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# Aminium Salts Induced Desulphurization of Allyl and Diallyl Thiiranes. Synthesis of Dienes and Trienes

Vincenzo Caló,\* Luigi Lopez,\* Angelo Nacci, Giuseppe Mele

CNR Centro di Studio sulle Metodologie Innovative di Sintesi Organiche, Dipartimento di Chimica, Università di Bari, via Orabona 4-70125 Bari, (Italy)

Abstract: Catalytic amounts of aminium salts A-B induce the conversion of methylene chloride in solutions of several allyl and diallyl episulphides 1-6 into the corresponding unsaturated derivatives 7-12. The desulphurization process, which occurs through a plausible chain electron-transfer mechanism, rapid and may proceed in a fashion that preserves the stereochemistry of the starting episulphide.

#### **INTRODUCTION**

Desulphurization of thiiranes, a useful procedure for the synthesis of olefins, can occur spontaneously,<sup>1</sup> thermally,<sup>2</sup> or with a wide variety of reagents, which includes trivalent phosphorous compounds,<sup>3</sup> organometallic reagents,<sup>4</sup> iron carbonyl complexes,<sup>5</sup> metals,<sup>6</sup> and peculiar selenium derivatives, such as 3-methyl-2-selenoxobenzothiazole.<sup>7</sup> The majority of these reactions, requiring more than an equivalent amount of the reagent to thiiranes, take place stereospecifically, but in the case of *cis*-thiiranes they are accompained by the formation of the more stable *trans*-alkenes.<sup>8</sup> However, to date the only efficient catalytic desulphurization procedure, although limited to the synthesis of tetra and triarylsubstituted olefins, involves the use of aminium salts as initiators.<sup>9</sup>

In this context, as part of our continuing studies on the aminium salt induced generation and evolution of radical cations from different classes of organic substrates,<sup>10</sup> we disclose here that catalytic amounts of aminium salts, such as *tris*-(4-bromophenyl)-aminium hexachloroantimonate (A), [ $E^{red} = 1.16 \text{ V}$ . vs SCE],<sup>11</sup> or *tris*-(2,4-dibromophenyl) aminium hexachloroantimonate (B), [ $E^{red} = 1.66 \text{ V}$ . vs SCE],<sup>12</sup> induce the *facile* desulphurization of several synthesized allyl and diallyl thiranes (1-6),<sup>13</sup> under mild conditions, through a plausible chain electron transfer mechanism. Detailed mechanistic studies substantiate that the reactions may proceed stereospecifically. On the other hand, increasing the amounts of the aminium salts, added to the reaction mixtures, will favour the isomerization of the alkenes into the more stable isomers, through an electron-transfer mechanism.

## **RESULTS AND DISCUSSION**

Starting materials (1-6) have been synthesized by reaction of the appropriate  $\alpha$ -ketosulphides of benzothiazole, *i.e.* 1-(benzothiazolyl-2-thio)-propanone<sup>14</sup> and/or 2-(benzothiazolyl-2-thio)-1-phenyl-ethanone,<sup>13</sup> with allylic carbonates in the presence of palladium acetate and triphenyl phosphine as catalysts. The reactions, carried out in dichloromethane under nitrogen at room temperature, yield the corresponding  $\alpha$ , and  $\alpha$ , $\alpha$ -diallyllated ketosulphides, showing the expected <sup>1</sup>H,<sup>13</sup>C NMR, IR and mass spectra. The latter, by reduction with sodium borohydride in isopropanol, directly afford the corresponding episulphides (50-90 %), together with 2hydroxybenzothiazole, as by product, easily discharged by washing the ethereal mixtures with a sodium carbonate (10 %) solution, (scheme 1).<sup>14</sup>

As previously reported by us,<sup>15</sup> this process is characteristic for  $\beta$ -hydroxy sulphides of benzothiazole. In fact, other  $\beta$ -hydroxy sulphides do not react, under the same reaction conditions, to give episulphides.

Scheme 1



R= Me, Ph; R'= H, Et, Ph

All the intermediates and episulphides have been isolated and fully characterized by physical and spectral data, as reported for one of them in the experimental section.

