Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 9111–9116

TETRAHEDRON

Acetyl chloride–ethanol brings about a remarkably efficient conversion of allyl acetates into allyl chlorides

Veejendra K. Yadav* and K. Ganesh Babu

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

Received 11 July 2003; revised 29 August 2003; accepted 18 September 2003

Abstract—AcCl–EtOH transforms primary and secondary allyl acetates into allyl chlorides that retain the olefinic bond in the more stable position. Whereas secondary allyl alcohols also react with almost the same efficacy as the acetates, the reactions of primary allyl alcohols that possess 1,2-disubstituted alkenes are very slow. The products are isolated in high state of purity simply by removal of the volatiles.

1. Introduction

The transformation of an allyl alcohol into its chloride can be achieved in several ways. The classical method involving the reaction with $SOCl_2$ generates the rearranged chloride exclusively from both primary and secondary alcohols.[1] MsCl–LiCl,[2] Ph_3P–CCl_4,[3] $ZnCl_2$–diethylazodicarboxylate–Ph_3P,[4] *N*-halosucciniimide–Me_2S,[5] TsCl–DMAP,[6] and tetramethyl-α-haloenamines[7] achieve the transformation of primary alcohols containing trisubstituted olefins into the corresponding primary chlorides. TMSCl–SeO_2[8] and $BiCl_3$[9] are nonspecific reagents that yield both the unrearranged and the rearranged chlorides. Several of these reagents are expensive, not readily available, toxic and unfriendly to the environment. Furthermore, they require aqueous workup and chromatographic purification of the product. Thus, there is scope for methods that avoid several or all of the above difficulties.

We report herein a simple, inexpensive, rapid and high yielding protocol for the conversion of allyl acetates (and allyl alcohols) into allyl chlorides bearing the π-bond in the more stable position using reagents as simple as AcCl and EtOH. To our best information, no method for the direct transformation of allyl acetates into allyl chlorides has hitherto been reported in the literature. The products are isolated in high yields simply by removing the volatiles. The requisite acetates were prepared very conveniently by following a known protocol.[10]

2. The reaction of allyl acetates with AcCl–EtOH

An allyl acetate (1 mmol) and EtOH (8 mmol) were mixed with AcCl (8 mmol) at 23°C. The contents were stirred magnetically until the reaction was complete by TLC. The volatiles were removed on a rotovap under water aspirator pressure to obtain the product. Using this simple protocol, several allyl acetates were transformed into allyl chlorides in excellent yields. The results are collected in Table 1.

The cinnamyl acetate was converted into cinnamyl chloride in 30 min (entry 1). A reaction on 10 mmol scale proceeded just as well. 2-Acetoxymethyl-2-cyclohexen-1-one gave 2-chloromethyl-2-cyclohexen-1-one exclusively in 5 min (entry 2). Geranyl acetate gave (*E*)-1,7-dichloro-3,7-dimethyl-2-octene predominantly (entry 3). Likewise, neryl acetate gave (*Z*)-1,7-dichloro-3,7-dimethyl-2-octene predominantly (entry 4). The geometry of the 2,3-double bond in both the geranyl acetate and the neryl acetate was retained. Obviously, trisubstituted alkenes also reacted under the conditions and added the elements of HCl in Markovnikov fashion.

