Journal of Organometallic Chemistry, 292 (1985) 133–144
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CROSS-COUPLING REACTIONS BETWEEN SOME ALLYL, HOMOALLYL, AND HOMOPROPARGYL SUBSTRATES AND TRIALKYLALANES OR DIALKYL- AND DIARYL-MAGNESIUM DERIVATIVES *

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(Received February 21st, 1985)

Summary

Trialkylalanes and dialkyl- and diaryl-magnesium derivatives can be cross-coupled with allyl ethers and esters, sulphides, and quaternized allylamines. The reactions proceed uncatalyzed either with mild conditions or in the presence of copper complex catalysts to result in high yields of mono- and di-olefins of various structures.

The alkylation of homoallyl or homopropargyl tosylates by trialkylalanes is accompanied by cyclization, which leads to alkyl-substituted cyclopropanes, i.e. cyclobutenes and cyclopropylidenes.

Introduction

Substitution reactions involving organometallic non-transition metal compounds, mostly Grignard reagents [1,2], have recently attained much interest and have been extensively used to build carbon chains. Vinyl, allyl, and aryl halides as well as ethers and esters were used very often as active substrates for the process. These reactions being affected by metal complex catalysts, which also affect the regio- and stereo-selectivity of the cross-coupling as well as the yield of substitution products which can be considerably augmented [2,3].

The present paper considers the interaction of trialkylalanes, dialkyl- or diaryl-magnesium compounds, with allyl ethers, esters, thioesters, or amines; this interaction has been explored insufficiently. Furthermore, the paper represents our investigations of homoallyl and homopropargyl substrates in substitution reactions of tosylates of homoallyl and homopropargyl alcohols by organoaluminium compounds (OAC).

* Dedicated to Prof. O.A. Reutov on the occasion of his 65th birthday.

0022-328X/85/$03.30

Discussion

A possibility of substituting allyl acetates by alkylalanes was demonstrated by the interactions of geraniol or *cis–trans*-carveol acetates and Et_3Al or i-Bu_3Al [4,5]. The uncatalyzed reactions proceeded in mild conditions (−78°C) to lead to cross-coupling products in 66–85% yields. We extrapolated this method at some other allyl substrates to compare the behaviour of primary and secondary allyl acetates as well as of acetates containing electron-donor substituents in the γ-position to the leaving group. The compounds allyl- (I), crotyl- (II), cinnamyl- (III), sorbyl- (IV), 2,7-octadienyl- (V), 2-pentenyl- (VI), 2-cyclohexenyl- (VII) acetates and trialkylalanes R_3Al (R = Et, i-Bu, n-Hex) were selected to be the starting reactants. The reactions were carried out in hexane or in CH_2Cl_2 at room temperature for 2–5 hours, the

TABLE 1

EFFECT OF THE ALLYL ACETATE STRUCTURE ON THE YIELD OF CROSS-COUPLING PRODUCTS IN REACTIONS WITH TRIALKYLALANES [a]

Alcohols ←(b)— R⁄⁄OAc + R'_3Al —(a)→ R⁄⁄R' (α) + R(R')⁄ (γ)

Acetate		R'_3Al	Hydrocarbon yield (%) α	γ
OAc	(I)	Hex_3Al	trace	(55 [b])
OAc	(II)	Hex_3Al	trace	(63 [b])
Ph OAc	(III)	i-Bu_3Al	100	
—		Hex_3Al	82	
OAc	(IV)	i-Bu_3Al	100	
OAc	(V)	Et_3Al	41	(89 [b])
—		Hex_3Al	26	(86 [b])
OAc	(VI)	i-Bu_3Al	100	
—		Hex_3Al	81	
OAc	(VII)	i-Bu_3Al	100	

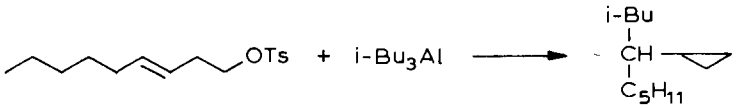
[a] Reactions of crotyl (II), cinnamyl (III), and octadienyl (V) acetates with trialkylalanes were not regioselective and led to α/γ-isomeric hydrocarbons in 70/30 or 60/40 ratios. [b] The reaction was carried out with the additions of CuBr and $FeCl_3$ (7–10 mol%).

