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CHEMISTRY OF ORGANOSILICON COMPOUNDS

CC*. ALLYL COUPLING REACTIONS OF ALLYLSILANES AND ALLYLSTANNANES WITH ALLYLIC HALIDES, ETHERS AND ACETATES PROMOTED BY A LEWIS ACID

AKIRA HOSOMI, TAKAFUMI IMAI, MASAHIKO ENDO and HIDEKI SAKURAI
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 (Japan)

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Summary

Facile allyl couplings between allylsilanes or allylstannanes and various allylic substrates such as halides, ethers or acetates promoted by a Lewis acid, leading to 1,5-dienes with regiospecific transposition in the allylic part of allylmetallics have been observed. The combination of allylstannanes with allylic acetates promoted by bis(diethylaluminum) sulfate gives the most satisfactory results. The factors influencing the regioselectivity with respect to allylic substrates are discussed.

Introduction

Allyl couplings which are usually accomplished by Wurtz-type couplings between allylic organometallics and allylic halides [2–5] are important reactions in organic synthesis, especially for the synthesis of various natural products. However, the regioselectivity, especially with respect to the organometallics, of the reactions cannot be sufficiently controlled at present, except for specially designed reactions [6–11]. Generally a mixture of four regioisomers from every possible combination of these two reagents is obtained. During the course of studies on the application of allylsilanes to organic synthesis [12], we found that not only mono-allylated products but also doubly allylated ones were formed by the stepwise reaction of allylic silanes with α,β-unsaturated acetals in the presence of a Lewis acid [12f]. In this paper we report that allylsilanes (I) and allylstannanes (II) are useful and convenient reagents for allyl couplings with allylic halides, ethers and acetates, affording only cross-cou-

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[*] Presented in part at the 37th Annual Meeting and the Tohoku Regional Meeting of the Chemical Society of Japan [1].

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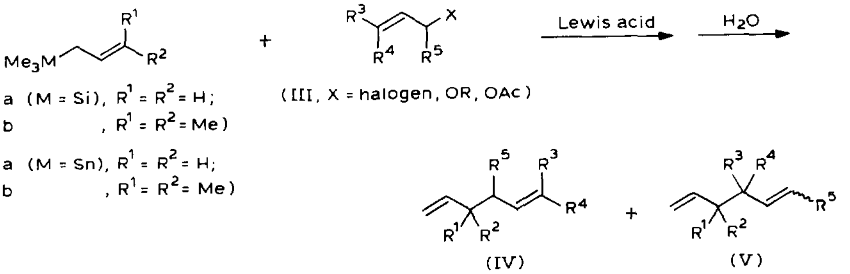
pled 1,5-dienes with regiospecific transposition in the allylic part of the allylmetallics (eq. 1)*.



(1)

Results and discussion

Allyl couplings with allylsilanes

Allylic ethers and halides activated by titanium chloride ($TiCl_4$) reacted with allyltrimethylsilane (Ia) at −78°C to give a mixture of two regioisomeric 1,5-dienes (IV and V) in fairly good yield. The results are listed in Table 1. In these reactions, only cross-coupling, but not homocoupling, took place cleanly. Trimethylsilyl ethers of allylic alcohols, similarly to methyl ethers, afforded cross-coupled 1,5-dienes. Titanium chloride was the most effective activator for the reaction using allylsilanes among various Lewis acids such as aluminum chloride and stannic chloride. Boron trifluoride etherate was too weak to activate the reaction with allylsilanes.

The yields of the 1,5-dienes depend on both the reaction temperature and the reaction time. Thus, at −78°C, the reaction of Ia with 3-methoxy-1-heptene (IIIa) gave a mixture of IVa and Va in 89% yield after 3 h. However, at 0°C, the yield decreased to less than half this value. At a higher temperature and for a prolonged reaction time, polymerization of the starting materials and the resulting 1,5-dienes takes place considerably in competition with the allyl coupling due to the strong acidic conditions.

Although considerable polymerization took place diminishing the yield and producing a viscous oil, particularly in the case of primary allylic ethers and halides such as prenyl ethers and halides, secondary alkyl substrates gave the most satisfactory results, as can be seen in Table 1. Tertiary allylic ethers could not enter the reaction.

