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Alkenyl alane–pyridine complexes in a new synthesis of aryl alk-1-enyl sulfoxides

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Abstract—A new and an efficient synthesis of aryl alk-1-enyl sulfoxides is reported. The reaction between alane–pyridine complexes, triphenylphosphine, and sulfonyl chlorides affords the title products in good to excellent yields (70–94%) in short reaction times using mild conditions. The optimal ratio between reagents (alane–pyridine/PPh_3/sulfonyl chloride 1.00/1.35/0.92) was obtained performing a chemiometric analysis. A rationale for the reaction was advanced.

1. Introduction

α,β-Unsaturated sulfoxides are well known as useful reagents in organic synthesis.[1] Despite their widespread interest, synthetic pathways to this class of compounds are tedious or time-consuming, or require commercially unavailable reagents. Among the extensively reviewed approaches to α,β-unsaturated sulfoxides,[2] the most general ones are: controlled oxidation of the corresponding sulfides,[3] condensation starting from carbonyl compounds,[4] and alkylation of sulfinates with organometallic reagents.[5]

In a previous work[6] we described an improvement of the Reinheckel procedure[7] to prepare aryl as well as alkyl alk-1-enyl sulfoxides. The reported reaction[6] is rather general, but it is carried out under drastic conditions and affords the products in a 50% yield referred to the alkenyl alane; these drawbacks constitute a limitation to the synthetic applicability of our previous protocol.

Dialkyl alk-1-enyl alanes are useful reagents in organic synthesis when an unsaturated chain has to be transferred;[8] we thus considered their employment in the direct synthesis of alkenyl sulfoxides.

In the context of a study on the chemistry of α,β-unsaturated sulfoxides,[6] multigram amounts of these intermediates were needed; an easy and cost-effective synthetic procedure was thus required. Use of aryl sulfonyl chlorides and of triphenylphosphine as reducing agents seemed to be reasonable in view of their low cost and commercial availability. In a preliminary experiment a low yield (35%) of *p*-tolyl hex-1-enyl sulfoxide, recovered in a 1:1 ratio with the corresponding sulfone was obtained by reacting tosyl chloride and triphenylphosphine with an hexane/THF solution of alkenyl alane at room temperature. The ratio between products was found to be independent of the temperature (0–25 °C) as well as the solvent (THF and CH_2Cl_2).

Taking into account that coordination of dialkyl alk-1-enyl alanes with amines seems to enhance[9] the hardness of the unsaturated chain, we decided to employ alkenyl alane–pyridine complexes[10] to increase the selectivity of the process.

In a further reaction, tosyl chloride was added at room temperature to the preformed alane–pyridine complex **1**, as shown in Scheme 1.

In the reported conditions, the organometallic reagent **1** is unreactive toward sulfonyl chloride. An immediate reaction occurs when triphenylphosphine is added, giving *p*-tolyl hex-1-enyl sulfoxide, *p*-tolyl hex-1-enyl sulfone, and *p*-tolyl *iso*-butyl sulfoxide in a 2.5/2.5/1.0 ratio (overall yield 60%, Table 1, entry 1).

Reaction temperature has in this case a remarkable effect on the selectivity in the desired product: alkenyl sulfoxide is recovered as the sole product in a 50% yield when the reaction is performed at 0 °C (Table 1, entry 2).

No reaction occurs at temperatures lower than −30 °C (Table 1, entry 3), and different alk-1-enyl alanes give

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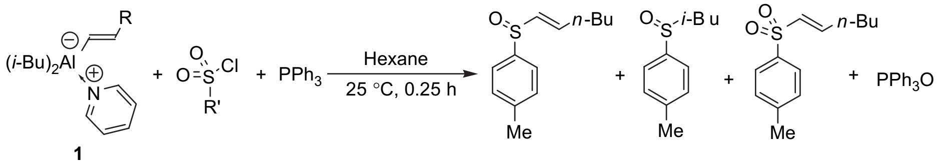


Scheme 1. Reaction of tosyl chloride with **1** in the presence of triphenylphosphine.

similar results. It has to be underlined that although only a 50% yield is obtained, conversion of the sulfonyl chloride, as well as oxidation of triphenylphosphine, is always complete.