Typical experimental conditions for the conversion of the episulphides into dienes and trienes are as follows: catalytic amounts of aminium salts (A-B) are rapidly added to freshly distilled methylene chloride solutions of allyl and diallyl episulphides (1-6), while stirring at room temperature. The intensely blue or green colour of the solutions, depending on the aminium salts used, fades, with the exception for substrate 4, within a few minutes. Analyses of the reaction mixtures, monitored by TLC, GC, GC/MS, and <sup>1</sup>H-NMR spectroscopy until completion, reveal the disappearance of the starting materials and the formation of new products 7-12, together with trace amounts of the corresponding amines, eq.1.

1:  $R^1 = H$ ,  $R^2 = C_6H_5$ ,  $R^3 = R^4 = allyl$ ; 2:  $R^1 = R^4 = H$ ,  $R^2 = C_6H_5$ ,  $R^3 = CH_2(CH_3)C=CH_2$ ; 3:  $R^1 = H$ ,  $R^2 = C_6H_5$ ,  $R^3 = R^4 = CH_2CH=CHCH_2CH_3$ ; 4:  $R^1 = H$ ,  $R^2 = CH_3$ ,  $R^3 = R^4 = cinnamyl$ ; 5:  $R^1 = R^4 = H$ ,  $R^2 = C_6H_5$ ,  $R^3 = cinnamyl$ ; 6:  $R^1 = R^4 = H$ ,  $R^2 = C_6H_5$ ,  $R^3 = allyl$ .

Data concerning the experimental conditions of the desulphurization of representative episulphides, together with the physical and spectral data of the reaction products are reported in the experimental section.

Aminium salts,  $\hat{A}$ ,  $\hat{B}$ , have been found to efficiently promote a great variety of reactions on electron rich substrates, and in most of the studied cases, 10,16-18 it was ascertained that the role of the aminium salts is as one-electron oxidants, acting as initiators in cation-radical chain mechanisms, modelled upon Ledwith<sup>16</sup> and Nelsen's <sup>17</sup> proposals. However, it has also been claimed that the real function of aminium salts might be to trigger an acid catalyzed process. <sup>10d,19</sup>

In our case, the mechanism operating in this synthetic procedure might be rationalized on the basis of the peculiar features of the reagents involved. In fact, the powerful aminium salt oxidants can induce electron-transfer reactions on substrates 1-6 with the formation of the corresponding radical cations  $(1-6)^+$  and neutral amines,<sup>9</sup> scheme 2.





The efficiency of this initiation step, strictly related to the higher (aromatic substituted ones 1-3,5,6), or minor (4) susceptibility of the episulphides to oxidation by an electron-transfer pathway, directly influences the rate, but not the overall process. In fact, even in the case in which this initiation step was strongly endothermic, as with 4, the requirement that the intermediate radical cations could irreversibly evolve into different species, appearsto be more fundamentalthan the endothermicity. Thus, in our opinion, the driving reaction force, that could account for the experimental results, is the subsequent isomerization of the closed radical cations into the corresponding ring opened ones, followed by the desulphurization process, with the contemporary formation of the unsaturated radical cations. Finally, these latter afford the reaction products by an electron transfer process with the starting episulphides, as the more plausible termination step.

Since no other products than dienes and trienes are observed, it is of interest to notice that, in particular with diallyl thiiranes 1-3, showing more than one oxidizable site, the stereochemistry of the double bonds are preserved.