Reactions with 3-methyl-2-butenyltrimethylsilane (Ib) demonstrate that the regiospecificity in the allylic part of the allylsilanes is absolutely controlled [12]. However, two regioisomers with respect to the allylic group of the allylic substrates were obtained regioselectively as a mixture from the reaction of unsymmetrically substituted allylic substrates with I, where the carbon–carbon bond formation took place predominantly at the less substituted carbon atom of the allylic group. For example, 3-methoxy-1-heptene (IIIa) and 3-trimethylsiloxy-1-heptene (IIIb), which

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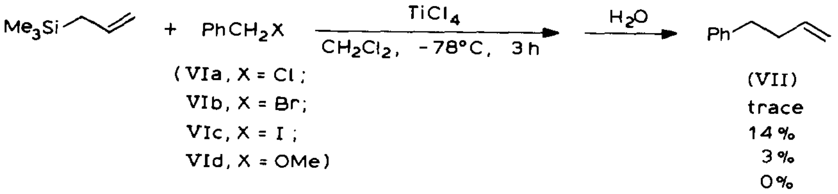
* When we had almost completed our work, we learnt that two groups had recently reported allyl coupling reactions using allylsilanes, by the promotion of the Lewis acid or trimethyloxonium ion. See refs. 7c and 7d.

generate incipiently primary and secondary carbocationic species at the γ and α sites of the allylic group with the aid of titanium chloride, afford a mixture of two regioisomers (IV and V), of which 70–80% is the sterically less hindered regioisomer (V) in preference to the other isomer (IV).

It has been found that, instead of allylic substrates, benzyl halides (VIa–c), but not benzyl ether (VId), react with Ia to give 4-phenyl-1-butene (VII), though in a low yield (eq. 2).



(2)

Allyl couplings with allylstannanes

Since allylstannanes display a higher reactivity towards electrophiles than allylsilanes [13], it has been observed that a weak Lewis acid such as boron trifluoride etherate is sufficient to activate carbon electrophiles [13d,e]. Moreover, it is well known that organoaluminums reveal strong Lewis acidity, especially towards oxygen-containing substrates such as ethers and acetates, to give the corresponding 1 : 1 complexes [14]. Therefore, the problems that we encountered in the allylsilane-$TiCl_4$ system, namely, the drawbacks that primary allylic substrates cannot be effectively activated and both starting materials and products tend to undergo polymerization under the reaction conditions, are successfully solved by utilizing allylstannanes (II) instead of allylsilanes (I), and bis(diethylaluminum) sulfate [14a] instead of titanium chloride. Indeed, 1,5-dienes are obtained in good yields without polymerization even under the condition of heating to reflux. The results are summarized in Table 2. In the reaction of II, boron trifluoride etherate was also effective as an activator of the allylic substrates, although polyolefinic substrates such as geranyl acetate and chloride failed to give allyl coupling products probably due to polymerization and/or other side reactions. Both allylic chlorides and acetates can be successfully used for allyl couplings promoted by bis(diethylaluminum) sulfate to give the corresponding cross-coupled 1,5-dienes in considerably high yields, although these two substrates bring about different regiochemical outcomes.

Allyl transfer from allylstannanes proceeded in a regiospecific fashion. Although, even in these reactions, the regiochemistry with respect to allylic substrates could not be sufficiently controlled, it is worthwhile noting that the regioselectivity depends on the structure of the allylic substrates, as discussed below. However, the synthetic utility of the present reactions was mostly displayed by the complete cross-coupling reactions between allylic organometallics and allylic substrates, the ready accessibility of the starting materials, and the simple manipulation of the conversion.

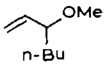
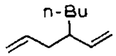
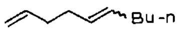
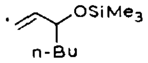
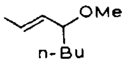
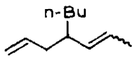
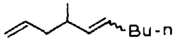
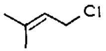
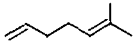
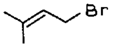
Regioselectivity in the cross-coupling reactions

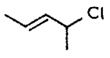
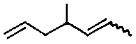
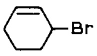
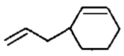
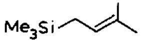
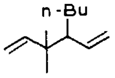
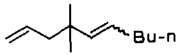
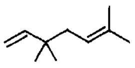
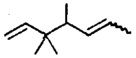
The results listed in Table 1 indicate that, with allylsilanes (I), allyl ethers and allyl halides activated by titanium chloride as a Lewis acid selectively afforded a mixture of the regioisomers of the corresponding cross-coupled 1,5-dienes which