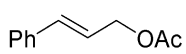
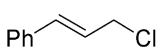
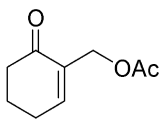
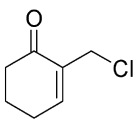
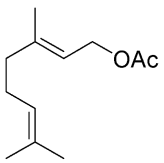
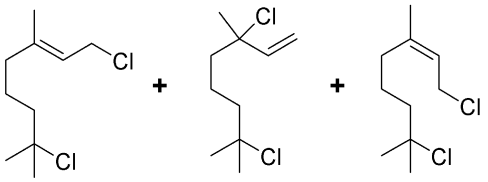
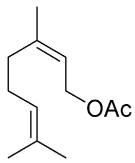
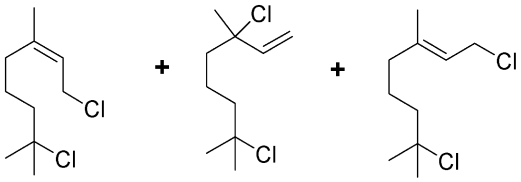
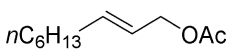
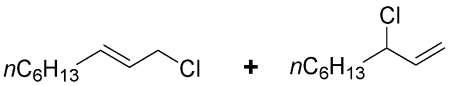
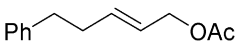
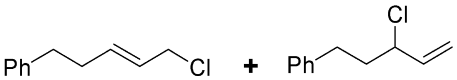
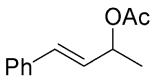
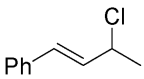
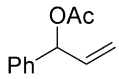
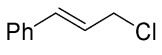
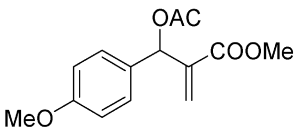
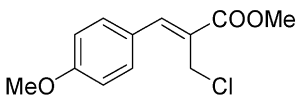
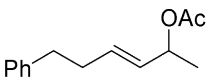
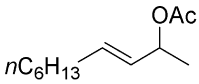
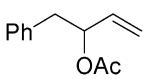
(*E*)-2-Nonen-1-ol acetate gave a 6.7:1 mixture of (*E*)-1-chloro-2-nonene and 3-chloro-1-nonene (entry 5). The reaction was complete in 150 min. (*E*)-5-Phenyl-2-penten-1-ol acetate gave a 6.3:1 mixture of (*E*)-5-phenyl-1-chloro-2-pentene and 5-phenyl-3-chloro-1-pentene (entry 6). This constitutes an efficient preparation of primary allyl chlorides from the corresponding primary allyl acetates. The experimental simplicity and the ease of product isolation easily offset the difficulty arising from the small amount of the rearranged chloride that is also formed.

The secondary allyl acetates also reacted very well. (*E*)-4-Phenyl-3-buten-2-ol acetate gave (*E*)-2-chloro-4-phenyl-3-butene exclusively (entry 7). 1-Phenyl-2-propene-1-ol

Keywords: allyl acetate; allyl alcohol; allyl chloride.
* Corresponding author. Tel.: +91-512-2597439; fax: +91-512-2597436; e-mail: vijendra@iitk.ac.in

0040–4020/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.tet.2003.09.063

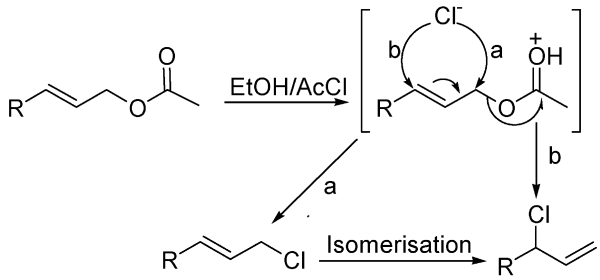
Table 1. Conversion of allyl acetates/alcohols into allyl chlorides.[a] The values given in the parentheses are for the reactions of the corresponding allyl alcohols

Entry	Substrate	Time (min)	Product(s)	Yield (%)
1		30 (30)		96 (91)
2		5		96
3		15 (15)	 (a) (b) (c)	95 (93)[b,c]
4		15 (15)	 (a) (b) (c)	93 (94)[b,d]
5		150 (1440)		94 (−)[b,e]
6		150 (1440)		95 (−)[b,f]
7		30 (30)		95 (93)[g]
8		10 (15)		91 (91)
9		5		96
10		45 (45)		94 (92)[b,h]
11		30 (30)		92 (94)[b,h]
12		45 (60)		89 (89)[b,i]

[a] The ratio acetate/AcCl/EtOH was 1:8:8.
[b] The ratios were calculated from the relative ^{1}H NMR integrals.
[c] a/b/c=13.6:5.0:1 (9.4:2.1:1).
[d] a/b/c=6.1:1.6:1 (5.4:1.2:1).
[e] The ratio of the normal and the rearranged chlorides was 6.7:1. ^{1}H NMR of the chlorides was identical with reported data.[11]
[f] The ratio of the normal and the rearranged chloride was 6.3:1.
[g] The ^{1}H NMR of the chloride was identical with reported data.[12]
[h] 1:1 Mixture of chlorides was formed.
[i] The ratio of the rearranged and normal chloride was 2.3:1 (2.1:1).

