Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1992, **2**(1), 28–29
Mendeleev Communications

Novel Regioselective β-Hydrovinylation of Terminal Alkenes in the Presence of Metallocomplexed Catalysts

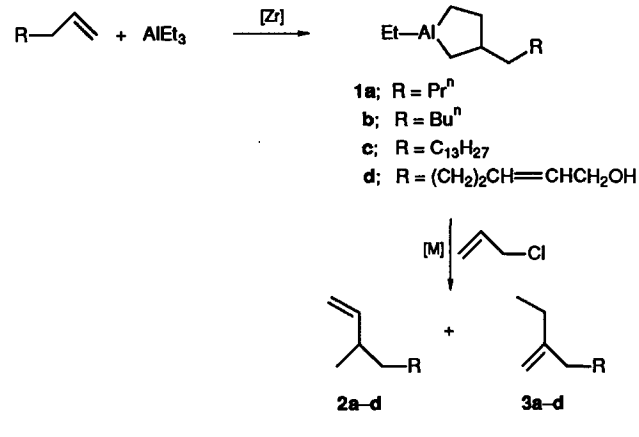
Usein M. Dzhemilev, Askhat G. Ibragimov* and Aleksei P. Zolotarev

Institute of Organic Chemistry, Ural Branch of the Russian Academy of Sciences, 450054 Ufa, Russia. Fax: +7 3472 223 569

A novel method for the synthesis of 2-vinylalkanes by reaction of 3-alkyl-substituted aluminacyclopentanes with functionalized allyl compounds in the presence of catalytic amounts of Ni or Co complexes is proposed.

We have recently reported the transformation of 3-alkyl-substituted aluminacyclopentanes (ACPs)[1,2] into cyclobutane[3] or cyclopropane[4] derivatives in the presence of catalytic amounts of $Ni(acac)_2$ (Hacac = acetylacetone) or palladium phosphine complexes.

This communication is concerned with the study of a novel reaction of 3-alkyl-substituted ACPs with functionalized alkyl compounds. The initial ACPs **1** were prepared by a catalytic cyclometallation of hex-1-ene, hept-1-ene, hexadec-1-ene and octa-2,7-dienol with $AlEt_3$.[1,2] In the presence of a threefold excess of allyl chloride or allyl ethers, the synthesized ACPs were found to transform into 2-vinylalkanes after hydrolysis under the influence of the three-component catalysts $Ni(acac)_2$–PPh_3–Bu^i_2AlH or $Co(acac)_3$–PPh_3–Bu^i_2AlH (1:4:8). For example, ACPs **1a–d** formed 3-methyl-1-vinylalkanes **2a–d** in 75% yield in the presence of 5 mol% phosphine complexes of Ni or Co in a ratio of **1**: $CH_2{=}CHCH_2Cl$ = 1:3 for 10 h at 20 °C after hydrolysis of the reaction mixture with aqueous HCl. An equimolar amount of propylene was liberated in the reaction. During each run, 2-vinylalkanes **2a–d** were formed, along with their structural isomers **3a–d** in 5–8% yields (Scheme 1).

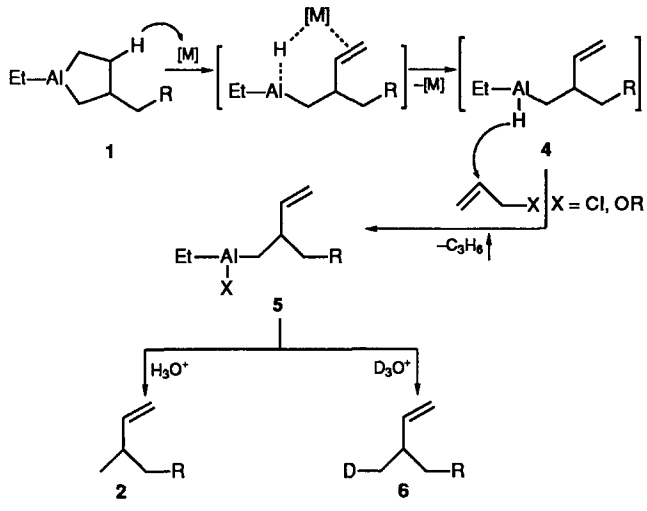


Scheme 1 [M] = Ni or Co complex

Table 1 Effects of solvent, nature of catalyst and allyl substrate on the yield of 3-methyl-n-heptadec-1-ene **2c** (5 mol% [M], 10 h, 20 °C)