(Continued on p. 102)

TABLE 1

ALLYL COUPLINGS OF ALLYLSILANES (I) WITH ALLYLIC SUBSTRATES (III) PROMOTED BY A LEWIS ACID [a]

Entry	Allylsilane	Allylic compound	1,5-Dienes		Yield (%) [b] (Ratio of IV/V) [c]
			IV	V	
1	 (Ia)	 (IIIa)	 (IVa)	 (Va)	67, 89 [c] (21/79)
2	Ia	 (IIIb)	IVa	Va	60 (30/70)
3	Ia	 (IIIc)	 (IVb)	 (Vb)	75 (35/65) [d]
4	Ia	 (IIId)	 (IVc) [e]	 (Vc)	4 (100/0)
5	Ia	 (IIIe)	IVc [e]	Vc	7 (100/0)

6	Ia	 (IIIf)	 (IVd)		45, 88 [c]
7	Ia	 (IIIg)	 (IVe)		75 [c]
8	 (Ib)	IIIa	 (IVf)	 (Vf)	33 (30/70)
9	Ib	IIId	 (IVg)	 (Vg)	10 (100/0)
10	Ib	IIIe	IVg	Vg	12 (100/0)
11	Ib	IIIf	 (IVh)		78

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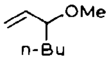
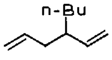
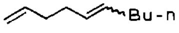
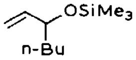
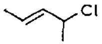
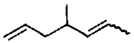
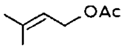
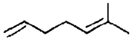
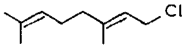
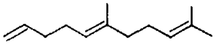
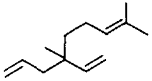
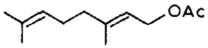
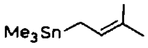
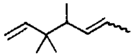
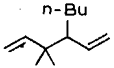
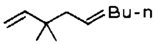
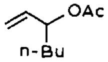
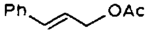
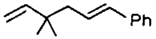
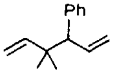
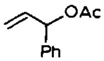
[a] All reactions were carried out at −78°C for 3 h in CH_2Cl_2. [b] Yield after isolation unless otherwise noted. [c] Determined by GLC. [d] Determined by NMR. [e] 6-Chloro-2-methyl-3-heptene (VIII) was obtained in 6% yield for entry 4 and in 13% yield for entry 5.

TABLE 2

ALLYL COUPLINGS OF ALLYLSTANANES (II) WITH ALLYLIC SUBSTRATES (III) PROMOTED BY BIS(DIETHYLALUMINUM) SULTATE[a]

Entry	Allylstannane	Allylic compound	1,5-Dienes		Yield (%)[b] (Ratio of IV/V)[c]
			IV	V	
1	 (IIa)	 (IIIa)	 (IVa)	 (Va)	70 (21/79)
2	IIa	 (IIIb)	IVa	Va	55 (24/76)
3	IIa	 (IIIf)	 (IVd)		100[c]
4[d,e]	IIa	IIIf	IVd		40[c]
5	IIa	 (IIIh)	 (IVc)	 (Vc)	100[c] (41/59)
6	IIa	 (IIIi)	 (IVi)	 (Vi)	51 (18/82)
7	IIa	 (IIIj)	IVi	Vi	41 (82/18)

8	 (IIb)	IIIf		 (IVh)	88 [c]
9 [d,e]	IIb	IIIf		IVh	74 [c]
10	IIb	IIIb	 (IVf)	 (Vf)	55 (24/76)
11	IIb	 (IIIk)	IVf	Vf	67 [c] (20/80)
12	IIb		 (IVj)	 (Vj)	67 (53/47)
13 [d,e]	IIb	IIIl	IVj	Vj	35 [c] (80/20)
14	IIb	 (IIIm)	IVj	Vj	94 [c] (53/47)
15 [d,e]	IIb	IIIm	IVj	Vj	32 [c] (12/88)

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[a] All reactions were carried out in benzene/hexane (1/1) at reflux for 16 h unless otherwise noted. [b] Yield after isolation was not always optimized. [c] Determined by GLC. [d] Reactions were carried out in CH_2Cl_2, using $BF_3 \cdot OEt_2$ as an activator. [e] The reaction was carried out at −78°C for 3 h. [f] The reaction was conducted at room temperature for 0.5 h.

were predominantly bonded to the sterically less hindered site of the allylic group of the allylic substrates while the transfer of the allyl group from the allylsilanes to the allylic substrates occurred in a cleanly regiospecific way (entries 8–11 in Table 1).