acetate (entry 8) and methyl 3-acetoxy-3-(4-methoxyphenyl)-2-methylidenepropionate (entry 9) gave the rearranged chlorides exclusively. The (*E*)-geometry of the π-bond in methyl 3-(4-methoxyphenyl)-2-chloromethylacrylate (entry 9) was determined from nOe studies. The irradiation of CH_2Cl resulted in enhancement of the absorption for two aromatic protons.

The acetates of 6-phenyl-3-hexene-2-ol (entry 10) and 3-decen-2-ol (entry 11) delivered 1:1 mixtures of the isomeric chlorides. ^{1}H NMR analysis of aliquots of the reaction of 3-decen-2-ol acetate that were withdrawn at intervals of 5 min from the commencement of the reaction and quenched immediately with water showed the presence of the corresponding isomeric alcohols in 1:1 ratio, though in very small amounts, along with a 1:1 mixture of the above isomeric chlorides. A similar result was obtained from the reaction of 6-phenyl-3-hexen-2-ol acetate. The formation of only small amounts of the isomeric alcohols in comparison to the isomeric chlorides suggests an enormously efficient capture by the chloride ion of either the allyl cation formed from ionization of the protonated allyl acetate or the protonated allyl acetate itself through S_N2/S_N2' pathways as shown below. Although we have evidence for both, we prefer the latter to accommodate the successful reactions of the acetates of 2-nonen-1-ol and 5-phenyl-2-penten-1-ol (vide supra) and the failures of the corresponding alcohols (vide infra).



The equal distribution of the two isomeric chlorides suggests equal propensity of attack by chloride ion on either terminus of the allyl system. This is due probably to the secondary nature of both the termini and the energetically similar disubstituted nature of the π-bond in both the isomers. The reaction of 1-phenyl-3-butene-2-ol acetate gave a mixture of the rearranged and the normal chlorides in the ratio 2.3:1 (entry 12). The larger amount of the rearranged chloride than that of the normal chloride is likely to be a consequence of both the (a) faster S_N2 attack on a primary center than that at a secondary center and (b) higher π-bond stability for its higher substitution.

^{1}H NMR analysis of aliquots, withdrawn at 30 min intervals, of the reaction of (*E*)-2-nonen-1-ol acetate was undertaken to explore the origin of the rearranged chloride. The results are collected in Table 2. The secondary chloride is obviously a product of isomerization of the primary chloride as the concentration of the secondary chloride increased with the increase in reaction duration. The primary chloride itself is a product of bimolecular displacement of the acetate function by chloride ion (vide infra).

Table 2. Reaction of 2-nonen-1-ol acetate with AcCl–EtOH. A case study of products distribution (primary vs secondary chlorides) against reaction time

Entry	Time (min)	Ratio (1°:2° chloride)[a]	% Conversion
1	030	>20:1	30
2	060	10:1	55
3	090	7.7:1	80
4	120	7.5:1	95
5	150	6.7:1	100

[a] The ratio was determined from the ^{1}H integrals of CH_2Cl (δ 4.04) and C*H*Cl (δ 4.36–4.31) absorptions.

3. The reaction of allyl alcohols with AcCl–EtOH

We have also studied the reactions of allyl alcohols with AcCl–EtOH to ascertain (a) whether indeed the chloride formation via the acetate route was necessary, and, if yes, (b) whether the acetate pathway was any better than the alcohol pathway. These results are also collected in Table 1. Several features deserve comment. The primary alcohols such as 2-nonen-1-ol (entry 5) and 5-phenyl-2-penten-1-ol (entry 6) that had 1,2-disubstituted olefins reacted extremely slow as only traces of chlorides were formed even after 24 h. There was no improvement in the reaction even when 16 equiv. of AcCl and EtOH each were used. In contrast, cinnamyl alcohol (entry 1), geraniol (entry 3) and nerol (entry 4) underwent smooth transformation to give cinnamyl chloride, (*E*)-1,7-dichloro-3,7-dimethyl-2-octene and (*Z*)-1,7-dichloro-3,7-dimethyl-2-octene, respectively, along with the rearranged chlorides in the last two instances in high yields.

