

Proazaphosphatrane $P(RNCH_2CH_2)_3N$ ($R = Me, i\text{-Pr}$)-Catalyzed Isomerization of Allylaromatics, Allyl Phenyl Sulfide, Allyl Phenyl Sulfone, and *bis*-Allylmethylene Double Bond-Containing Compounds

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Abstract: Using a proazaphosphatrane catalyst, $P(RNCH_2CH_2)_3N$ ($R = Me, i\text{-Pr}$), allylaromatics and allyl phenyl sulfide were selectively isomerized to the corresponding vinyl isomers in yields up to > 99% in CH_3CN at 40 °C. Efficient transformation of allyl phenyl sulfone at ambient temperature afforded an isomerization/dimerization product in > 95% yield. Conjugation of *bis*-allylmethylene double bond-containing compounds gave the corresponding conjugated isomers for *cis,cis*-9,12-octadecadienol and its methyl ether in yields up to 97%, and desilyla-

tion/conjugation products were obtained from the catalytic reaction of the trimethylsilyl ether of *cis,cis*-9,12-octadecadienol. The reaction mechanism is discussed based upon the 1H and ^{31}P NMR-monitored reactions in CD_3CN or CH_3CN under the reaction conditions.

Keywords: allylic compounds; isomerization; methylene-interrupted diene compounds; proazaphosphatrane; $P(RNCH_2CH_2)_3N$

Introduction

Ever since Shimizu and Blum first reported the isomerization of allylbenzene using Natta-type catalyst^[1a] and platinum complex catalysts,^[1b] a wide array of complexes of transition metals, such as palladium,^[2] ruthenium,^[3] rhodium,^[4] nickel,^[5] cobalt,^[6] iron,^[7] titanium,^[7b,8] and zirconium^[8d,9] have been utilized for this purpose. Organolanthanide complexes Cp_3Y catalyzed the isomerization of allylbenzene to achieve a *trans/cis* ratio of 91/9 for the corresponding isomerized products.^[10] Isomerizations of *p*-allylanisole^[2b,3a,4c] and safrole^[6a,7b,8a,8c,11] were also realized with transition metal catalysts, respectively. 2,4-Dimethoxyallylbenzene was even isomerized on Pb/Al_2O_3 .^[12] Base-catalyzed isomerizations of allylaromatics have been reviewed.^[13] Potassium fluoride on alumina isomerized safrole in 76% yield,^[14] while KOH or *t*-BuOK isomerized safrole to form the corresponding *trans* product in 99% yield in

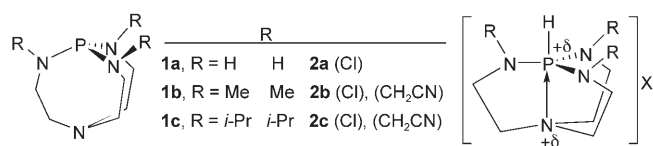
the absence of a solvent.^[15] In absolute ethanol, allylbenzenes were isomerized to the *trans* products with sodium ethoxide under refluxing conditions.^[16] Allylbenzene was isomerized with K_2CO_3 and a phase-transfer catalyst.^[17] Using polyethylene glycol as the phase-transfer catalyst KOH also isomerized *p*-allylanisole.^[18] Under phase-transfer conditions allylbenzene was also isomerized with aqueous NaOH in hydrocarbon solvents.^[19] Under microwave irradiation KOH in alcohols efficiently isomerized safrole and eugenol.^[20] The electrogenerated triphenylmethyl anion acted as a base to isomerize allylaromatics.^[21]