From the mechanistic point of view, the present allyl coupling reaction is essentially similar to the reactions of allylsilanes with carbon electrophiles reported by us previously [12]. Although the α (S_N2 reaction) or γ substitution (S_N2' reaction) with respect to the allylic substrates cannot be sufficiently controlled in this reaction, the regioselectivity obtained in Table 1 may be reasonably attributed to the steric effect around the reaction sites where positive charge develops to a small extent by the complexation of a leaving group, X, with titanium chloride, as shown in Scheme 1. Thus, the γ position of allylic substrates (IIIa–IIIc), though a less electron-deficient carbon center, is a more reactive site than the α-position towards allylsilanes, since the secondary α site activated by the bulky titanium chloride may be sterically more hindered than the unsubstituted γ site. On the other hand, it is reasonably understood that the α site is more reactive in the prenyl substrates (IIId and IIIe), because of both electronic and steric reasons.

more reactive site for IIIa-IIIc
(less sterically hindered although
less electron-deficient)

more reactive site for IIId and IIIe
(less sterically hindered and more
electron-deficient)

SCHEME 1

In the case of allylstannanes (II), the regiospecificity with respect to the allylmetallics was also demonstrated by the experiments with 3-methyl-2-butenyltrimethylstannane (IIb), while the regioselectivity of the allylic substrates depends on the steric environment around the α and γ sites of the allylic group and, in addition, on the degree of interaction between the activator and the leaving group of the substrate. Thus the difference in the coordinating ability of aluminum or boron towards oxygen or chlorine which causes charge polarization in the allylic substrates governs the regioselectivity of the present allyl couplings.

Judging from the large bond energy between aluminum and oxygen, the aluminum reagent coordinates strongly to the functional group and activates oxygen-containing substrates in particular [14]. As a result, cleavage of the carbon–oxygen bond proceeds to a large extent, producing the corresponding allyl cationic species. For example, the allyl ethers IIIa and IIIb, activated by bis(diethylaluminum) sulfate revealed similar regiochemical outcomes (entries 1 and 2 in Table 2). Moreover, it is important to note that two regioisomeric allyl acetates, IIIl and IIIm, promoted by bis(diethylaluminum) sulfate afforded a mixture of two regioisomers (IVj and Vj) in approximately equal ratios (entries 12 and 14 in Table 2). Apparently the positive charge develops to a considerable extent by the activation of allylic acetates and ethers with the aluminum compound, and consequently, steric and electronic effects of the substituent on the α or γ site of the allyl acetates decide the proportions of regioisomers IV and V. Thus for geranyl acetate (IIIj), in which the allylic cation delocalized over the primary (α site) or tertiary (γ site) carbon center, substitution took place mainly at the α site of the allylic part to give a regioisomer (IVi) predominantly (entry 7).

The interaction of the aluminum reagent with a chlorine atom is very weak [14e] so that the allylic chloride activated by bis(diethylaluminum) sulfate cannot produce a free allylic carbocation, hence the α site of the allylic group is sterically more crowded due to the complexation of the aluminum reagent that aggregates highly in hydrocarbon solvent [14a]. As a result, the reaction of geranyl chloride (IIIi) proceeds mostly via an S_N2' pathway to give a regioisomeric mixture of IVi and Vi in a ratio of 18/82 (entry 6).

On the other hand, the activation of allylic acetates with boron trifluoride etherate is not so strong, but the steric hindrance at the α site due to the complexation of the Lewis acid with the ester carbonyl group is not increasing so much in these cases. Therefore the reaction occurred at the more electron-deficient carbon center and proceeded chiefly via an S_N2 pathway. Thus, IIIl gave a mixture of IVj and Vj in a ratio of 80/20 selectively, while from regioisomer IIIm, the formation of Vj predominated over IVj in a ratio of 88/12.