Secondary alcohols were also conveniently transformed into isomeric chlorides. As above with the corresponding acetates, 4-phenyl-3-buten-2-ol (entry 7) reacted without rearrangement, 1-phenyl-2-propene-1-ol (entry 8) gave exclusively the rearranged chloride, and 1-phenyl-3-butene-2-ol (entry 12) gave a 2.1:1 mixture of chlorides wherein the rearranged isomer predominated. 6-Phenyl-3-hexen-2-ol (entry 10) and 3-decen-2-ol (entry 11) offered an almost 1:1 mixture of the isomeric chlorides.

The rapid reactions of cinnamyl alcohol, geraniol and nerol in comparison to those of 2-nonen-1-ol and 5-phenyl-2-penten-1-ol could be attributed to the higher stability and, hence, faster generation of carbocations in the former examples. The product-stability controlled the regioselectivity and, thus, predominantly the primary chlorides were formed from cinnamyl alcohol, geraniol and nerol. The generation of allyl cations from secondary allyl alcohols was also smooth and the reaction proceeded with much facility. These results with 2-nonen-1-ol and 5-phenyl-2-penten-1-ol are at variance from those obtained from the corresponding acetates that reacted rapidly and with high regioselectively.

A comparison of the data in Table 1 suggests that in so far as the transformation of substrates like 2-nonen-1-ol and 5-phenyl-2-penten-1-ol into the corresponding primary allyl chlorides is concerned, the reaction via the acetate is the sole choice. The results for the reactions of other primary and secondary allyl alcohols and acetates are almost similar.

The acetate route, however, offered cleaner products in somewhat improved yields.

4. Conclusion

We have presented a rapid, operationally simple, inexpensive, and high yield protocol for the transformation of allyl acetates into allyl chlorides using AcCl–EtOH combination as a source of in situ HCl. The primary allyl alcohols with simple 1,2-disubstituted π-bonds such as 2-nonen-1-ol and 5-phenyl-2-penten-1-ol do not react. In contrast, the corresponding acetates reacted smoothly with high regioselectivity to furnish the primary chloride almost exclusively.

5. Experimental

5.1. General

IR spectra were recorded on Bruker Vector 22 FTIR spectrophotometer in CH_2Cl_2 solution. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-LA400 in $CDCl_3$. The ^1H and ^{13}C positions are reported in δ value relative to TMS (internal standard) and the central line for $CDCl_3$, respectively. The solvents were removed under reduced pressure on a rotovap. The chromatographic separations, whenever required, were performed by silica gel (100–200 mesh) column chromatography using mixtures of EtOAc and hexanes. 2-Hydroxymethyl-2-cyclohexen-1-one,[13] 3-hydroxy-3-(4-methoxyphenyl)-2-methylidenepropionate,[14] 5-phenyl-3-penten-1-ol[15a] and 1-phenyl-3-buten-2-ol[15b] were prepared using literature protocols.

5.1.1. (*E*)-4-Phenyl-3-buten-2-ol. 4-Pheyl-3-buten-2-one (2 mmol, 292 mg) was dissolved in methanol (5 mL) and cooled to 0°C. $NaBH_4$ (76 mg, 2 mmol) was added to it in one portion under stirring. A vigorous gas evolution was noticed and the reaction mixture was allowed to stir for 15 min. MeOH was evaporated and the residue was taken in Et_2O and washed with saturated aqueous NH_4Cl, water, and brine, in that order. The residue left after solvent removal was filtered through a short silica gel column to afford the alcohol; 280 mg, 95% (colorless liquid).[16]