The chemical proof, accounting for such a mechanism, derive from the following experimental observations: (a) addition to the reaction solutions of equivalent amounts of aminium salts and 1,4-diazabicylo [2,2,2] octane (DABCO)  $[E^{red} = 0.64 \text{ V}. vs \text{ SCE}]^{20}$  inhibits the desulphurization of the episulphides. This inhibition, in our opinion, is due to a faster electron-transfer process between A or B and DABCO, rather than to its basic property. In fact, similar reactions, carried out in the presence of a non oxidizable base, with reactivity restricted to protons, such as 2,6-di-tert-butyl-pyridine (DBP) [E<sup>red</sup>= 1.85 V. vs SCE],<sup>17,18</sup> in molar excess over the aminium salts initiators, appear retarded, but not inhibited; (b) treatment of methylene chloride solutions of 3phenyl-2,2-bis[2-propen-1-yl], or 2-(E)-3-phenyl-2,2-bis[2-penten-1-yl]-thiiranes 1,3 with catalytic amounts of aminium salt A (10 mol %) afford, within 10 mins, the corresponding 4-(phenyl)methylidene-1,6-heptadiene 7. and (3E),(8E)-6-phenyl)methylidene-undecadiene 9. Similar reactions, performed on methylene chloride solutions of (3E)-3-phenyl-2-[3-phenyl-2-propen-1-yl] thiirane 5, and 3-phenyl-2-[2-propen-1-yl] thiirane 6, as mixtures of the (Z) and (E) isomers in the ratios 90/10 and 80/20, afford mixtures of the corresponding dienes 11 and 12 in the ratios 70/30 and 55/45, respectively. These results have been recorded by <sup>1</sup>H-NMR spectroscopy on deuterochloroform solutions, obtained as follows. The original methylene chloride solutions, after total conversion of the episulphides determined by tlc, are quenched with a methylene chloride solution of **DABCO** (10%). The solvent is removed in *vacuo*, and the residues, dissolved in deuterochloroform, are rapidly analyzed by <sup>1</sup>H-NMR spectroscopy. Increasing amounts of the more stable (E) isomers are observed avoiding the quenching, or adding, directly in the NMR test tube, a small amount of the aminium salt; (c) the conversion of the non aromatic episulphide, i.e, (2E)-3-methyl-2,2-bis[3-phenyl-2-propen-1-yl]thiirane 4, the much less susceptible one to oxidation, into the corresponding 4-(methyl)methylidene-1,6-diphenyl-1,5hexadiene 10 requires, not only catalytic amounts of the more powerful aminium salt oxidant, namely, B, but also a longer reaction time (overnight).

Stereochemical studies have been performed on 3-phenyl-2-[2-methyl-2-propen-1-yl] thiirane 2, obtained, as depicted in the scheme 1, as pure (Z) isomer. The geometry of this episulphide has been established by its conversion to the corresponding (Z)-1-phenyl-4-methyl-1,4-pentadiene 8, by reaction with 3-methyl-2-selenoxobenzothiazole, occurring, as reported, stereospecifically, 7,14

Treatment of a methylene chloride solution of 2 with catalytic amounts of aminium salts A or B (10 mol %) leads to mixtures of both (Z) and (E) dienes, whose ratios range between 70/30 and 50/50 in relation to the oxidizing power of the aminium salts. However, the same reaction, performed in deuterochloroform in the presence of a reduced amount of the initiator A (1 mol %) and followed by <sup>1</sup>H-NMR, envisages a slower (2 h), but stereospecific conversion into the (Z)-isomer 8. Furthermore, increasing amounts of the aminium salt.

directly added to the NMR test tube, evidentiate the isomerization of the previous (Z)-diene into the more stable (E)-isomer.

Conventional aromatic episulphides, such as *trans* or *cis*-2,3-diphenyl thiiranes, and 2-phenylthiirane, by reaction with catalytic amounts of aminium salts,<sup>9</sup> afford the corresponding alkenes (*trans, cis/trans* mixture of stilbenes and phenylethylene), respectively, in a time scale consistent with that observed for the other aromatic episulphides. Furthermore, the desulphurization of *cis*-stilbene thiirane, and the following isomerization of *cis*-stilbene into the more stable *trans*-isomer can be controlled by using a reduced amount of aminium salt as initiator.

In conclusion, the easy procedure, and the high yields of the isolated reaction products are evidence of the potential of this method as a valuable synthetic tool for the preparation of several functionalized dienes and trienes.

## EXPERIMENTAL SECTION

Melting points were determined on an electrothermal apparatus and are uncorrected. <sup>1</sup>H-and <sup>13</sup>C-NMR spectra were recorded on a Brucker-500 MHz instrument, chemical shifts are reported in parts per million ( $\delta$ ), solvent CDCl<sub>3</sub>. IR and MS spectra were performed, respectively, on a Perkin-Elmer FT-1710 (KBr pellets), and on Hewlett-Packard GC/Mass MSD 5970 instruments. GC analyses were carried out on a Hewlett-Packard gas chromatograph, model 5750 B, on columns (1/4"x15 feet) packed with SP 2100 (5% on Supelcoport 100/120). TLCs were performed on silica gel sheets with fluorescent indicator (Stratocrom SIF-Carlo Erba). Dichloromethane was purified by washing with sulphuric acid solution, distillation over calcium hydride and then stored in the dark under a nitrogen atmosphere and over molecular sieves. The starting materials 1-6 have been synthesized according to the procedure reported in ref. 14. DABCO, DBP, commercial samples from Aldrich Co, have been dried before use. Aminium salts A, B have been synthesized following the procedure reported in refs 11,12.