The nature of the amine used is critical for the outcome of the reaction, for example, when triethylamine is used instead of pyridine (Table 1, entry 4), only 30% of the sulfoxide is recovered, together with the corresponding sulfone. It is worth noting that results obtained with the use of triethylamine are quite similar to those observed when uncomplexed organoalanes are employed; it is known that triethylamine is a weak ligand for organoalanes,[11] which probably react as uncomplexed species.

We analyzed the effect of different solvent mixtures to increase the yield. Coordinating solvents can dramatically modify the reactivity of organoaluminum reagents, so in a further reaction hexane was used. Sulfoxide was recovered in this case in a very low yield (25%) and appreciable amounts of the corresponding sulfone (20%) and *S*-*p*-tolyl 4-methylbenzenesulfonothioate (20%) were recovered (Table 1, entry 5). On the other hand, the reaction is considerably slower (3 h at 0 °C) when THF is used (Table 1, entry 6). In these conditions complete chemoselectivity and an 81% yield is obtained.

These data suggested that coordinating solvents slow down the reaction, and polar solvent mixtures enhance the yield. Dichloromethane was thus used, in consideration of its quite large polarity and low coordinating strength; the sulfoxide was eventually recovered in a very good yield (83%) after a few minutes (Table 1, entry 7).

Table 1. Reaction of **1** with *p*-toluenesulfonyl chloride in the presence of triphenylphosphine

Entry[a]	Solvent	Temperature (°C)	Sulfoxide[b]	Sulfone[b]	Time (h)[c]
1	THF/hexane 1/1	25	25[d]	25	0.25
2	THF/hexane 1/1	0	50	0	0.25
3	THF/hexane 1/1	−30	0[e]	0	2
4	THF/hexane 1/1	0	30[f]	35	0.25
5	Hexane	0	25[g]	20	0.25
6	THF	0	81	0	3
7	CH_2Cl_2	0	83	0	0.10

[a] All reactions were performed using **1**/PPh_3/$ArSO_2Cl$=1.0/0.9/0.9 ratio.
[b] Calculated on the isolated, chemically pure product.
[c] Necessary to achieve maximum yield (GLC).
[d] *iso*-Butyl *p*-tolyl sulfoxide (10%) was also recovered.
[e] Complete disappearance of sulfonyl chloride and oxidation of triphenylphosphine was observed.
[f] Et_3N was used instead of pyridine.
[g] *S*-*p*-Tolyl 4-methylbenzenesulfonothioate (20%) was recovered from the reaction mixture.

Basicity is a factor, which greatly influences the outcome of the reaction; pyridine, isoquinoline, and 4-ethyl pyridine give identical yields in the sulfoxide, while the more basic 4-(*N*,*N*-dimethylamino) pyridine does not lead to any product formation. These data suggest that the organoalane must be able to decomplex from pyridine to react with sulfonyl chloride.

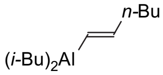
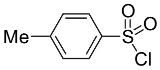
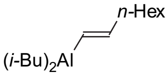
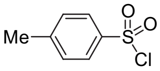
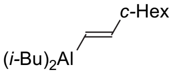
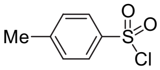
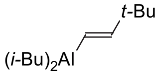
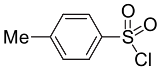
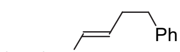
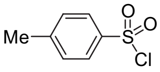
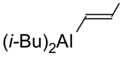
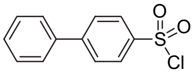
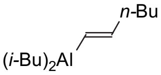
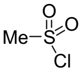
Further optimization of the yield was achieved using a chemiometric analysis; the influence of the **1**/Ph_3P/TsCl ratio on the yield was taken into consideration, performing a total of 9 reactions and applying a Doehlert design.[12]

The analysis showed that the yield is maximum at the point corresponding to a ratio **1**/Ph_3P/TsCl=1.00/1.35/0.92.[13] Furthermore, the study suggested that the ratio between the reagents should be strictly controlled in order to achieve a good yield.

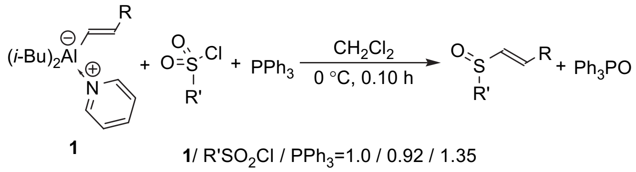
A further experiment was carried out using the optimized values found and an excellent (94%) yield of the desired sulfoxide was obtained (Table 2, entry 1).