5.1.2. (*E*)-2-Nonene-1-ol. To a suspension of NaH (2.4 mmol, 58 mg) in THF (2 mL) was added triethyl phosphanoacetate (2.4 mmol, 0.48 mL) in THF (2 mL) at 0°C slowly with stirring. The mixture was allowed to stir for 30 min. Heptanal (2 mmol, 228 mg) in THF (4 mL) was added slowly at the same temperature and the reaction mixture was stirred overnight. It was diluted with Et_2O and washed with saturated aqueous NH_4Cl, water, and brine, in that order. Concentration and filtration of the residue through a short silica gel column afforded ethyl (*E*)-2-nonenate; 294 mg, 80% (colorless liquid).[17]

DIBAL-H (2 mmol) was added slowly to a solution of ethyl 2-noneate (1 mmol, 184 mg) in toluene (2 mL) at 0°C under stirring. The mixture was stirred at the same temperature for 1 h and then diluted with Et_2O. The ether solution was washed with 2% cold aqueous HCl, H_2O, and brine, in that order. Concentration and filtration through a short silica gel column gave the desired alcohol; 128 mg, 90% (colorless liquid).

5.1.3. (*E*)-6-Phenyl-3-hexen-2-ol. To a suspension of NaH (1.65 mmol, 40 mg) in THF (2 mL) was added diethyl (2-oxopropyl)phosphonate (1.65 mmol, 320 mg) in THF (4 mL) at 0°C slowly with stirring. The mixture was allowed to stir for 5 min. 3-Phenyl-1-propanal (1.5 mmol, 195 mg) in THF (4 mL) was added slowly and the reaction mixture was stirred overnight. It was diluted with Et_2O and washed with saturated aqueous NH_4Cl, water, and brine, in that order. Concentration and filtration of the residue through a short silica gel column afforded (*E*)-6-phenyl-3-hexen-2-one; 214 mg, 82% (colorless liquid).[18]

(*E*)-6-Pheyl-3-hexen-2-one (1.23 mmol, 214 mg) was dissolved in methanol (2.5 mL) and cooled to 0°C. $NaBH_4$ (1.23 mmol, 46 mg) was added to it in one portion under stirring. A vigorous gas evolution was noticed and the reaction mixture was allowed to stir for 15 min. MeOH was evaporated and the residue was taken in Et_2O, washed with saturated aqueous NH_4Cl, water, and brine, in that order. The residue left after solvent removal was filtered through a short silica gel column to afford (*E*)-6-phenyl-3-hexen-2-ol; 208 mg, 96% (colorless liquid).[19]

5.1.4. (*E*)-3-Decen-2-ol. To a suspension of NaH (2.4 mmol, 58 mg) in THF (3 mL) was added diethyl (2-oxopropyl)phosphonate (2.4 mmol, 464 mg) in THF (5 mL) at 0°C slowly with stirring. The mixture was allowed to stir for 5 min. Heptanal (2 mmol, 228 mg) in THF (5 mL) was added slowly and the reaction mixture was stirred overnight. It was diluted with Et_2O and washed with saturated aqueous NH_4Cl, water, and brine, in that order. Concentration and filtration of the residue through a short silica gel column afforded (*E*)-3-decen-2-one; 262 mg, 85% (colorless liquid).[20]

(*E*)-3-Decen-2-one (1.0 mmol, 154 mg) was dissolved in methanol (2.5 mL) and cooled to 0°C. $NaBH_4$ (1.0 mmol, 38 mg) was added to it in one portion under stirring. A vigorous gas evolution was noticed and the reaction mixture was allowed to stir for 15 min. MeOH was evaporated and the residue was taken in Et_2O and washed with saturated aqueous NH_4Cl, water, and brine, in that order. The residue left after solvent removal was filtered through a short silica gel column to afford (*E*)-3-decen-2-ol; 150 mg, 96% (colorless liquid).

5.1.5. Large scale reaction of cinnamyl acetate. AcCl (80 mmol, 5.7 mL) was added dropwise over 30 min to a stirred solution of cinnamyl acetate (10 mmol, 1.76 g) in EtOH (80 mmol, 4.7 mL) that was taken in a round bottom flask closed with a rubber septum. The stirring was continued at 30°C for 10 min. The volatiles were removed on a rotovap under reduced pressure to obtain the product, 1.46 g, 96%.