Isomerization of allyl sulfides has been reported with NaOH or NaOEt,^[22a, b] $Pd(PCy_3)_2$ ($PCy_3 =$ tricyclohexylphosphine),^[22c] or tris(2,4-pentanedionate)ruthenium.^[22d] Basic thermal isomerization of allyl aryl sulfides occurred in quinoline at 240 °C.^[23] Isomerization of allyl to vinyl sulfones catalyzed by various bases has received much attention from organic chemists.^[13,24] All-

yl phenyl sulfone was transformed into vinyl phenyl sulfone with NaOH in CH₂Cl₂ under phase transfer conditions.^[4c] Recently, the isomerization of allylic compounds and methylene-interrupted dienes was realized with the non-ionic phosphazene strong base P₂-Et.^[25] Conjugation of methylene-interrupted carbon-carbon double bonds has aroused much attention due to new potential applications of vegetable oils such as soybean oil and safflower oil, and polyunsaturated fatty acids and their derivatives.^[26] Transition metal complexes are known for this goal.^[27] Base-catalyzed conjugation of CH₂-interrupted carbon-carbon double bonds employed *t*-BuOK^[28] and alkali,^[29] respectively. Thionyl chloride^[30] and toluene-*p*-sulfonic acid^[31] were also reported as the catalysts for isomerization of fatty oils, methyl linoleate, and related esters. In the case of methyl linoleate, a *ca.* 80% isomerization yield was obtained *via* a radical-induced mechanism by iodine.^[32]

Using transition metal catalysts, dimerization, polymerization and hydrogenation were the side reactions in the above-mentioned isomerization or conjugation procedures. Under ionic basic conditions, geometrical selectivities for the conjugated dienes were higher than those using transition metal catalysts, but low yields of the corresponding products and loss of ester groups were quite common. Although these results have been achieved, more efficient procedures for isomerizing allylaromatic and fatty olefinic compounds are still being pursued.

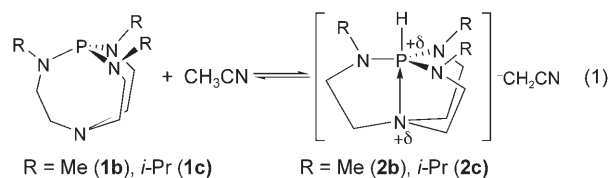
Synthetic applications of exceedingly strong non-ionic bases and catalysts of type **1** have been well documented since they were first reported from Verkade's laboratories.^[33–35] It has been demonstrated that the nucleophilicity and basicity of **1** stemming from transannular bond formation play important roles in the formation and stability of cationic intermediates of type **2** (Scheme 1). Both **1b** and **1c** are known strong non-ionic bases that can deprotonate acetonitrile,^[33d] benzylnitrile,^[33d] and other activated methylene groups,^[36] resulting in a variety of reactions initiated by anions such as ⁻CH₂CN generated by **1b** or **1c** from CH₃CN, etc. Our recent preliminary work demonstrated the catalytic dimerization of allyl phenyl sulfone by superbases of type **1**,^[37] which led us to investigate isomerization of allyl-containing or CH₂-interrupted carbon-carbon double bond-containing compounds by using **1b** and **1c** as the catalysts. Herein, we report the isomerization of allylaromatics, allyl phenyl sulfide, allyl phenyl sulfone, methylene-interrupted carbon-carbon double bond-containing *cis*-, *cis*-9,12-octadecadienol and its derivatives, in CH₃CN at 40 °C by using **1b** or **1c** as the catalyst. The highlights of the present work are: (a) Isomerization or conjugation proceeded under very mild conditions and the reactions were catalytic. (b) High yields and selectivities were achieved for the aimed products. (c) The reactions could be conveniently monitored by ¹H and ³¹P {¹H} NMR measurements.



Scheme 1.

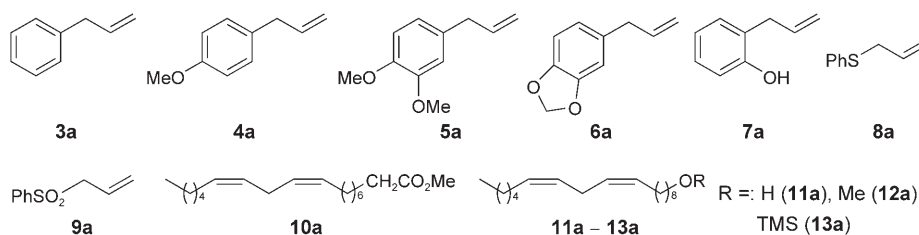
Results and Discussion

Proazaphosphatranes are powerful non-ionic bases forming remarkably stable azaphosphatranane cations **2a–c**. The conjugate acids, i.e., **2b** of superbase **1b**, and **2c** of superbase **1c** have been shown to have *pK_a* values of 32.90 and 33.63 in acetonitrile, respectively.^[35c] The equilibrium shown in Eq. (1) (Scheme 2) has been established in CH₃CN.^[35, 38]