Attention was directed toward the synthesis of different alkenyl sulfoxides. Various di-*iso*-butyl alk-1-enyl alanes and sulfonyl chlorides were tested using optimized reaction conditions, as shown in Scheme 2.

Table 2. Results obtained with different substrates

Entry[a]	Alkenyl alane	Sulfonyl chloride	Yield (%)[b]
1			94
2			94
3			92
4			89
5			88
6			70
7			35[c]

[a] All the reactions were performed using the optimized conditions shown in Scheme 2.
[b] Calculated on the isolated, chemically pure product.
[c] Complete consumption of sulfonyl chloride and oxidation of triphenylphosphine was observed.



Scheme 2. Reaction performed using optimized conditions.

The results, summarized in Table 2, show that the yield is independent of the nature of the alk-1-enyl alane used, as long as an alk-1-yne is employed as precursor in the preparation of the organometallic reagent. It is noteworthy that aryl sulfonyl chlorides give excellent yields while methyl sulfonyl chloride affords the corresponding sulfoxide in a low yield (35%, Table 2, entry 7).

It is to be noted that yields tend to decrease when the reaction is carried out on substrates whose structures are different from that of *p*-toluensulfonyl chloride and di-*iso*-butylhex-1-enylalane, since the reaction parameters were optimized for this particular couple of reagents. Trialkyls or dialkyl alkynylalanes[10d] were unreactive, even after prolonged reaction times.

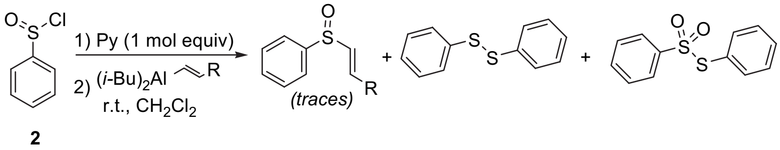
Some mechanistic investigations were finally performed to shed light on the mechanism.

Formation of sulfone as intermediate in the reaction can be ruled out according to the following observations: (i) when (*E*) *p*-tolyl hex-1-enyl sulfone is added to the reaction mixture described in Scheme 2, it is reduced only by the excess of Ph_3P present and (ii) the reduction process is considerably slow, requiring several hours to be complete.

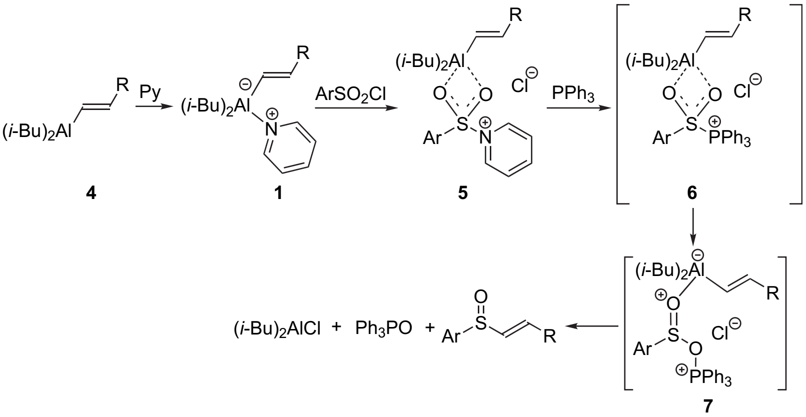
It is also possible to rule out the presence of sulfinyl chloride as a reaction intermediate. Direct reaction between sulfinyl chloride and dialkyl alk-1-enyl alanes in the presence of stoichiometric amounts of pyridine lead to the formation of many by products, where the sulfoxide is present only in traces (Scheme 3).

On the basis of these results, it was possible to propose the reaction pathway represented in Scheme 4.