reagent ratio being $ROAc/R_3Al$ 1/2. The experimental data (Table 1) demonstrated that the reaction followed two competitive pathways, i.e. alkylation (a) and nucleophilic attack of the carbonyl carbon by the alkyl (b). The ratio of (a)/(b) is strongly dependent on the allyl substrate structure. Thus, the reactions of allyl acetate (I) and crotyl acetate (II) with Hex_3Al do not yield cross-coupling products, the resulting mixtures are represented by unexpected hexylmethyl- and dihexylmethyl carbynals. The hydrocarbons in a 26% yield are obtained from acetate V and Hex_3Al, the yield reaches 41% in the case of Et_3Al. Catalytic amounts of CuBr, CuCl, and $FeCl_3$ lead to a pronounced change of the selective nucleophilic activity of organoaluminium reagents. Uncatalyzed cross-coupling product yields of I and II with Hex_3Al are 55–63%. Yields of alkylation products are increasing to 86–89% in the course of catalyzed interactions of V with trialkylalanes.

The electron-donor groups at the double bond assist the reactions to follow the cross-coupling pathway, thus resulting in high yields of the target products without catalysts. According to literature data [4], interactions of geranyl acetate and Et_3Al lead to hydrocarbons in a 75% yield. Quantitative yields of the alkylation products were observed with acetates III and IV (the effect of α-conjugation). Reactions of secondary acetates VI and VII with trialkylalanes also gave high yields (81–100%).

While investigating cross-coupling reactions of trialkylalanes with various organic electrophiles we have paid attention to homoallyl substrates, no data have been reported on their behaviour in reactions with organometallic reagents. However, the possibility of actual homoallylic interactions and rather ambiguous structures of the intermediates, resulting from skeletal isomerization, promoted broad studies of those systems in solvolytic reactions [6]. We have found that the alkyl-substituted cyclopropanes were formed in the course of homoallylic rearrangements as a consequence of interactions of trialkylalanes and tosylates of acyclic primary and secondary homoallylic alcohols.

1-Isobutylhexylcyclopropane (IX) was obtained quantitatively in the reaction of 3-nonene-1-ol tosylate (VIII) with $i\text{-}Bu_3Al$:



(VIII) (IX)

The alkylation reaction of 4-pentene-2-ol tosylate (X) by $i\text{-}Bu_3Al$ led to 1-methyl-2-isopentylcyclopropane (XI) (90%) *. Apart from IV, 4,6,-dimethyl-1-heptene (XII) (6%) and 7-methyl-3-octene (XIII) (4%) were produced. The total yield of hydrocarbons amounted to 74% (Scheme 1; Table 2). The high yield of cyclopropane hydrocarbons in the mixture (80–95%) was maintained with the growth of the alkylradical (CH_3, C_3H_7, Hex) α-positioned to a tosyl group (Table 2, tosylates XIV and XV), also when a methyl was introduced into the β-position of that group, and in the presence of an alkyl group at the double bond (tosylates XVI and XVIII).

Only change of the alkyl substituent at the cation center for an active electron-donor, phenyl, led to total suppression of the cyclization pathway in the reaction.

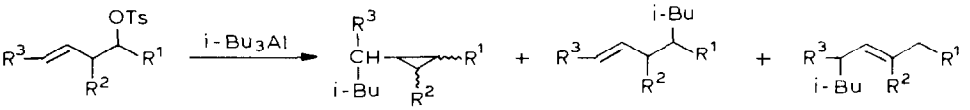
* Vicinal *cis*–*trans*-dialkylcyclopropanes were formed in a 1/1 ratio (GLC) in the course of reactions of homoallylic acyclic alcohols.

TABLE 2

THE REACTION MIXTURE COMPOSITIONS IN ALKYLATING TOSYLATES (X, XIV, XVIII)

No	Tosylate	Total yield (%)	Mixture composition	
			cyclopropanes (%)	olefins
1	X	74	XI (90)	(10)
2	XIV	66	XIX (80)	(20)
3	XV	quantitative	XX (81)	(19)
4	XVI	62	XXI (95)	absent
5	XVII	75	XXII (88)	(12)
6	XVIII	78	absent	

SCHEME 1

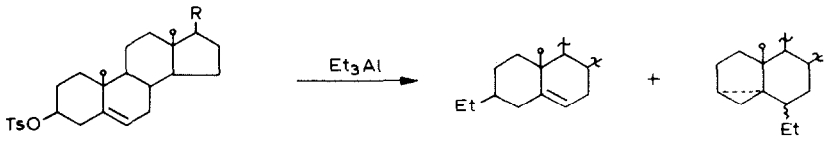


(X) (XIV-XVIII) (XI) (XIX-XXII) (XII) (XIII)