Scheme 2.

Using the superbase catalysts **1b** or **1c** allylaromatics **3a–7a** (Scheme 2) were exclusively conjugated to vinylaromatics with the corresponding *trans*-isomers as the major products (Table 1), while *cis*-isomers are predominantly formed from isomerization of the same substrates by means of transition metal complexes or ionic bases. Substituent(s) on the phenyl group lessened the reaction rate. Predominant formation of *trans* vinyl products suggests that the allyl anion formed during the reaction by deprotonation of the substrate with the *in situ* generated ⁻CH₂CN anion lived long enough to afford the more thermodynamically stable diastereoisomers. With 10–50 mol % of the proazaphosphatranane catalysts, 100% conversion for the allylaromatics **3a–6a** and up to 99% isolated yields for the conjugated products were obtained (Table 1). Under the same conditions, *trans*- β -methylstyrene, i.e., (*E*)-**3b**, did not undergo isomerization to form allylbenzene **3a** as monitored proton NMR measurements, revealing that the superbases cannot deprotonate vinylic CH or non-activated CH₃ functions. Conjugation reactions of **3a–6a** were also carried out in CD₃CN in a 5-mm NMR tube at 40 °C and monitored by ¹H NMR determinations. With 0.05 equivs. of **1b**, allylbenzene (**3a**), was conjugated to (*E*)-1-phenylpropene [(*E*)-**3b**] in 50% yield over a period of 14 hours, and the ³¹P NMR spectrum of the reaction mixture only exhibited three equal intensity lines which centered at $\delta_{(P-D)} = -10.4$ ppm and are assigned to the deuterated form of **1b**, i.e., **1bD⁺**. The result

Table 1. Isomerization of allylaromatics using **1b** or **1c** as the catalyst.^[a]

Substrate	Base (equivs.)	Time [h]	Conversion ^[b] [%]	Eluent ratio ^[c]	Product	Yield ^[d] [%] (<i>E/Z</i>)
3a	1b (0.1)	24	100	10:1		94.0 ^[e] (99/1)
3a	1c (0.1)	10	100	10:1		93.0 ^[e] (98/2)
4a	1b (0.4)	72	90.2	10:1		90.0 (94/6)
4a	1c (0.15)	60	100	10:1		96.3 (94/6)
5a	1b (0.2)	120	48.0	5:1		47.4 (89/11)
5a	1b (0.5)	120	90.1	5:1		90.0 (89/11)
5a	1c (0.4)	96	100	5:1		99.4 (90/10)
6a	1b (0.3)	60	100	10:1		98.0 (93/7)
6a	1c (0.15)	30	100	10:1		95.3 (94/6)
7a	1b (0.82)	72	–	5:1		–
7a	1b (1.57)	96	37.0	5:1		36.0 (91/9)
7a	1c (1.57)	96	43.0	5:1		42.0 (92/8)

^[a] Reaction conditions: 0.1 MPa, 40 °C; substrate, 1.0 mmol; CH₃CN, 5 mL.

^[b] Determined by ¹H NMR.

^[c] *n*-Hexane/THF.

^[d] Isolated yields from TLC or column chromatography on silica gel, products are >98% purity by ¹H NMR measurements.