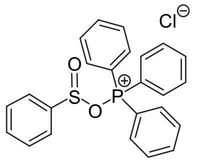
Experimental evidences for the formation of some intermediates were obtained via ^1H and ^{13}C NMR spectroscopy. As reported in the Section 2 there is a remarkable change in the chemical shift when the organoalane **4** is converted into its pyridinated form **1**. Addition of tosyl chloride causes the formation of a new species whose chemical shifts significantly differ both from the tosyl chloride–pyridine adduct and from pyridinated organoalane **1**. The absence of characteristic signals of uncomplexed organoalane **4** support the possible formation of intermediate **5**; this structure is consistent with the drift of signals observed in ^1H and ^{13}C NMR spectra. It is reported that triphenylphosphine is able to reduce sulfonyl chlorides even in very mild conditions,[14] phosphorous in this process firstly adds to the sulfur atom. It is then likely for intermediate **6** to exist in the reaction. This could further evolve to **7**, which would finally afford the product. Direct evidences for the presence of intermediates **6** and **7** could not be obtained due to the fast conversion of **5** in the reaction product. However, a sulfinyl chloride-triphenylphosphine oxide adduct was prepared by reacting benzenesulfinyl chloride with triphenylphosphine oxide; evidences for the formation of the adduct were brought by the shift of the ^{31}P signal upfield by 3.6 ppm with respect to triphenylphosphine oxide. The resulting intermediate **3**, whose postulated structure is reported in Figure 1, was added to stoichiometric amounts of dialkyl alk-1-enyl alanes. In these reaction conditions aryl alk-1-enyl sulfoxides were recovered in 35–45% yields, both using uncomplexed or pyridinated organoalanes, although reaction conditions were not optimized. This fact



Scheme 3. Reaction between benzenesulfinyl chloride and dialkyl alk-1-enyl alanes in the presence of pyridine.



Scheme 4. Proposed reaction pathway for formation of sulfoxides.



3

Figure 1. Adduct of sulfinyl chloride with triphenylphosphine oxide.

supports the presence of **7** as an intermediate in the studied reaction.

The mechanism reported in Scheme 4 has not been studied in detail, and should be then regarded only as a reasonable rationale for the reported reaction; it however succeeds in the explanation of experimental and spectroscopic evidences, which emerged during this study. Moreover, the above discussed influence of the basicity of ligands on the reaction outcome is clearly evidenced; when the organoalane forms very strong complexes with the ligand, intermediate **5** is not likely to form.

In conclusion, we report a new procedure, which allows the synthesis of aryl alk-1-enyl sulfoxides starting from readily available sulfonyl chlorides and dialkyl alkenyl alanes, in a one-pot procedure. This protocol was optimized studying the solvent effect and using a chemiometric approach, and makes possible to synthesize the title compounds in excellent yields, with short reaction times. Due to the stereoselectivity both of hydroalumination step and of subsequent sulfoxides formation step, the whole process affords pure *E* isomers (GLC and NMR analyses). A reasonable reaction mechanism, which explains the experimental details of this reaction, was provided; NMR spectroscopy evidences and appropriate reactions were brought to support this hypothesis.

Furthermore this method represents, to the best of our knowledge, the first employ of pyridinated dialkyl alk-1-enyl alanes in organic synthesis.

2. Experimental

2.1. General

All reactions were performed in apparatus dried by replicated vacuum-nitrogen cycles under an inert atmosphere (N_2). Solvents were dried by standard procedures. Pyridine was refluxed over, and distilled from, KOH. Triphenylphosphine (Aldrich) was used as received. DIBAL-H was prepared starting from $Al(i\text{-}Bu)_3$. GLC analyses were performed on a Perkin–Elmer 8500 instrument [ZB1 column (15 m×0.25 mm), film 0.25 μm] equipped with a flame ionization detector and a split–splitless injector, with He as carrier gas. Thin layer chromatography (TLC) analyses were performed on silica gel 60 plates (Fluka) and purifications were carried out with silica gel 60 (Fluka, 230–440 mesh) using ethyl acetate as solvent. ^{1}H and ^{13}C NMR (200 and 50 MHz, respectively) spectra were recorded on a Varian Gemini 200 spectrometer; all NMR data were obtained using $CDCl_3$ solutions. Chemical shifts (δ, ppm) are referenced to tetramethylsilane (TMS) (^{1}H NMR) or $CDCl_3$ (^{13}C NMR) as an internal standard. Mass spectra (*m*/*z*, *I*%) were taken on a 5980 Hewlett–Packard GC instrument, equipped with a HP-5MS column (30 m×0.25 mm, film 0.25 μm) interfaced with a Hewlett–Packard 5995A instrument, with He as carrier gas. Indicated yields are reported on the isolated, chemically pure products.