(R^1 = CH_3, R^2 = R^3 = H (X-XIII)
R^1 = C_3H_7, R^2 = R^3 = H (XIV, XIX)
R^1 = C_6H_{13}, R^2 = R^3 = H (XV, XX)
R^1 = R^2 = CH_3, R^3 = H (XVI, XXI)
R^1 = CH_3, R^2 = H, R^3 = C_3H_7 (XVII, XXII)
R^1 = C_6H_5, R^2 = R^3 = H (XVIII))

The behaviour of tosylates of steroid and terpenoid homoallyl alcohols was followed in those reactions. The reactions of 3β-tosyloxy-Δ^5-cholestene (XXIII) and -androstene (XXIV) with Et_3Al were accompanied by homoallylic rearrangement as occurred with the acyclic substrates to lead to quantitative yields of steroids XXV–XXVIII, where the hydrocarbon ratios XXVII/XXV and XXVIII/XXVI were about 6/1.

SCHEME 2

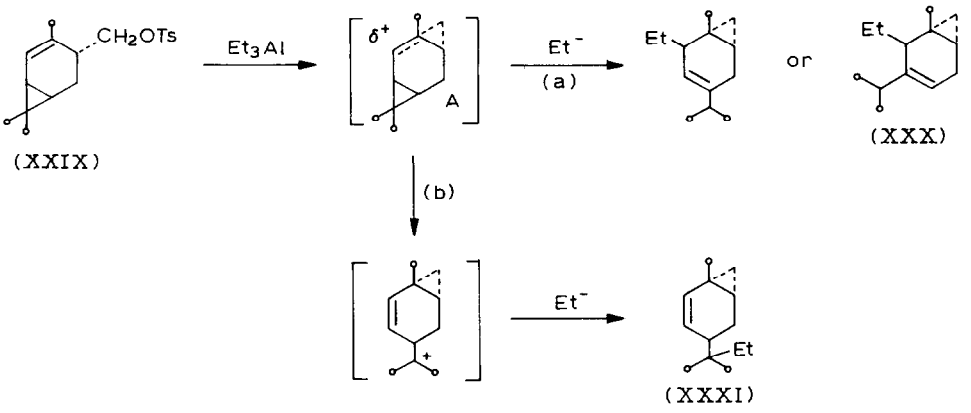


(R = CH_3 (XXIV, XXVI, XXVIII;
R = C_8H_{17} XXIII, XXV, XXVII)). (XXV, XXVI) (XXVII, XXVIII)

The homoallylic rearrangement also took place in the case of reactions of tosylate (XXX) of 4-α-oxymethyl-Δ^2-carene with Et_3Al. Under these reaction conditions, ring opening of the cyclopropane bearing a geminal methyl group was observed to be effected by Et_3Al as the Lewis acid (pathway (a)) and followed by retro-homoallylic rearrangement (pathway (b)). As a result, derivatives of a menthene series: 1-methyl-2-ethyl-3- or 4(1^1-methylethyl)bicyclo[4.1.$0^{1,6}$]-heptene-3 (XXX) and 1-

methyl-4(1^1,1^1-dimethylpropylbicyclo[4.1.$0^{1,6}$]heptene-2-(XXXI) were produced in 45 and 40% yields, respectively (Scheme 3).

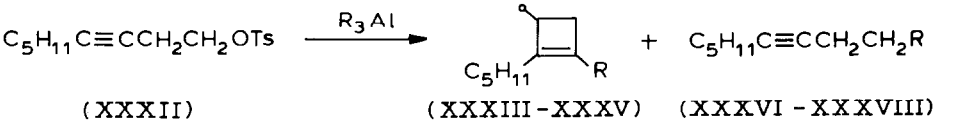
SCHEME 3



The behaviour of homopropargyl systems in nucleophilic substitution is of interest though it has not been yet studied deeply. The few papers concerned with the subject [7,8] reported solvolysis reactions involving homopropargyl species.

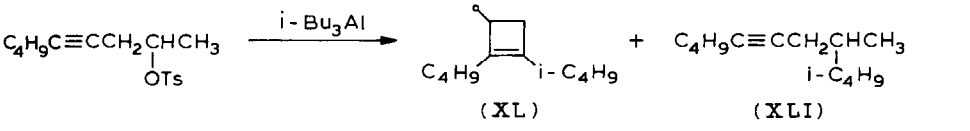
We have found that coupling reactions of trialkylalanes with tosylates of 4-alkyl- or 4-phenyl-substituted 3-butyne-1-ols involved the triple bond to result either in alkyl-cyclobutenes or in -cyclopropylidenes with regard to the substituent.