Experimental

Infrared spectra were taken on a Hitachi EPI-G2 spectrometer. NMR spectra were recorded on Varian T-60, EM-390 and HA-100 spectrometers. Mass spectra were taken on Hitachi RMU-60 and JEOL JMS-300D GC-MS spectrometers. Gas chromatographic analyses and collections were carried out on Hitachi Model 063 and 163 gas chromatographs equipped with a thermal conductivity detector.

Materials

Allylsilanes [15] and allylstannanes [16] were prepared from the corresponding allylic Grignard reagents and trimethylchlorosilane or trimethylchlorostannane [17], respectively, by the similar procedures to those cited in the literature. 2-Propenyltrimethylsilane (Ia): b.p. 83°C, n_D^{17} 1.4096 (ref. 15a b.p. 84.9°C (737 Torr), n_D^{20} 1.4074, 3-methyl-2-butenyltrimethylsilane (Ib): b.p. 58°C (60 Torr), n_D^{17} 1.4302 (ref. 18 b.p. 132°C (739 Torr), n_D^{20} 1.4290). 2-Propenyltrimethylstannane (IIa): b.p. 128°C (ref. 19 b.p. 128°C). 3-Methyl-2-butenyltrimethylstannane (IIb): b.p. 69°C (35 Torr). Allylic ethers were obtained according to Williamson's ether synthesis [20]. Silyl ethers, allylic halides and allylic acetates were prepared by essentially the similar methods as those in the literature. 3-Methoxy-1-heptene (IIIa): b.p. 61°C (70 Torr), n_D^{20} 1.4314. 3-Trimethylsiloxy-1-heptene (IIIb) [21]: b.p. 59°C (18 Torr), n_D^{20} 1.4174. 4-Methoxy-2-octene (IIIc): b.p. 51°C (24 Torr), n_D^{20} 1.4239. 1-Chloro-3-methyl-2-butene (IIId): b.p. 50°C (94 Torr), n_D^{20} 1.4524 (ref. 22 b.p. 52°C (100 Torr), n_D^{20} 1.4450). 1-Bromo-3-methyl-2-butene (IIIe): b.p. 52°C (64 Torr), n_D^{20} 1.4954 (ref. 23 b.p. 64°C (67 Torr)). 4-Chloro-2-pentene (IIIf): b.p. 44°C (120 Torr), n_D^{20} 1.4335 (ref. 24 b.p. 57°C (200 Torr), n_D^{20} 1.4328). 3-Bromocyclohexene (IIIg): b.p. 62°C (21 Torr), n_D^{20} 1.5343 (ref. 25 b.p. 80°C (35 Torr)). 3-Acetoxy-1-phenylpropene (IIIf): b.p. 125°C (2 Torr) (ref. 26 b.p. 114°C (1 Torr)). 1-Chloro-3,7-dimethylocta-2,6-diene (IIIi) [27]: b.p. 94°C (16 Torr). 3-Acetoxy-2-heptene (IIIk) [28]: b.p. 82°C (13 Torr). 3-Acetoxy-3-phenylpropene (IIIm): b.p. 105°C (19 Torr) (ref. 29 b.p. 133–136°C (17 Torr)). Benzyl iodide (VIc) [30]: b.p. 101°C (15 Torr), n_D^{20} 1.6541. Benzyl methyl ether (VId): b.p. 58°C (17 Torr), n_D^{20} 1.5030 (ref. 31 b.p. 170°C, n_D^{20} 1.5032).

Bis(diethylaluminum) sulfate was prepared from diethylaluminum chloride and anhydrous sodium sulfate in hexane/benzene (1/1) by the previously reported method [14]. All other materials used are commercially available and were purified by distillation before use.