2.1.1. Hydroalumination of alkynes. In a typical procedure, a hexane solution of DIBAL-H (1.0 mL, 1 mmol) was slowly added to a cooled (0 °C) hexane solution (25 mL) of the alkyne (1.1 mmol, freshly distilled). The mixture was then refluxed for 5 h, cooled to room temperature, the hexane was eliminated in vacuo (15 mmHg), replaced with CH_2Cl_2 (25 mL) and the solution was used without further purifications.

2.1.2. Synthesis of unsolvated diethyl hex-1-ynyl alane.[10d] In a typical procedure, triethylamine (5.5 mL, 0.075 mmol, freshly distilled) and an hexane solution (25 mL) of hex-1-yne (0.6 mL, 1 mmol, freshly distilled) were added to a cooled (0 °C) hexane solution (25 mL) of DIBAL-H (1.0 mL, 1 mmol). After stirring for 2 h at 0 °C the mixture was allowed to warm at room temperature, the solvent was eliminated at reduced pressure (15 mmHg), replaced with CH_2Cl_2 (25 mL) and the solution was used without further purifications.

2.1.3. Reaction between dialkyl alk-1-enyl alane–pyridine complexes and sulfonyl chlorides in the presence of triphenylphosphine. In a typical procedure, pyridine (0.8 mL, 1 mmol) was added to a cooled (0 °C) solution of the required organoalane (1 mmol) in the appropriate solvent (25 mL). The solution was stirred for 10 min, then sulfonyl chloride (175 mg, 0.92 mmol) and triphenylphosphine (353 mg, 1.35 mmol) were added at once as solids. The mixture was stirred for 15 min or until the maximum yield was achieved (GLC and TLC), then deposed over a short column (5 cm) of silica gel and eluted with dichloromethane (200 mL). The solution was dried (Na_2SO_4) and the solvent evaporated in vacuo. The crude product was further purified by flash chromatography.

2.1.4. Characterization of the prepared compounds. For each synthesized compound flash chromatography condition, yield, physical state, R_f data, mass spectroscopy data, ^{1}H and ^{13}C NMR data are reported.

2.1.4.1. (*E*) 4′-Methylphenyl hex-1-enyl sulfoxide.[15] Petroleum ether/Ethyl Acetate 80/20; 94%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.20; GC–MS (*m*/*z*, *I*%): 222 ($M^{\bullet +}$, 5), 206 (11), 174 (67), 131 (100), 123 (29), 91 (29); ^{1}H NMR: 7.50–7.30 (4H, m, Ar), 6.59 (1H, dt, *J* 15.0 Hz, *J*′ 7.0 Hz, SOCH*CH*), 6.20 (1H, dt, *J* 15.0 Hz, *J*′ 1.5 Hz, SO*CH*CH), 2.40 (3H, s, Ar*CH*$_3$), 2.22 (2H, dtd, *J* 7.0 Hz, *J*′ 6.6 Hz, *J*″ 1.5 Hz, CHCH*CH*$_2$), 1.50–1.20 (4H, m, *CH*$_2$*CH*$_2$CH$_3$), 0.88 (3H, t, *J* 7.0 Hz, CH$_2$*CH*$_3$); ^{13}C NMR: 141.5, 141.4, 141.2, 135.3, 130.2, 124.8, 31.9, 30.4, 22.3, 21.6, 14.0; Anal. Calcd for $C_{13}H_{18}OS$: C, 70.24; H, 8.17; S, 14.39%. Found: C, 70.12; H, 8.14; S, 14.44%.

2.1.4.2. (*E*) 4′-Methylphenyl oct-1-enyl sulfoxide.[15] Petroleum ether/Ethyl Acetate 80/20; 94%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.21; GC–MS (*m*/*z*, *I*%): 250 ($M^{\bullet+}$, 4), 234 (30), 202 (56), 163 (29), 131 (100), 124 (49), 118 (51), 105 (18), 91 (36), 77 (9); ^{1}H NMR: 7.54–7.46 (2H, m, *o*-Ar), 7.35–7.26 (2H, m, *m*-Ar), 6.59 (1H, dt, J 15.4 Hz, J' 7.0 Hz, SOCH*CH*), 6.20 (1H, dt, J 15.4 Hz, J' 1.4 Hz, SO*CH*CH), 2.40 (3H, s, Ar$\mathit{CH_3}$), 2.21 (2H, dtd, J 6.2 Hz, J' 7.0 Hz, J'' 1.4 Hz, CH$\mathit{CH_2}$), 1.50–1.20 (8H, m, $(\mathit{CH_2})_4\mathrm{CH_3}$), 0.86 (3H, J 6.6 Hz, $\mathrm{CH_2}\mathit{CH_3}$); ^{13}C NMR: 141.5, 140.9, 134.8, 129.8, 124.4, 31.8, 31.3, 28.5, 27.9, 22.4, 21.2, 13.9; Anal. Calcd for $C_{15}H_{22}OS$: C, 71.96; H, 8.86; S, 12.78%. Found: C, 71.87; H, 8.73; S, 12.91%.