The reactions of 3-nonyne-1-ol tosylate (XXXII) with Et_3Al, i-Bu_3Al or Hex_3Al gave alkyl-substituted cyclobutenes XXXIII–XXXV, their contents in the reaction mixtures being 78–90%. Together with the cyclic hydrocarbons the reaction leads to the formation of alkynes XXXVI–XXXVIII. The total hydrocarbon yields being 60–100%.



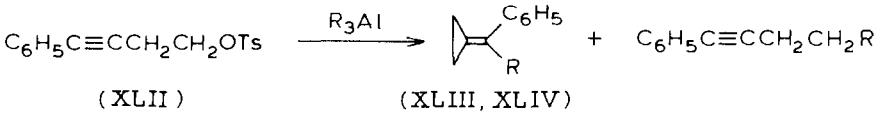
(R = C_2H_5 ; R = i-C_4H_9; R = C_6H_{13})

Alkylation of 4-nonyne-2-ol tosylate (XXXIX) by i-Bu_3Al led to quantitative yields of 1-isobutyl-2-butyl-3-methyl-1-cyclobutene (XL) (40%) and 8,10-dimethyl-5-undecyne (XLI) (60%).



The reaction of 4-phenyl-3-butyne-1-ol tosylate (XLII) with Et_3Al or i-Bu_3Al was accompanied by homopropargyl rearrangement resulting in that case in the com-

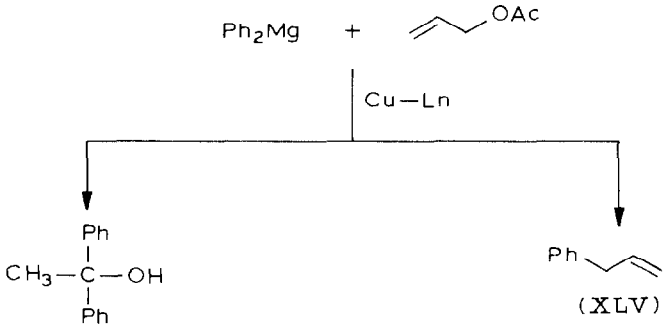
pounds 4,4[1]-phenylethyl- and 4,4[1]-phenylisobutyl-cyclopropylidenes (XLIII and XLIV), in 100 and 73% yields, respectively.



(R = Et, i-C_4H_9)

Thus, it was demonstrated that trialkylates could be easily involved in cross-coupling reactions with allyl acetates. The skeletal rearrangements in the course of the substitution reactions of tosylates of homoallylic and homopropargylic alcohols by trialkylalanes resulted in formation of alkyl-substituted cyclopropanes, cyclobutenes, and cyclopropylidenes in high yields. Those reactions are novel promising methods for synthesizing the cyclic hydrocarbons mentioned above. We were the first group who studied the interactions of dialkyl- and diaryl-organomagnesium reagents and allyl ethers, esters, thioesters, and amines comparing the reactivity of trialkylalanes to that of dialkylmagnesium derivatives in their cross-coupling reactions with allylic electrophiles, and to enlarge the application scope of the methods.

The optimal conditions for these processes were chosen using the cross-coupling reaction of diphenylmagnesium with allyl acetate. The absence of a catalyst made diphenylmagnesium, as well as trialkylalanes, attack mainly the ester group and, as a result, diphenylmethylcarbynol was formed. The yields of allylbenzene (XLV) in these experiments were less than 10%. Further investigations were carried out in the presence of transition metal complex catalysts. Our studies were concerned with the effect of the type of metal, the structure of the electron-donor ligand, and the solvent used on the yields and composition of the reaction products. The highest catalytic activity was observed with Cu salts activated by PPh_3 (Table 3). The presence of Cu salts gave rise to higher yields of XLV, up to 40%. Activation by PPh_3 caused the formation of XLV in a 98% yield exclusively.



The scope of the electron-donor ligands and solvents tested revealed the highest yields of XLV when THF, Et_2O, and dioxane were used in the presence of PPh_3 (Table 4).

Thus, further experiments were realized with the catalytic system $Cu(acac)_2PPh_3$ in THF (4 h, 40°C). Under such conditions Ph_2Mg and Hex_2Mg were involved in

TABLE 3

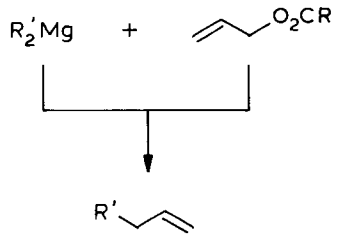
THE EFFECT OF THE CATALYST TYPE ON YIELDS AND COMPOSITIONS OF THE PRODUCTS IN THE REACTION OF Ph_2Mg WITH ALLYL ACETATE

(Reaction conditions: Solvent THF; 40°C, 4 h; Cu/PPh_3/(allyl acetate)/Ph_2Mg 1/2/50/25)

Catalyst	Yield[XLV] (%)	Catalyst	Yield[XLV] (%)
$Cu(acac)_2$	98	(*ortho*-OH-$C_6H_4CO_2)_2Cu$	77
Li_2CuCl_4	96	$CuCl_2$	65
CuI	96	$CuCl_2$	42
CuBr	79	–	7

the reaction with allyl esters of acryl, methacryl, cinnamic, and benzoic acids to result in high yields of XLV and 1-nonene XLVI.