#### Synthesis of (Z)-2-(2-methyl-2-propen-1-yl)-3-phenyl thiirane (2)

To a solution of 1-phenyl-2-(benzothiazolyl-2-thio)-4-methyl-4-penten-1-one (474 mg, 1.4 mmol) in isopropanol (10 ml) was added portionwise, under stirring at room temperature, an equimolecular amount of sodium borohydryde (53 mg, 1.4 mmol). The suspension was monitored by tlc (petroleum ether/ethylacetate 10/1, v/v) until the total disappearance of the ketosulphide (24 h). The solvent was removed in vacuo and the residue, dissolved in diethyl ether (30 ml). The ethereal solution was washed twice with a sodium carbonate solution (5 %), then dried over dry sodium sulphate. The solvent removed *in vacuo* leaves, almost pure, 200 mg (75 %) of the episulphide (Z)-2-(2-methyl-2-propen-1-yl)-3-phenyl thiirane **2**.

The spectral data relating to 1-phenyl-2-(benzothiazolyl-2-thio)-4-methyl-4-penten-1-one and thiirane 2 are reported in succession::

<sup>1</sup>H-NMR: 1.79-1.82 (3H, m, allylic CH<sub>3</sub>); 2.69 (1H, dd, J = 14.6 and 7.1 Hz, allylic CH<sub>2</sub>); 2.95 (1H, dd, J = 14.6 and 7.6 Hz, allylic CH<sub>2</sub>); 4.78-4.81 (2H, m, vinyl protons); 5.99 (1H, t, 7.6 Hz, CHCO); 7.25-7.35 (1H, m, aromatic proton); 7.37-7.42 (1H, m, aromatic proton); 7.43-7.49 (2H, m, aromatic protons); 7.52-7.60 (1H, m, aromatic proton); 7.70-7.75 (1H, m, aromatic proton); 7.77-7.82 (1H, m, aromatic proton); 8.09-8.15 (2H, m, aromatic protons). <sup>13</sup>C-NMR: 22.5, 40.0, 48.9, 113.0, 114.5, 121.1, 121.6, 125.5, 126.0, 128.7, 128.8, 133.5, 135.8, 141.2, 152.7, 164.6, 196.5. ir (liquid film)  $\upsilon$ : 901, 1652, 1686, 1738 cm<sup>-1</sup>.

<sup>1</sup>H-NMR: 1.64-1.68 (3H, m, CH<sub>3</sub>); 1.91 (1H, dd, J= 15.8 and 8.0 Hz, allylic CH<sub>2</sub>); 2.20 (1H, dd, J= 15.8 and 5.6 Hz, allylic CH<sub>2</sub>); 3.26 (1H, ddd, J= 8.0, 7.0 and 5.6 Hz, PhCH(S)CH); 4.17 (1H, d, J= 7.0 Hz, PhC<u>H</u>(S)CH); 4.67-4.71 (1H, m, vinyl proton), 4.72 (1H, m, vinyl proton); 7.24-7.39 (5H, m, aromatic protons). <sup>13</sup>C-NMR: 22.7, 38.6, 40.2, 42.3, 111.2, 127.4, 127.9, 129.2, 135.4, 143.5. MS (olefin) (m/e %) 158 (18), 143 (100), 129 (56), 128 (68), 115 (52), 91 (21), 80 (16), 77 (12), 65 (10), 51 (11). The geometry of this episulphide was established by its conversion into the corresponding (Z)-olefin by reaction with 3-methyl-2-selenoxobenzothiazole.<sup>9</sup> Thus, 3-methyl-2-selenoxobenzothiazole (205 mg, 0.9 mmol) and 2 (171 mg, 0.9 mmol), dissolved in 5 ml of dichloromethane, containing trifluoroacetic acid (207 mg, 1.82 mmol), were refluxed for 2h. After filtration of the selenium and evaporation of the solvent, the residue was chromatographed on silica gel (eluant: petroleum ether/ethyl acetate 5/1, v/v) to give a pale yellow oil (137 mg,

72% yield), which shows spectral data consistent with that of the olefin 8, synthesized by us through the aminium salt-induced procedure.