Allyl coupling reactions of allylsilanes (I) or allylstannanes (II) with allylic substrates (III) promoted by a Lewis acid

General procedure. In a 20-ml two-necked flask equipped with a Dimroth condenser with a drying tube and a dropping funnel, titanium chloride (2 mmol) and 2 ml of dry dichloromethane were placed under nitrogen. To this, a mixture of an allylsilane (2 mmol) and an allylic substrate (2 mmol) in dichloromethane (2 ml) was added at −78°C and the resulting mixture was stirred for 3 h at −78°C. After hydrolysis, ether extraction and drying, the ethereal solution was concentrated, and then the 1,5-dienes (IV + V) were isolated by silica gel column or thin-layer chromatography. Each isomer of the 1,5-dienes was separated by preparative GLC. When bis(diethylaluminum) sulfate (1 mmol) was used as the promotor, the reaction involving an allylstannane was carried out in a 1 mmol-scale experiment in benzene/hexane (1/1) (4 ml) at reflux for 16 h. For boron trifluoride etherate, dichloromethane was used as the solvent. The physical properties and spectroscopic data of the 1,5-dienes are given below.

3-Butyl-1,5-hexadiene (IVa). An oil; n_D^{22} 1.4267; MS (m/e 138 (0.4%, M^+), 55 (100%); NMR δ (CCl_4) 0.83 (m, 3H, CH_3C), 1.20 (m, 6H, CH_2), 1.97 (m, 3H, $=CCH_2CHC=$), 4.82 (m, 4H, $CH_2=$), 5.43 (m, 2H, CH=); IR (neat) (cm^{-1}) 3075m, 2955s, 2925s, 2860m, 1640m, 1484w, 996w, 912m. Anal. Found: C, 86.61; H, 13.36. $C_{10}H_{18}$ calcd.: C, 86.88; H, 13.12%.

1,5-Decadiene (Va). An oil; n_D^{17} 1.4374; MS (m/e) 138 (3%, M^+), 55 (100%); NMR δ (CCl_4) 0.86 (m, 3H, CH_3C), 1.26 (m, 4H, CH_2), 1.92 (m, 2H, $CH_2C=$), 2.03 (m, 4H, $CH_2C=$), 4.87 (m, 2H, $CH_2=$), 5.30 (m, 2H, $CH{=}CH$), 5.50 (m, 1H, $CH=$); IR (neat) (cm^{-1}) 3075w, 2955s, 2920s, 2850m, 1640m, 1449w, 993w, 970m, 918s. Anal. Found: C, 86.74; H, 13.09. $C_{10}H_{18}$ calcd.: C, 86.88; H, 13.12%.

4-Butyl-1,5-heptadiene [32] (IVb). An oil; n_D^{22} 1.4377; NMR δ (CCl_4) 0.83 (m, 3H, CH_3C), 1.19 (m, 6H, CH_2), 1.61 (d, J 5 Hz, 3H, $CH_3C=$), 1.95 (m, 3H, $=CCH_2CHC=$), 4.85 (m, 2H, CH_2), 5.18 (m, 2H, CH=CH), 5.58 (m, 1H, CH=); IR (neat) (cm^{-1}) 3070w, 2950s, 2900m, 1637w, 1434w, 1375w, 993w, 968m, 909m. Anal. Found: C, 86.46; H, 13.54. $C_{11}H_{20}$ calcd.: C, 86.76; H, 13.24%.

4-Methyl-1,5-decadiene (Vb). An oil; n_D^{22} 1.4352; NMR δ (CCl_4) 0.85 (m, 3H, CH_3C), 0.90 (d, J 6.5 Hz, 3H, CH_3C), 1.25 (m, 4H, CH_2), 1.92 (m, 5H, $CHC=$), 4.85 (m, 2H, CH_2), 5.24 (m, 2H, $CH{=}CH$), 5.54 (m, 1H, $CH=$); IR (neat) (cm^{-1}) 3080w, 2960s, 2925s, 2870m, 1641w, 1457w, 1379w, 996w, 972m, 916m. Anal. Found: C, 86.73; H, 13.33. $C_{11}H_{20}$ calcd.: C, 86.76; H, 13.24%.

6-Methyl-1,5-heptadiene (IVc). An oil; n_D^{22} 1.4322 (ref. 6 n_D^{20} 1.4316); NMR δ (CCl_4) 1.62 (m, 3H, $CH_3C=$), 1.70 (m, 3H, $CH_3C=$), 2.07 (m, 4H, $CH_2C=$), 4.85 (m, 3H, $CH=$), 5.72 (m, 1H, $CH=$); IR (neat) (cm^{-1}) (3070m, 2940s, 2915s, 1855s, 1634m, 1439m, 1375m, 1111w, 990w, 910m, 836w. Anal. Found: C, 87.10; H, 12.80. C_8H_{14} calcd.: C, 87.19; H, 12.81%.