The structure of the acid residue in allyl esters did not influence the yields of the cross-coupling product (average 79–90%). Besides this, the reactivity of Hex_2Mg was higher than that of Ph_2Mg towards allyl compounds.



(XLV , R' = Ph ;
XLVI, R' = C_6H_{13})

(R = $CH_2CH{=}CH_2$; $CH_2CH{=}CHPh$; $CH_2C(CH_3){=}CH_2$; Ph)

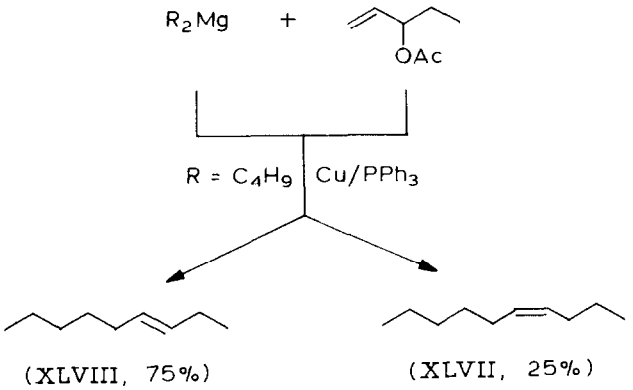
TABLE 4

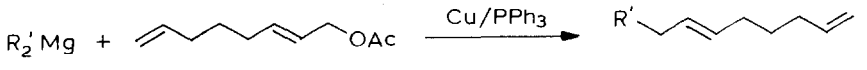
THE EFFECTS OF SOLVENT TYPE AND ACTIVATOR STRUCTURE ON YIELDS OF XLV

(Reaction conditions: Solvent THF, 40°C, 4 h; $Cu(acac)_2$/(ligand-activator)/(allyl acetate)/Ph_2Mg 1/2/50/25)

Solvent	Yield[XLV] (%)	Ligand-activator	Yield[XLI] (%)
THF	98	Ph_3P	98
Dioxane	90	$(PhO)_3P{=}O$	90
Diethyl ether	75	α,α-dipyridine	70
Dipropyl ether	65		
Diglyme	50	$(i\text{-}C_3H_7O)_3P$	60
Sulfolane	41	$Ph_3P{=}O$	63
Benzene	37	$(C_6H_{13}O)_3P$	62
Heptane	15	$(PhO)_3P$	30

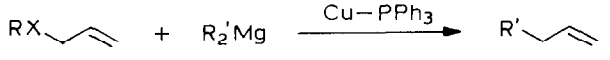
All our attempts to produce branched olefins by coupling Bu_2Mg with 3-acetoxy-1-pentene failed. Irrespective of the reaction conditions, each experiment gave *cis*- and *trans*-3-nonenes (XLVII, XLVIII) in a 1/2 ratio. 1,6*E*-Dienes (XLIX, L) were formed from 2,7-octadienyl acetate and Ph_2Mg, Hex_2Mg or Bu_2Mg.





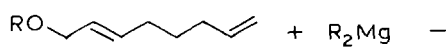
(XLIX, R' = Ph;
L, R' = Bu;
LI, R' = C_6H_{13})

Cross-coupling of Ph_2Mg, Bu_2Mg, or Hex_2Mg with allyl ethers and thioesters catalyzed by Cu complexes also led to mono- (XLV, XLVI, LII) and di-olefins (XLIX–LI) in high yields.