^[e] >99% yield according to GC analysis of the reaction mixture but the isolated yields are lower than the reported results due to the volatility of the product.

also revealed that all the catalyst was deuterated by the solvent and the ⁻CD₂CN anion was generated during the reaction. 64 hours later 74% of **3a** was conjugated and the ³¹P NMR measurements showed no further increase of its conversion upon extending the reaction time. However, **3a** was completely conjugated to (*E*)-**3b** in CD₃CN within 24 hours by means of 0.10 equiv. of **1b** as the catalyst and a major singlet at 119.3 ppm for the remaining catalyst and three equal intensity lines centered at –10.4 ppm for **1bD**⁺ were observed in the phosphorus NMR spectrum of the reaction mixture at the end of the reaction. Apparently, a sufficient concentration of the catalyst is necessary during the reaction, that is, continuous generation of the catalytic species ⁻CH₂CN anion as shown in Eq. (1), is necessary for a complete isomerization. With less than 1.0 equiv. of **1b** or **1c**, 2-hydroxyallylbenzene (**7a**), could not be isomerized under the reaction conditions. The ³¹P NMR measurement of the reaction mixture in CD₃CN revealed only a singlet at δ_{(P-H)}} = –9.9 ppm characteristic of **2b** or **2c**, suggesting deprotonation of the phenolic OH group in **7a** to form species **A** [Eq. (2)]. This deprotonation process ended up within one hour. ³¹P NMR meas-

urement of the mixture of **7a** and 0.2 equivs. of **1b** in CD₃CN at 40 °C revealed that **1b** was predominantly converted to form **A** [singlet, δ_{(P-H)}} = –9.9 ppm] by extracting a phenolic proton from **7a**, and only trace of **1bD**⁺, i.e., species **B** [evidenced by the three-line resonance at δ_{(P-D)}} = –10.4 ppm] was detected. These results indicate, not unexpectedly, that **1b** and **1c** deprotonated the hydroxy group of **7a** substantially faster than they did to the solvent, CD₃CN or CH₃CN [Eq. (2)]. Only by using excess of the superbases, e.g., 1.57 equivs. of **1b** or **1c** (Table 1), **7a** was moderately isomerized and the corresponding product was isolated in 36% and 42% yield, respectively. That the ⁻CH₂CN anion initiates these isomerization is shown by the virtual absence of these transformations in other solvents such as benzene, toluene, and THF. It should be noted that the electron-donating substituent(s) in **4a–6a** and 2-phenolate anion from **7a** remarkably decreased the conjugation rates as compared with that of **3a**, presumably because of reduction in acidity of the methylene proton in the allyl groups of **4a–7a** (Table 1). In all cases listed in Table 1, *cis*-1-arylpropenes were formed as the minor products and the superbases **1c** exhibited higher catalytic activity than **1b**.

Table 2. Conjugation of allyl phenyl sulfide, allyl phenyl sulfone and conjugation of compounds containing CH₂-interrupted carbon-carbon double bonds.^[a]

Substrate	Base (equiv)	Time [h] ^[b]	Eluent ratio ^[c]	Product	Yield ^[d] [%] (isomer ratio)
8a	1b (0.1)	15	A (15:1)		93.0 (<i>E/Z</i> , 48/52)
8a	1c (0.1)	13	A (15:1)		95.5 (<i>E/Z</i> , 48/52)
9b	1b (0.025)	15 ^[e]	A (1:1)		96.3
9a	1c (0.025)	15 ^[e]	A (1:1)		95.0
10a	1b (0.8)	36 ^[f]	A (1:1)		40.5 (10b/10c , 1/1)
10a	1c (0.8)	49 ^[g]	A (1:1)	10b + 10c	44.0 (1/1)
11a	1b (0.3)	65	B (10:1)		97.0 (11b/11c , 1/1)
11a	1c (0.2)	65	B (10:1)	11b + 11c	97.1 (1/1)
12a	1b (0.4)	120	A (10:1)		50.0 (12b/12c , 1/1)
12a	1c (0.4)	120	A (10:1)	12b + 12c	93.2 (1/1)
13a	1b (0.3)	80	B (10:1)		96.4 (11b/11c , 1/1)
13a	1c (0.2)	66	B (10:1)	11b + 11c	96.9 (1/1)
13a	1c (0.2)	48 ^[h]	B (10:1)		38.2 (13b/13c , 1/1)
					47.8 (11b/11c , 1/1)
					6.6 (11a)

^[a] Reaction conditions : 0.1 MPa, 40 °C; CH₃CN, 5 mL; substrate, 1.0 mmol.