4-Methyl-1,5-heptadiene (IVd). An oil; n_D^{16} 1.4257 (ref. 6 n_D^{20} 1.4231); NMR δ (CCl_4) 0.93 (d, J 6.5 Hz, 3H, CH_3C), 1.61 (d, J 5 Hz, 3H, $CH_3C=$), 1.98 (m, 3H, CH=), 4.89 (m, 2H, CH_2), 5.25 (m, 2H, $CH{=}CH$), 5.57 (m, 1H, $CH=$); IR (neat

(cm^{-1}) 3070m, 2960s, 2920s, 1636w, 1445w, 1434w, 1372w, 990w, 964m, 909m. Anal. Found: C, 87.37; H, 13.08. C_8H_{14} calcd.: C, 87.19; H, 12.81%.

3-Allylcyclohexene (IVe). An oil; n_{D}^{21} 1.4657; NMR δ (CCl_4) 1.2–1.8 (m, 4H, CH_2), 1.85–2.2 (m, 5H, $CH_2C=$), 4.97 (m, 2H, $CH_2=$), 5.57 (m, 3H, $CH=$); IR (neat) (cm^{-1}) 3070w, 3010m, 2915s, 2930m, 1633w, 1431w, 990w, 908m, 720w, 687w. Anal. Found: C, 88.25; H, 11.51. C_9H_{14} calcd.: C, 88.45; H, 11.55%.

3,3-Dimethyl-3-butyl-1,5-hexadiene (IVf). An oil; NMR δ (CCl_4) 0.87 (m, 3H, CH_3C), 0.91 (s, 6H, CH_3C), 1.0–1.6 (m, 6H, CH_2), 1.87 (m, 1H, CH), 4.83 (m, 4H, $CH_2=$), 5.41 (dd, J 17 Hz, J 8.5 Hz, 1H, $CH=$), 5.52 (m, 1H, $CH=$); IR (neat) (cm^{-1}) 3080m, 2965s, 2935s, 2870m, 1641m, 1469w, 1418w, 1385w, 1371w, 1007m, 918s.

3,3-Dimethyl-1,5-decadiene (Vf). An oil: n_{D}^{20} 1.4398; NMR δ (CCl_4) 0.83 (m, 3H, CH_3C), 0.89 (s, 6H, CH_3C), 1.26 (m, 4H, CH_2), 1.88 (m, 4H, $CH_2C=$), 4.77 (dd, J 10, J 1.8 Hz, 1H, $CH=$), 4.77 (dd, J 18, J 1.8 Hz, 1H, $CH=$), 5.25 (m, 2H, $CH=CH$), 5.69 (dd, J 18, J 10 Hz, 1H, $CH=$); IR (neat) (cm^{-1}) 3080w, 2960s, 2925s, 2875s, 1640w, 1467w, 1413w, 1380w, 1375w, 1003w, 973m, 913m. Anal. Found: C, 86.59; H, 13.52. $C_{12}H_{22}$ calcd.: C, 86.67; H, 13.33%.

3,3,6-Trimethyl-1,5-heptadiene (IVg). An oil; n_{D}^{22} 1.4387 (ref. 6 n_{D}^{20} 1.4391); NMR δ (CCl_4) 0.92 (s, 6H, CH_3C), 1.54 (m, 3H, $CH_3C=$), 1.62 (m, 3H, $CH_3C=$), 1.92 (m, 2H, $CH_2C=$), 4.86 (m, 3H, $CH=$), 5.63 (m, 1H, $CH=$); IR (neat) (cm^{-1}) 3080w, 2965s, 2920s, 2975w, 1635w, 1450w, 1411w, 1373w, 1009w, 912w. Anal. Found: C, 86.94; H, 12.98. $C_{10}H_{18}$ calcd.: C, 86.88; H, 13.12%.

