CH ₄), 1,60 d (6H, CH ₄) 1,75 m (3H, CH ₂ and CH), 4,73 m (1H, C=C=CH)		124
3-Methyl-3,4-heptadiene (V)	40-42 (45)	1,4425	1970	0,88 t (6H, CH ₃), 1,58 d (3H, CH ₃) 1,80 m (4H, CH ₂), 4,97 m (1H, C=C=CH)		110
3-Methyl-3,4-undecadiene (VI)	53-55 (1)	1,4495	1980			166
2. Phenyl-2, 3-hexadiene (VII)	60-62 (1)	1,5539	1950	0,96 t (3H, CH ₂), 1,97 d (3H, CH ₃), 2,24 m (2H, CH ₂), 5,34 m (1H, $C = C = CH$) 7,16m (5H, CeH ₂)		158
1-Phenyl-1,2-pentadiene (VIII)	55-56 (1)	1,5575	1965	0.98 t (3H, CH ₃), 1.96 m (2H, CH ₃) 5,45 m and 5,93 m (2H, HC=C=CH) 7,08 m (5H, C ₆ H ₃)		144
2-Methyl-4-phenyl-2,3-hexadiene (JX)	68-70 (2)		1950	1,00 t (3H, CH ₂), 1,73 s (6H, CH ₃) 2,88 q (2H, CH ₂), 7,15 m (5H, C ₆ H ₃)		172
2-Methy1-4-ethy1-2,3,5-hexatriene (X)	39-41 (20)	1,4789	1950, 3095 3020, 995 900, 1620	0,90 t (3H, CH ₃), 1,63 s (6H, CH ₃) 2,00 q (2H, CH ₂), 4,88 m and 6,10 m (3H, CH ₂ =CH)	221 (4,15)	122

Physical Constants and Spectral Characteristics of the Allenes TABLE 5.

)) 150	() 178	202) 230	218	() 136
27 (4,00	25 (4,16	24 (4,27	25 (4,19		28 (4,05
		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~~~~~~~		∾ 
0,83 d (6H, CH ₃ ), 1,66 s (6H, CH ₃ ) 1,85 m (3H, CH ₂ and CH), 4,86 m and 6,10 m (3H, CH ₂ =CH)	$\begin{array}{rcl} 0.82 & t & (3H, \ {\rm CH}_3), \ 1.25 {\rm m} & (8H, \ {\rm CH}_2), \\ 1.66 & (6H, \ {\rm CH}_3), \ 1.93 {\rm m} & (2H, \ {\rm CH}_2), \\ 4.92 {\rm m} \ {\rm and} \ 8.10 {\rm m} & (3H, \ {\rm CH}_2={\rm CH}) \end{array}$	1,33–2,08 m (11H, CH ₂ and CH) 1,63 s (6H, CH ₃ ), 5,55 s (2H, CH=CH) 4,92 m and 6,12 m (3H, CH ₂ =CH)	0,75 s (3H, CH ₃ ), 1,10 s (3H, CH ₃ ), 1,60 s (6H, CH ₃ ), 1,75m (11H, CH ₂ and CH) 4,83 m and '6,04 m (3H, CH ₂ =CH)	0.78 s (3H, CH ₃ ), 0.93 t (3H, CH ₃ ), 1,16 s (3H, CH ₃ ), 1,58 d (3H, CH ₃ ), 1,82 m (3H, CH ₂ ), 1,82 m (13H, CH ₂ and CH), 4,83 m (1H, $C$ =C=CH)	
1950, 3095 3020, 995 900, 1620	1945, 3095 3020, 995 900, 1615	1945, 730 3090, 3025 995, 900 1650, 1615	1950, 3095 3020, 995 900, 1615	1970	1960, 3040 1640, 740
1,4760	1,4730	1,5150	1,5083		1,5130
59-60 (12)	53–55 (1)	85-87 (2)	75-77 (0,2)	8385 (1)	88-90
2-Methyl-4-isobutyl-2,3,5-hexatriene (XI)	2-Methyl-4-hexyl-2,3,5-hexatriene (XI)	2-Methyl-4-vinyl-6-(3 -cyclohexenyl)- 2,3-hexadiene (XIII)	2-Methyl-4-myrtanyl-2,3,5-hexa- triene (XIV)*	1-Myrtany1-3-methy1-1,2-pentadiene. (XV)	3-Methyl-3,4,6-nonatriene (XVI)

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* $[\alpha]_{D}^{20} - 51.3$  (C 7.6, heptane).

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in the presence of 5 mole% of FeCl₃ for 1 h at 20°C, and was highly exothermic. The reactivity of the unsaturated radical was greater than that of the alkyl radical, since allenes with butenyl and ethyl radicals were formed in equal amounts. From the stoichiometry, the ratio of allenes (V) and (XVI) should be 2:1. Noteworthy is the instability of the 3-methyl-3,4,6-nonatriene formed in the reaction, which on storage at  $-5^{\circ}$ C had almost completely polymerized within two days of preparation. The other allenes could be stored under these conditions for several months. The reactivity of propargyl derivatives in the substitution reaction is partly determined by the nature of the leaving group. To elucidate this point, the trifluoroacetate, p-nitrobenzoate, and trimethylsilyl ether of methylethylethynylcarbinol were reacted with TEA. In all cases, the reactions were carried out in boiling ether for 3 h in the presence of 5% of FeCl₃. No reaction occurred with the p-nitrobenzoate. The reaction of TEA with methylethylethynylcarbinol trifluoroacetate and trimethylsilyl ether gave the allene in much smaller yields than when the acetate was employed; the selectivity of the reaction was reduced, and the amounts of polymeric products increased. Thus, the use of the acetoxy-group as the leaving group was the most effective