^[b] The conversion is 100% unless stated otherwise.

^[c] A = *n*-hexane/EtOAc, B = *n*-hexane/THF.

^[d] Isolated yields by TLC or column chromatography on silica gel.

^[e] At 23 °C.

^[f] Mass recovery, 97.2%.

^[g] Mass recovery, 95.6%.

^[h] Conversion of **13a** is 97.0%.

Allyl phenyl sulfide (**8a**) was isomerized to 1-phenylthiopropene, i.e., (*E/Z*)-**6b** in 93% yield using **1b** and in 95.5% yield using **1c** as the catalyst with an *E/Z* ratio close to 1.0, respectively (Table 2). The phenylthio group obviously activates the allylic methylene group in **8a** because methyl allyl sulfide, diallyl sulfide, and

benzyl allyl sulfide could not be isomerized under the same conditions. An attempt to isomerize allyl phenyl ether with **1b** or **1c** did not succeed either. Although **1b** and **1c** are capable of desulfurizing a variety of organic sulfides,^[39] they showed no reactivity to **8a,b**. Allyl phenyl sulfone (**9a**) was efficiently dimerized in

CH₃CN by means of 2.5 mol % of **1b** or **1c** as the catalyst and an isomerization/dimerization product was isolated in >95% yields. No reaction occurred with **9a** in the absence of a protic solvent such as CH₃CN under the reaction conditions, which suggests that the superbases itself does not deprotonate the sulfone to initiate the reaction.

Conjugation of methyl linoleate (**10a**) in CH₃CN at 40 °C using the superbases catalysts only afforded the corresponding products **10b** and **10c** (**10b/10c** = 1/1) in 40–44% yields (Table 2). The isomer ratio was determined by GC-MS. About 14% destruction of the ester group was observed to form RCH₂C(=O)CH₂CN by attack of the ⁻CH₂CN anion generated *in situ* by the catalyst on the ester group according to the ¹H NMR measurement of the isolated product. Proton NMR monitored reactions of **10a** catalyzed by **1b** or **1c** in CD₃CN at ambient temperature or 40 °C revealed that fast H-D exchange between the α-CH₂ group to the ester group and CD₃CN/⁻CD₂CN led to deuterated methyl linoleate (RCH₂CD₂COOMe, **D**) from which a fast equilibrium was established as shown in Scheme 3. In CH₃CN such an equilibrium consumed a considerable amount of anion ⁻CH₂CN generated by the superbases catalyst and thus lessened the deprotonation of 11-CH₂ in **10a**, remarkably decreasing the conjugation rates and efficiency. Unexpectedly, *cis,cis*-9,12-octadecadienol (**11a**) was isomerized to its corresponding conjugate alcohols **11b** and **11c** (**11b/11c** = 1.0) in CH₃CN at 40 °C in 97% yield by using **1b** or **1c** as the catalyst (Table 2). The conjugation reaction of **11a** was carried out in CD₃CN at 40 °C using **1b** or **1c** as the catalyst and was monitored by ³¹P NMR measurements. The following results were observed. Considerable amounts of the superbases catalyst survived during the reaction (singlet, δ_p: 119.4 ppm for **1b**; 118.2 ppm for **1c**) and the catalyst was predominantly transformed into its deuterated form, i.e., **B** [three equal intensity lines centered at δ_(p-D): -10.4 ppm for **1bD**⁺ and -11.2 ppm for **1cD**⁺] and only detectable amounts of the protonated form, i.e., **2b** or **2c**, were observed [singlet, δ_(p-H): -10.0 ppm for **2b**; -10.1 ppm for **2c**].