5.2. General procedure for the conversion of alcohols into chlorides

AcCl (8 mmol, 0.57 mL) was added dropwise to a solution

of alcohol (1 mmol) in EtOH (8 mmol, 0.47 mL). The reaction flask was stoppered tightly and the contents were stirred at 23°C. After the reaction was complete to TLC, the volatiles were removed on a rotovap under reduced pressure to obtain the product.

5.2.1. Methyl-3-acetoxy-3-(4-methoxyphenyl)2-methylidinepropionate (colorless liquid). ^{1}H NMR was in accordance to the reported data.[21]

5.2.2. 2-Acetoxymethyl-2-cyclohexen-1-one (colorless liquid). ^{1}H NMR was in accordance to the reported data.[22]

5.2.3. (*E*)-2-Acetoxy-6-phenyl-3-hexene (colorless liquid). ^{1}H NMR was in accordance to the reported data.[23]

5.2.4. (*E*)-2-Acetoxy-3-decene (colorless liquid). IR cm^{-1} 1738, 1667, 1460, 1374, 1243, 1025. ^{1}H NMR δ 5.73–5.66 (td, J=15.4, 6.8 Hz, 1H), 5.48–5.42 (qdd, J=15.4, 6.8, 1.0 Hz, 1H), 5.34–5.28 (quintet, J=6.8 Hz, 1H), 2.03 (s, 3H), 2.03–2.01 (m, 2H), 1.36–1.28 (m, 8H), 1.29 (d, J=6.8 Hz, 3H), 0.88 (t, J=6.7 Hz, 3H). ^{13}C NMR δ 170.3, 133.4, 129.3, 71.2, 32.1, 31.6, 28.9, 28.8, 22.5, 21.4, 20.3, 14.0. Anal. calcd for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19. Found: C, 72.50; H, 10.94.

5.2.5. Mixture of (*E*)-1,7-dichloro-3,7-dimethyl-2-octene,[24] (*Z*)-1,7-dichloro-3,7-dimethyl-2-octene and 3,7-dichloro-3,7-dimethyl-1-octene (colorless liquid). IR cm^{-1} 1661, 1452, 1372, 1255, 1117, 741, 672, 566.

Characteristic ^{1}H signals for (Z)-1,7-dichloro-3,7-dimethyl-2-octene. ^{1}H NMR δ 4.08 (d, J=8.3 Hz, 2H), 2.15 (t, J=7.3 Hz, 2H).

Characteristic ^{1}H signals for 3,7-dichloro-3,7-dimethyl-1-octene (liquid). ^{1}H NMR δ 6.03–5.96 (dd, J=17.1, 10.7 Hz, 1H), 5.27 (d, J=17.1 Hz, 1H), 5.12 (d, J=10.7 Hz, 1H). Anal. calcd for $C_{10}H_{18}Cl_2$: C, 57.67; H, 8.72. Found: C, 57.54; H, 8.60.

5.2.6. (*E*)-Methyl-3-(4-methoxyphenyl)-2-chloromethylacrylate (colorless liquid). IR cm^{-1} 1708, 1602, 1512, 1439, 1308, 1259, 1217, 1177, 1091, 1030, 836. ^{1}H NMR δ 7.83 (s, 1H), 7.56 (d, J=8.5 Hz, 2H), 6.98 (d, J=8.5 Hz, 2H), 4.52 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H). ^{13}C NMR δ 167.0, 160.9, 143.7, 131.8, 126.6, 125.8, 114.4, 55.3, 52.3, 39.6. Anal. calcd for $C_{12}H_{13}ClO_3$: C, 59.99, H, 5.46. Found: C, 59.80; H, 5.30.

5.2.7. 2-Chloromethyl-2-cyclohexen-1-one (colorless liquid). IR cm^{-1} 1670, 1265, 742. ^{1}H NMR δ 7.15 (t, J=4.0 Hz, 1H), 4.22 (s, 2H), 2.50–2.44 (m, 4H), 2.07–2.00 (m, 2H). ^{13}C NMR δ 197.4, 149.3, 136.0, 40.9, 38.1, 26.0, 22.6. Anal. calcd for C_7H_9ClO: C, 58.32; H, 6.30. Found: C, 58.20; H, 6.15.