Solvent[a]	Yield **2c** (%)	Allyl substrate[b]	Yield **2c** (%)	Catalyst[c]	Yield **2c** (%)
Hexane	75	$CH_2{=}CHCH_2Cl$	75	$Ni(acac)_2$:	
Pentane	74	$MeOCH_2CH{=}CH(CH_2)_3CH{=}CH_2$	64	:Ph_3P:Bu^i_2AlH = 1:4:8	75
Cyclohexane	74	$(CH_2{=}CHCH_2)_2O$	58	$Co(acac)_3$:	
Benzene	72	$PhOCH_2CH{=}CH_2$	56	:Ph_3P:Bu^i_2AlH = 1:4:8	68
THF[d]	70	$BuOCH_2CH{=}CH_2$	5	$Pd(aca)_2$:Ph_3P:Bu^i_2AlH = 1:4:8	0
Ether	68	$N(CH_2CH{=}CH_2)_3$	0	$Cu(acac)_2$:Ph_3P = 1:2	0

[a] $Ni(acac)_2$:Ph_3P:Bu^i_2AlH = 1:4:8, $CH_2{=}CHCH_2Cl$:$AlEt_3$ = 3:1. [b] $Ni(acac)_2$:Ph_3P:Bu^i_2AlH = 1:4:8, allyl substrate:$AlEt_3$ = 3:1. [c] $CH_2{=}CHCH_2Cl$:$AlEt_3$ = 3:1. [d] THF = tetrahydrofuran.



Scheme 2 [M] = Ni or Co complex

In the absence of a catalyst complex or allyl compounds, the ACPs studied were never transformed into 2-vinylalkanes. The nature of the solvent has no effect on the yield of vinylalkanes **2**, but the yields of the latter compounds were highly dependent on the structure of the initial allyl compound (Table 1). A number of Fe-, Co-, Ni-, Pd-, and Ir-based catalysts were studied in this reaction, and the highest yields were obtained in the presence of either a cobalt- or nickel-containing catalytic system.

With regard to a mechanism for the β-vinylation reaction of terminal alkenes, it may be assumed that the role of low-valent transition metal complexes consists of the catalysis of hydride transfer of the β-hydrogen atom in the formed ACPs with further generation of aluminium hydrides **4** and **5**. Aluminium hydrides **4** reduce allyl compounds (allyl chloride, allyl ethers) to propylene,[6] and are thus transformed into related aluminium halides or alkoxides **5**. Hydrolysis of the latter leads to 2-vinylalkanes **2**, and deuteriolysis leads to the related 1-deuterio-2-vinylalkanes **6** (Scheme 2). Compounds **1**, **2**, **5** and **6** were identified by spectroscopic methods.

The developed method for β-hydrovinylation of terminal alkenes into 3-methylalk-1-enes **2** *via* the formation *in situ* of 3-substituted aluminacyclopentanes **1** offers a promising new route for the homologation of terminal alkenes.

Received: Moscow, 26th April 1991
Cambridge, 11th July 1991; Com. 1/02112E

References

1 U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 207.
2 U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2831.
3 U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2152.
4 U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1190.
5 G. Henrici-Olivé and S. Olivé, *Koordinatsiya i katalyuz* (Coordination and catalysis), Mir, Moscow, 1980, p. 174 (in Russian).
6 G. A. Tolstikov and V. P. Yur'ev, *Aluminiiorganitcheski sintez* (Organoaluminium synthesis), Nauka, Moscow, 1979,p. 265 (in Russian).