These results reveal that both superbases **1b** and **1c** deprotonated the hydroxy group of **11a** and its corresponding conjugate alcohols very slowly, and they predominantly dedeuterated (or deprotonated) the solvent CD₃CN (or CH₃CN) to generate ⁻CD₂CN (or ⁻CH₂CN) anions to initiate the conjugation reaction. Such a slow deprotonation of alcohol was confirmed

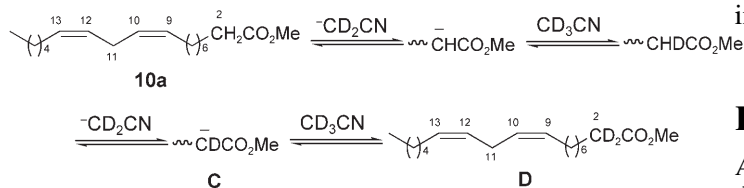
by subjecting the solution of **1b** or **1c** in CH₃OH to the reaction conditions. Six days later ³¹P NMR determination of the reaction mixture still revealed the presence of the superbases in CH₃OH. In the presence of 3.0 equivs. of water **1b** survived in CD₃CN at 40 °C for 3 days. Somehow, the methyl ether of **11a**, i.e., **12a**, underwent the conjugation much less efficiently than **11a** did (Table 2), and the corresponding conjugate ether isomers **12b/12c** (1:1) were only obtained in 93% yield over a period of 5 days and unreacted **12a** was recovered. The superbases catalysts exhibited much higher activity than *n*-BuLi which metalated and isomerized **11a** and **12a** in *n*-hexane or Et₂O in up to 75% yield.^[40] The TMS ether (TMS = trimethylsilyl) of **11a**, i.e., **13a**, was unexpectedly conjugated/desilylated to equivalent amounts of **11b** and **11c** in >96% yields with complete conversion of the TMS ether (Table 2). A shorter reaction time led to an incomplete conversion of **13a** (94.6% conversion using **1c** as the catalyst over a period of 48 hours). From the above incomplete reaction of **13a**, the corresponding conjugated TMS ethers, i.e., **13b** and **13c** (1:1), isomerization–desilylation products **11b** and **11c** (1:1), and the desilylated alcohol **11a** were isolated in 38.2%, 47.8%, and 6.6% yields, respectively (Table 2). These results have demonstrated that ⁻CH₂CN anions generated by the superbases catalysts not only initiated conjugation of CH₂-interrupted carbon-carbon double bonds but also desilylated the silyl ether to form the alcohol.^[41] A conjugation-desilylation/desilylation-conjugation mechanism is proposed to explain the reactions of **13a** in CH₃CN using **1b** or **1c** as the catalyst (Scheme 4). It is clear that the conjugated silyl ethers **12b/12c** and the desilylated alcohol **11a** were the reaction intermediates. Under the same conditions **1c** showed higher catalytic activity than **1b** for all the reactions and a reactivity order **11a** > **13a** > **12a** > **10a** was observed.

Conclusions

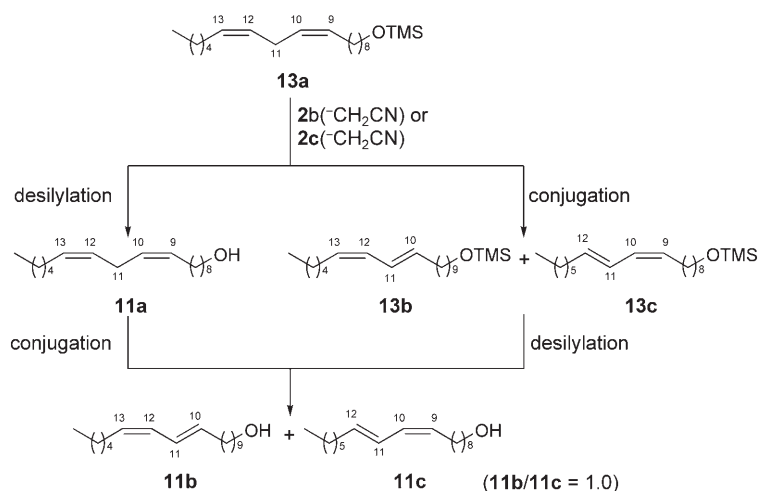
An efficient approach to isomerize allylaromatics, allyl sulfide, allyl sulfone, and CH₂-interrupted carbon-carbon double bonds-containing compounds by the non-ionic proazaphosphatrane catalysts P(RNCH₂CH₂)₃N (R = Me, *i*-Pr) was achieved under mild conditions. The high yields and selectivities for propenylaromatics and long-chain *cis,trans*-conjugated diene derivatives offer promising alternative routes to these compounds in organic synthesis.