5.2.8. Mixture of (*E*)-5-phenyl-1-chloro-2-pentene and 5-phenyl-3-chloro-1-pentene (6.3:1) (colorless liquid). IR cm^{-1} 1666, 1603, 1495, 1453, 1251, 967, 748, 699.

Characteristic ^{1}H signals for (E)-5-phenyl-1-chloro-2-pentene (major isomer). δ 5.84–5.77 (td, J=15.1, 6.6 Hz, 1H), 5.68–5.61 (qtd, J=15.1, 7.1, 0.7 Hz, 1H), 4.02 (d, J=7.1 Hz, 2H), 2.38 (q, J=7.6 Hz, 2H).

Characteristic ^{1}H signals for 5-phenyl-3-chloro-1-pentene (minor isomer). δ 5.96–5.87 (m, 1H), 5.28–5.24 (qd, J=17.0, 0.8 Hz, 1H), 5.17–5.14 (dd, J=10.1, 0.8 Hz, 1H), 4.34–4.29 (dt, J=7.4, 7.1 Hz, 1H), 2.17–2.08 (m, 2H). ^{13}C NMR (mixture) δ 141.4, 135.0, 128.50, 128.48, 128.4, 128.3, 126.5, 126.1, 125.9, 116.8, 62.2, 45.3, 39.7, 35.2, 33.8, 32.5. Anal. calcd for $C_{11}H_{13}Cl$: C, 73.13; H, 7.25. Found: C, 73.00; H, 7.15.

5.2.9. Mixture of (*E*)-6-phenyl-2-chloro-3-hexene and (*E*)-6-phenyl-4-chloro-2-hexene (1:1) (colorless liquid). IR cm^{-1} 1453, 1374, 1244, 1046, 1028, 740, 700.

Characteristic ^{1}H signals for (E)-6-phenyl-2-chloro-3-hexene. δ 4.55–4.48 (quintet, J=7.0 Hz, 1H), 2.38–2.33 (m, 2H), 1.56 (d, J=6.6 Hz, 3H).

Characteristic ^{1}H signals for (E)-6-phenyl-4-chloro-2-hexene. δ 4.34–4.29 (dt, J=8.2, 6.2 Hz, 1H), 2.18–2.02 (m, 2H), 1.73–1.71 (dd, J=6.3, 1.5 Hz, 3H). ^{13}C NMR (mixture) 141.4, 140.9, 132.8, 131.9, 131.4, 128.7, 128.5, 128.44, 128.43, 128.3, 126.0, 125.9, 62.7, 58.3, 40.2, 35.3, 33.6, 32.7, 25.4, 17.5. Anal. calcd for $C_{12}H_{15}Cl$: C, 74.03; H, 7.77. Found: C, 73.82; H, 7.62.

5.2.10. Mixture of (*E*)-2-chloro-3-decene and (*E*)-4-chloro-2-decene (1:1) (colorless liquid). ^{1}H NMR was in accordance to the reported data.[12]

5.2.11. Mixture of (*E*)-1-chloro-4-phenyl-2-butene and 2-chloro-1-phenyl-3-butene (2.3:1) (colorless liquid). IR cm^{-1} 1665, 1603, 1495, 1452, 1251, 966, 748, 699.

Characteristic ^{1}H signals for (E)-1-chloro-4-phenyl-2-butene. δ 5.72–5.64 (td, J=15.1, 7.1 Hz, 1H), 4.06 (d, J=7.1 Hz, 2H), 3.40 (d, J=6.8 Hz, 2H).

Characteristic ^{1}H signals for 2-chloro-1-phenyl-3-butene. δ 5.23–5.19 (dd, J=16.8, 0.7 Hz, 1H), 5.14–5.11 (dd, J=10.3, 0.7 Hz, 1H), 4.58–4.52 (q, J=7.4 Hz, 1H), 3.13–3.11 (dd, J=7.1, 2.2 Hz, 2H). Anal. calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65. Found: C, 72.18; H, 6.61.