2.1.4.3. (*E*) 4′-Methylphenyl 2-cyclohexylethenyl sulfoxide.[16] Petroleum ether/Ethyl Acetate 80/20; 92%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.19; GC–MS (*m*/*z*, *I*%): 234 ($M^{\bullet+}$, 5), 219 (18), 218 (100), 186 (18), 136 (36), 109 (71), 67 (63); ^{1}H NMR: 7.53–7.46 (2H, m, *o*-Ar), 7.33–7.27 (2H, m, *m*-Ar), 6.56 (1H, dd, J 15.0 Hz, J' 6.6 Hz, SO*CH*CH), 6.15 (1H, dd, J 15.0 Hz, J' 1.1 Hz, SOCH*CH*), 2.40 (3H, s, Ar$\mathit{CH_3}$), 2.20–2.10 (1H, m, $\mathit{CH}(\mathrm{CH_2})_2$), 1.90–1.60 (5H, m, $\mathrm{CH_{cycle}}$), 1.40–1.10 (5H, m, $\mathrm{CH_{cycle}}$); ^{13}C NMR: 146.0, 141.5, 141.4, 133.3, 130.2, 124.8, 40.5, 37.8, 32.0, 31.9, 26.0, 25.9, 21.6; Anal. Calcd for $C_{15}H_{20}OS$: C, 77.54; H, 8.12; S, 12.89%. Found: C, 77.45; H, 8.07; S, 13.01%.

2.1.4.4. (*E*) 4′-Methylphenyl 3,3-dimethyl-but-1-enyl sulfoxide.[17] Petroleum ether/Ethyl Acetate 80/20; 89%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.22; GC–MS (*m*/*z*, *I*%): 222 ($M^{\bullet+}$, 2), 206 (6), 191 (11), 174 (53), 159 (100), 137 (17), 123 (26), 91 (25), 77 (8), 65 (14), 57 (16); ^{1}H NMR: 7.52–7.42 (2H, m, *o*-Ar), 7.32–7.23 (2H, m, *m*-Ar), 6.60 (1H, J 15.4 Hz, SOCH*CH*), 6.11 (1H, d, J 15.4 Hz, SO*CH*CH), 2.49 (3H, s, $\mathrm{ArCH_3}$), 1.16 (9H, s, $\mathrm{C(CH_3)_3}$); ^{13}C NMR: 151.0, 141.5, 141.4, 131.3, 130.2, 124.9, 34.4, 29.0, 21.6; Anal. Calcd for $C_{13}H_{18}OS$: C, 70.24; H, 8.17; S, 14.13%. Found: C, 70.20; H, 8.07; S, 14.20%.

2.1.4.5. (*E*) 4′-Biphenyl hex-1-enyl sulfoxide. Petroleum ether/Ethyl Acetate 80/20; 70%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.18; GC–MS (*m*/*z*, *I*%): 284 ($M^{\bullet+}$, 3), 268 (46), 236 (100), 225 (15), 193 (99), 185 (62), 178 (40), 165 (23), 152 (71), 141 (14), 115 (16), 77 (7), 55 (12), 41 (16); ^{1}H NMR: 7.90–7.65 (5H, m, Ph), 7.60–7.45 (4H, m, SOAr), 6.74 (1H, dt, J 15.4 Hz, J' 6.6 Hz, SOCH*CH*), 6.36 (1H, dt, J 15.4 Hz, J' 1.4 Hz, SO*CH*CH), 2.34 (2H, dtd, J 6.6 Hz, J' 6.0 Hz, J'' 1.4 Hz, CH$\mathit{CH_2}$), 1.60–1.30 (4H, m, $\mathit{CH_2CH_2}\mathrm{CH_3}$), 0.99 (3H, t, J 6.6 Hz, $\mathrm{CH_2}\mathit{CH_3}$); ^{13}C NMR: 144.2, 143.0, 142.1, 140.0, 134.9, 129.2, 128.4, 128.3, 127.5, 125.3, 32.0, 30.4, 22.4, 14.1; Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.10; S, 11.25%. Found: C, 76.23; H, 7.01; S, 11.20%.