(XLV, XLVI, LII)

(X = O, S; R = C_4H_9, C_6H_5, $CH_2CH{=}CH_2$;
R' = Ph (XLV), C_6H_{13} (XLVI), Bu (LII))

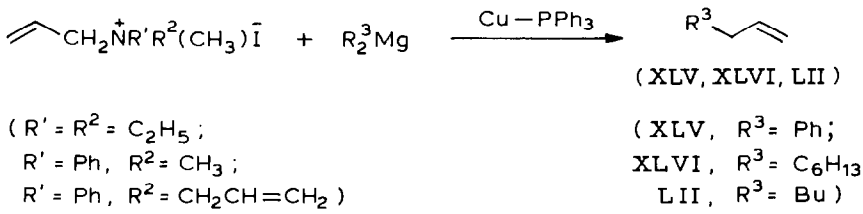


(R = CH_3, Et, Ph)

(XLIX, R' = Ph;
L, R' = Bu;
LI, R' = C_6H_{13})

Unlike ethers and esters, dialkylamines interacted with the Grignard reagents presented above to give cross-coupling products in low yields (< 10%). However, allylamines with a more polarized N–C bond (ammonium salts) were readily involved in the reaction with diaryl- and dialkyl-magnesium derivatives to give reasonable yields of monoolefins.

To summarize: the cross-coupling of dialkylmagnesium derivatives with allyl



ethers and esters, sulphides, and quaternized allylamines, catalyzed by Cu salts, should be seen as an effective approach to mono- and di-olefins of various structure.

Experimental

IR spectra were recorded on IR-20 Spectrophotometer (thin layer). PMR spectra on "Tesla BS-467" (60 MHz) and on "Tesla BS-567" (100 MHz), TMS and $CDCl_3$ were used as solvents. Mass spectra were recorded on a MX-1306 device (70 eV), ionization chamber temperature 150°C. GLC analyses were carried out by "Chrom-5" with the columns 1.2 m × 3 mm and 2.4 m × 3 mm, 5% SE-30, on Chromaton N-AW-DMCS, helium was used as carrier gas (50 ml/min). Preparative separation was carried out with "Perkin–Elmer F-21" with the columns 5 m × 8 mm, 5% SE-30 and 15% PEG-6000 on Chromaton N-AW, helium as the carrier gas (300 ml/min).

Dialkylmagnesium derivatives were obtained as in ref. 9,10; trihexylaluminium as in ref. 11; acetate (IV) was produced from sorbic acid by methylation and reduction by $LiAlH_4$ of methyl sorbate as in ref. 12; alcohol acetylations were accomplished in accordance with the usual technique. The derivatives of 2,7-octadiene were produced by butadiene telomerization with the related alcohols and AcOH as in ref. 13; 3-nonene-1-ol was produced from 1-octene and paraformaldehyde [14], and 4-octene-2-ol from hexene-1 according to ref. 15. 4α-Oxymethyl-Δ^2-carene was obtained from Δ^3-carene as in ref. 16. Alcohol tosylations following the usual technique. Olefins (XLV, XLVI, LII) and 1,6-diene were identified by comparison with the known substances [17,18].

Interactions of allyl acetates and trialkylalanes (general technique)

Trialkylalane (0.02 mol of 1.5–2 *M* solution in hexane or CH_2Cl_2) was added dropwise to a solution of acetate (0.01 mol) in hexane or CH_2Cl_2. A catalyst (7–10 mol%) was added to the acetate. The reaction came to an end immediately after dropping was completed or in several hours, which depended on the reagents employed. The reaction mass was diluted by ester and decomposed by H_2O and, then, by 10% HCl solution. The mixture was extracted by ester and washed by $NaHCO_3$ solution, H_2O, and dried by $MgSO_4$.

Interaction of acetate III and i-Bu_3Al and Hex_3Al

5-Methyl-1-phenyl-1-hexene (LIII), 5-methyl-3-phenyl-1-hexene (LIV), 1-phenyl-1-nonene (LV), and 3-phenyl-1-nonene (LVI) were obtained according to the technique described. Isomers LIII–LVI were separated by the preparative GLC.

LIII: n_d^{20} 1.5195. ^1H NMR spectrum (δ (ppm)): 0.8 d (6H $\begin{matrix}\text{Me}\\ \diagup\\ \text{C}\\ \diagdown\\ \text{Me}\end{matrix}$), 1.4 m (3H, CH_2), 2.1 m(2H,CH_2C=C), 6.0 m (2H, CH=CH), 7.0 m (5H,C_6H_5), *m/z* 174.

LIV: n_d^{20} 1.4961. ^{1}H NMR spectrum (δ (ppm)): 0.8 d (6H $\begin{matrix}\text{Me}\\ \diagup\\ \text{Me}\end{matrix}$>C), 1.45 m (3H, CH_2), 3.2 m (1H, CHC_6H_5), 4.8 m (2H, CH_2=C), 5.45–6.1 m (1H, CH=CH), 7.0 m (5H, C_6H_5), *m/z* 174.

LV: n_d^{20} 1.5142. ^{1}H NMR spectrum (δ (ppm)): 0.9 t (3H, CH_3), 1.35 m (10H, CH_2), 2.2 m (2H, CH_2–C=C), 6.1 m (2H, CH=CH), 7.2 m (5H, C_6H_5), *m/z* 202.