Also studied were the reactions of propargyl acetates with alkylchloralanes and alkylalkoxyalanes, which present the possibility of nucleophilic attack on the substrate not only by an organic radical, but also by the Cl⁻ and  $OC_4H_9$  ions. As will be seen from the equation for the reaction of 1-acetoxy-1-ethynylcyclohexane with ethylchloralanes, in the case of  $(C_2H_5)_2$ -AlCl the reaction affords the ethyl-substituted allene, with partial elimination of the acetoxy-group to form the corresponding enyne. In the case of  $C_2H_5AlCl_2$ , the latter reaction predominates with the simultaneous formation of the chloroallene



When diethylbutoxyaluminum reacts with the acetate (II), only the ethyl radical participates in allenic rearrangement, and after 4 h at 20°C the corresponding allene (X) is formed in 28% yield. Thus, the introduction of an alkoxy group into the OAC results in a reduction in the reactivity of this reagent in comparison with the trialkylalane. For the synthesis of allenes, the OAC can be advantageously used in the form of the atomic complexes MeAlR₄. These compounds are obtained by the reaction between trialkylalanes and alkali metals [6], or by the catalytic hydroaluminization of olefins with LiAlH₄ [7].

It has been shown experimentally that atomic complexes are highly reactive in substitution reactions, as shown by the reduction in the reaction temperature as compared with trialkylalanes, although the preparative yields of allenes are somewhat lower (Table 4).



We have thus shown that organoaluminum compounds may be used advantageously in the synthesis of allenes.

#### EXPERIMENTAL

PMR spectra were obtained on Tesla instruments (60 and 100 MHz) for solutions of the compounds in CCl₄, relative to HMDS. IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra were obtained on an MX-13-03 spectrometer, with ionizing electron energies up to 70 eV. UV spectra were recorded on a Specord UV-VIS instrument (in alcoholic solution). Specific rotations were measured on a Perkin-Elmer-141 polarimeter. GLC analyses were carried out on a Khrom-41 instrument, on a column 2.4 m  $\times$  3 mm with 5% SE-30 on Chromaton N-AW-DMCS, carrier gas helium (40 ml/min). Preparative separation was carried out in a Khrom-31 apparatus, 1.5 m  $\times$  10 mm, 20% SE-301 on Chromaton N-AW, helium flow rate 300 ml/min. The

propargyl alcohol starting materials were obtained as in [8, pp. 44 and 81]. Propargyl acetates were obtained by standard methods, by reaction of the alcohols with acetic anhydride in pyridine, or as described in [8, p. 196], and the organoaluminum compounds by the methods described in [6, 7, 9].

General Method of Synthesis of Allenes. To a solution of 20 mmole of the acetate of the acetylenic alcohol in 10 ml of ether were added successively with stirring at 20°C 0.6-1 mmole of FeCl₃ in 10 ml and 21 mmole of AlR₃ in 20 ml of ether. The mixture was kept at  $\sim$ 20°C or heated (see Table 2), and hydrolyzed with water followed by 10% HCl. The organic layer was extracted with ether, dried over MgSO₄, evaporated, and distilled. The properties of the allenes (III)-(XVI) are given in Table 5.

Reaction of 1-Acetoxy-1-ethynylcyclohexane with Ethylchloralanes. To a solution of 3.2 g (20 mmole) of 1-acetoxy-1-ethynylcyclohexane in 10 ml of THF was added with stirring at 20°C 0.28 g (2 mmole) of CuBr in 10 ml of THF and 2.1 g (21 mmole) of Et₂AlCl in 20 ml of THF. The mixture was boiled for 4 h and worked up in the usual way. Distillation afforded 1.9 g of a mixture of the allene (III) and 1-ethynylcyclohexene (XX) in a ratio of 67:33. The enyne (XX) was isolated preparatively. IR spectrum ( $\nu$ , cm⁻¹): 3300, 2095 (CECH), 3035, 810, 1630 (C=CH). PMR spectrum ( $\delta$ , ppm): 1.66 m (4H, CH₂), 2.10 m (4H, CH₂), 2.66 s (1H, CECH), 6.16 m (1H, C=CH). m/z 106. UV spectrum:  $\lambda_{max}$  224 nm,  $\varepsilon$  11,600.

The reaction of 1-acetoxy-1-ethynylcyclohexane with EtAlCl₂ was carried out as described above. From 3.3 g of the acetate and 2.8 g of the OAC was obtained 2 g of a mixture of (XX) and 1,1-pentamethylene-3-chloro-1,2-propadiene (XXI) in a ratio of 63:37. The allene (XXI) was isolated preparatively. IR spectrum ( $\nu$ , cm⁻¹): 1960 (C=C=C). PMR spectrum ( $\delta$ , ppm): 1.56 m (6H, CH₂), 2.15 m (4H, CH₂), 5.78 m (1H, C=C=CH). m/z 142.5.

# CONCLUSIONS

1. A new, convenient method for the preparation of allenes has been developed, based on the reaction of substituted propargyl acetates with organoaluminum compounds in the presence of transition metal salts or complexes.

2. The best results were obtained using trialkylalanes and tetraalkylaluminates. The most active catalysts were iron and palladium compounds.

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