2.1.4.6. (*E*) 4′-Methylphenyl 4-phenyl but-1-enyl sulfoxide.[17] Petroleum ether/Ethyl Acetate 80/20; 88%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.18; GC–MS (*m*/*z*, *I*%): 270 ($M^{\bullet+}$, 1), 254 (5), 222 (17), 163 (21), 131 (110), 123 (14), 91 (73), 77 (10), 65 (16); ^{1}H NMR: 7.55–7.20 (9H, m, Ph+SOAr), 6.69 (1H, dt, J 15.4 Hz, J' 7.4 Hz, SOCH*CH*), 6.28 (dt, J 15.4 Hz, J' 1 Hz, SO*CH*CH), 2.87 (2H, t, J 7.2 Hz, $\mathrm{SOCH_2}$), 2.63 (2H, dtd, J 7.0 Hz, J' 7.4 Hz, J'' 1, 2.0 Hz, $\mathit{CH_2}$Ph), 2.49 (3H, s, $\mathrm{CH_2}\mathit{CH_3}$); ^{13}C NMR: 141.6, 141.1, 140.7, 139.5, 136.0, 130.3, 128.8, 128.7, 126.5, 125.0, 34.6, 33.8, 21.7; Anal. Calcd for $C_{17}H_{18}OS$: C, 75.52; H, 6.72; S, 11.84%. Found: C, 75.42; H, 6.67; S, 11.93%.

2.1.4.7. (*E*) Methyl hex-1-enyl sulfoxide.[18] Ethyl Acetate 100%; 35%; yellowish oil; R_f (20% Petroleum ether/Ethyl Acetate) 0.15; GC–MS (*m*/*z*, *I*%): 146 ($M^{\bullet+}$, 49), 129 (11), 117 (12), 103 (10), 81 (51), 55 (100), 41 (72); ^{1}H NMR: 6.49 (1H, dt, J 15.0 Hz, J' 6.6 Hz, SOCH*CH*), 6.27 (1H, dt, J 15.0 Hz, J' 1.5 Hz, SO*CH*CH), 2.60 (3H, s, $\mathrm{SOCH_3}$), 2.24 (2H, dtd, J 7.0 Hz, J' 6.4 Hz, J'' 1.5 Hz, CH$\mathit{CH_2}$), 1.55–1.25 (4H, m, $\mathit{CH_2CH_2}\mathrm{CH_3}$), 0.91 (3H, t, J 7.0 Hz, $\mathrm{CH_2}\mathit{CH_3}$); ^{13}C NMR: 141.2, 134.2, 41.0, 31.9, 30.4, 22.4, 14.0; Anal. Calcd for $C_7H_{14}OS$: C, 57.50; H, 9.66; S, 21.89%. Found: C, 57.59; H, 9.74; S, 21.84%.

2.1.5. NMR of reaction intermediates. All NMR spectra were recorded on a Varian Infinity 300 spectrometer in C_6D_6 solution, using the residual signal of solvent (set exactly at 2134.2 Hz) as reference, and are expressed in Hertz.

2.1.5.1. (*E*) Di (*iso*-butyl) hex-1-enyl aluminum. ^{1}H NMR: 2242 (1H, dt, J_d 20.0 Hz, J_t 6.0 Hz, Al–CH=*CH*), 1770 (1H, dt, J_d 20.0 Hz, J_t 1.5 Hz, Al–*CH*=CH), 629.0 (2H, m, CH=CH–$\mathit{CH_2}$–), 601.0 (2H, m, $\mathrm{CH_2}\mathit{CH}\mathrm{(CH_3)_2}$), 390.0–345.0 (4H, m, =CH–$\mathrm{CH_2}$–$\mathit{CH_2}$–$\mathit{CH_2}$–), 330.3 (12H, s, $\mathrm{CH}(\mathit{CH_3})_2$), 227.0 (3H, t, J 7.0 Hz, $\mathrm{CH_2}$–$\mathit{CH_3}$), 111.0 (4H, d, J 7.0 Hz, Al–$(\mathit{CH_2}\mathrm{CH}–)_2$); ^{13}C NMR: 186.2, 126.3, 40.3, 29.4, 28.3 (2C), 26.8, 22.4, 13.7.