LVI: n_d^{20} 1.4935. ^{1}H NMR spectrum (δ (ppm)): 0.8 t (3H, CH_3), 1.0–1.7 m (10H, CH_2), 3.1 m (1H, CHC_6H_5) 4.9 m (2H, CH_2=C), 5.6–6.2 m (1H, CH=CH), 7.2 m (5H, C_6H_5), *m/z* 202.

Interactions of acetate IV and i-Bu$_3$Al

8-Methyl-2,4-nonadiene (LVII): B.p. 178–180°C, n_d^{20} 1.4583. ^{1}H NMR spectrum (δ (ppm)) 0.8 d (6H $\begin{matrix}\text{Me}\\ \diagup\\ \text{Me}\end{matrix}$>C), 1.0–1.5 m (3H, CH_2), 1.7 d (3H, CH_3C=C), 1.9 m (2H, CH_2C=C), 4.8–6.2 m (4H, CH=CH), *m/z* 138.

Interactions of acetate VI and i-Bu$_3$Al and Hex$_3$Al

4,6-Dimethyl-2-heptene (LVIII): B.p. 60°C 20 mmHg, n_d^{20} 1.4135. ^{1}H NMR spectrum (δ (ppm)): 0.8 d, 0.9 d (9H, CH_3), 1.2 m (3H, CH_2), 1.6 m (3H, CH_3C=C), 2.0 m (1H, CHC=C), 5.25 m (2H, CH=CH), *m/z* 126.

4-Methyl-2-decene (LIX): B.p. 75–77°C/20 mmHg, n_d^{20} 1.4270. ^{1}H NMR spectrum (δ (ppm)): 0.9 m (6H, CH_3), 1.2 m (10H, CH_2), 1.6 m (3H, CH_3C=C), 1.9m (1H, CHC=C), 5.25 m(CH=CH), *m/z* 154.

Interactions of acetate VII and i-Bu$_3$Al.

2-Isobutylcyclohexene-1 (LX): B.p. 68–70°C 20 mmHg, n_d^{20} 1.4547. ^{1}H NMR spectrum (δ (ppm)): 0.9 d (6H, CH_3), 1.1–1.5 m (3H, CH_2), 1.6 m (4H, CH_2 in a cycle), 1.75–2.3 m (3H, CH_2C=C), 5.6 m (2H, CH=CH), *m/z* 138.

Interactions of trialkylalanes and tosylates of homoallyl and homopropargyl alcohols.

The reactions were carried out in accordance with the general technique described for allyl acetates. Hydrocarbons XXX, XXI, XXXIII–XXXV, and XL–XLI were isolated by preparative GLC. The reaction mixtures obtained by interactions of trialkylalanes and homoallyl tosylates were oxidized by the calculated quantities of *p*-carbomethoxyperbenzoic acid in CH_2Cl_2 (+10°C, 4 days) and the remaining cyclopropanehydrocarbons described separated out. The reaction mass was filtered out and the precipitate washed by ether. The organic extracts were washed by the soda solution, H_2O, and dried by $MgSO_4$. The mixture of cyclopropane hydrocarbons and epoxides was separated by GLC on a column with Al_2O_3; for hydrocarbons, the eluent pentane was employed, for α-oxides, pentane diethyl ether (10/1).

1-Isobutylhexylcyclopropane (IX): n_d^{20} 1.4350, ^{1}H NMR spectrum (δ (ppm)): 0.6 and 0.35 m (5H, H cyclic), 0.8, 1.2, and 1.5 m (21 H, CH_3, CH_2, CH), *m/z* 182.

1-Methyl-2-isopentylcyclopropane (XI): n_d^{20} 1.4130, ^{1}H NMR spectrum (δ (ppm)): 0.08 and 0.4 m (4H, H cyclic), 0.88 and 1.23 m (13H, CH_3, CH_2), 1.66 m (1H, CH), *m/z* 126.

1-Propyl-2-isopentylcyclopropane (XIX): n_d^{20} 1.4260, ^{1}H NMR spectrum (δ

(ppm)): 0.06–0.5 m (4H, H cyclic), 0.8 and 1.2 m (17H, CH_3, CH_2), 1.7 m (1H, CH), *m/z* 154.

1-Hexyl-2-isopentylcyclopropane (XX): n_d^{20} 1.4380, ^{1}H NMR spectrum (δ (ppm)): 0.0–0.3 m (4H, H cyclic), 0.85 and 1.25 m (24H, CH_3, CH_2), *m/z* 196.