Experimental Section

All the reactions and solvent treatments were carried out under a nitrogen or argon atmosphere. Acetonitrile was distilled over calcium hydride. Compound **8a** was prepared as re-



Scheme 3.



Scheme 4.

ported,^[22a] **11a** (from TCI America Co.) and other chemicals were used as received.

General Procedure for 1b- and 1c-Catalyzed Isomerization or Conjugation

In a 25-mL flask was dissolved a catalytic amount of **1b** or **1c** in 5.0 mL of dry acetonitrile. To this mixture was added 1.0 mmol of the substrate and the mixture was stirred at 40 °C. The reaction time was approximately the same as that necessary for completion of the same reaction on a 0.1–0.2 mmol scale of the substrate in CD₃CN (0.7 mL) in a 5-mm NMR tube under the same reaction conditions. After the reaction mixture had been stirred for the stated time, the reaction mixture was concentrated under reduced pressure and isolated by column chromatography or TLC on silica gel. The products were subject to NMR and GC-MS analyses, and >98% NMR purity was obtained for all the products.

Preparation of 12a

To a mixture of **11a** (0.815 g, 3.0 mmol) and CH₃I (0.45 g, 3.2 mmol) in 10 mL of DMSO, 1.50 g of KOH was added and the mixture was stirred at ambient temperature for 30 minutes. 100 mL of water were then added and the mixture was extracted with EtOAc (3 × 40 mL). The organic layer was dried over MgSO₄, filtered and all the volatiles evaporated under reduced pressure. Isolation by column chromatography on silica gel with *n*-hexane/EtOAc (15:1) afforded **12a** as a colorless liquid; yield: 0.538 g (64%).

Preparation of 13a

To a stirred mixture of **11a** (7.40 g, 27.7 mmol) and trimethylsilyl chloride (3.32 g, 30.4 mmol) in THF at 0 °C, 3.64 g (36 mmol) of Et₃N were added. After the reaction was complete within 3 hours, 150 mL of water were added and the mixture was extracted with CH₂Cl₂ (3 × 100 mL). The organic layer was dried over MgSO₄, filtered, and all the volatiles were removed under

reduced pressure. Distillation at 130 °C/0.68 torr afforded **13a** as a colorless liquid; yield: 8.4 g (89.3%); ¹H NMR (400 MHz, 23 °C, CDCl₃): δ = 5.33 (m, 4H, 2 CH=CH), 3.54 (t, 2H, OCH₂), 2.75 (t, 2H, 11-H), 2.03 (m, 4H, CH₂), 1.31 (m, 2H, CH₂), 1.27 (m and broad, 16H, 8 CH₂), 0.87 (t, 3H, CH₃), 0.08 [s, 9H, Si(CH₃)₃]; ¹³C{¹H} NMR (400 MHz, 23 °C, CDCl₃): δ = 130.2 and 128.0, 62.7, 32.7, 31.5, 29.7, 29.6, 29.5, 29.4, 29.3, 27.2, 25.8, 25.6, 22.6, 14.1 (CH₃), -0.4 [Si(CH₃)₃]; anal. calcd. for C₂₁H₄₂O₂Si: C 74.49, H 12.51; found: C 74.30, H 12.45.

Acknowledgements

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