3,3,4-Trimethyl-1,5-heptadiene (IVh). An oil; n_{D}^{18} 1.4441; NMR δ (CCl_4) 0.95 (d, J 6.5 Hz, 3H, CH_3C), 1.00 (s, 6H, CH_3C), 1.73 (d, J 4.8 Hz, 3H, $CH_3C=$), 1.98 (m, 1H, $CHC=$), 4.91 (dd, J 18.5, J 1.8 Hz, 1H, $CH=$), 4.94 (dd, J 9, J 1.8 Hz, 1H, $CH=$), 5.38 (m, 2H, $CH=CH$), 5.81 (dd, J 18.5, J 9 Hz, 1H, $CH=$); IR (neat) (cm^{-1}) 3080m, 2970s, 2930s, 2875s, 1637w, 1458m, 1412m, 1373m, 1005w, 970m, 911m. Anal. Found: C, 86.59; H, 12.91. $C_{10}H_{18}$ calcd.: C, 86.88; H, 13.12%.

6,10-Dimethyl-1,5,9-undecatriene (IVi). An oil; NMR δ (CCl_4) 1.62 (s, 6H, $=C(CH_3)_2$), 1.70 (m, 3H, $=CCH_3$), 2.07 (m, 8H, CH_2), 5.05 (m, 2H, CH_2), 5.60 (m, 3H, CH). Anal. Found: C, 87.07; H, 12.24. $C_{13}H_{22}$ calcd.: C, 87.64; H, 12.36%.

4,8-Dimethyl-4-vinyl-1,7-nonadiene (Vi). An oil: NMR δ (CCl_4) 0.90 (s, 3H, CCH_3), 1.60 (s, 6H, $=C(CH_3)_2$), 2.03 (m, 6H, CH_2), 4.90 (m, 4H, CH_2), 5.67 (m, 3H, CH). Anal. Found: C, 88.02; H, 12.41. $C_{13}H_{22}$ calcd.: C, 87.64; H, 12.36%.

3,3-Dimethyl-6-phenyl-1,5-hexadiene (IVj). An oil; MS (m/e) 186 (89%, M^+), 118 (100%), 116 (64%), 91 (46%), 41 (77%); NMR δ (CCl_4) 1.05 (s, 6H, CH_3), 2.18 (d, J 5.6 Hz, 2H, CH_2), 5.05 (m, 2H, $=CH_2$), 5.60–6.50 (m, 3H, $=CH$), 7.18 (s, 5H, Ph); IR (neat) (cm^{-1}) 3070w, 3010s, 2940s, 1640m, 1598m, 1440m, 1368m, 1350m, 945m, 890s. Anal. Found: C, 90.33; H, 9.91. $C_{14}H_{18}$ calcd.: C, 90.26; H, 9.74%.

3,3-Dimethyl-4-phenyl-1,5-hexadiene (Vj). An oil; MS (m/e) 186 (4%, M^+), 118 (100%), 116 (53%), 91 (29%), 69 (57%), 41 (63%); NMR δ (CCl_4) 0.94 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 3.03 (d, J 9.4 Hz, 1H, CH), 4.82–5.33 (m, 4H, CH_2), 5.60–6.50 (m, 2H, $=CH$), 7.18 (s, 5H, Ph); IR (neat) (cm^{-1}) 1640 (ν(C=C)), 920 (δ(C=C)). Anal. Found: C, 89.80; H, 9.44. $C_{14}H_{18}$ calcd.: C, 90.26; H, 9.74%.

4-Phenyl-1-butene (VII). An oil; n_{D}^{20} 1.5069 (ref. 33 n_{D}^{20} 1.5090); NMR δ (CCl_4) 2.17–2.80 (m, 4H, CH_2), 4.91 (m, 2H, $CH_2=$), 5.62 (m, 1H, $CH=$), 7.07 (m, 5H, C_6H_5); IR (neat) (cm^{-1}) 3060m, 3080m, 3025m, 2945s, 2855m, 1639m, 1602w, 1492m, 1450m, 1248w, 1030w, 994m, 910s, 836m, 745m, 728m, 698s.

2-Methyl-6-chloro-3-heptene (VIII). An oil; MS (m/e) 146 (2.2%, M^+), 95 (100%); NMR δ (CCl_4) 1.00 (d, J 5Hz, 6H, CH_3C), 1.23–2.32 (m, 6H, CH_2), 3.96 (m, 1H, $CHCl$), 5.33 (m, 2H, $CH{=}CH$); IR (neat) (cm^{-1}) 2955s, 2865s, 1640w, 1460s, 1368m, 1239m, 976w, 840s, 745s.

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