2.1.5.2. Pyridine. ^{1}H NMR: 2543 (2H, m, α-CH), 2101 (1H, tt, J_1 7.0 Hz, J_2 2.0 Hz, γ-CH), 2002 (2H, m, β-CH); ^{13}C NMR: 150.1, 135.2, 123.4.

2.1.5.3. Tosyl chloride. ^{1}H NMR: 2258 (2H, d, J 8.0 Hz, α-CH), 1936 (2H, d, J 8.0 Hz, β-CH), 503 (3H, s, –$\mathrm{CH_3}$); ^{13}C NMR: 146.1, 142.0, 129.9, 126.9, 21.0.

2.1.5.4. Tosyl chloride–pyridine complex. ^{1}H NMR: 2538 (2H, m, α-CH), 2263 (2H, d, J 8.0 Hz, α-CH), 2099 (1H, tt, J_1 7.0 Hz, J_2 2.0 Hz, γ-CH), 2000 (2H, m, β-CH), 1959 (2H, d, J 8.0 Hz, β-CH), 521 (3H, s, –$\mathrm{CH_3}$); ^{13}C NMR: 150.0, 146.4, 141.9, 135.3, 130.0, 126.9, 123.5, 21.1.

2.1.5.5. (*E*) Di (*iso*-butyl) hex-1-enyl aluminum pyridine complex. ^{1}H NMR: 2513 (2H, m, α-CH), 2038 (1H, tt, J_1 7.0 Hz, J_2 2.0 Hz, γ-CH), 1940 (2H, m, β-CH), 1935 (1H, dt, J_d 20.0 Hz, J_t 6.0 Hz, Al–CH=*CH*), 1895 (1H, dt, J_d 20.0 Hz, J_t 1.5 Hz, Al–*CH*=CH), 708 (2H, m, CH=CH–$\mathit{CH_2}$–), 646 (2H, m, $\mathrm{CH_2}\mathit{CH}\mathrm{(CH_3)_2}$), 480–405 (4H, m, =CH–$\mathrm{CH_2}$–$\mathit{CH_2}$–$\mathit{CH_2}$), 364 (12H, s, $\mathrm{CH}(\mathit{CH_3})_2$), 269 (3H, t, J 7.0 Hz, $\mathrm{CH_2}$–$\mathit{CH_3}$), 126 (4H, d, J 7.0 Hz, Al–$(\mathit{CH_2}\mathrm{CH}–)_2$); ^{13}C NMR: 149.2, 148.7, 137.4, 124.1, 124.0, 39.6, 32.0, 28.7 (2C), 27.3, 22.7, 14.2.

2.1.5.6. (*E*) Di (*iso*-butyl) hex-1-enyl aluminum pyridinate–tosyl chloride complex. ^{1}H NMR: 2514 (m, 2H, α-CH), 2263 (d, J 8.0 Hz, 2H, α-CH), 2061 (tt, J_1 7.0 Hz, J_2 2.0 Hz, 1H, γ-CH), 1959 (d, J 8.0 Hz, 2H, β-CH), 1950 (m, 2H, β-CH), 1929 (dt, J_d 20.0 Hz, J_t 6.0 Hz, 1H, Al–CH=*CH*), 1884 (dt, J_d 20.0 Hz, J_t 1.5 Hz, 1H, Al–*CH*=CH), 699 (m, 2H, CH=CH–$\mathit{CH_2}$–), 636 (m, 2H,

$CH_2CH(CH_3)_2$), 522 (s, 3H, $-CH_3$), 465–390 (m, 4H, $=CH-CH_2-CH_2-CH_2-$), 364 (s, 12H, $CH(CH_3)_2$), 265 (3H, t, J 7.0 Hz, CH_2-CH_3), 117 (4H, d, J 7.0 Hz, $Al-(CH_2CH-)_2$); ^{13}C NMR: 149.1, 148.5, 146.3, 141.9, 137.9, 130.0, 126.9, 124.3, 39.6, 32.0, 28.7 (2C), 27.3, 22.7, 21.1, 14.2.

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