Acknowledgements

Authors thank Council of Scientific and Industrial Research, Govt. of India, for support of this research. KGB thanks CSIR for Senior Research Fellowship.

References

1. Caserio, F. F.; Denis, G. E.; DeWolfe, R. H.; Young, W. G. *J. Am. Chem. Soc.* **1955**, *77*, 4182.
2. Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044.
3. Snyder, E. I. *J. Org. Chem.* **1972**, *37*, 1466.
4. Ho, P.-T.; Davies, N. *J. Org. Chem.* **1984**, *49*, 3027.

5. Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, *42*, 4339.
6. Chen, K.-M.; Joullie, M. M. *Tetrahedron Lett.* **1984**, *25*, 393.
7. Munyemana, F.; Frisque-Hesbain, A.-M.; Devos, A.; Ghosez, L. *Tetrahedron Lett.* **1989**, *30*, 3077.
8. Lee, J. G.; Kang, K. K. *J. Org. Chem.* **1988**, *53*, 3634.
9. Keramane, E. M.; Boyer, B.; Roque, J.-P. *Tetrahedron* **2001**, *57*, 1909.
10. Yadav, V. K.; Ganesh Babu, K.; Mittal, M. *Tetrahedron* **2001**, *57*, 7047.
11. (a) Sakurai, A.; Hayashi, T.; Hori, I.; Jindo, Y.; Oishi, T. *Synthesis* **1978**, 370. (b) Boughdady, N. M.; Chynoweth, K. R.; Hewitt, D. G. *Aust. J. Chem.* **1987**, *40*, 767.
12. Izawa, K.; Okuyama, T.; Sakagami, T.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6752.
13. Rezgui, F.; EI Gaied, M. M. *Tetrahedron Lett.* **1998**, *39*, 5965.
14. Basaviah, D.; Dharma Rao, P.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001.
15. (a) Hojo, M.; Sakuragi, R.; Okabe, S.; Hosomi, A. *Chem. Commun.* **2001**, *4*, 357. (b) Harada, T.; Akiba, E.; Oku, A. *J. Am. Chem. Soc.* **1983**, *105*, 2771. (c) Nanoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 316.
16. (a) Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454. (b) Ravikumar, K. S.; Baskaran, S.; Chandrasekaran, S. *J. Org. Chem.* **1993**, *58*, 5981. (c) Fuller, J. C.; Stangeland, E. L.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 257. (d) Nutaitis, C. F.; Bernardo, J. E. *J. Org. Chem.* **1989**, *54*, 5629.
17. Katzenellenbogen, J. A.; Utawanit, T. *J. Am. Chem. Soc.* **1974**, *96*, 6153.
18. (a) Fujii, M.; Nakamura, K.; Yasui, S.; Oka, S.; Ono, A. *Bull. Chem. Soc. Jpn* **1987**, *60*, 2423. (b) Takeuchi, R.; Kashio, M. *J. Am. Chem. Soc.* **1998**, *120*, 8647. (c) Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, *16*, 1007.
19. (a) Inomata, K.; Igarashi, S.; Mohri, M.; Yamamoto, T.; Kinoshita, H.; Kotake, H. *Chem. Lett.* **1987**, *4*, 707. (b) Larock, R. C.; Leung, W. Y. *J. Org. Chem.* **1990**, *55*, 6244.
20. Kourouli, T.; Kefalas, P.; Ragoussis, N.; Ragoussis, V. *J. Org. Chem.* **2002**, *67*, 4615.
21. (a) Shadakshari, U.; Nayak, S. K. *Tetrahedron* **2001**, *57*, 4599. (b) Mateus, C. R.; Almeida, W. P.; Coelho, F. *Tetrahedron Lett.* **2000**, *41*, 2533.
22. (a) Ishizaki, M.; Niimi, Y.; Hoshino, O. *Chem. Lett.* **2001**, 546. (b) Rezgui, F.; El Gaied, M. M. *Tetrahedron* **1997**, *53*, 15711.
23. Yamaguchi, J.; Tamada, Y.; Takeda, T. *Bull. Chem. Soc. Jpn* **1993**, *66*, 607.
24. Julia, M.; Roy, P. *Tetrahedron* **1986**, *42*, 4991.