1,2-Dimethyl-3-isopentylcyclopropane (XXI): n_d^{20} 1.4180, ^{1}H NMR spectrum (δ (ppm)): 0.0 m (3H, H cyclic), 0.8, 1.15 and 1.5 m (17 H, CH_3, CH_2, CH), *m/z* 140.

1-Methyl-2-(1-propyl-isopentyl)cyclopropane (XXII): n_d^{20} 1.4265, ^{1}H NMR spectrum (δ (ppm)): 0.15 m (4H, H cyclic), 0.9, 1.07–2.0 m (20H, CH_3, CH_2, CH), *m/z* 168.

6-Ethyl-3,5-cyclocholestane (XXVII) n_d^{20} 1.5080, $[\alpha]_D^{25}$ + 35.4° (7.07 $CHCl_3$). ^{1}H NMR spectrum (δ (ppm)): 0.09 dd (1H C^4, J_{gem} 5.0, $J_{3,4}$ 8.0 Hz), 0.40 dd (1H, C^4, J_{gem} 5.0, $J_{3,4}$ 8.0 Hz), 0.40 dd (1H, C^4, J_{gem} 5.0, $J_{3,4}$ 3.8 Hz), 0.70 s(3H, C^{18}), 0.83 s (3H, C^{19}), *m/z* 398.

6-Ethyl-3,5-cycloandrostane (XXVIII): n_d^{20} 1.5179, $[\alpha]_D^{25}$ + 13.5° (4.44 $CHCl_3$). ^{1}H NMR spectrum (δ (ppm)): 0.09 dd (1H, C^4, J_{gem} 4.8, $J_{3,4}$ 8.0 Hz), 0.40 dd (1H, C^4, J_{gem} 4.8, $J_{3,4}$ 3.8 Hz), 0.74 s (3H, C^{18}), 0.83 s (3H, C^{19}), *m/z* 286.

1-Methyl-2-ethyl-3- or 4(1^1-methylethyl)bicyclo[4.1.$0^{1,6}$]hepten-3 (XXX): n_d^{20} 1.4810, $[\alpha]_D^{25}$ − 9.3° (6.5 C_2H_5OH). ^{1}H NMR spectrum (δ (ppm)): 0.06 dd and 0.44 dd ($2H^7$), 0.82 t (3H, CH_3), 0.96 d (6H, CH_3^{10} + CH_3^{11}), 1.04 s (3H, CH_3^8), 1.54 m, 2.08 m, 2.26 m (CH_2CH), 5.2 m (1H, H^3), *m/z* 178.

1-Methyl-4-(1^1,1^1-dimethylpropyl)bicyclo[4.1.$0^{1,6}$]hepten-2 (XXXI): n_d^{20} 1.4855, $[\alpha]_D^{25}$ − 11.3° (9.6, C_2H_5OH). ^{1}H NMR spectrum (δ (ppm)): 0.5 dd and 0.8 dd ($2H^7$), 0.85 (3H, CH_3), 0.85 s and 0.86 s (6H, CH_3^{10} and CH_3^{11}), 1.2 s (3H, CH_3^8), 0.87–2.2 m (CH_2CH), 5.3 d (1H, H^2), 5.8 dd (1H, H^3), *m/z* 178.

1-Ethyl-4-penthyl-1-cyclobutene (XXXIII): n_d^{20} 1.4490. ^{1}H NMR spectrum (δ, (ppm)): 0.88 and 0.93 m (6H, CH_3), 1.3 m (6H, CH_2), 1.95 m (4H, CH_2–C=C), 2.22 (4H, CH_2–C=C), *m/z* 152.

4,4^1-Phenylethylcyclopropylidene (XLIII): n_d^{20} 1.3750. ^{1}H NMR spectrum (δ (ppm)): 1.2 m (7H, CH_3, n-cyclic), 2.6 q (2H, CH_2–C=C), 7.2m and 7.5 m (5H aromatic), *m/z* 158.

Cross-coupling of dialkylmagnesium derivatives with allyl compounds (general technique).

An organomagnesium reagent (2.5 mmol) was added (under argon with stirring) to a cooled (to −5°C) solution of 0.262 g Cu(acac) (1 mmol), of 0.524 g Ph_3P (2 mmol) and of the related allylic compound (50 mmol) in 10 ml of THF; the mixture was left for 10 min at 5°C. The mixture was taken into a thermostatted glass reactor and heated at 40°C (4 h). After the reaction was over, the catalyst was decomposed by a NH_4Cl saturated solution and extracted by an ether. After the solvent was removed, the residue was vacuum distilled.

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