## Conversion of episulphides 1-6 into unsaturated derivatives: general procedure

The required catalytic amount of aminium salt A or B (83-116 mg, 0.1 mmol) is rapidly added, at room temperature, to a stirred solution of the appropriate episulphide 1-6 (176-306 mg, 1mmol) in dry methylene chloride (10 ml). The intensely blue or green colour of the solution, depending on the aminium salt employed, fades, with the exception of substrate 4, within a few minutes. The progress of the reactions have been monitored by TLC, GC and GC/MS until completion. The solvent was removed in *vacuo*, and the reaction products 7-12, isolated by column chromatography (silica gel, light petroleum ether/ethylacetate 10/1 v/v), as pale yellow oils (114-215 mg, 80 % yield) fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, mass spectroscopy and comparison with authentic samples, synthesized as reported in the reference 14.

Product isolation, by column chromatography, simply entailed removal of the amines as by product, so that in most of the cases yields of the isolated products were just a trifle lower than gc yields.

## 4-(phenyl)methyliden-1,6-heptadiene (7)

<sup>1</sup>H-NMR: 2.91 (2H, dq, J = 6.9, 1.3 Hz, allylic CH<sub>2</sub>), 2.98 (2H, d, J = 6.5 Hz, allylic CH<sub>2</sub>), 5.07-5.16 (4H, m, CH=CH<sub>2</sub>), 5.82-5.93 (2H, m, CH=CH<sub>2</sub>), 6.40 (1H, s, CHPh), 7.16-7.37 (5H, m, aromatic protons). <sup>13</sup>C-NMR: 35.3, 41.5, 116.1, 116.6, 118.4, 126.3, 127.2, 128.1, 128.4, 135.9, 136.3, 144.0. MS (m/e %): 184 (M<sup>+</sup>,8), 169 (14), 155 (12), 143 (95), 128 (100), 115 (62), 91 (50), 77 (25), 65 (22), 51 (16), 39 (35).

### (Z)-1-phenyl-4-methyl-1,4-pentadiene (8)

<sup>1</sup>H-NMR: 1.76 (3H, m, allylic CH<sub>3</sub>); 2.97 (2H, d, J = 7.6 Hz, allylic CH<sub>2</sub>); 4.77-4.82 (2H, m, C=CH<sub>2</sub>); 5.74 (1H, dt, J = 11.5 and 7.6 Hz, C<u>H</u>=CHPh); 6.54 (1H, d, J = 11.5 Hz, CH=C<u>H</u>Ph); 7.20-7.40 (5H, m, aromatic protons). <sup>13</sup>C-NMR: 22.9, 36.6, 110.5, 126.6, 128.1, 128.6, 129.7, 130.3, 137.3, 144.6. MS (m/e %): 158 (M<sup>+</sup> 18), 143 (100), 129 (56), 128 (68), 115 (52), 91 (21), 80 (16), 77 (12), 65 (10), 51 (11). The same spectral data have been observed for the olefin synthesized as reported above. The isomerization into the more stable (E) isomer has been performend by addition to the reaction solution of increasing amounts of the aminium salt. After quenching, the solution worked up as usual, was analysed as deuterochloroform solution by <sup>1</sup>H-NMR spectroscopy: 1.41 (3H, m, allylic CH<sub>3</sub>); 2.88 (2H, d, J = 7.1 Hz, allylic CH<sub>2</sub>); 4.75-4.80 (2H, m, C=CH<sub>2</sub>); 6.21 (1H, dt, J = 15.8 and 7.1 Hz, C<u>H</u>=CHPh); 6.40 (1H, d, J= 15.8 Hz, CH=C<u>H</u>Ph); 7.25-7.40 (5H, m, aromatic protons).

### (3E,8E)-6-(phenyl)methyliden-undecadiene (9)

<sup>1</sup>H-NMR: 0.97 (3H, t, J = 7.5 Hz, CH<sub>3</sub>); 0.98 (3H, t, J = 7.5 Hz, CH<sub>3</sub>); 1.98-2.10 (4H, m, CH<sub>2</sub>CH<sub>3</sub>); 2.82 (2H, dt, J= 6.7, 1.1 Hz, allylic CH<sub>2</sub>); 2.88 (2H, d, J= 6.1 Hz, allylic CH<sub>2</sub>); 5.39-5.47 (2H, m, EtCH=C<u>H</u>); 5.48-5.57 (2H, m, EtC<u>H</u>=CH) [irradiating at  $\delta$  = 2.04 ppm: 5.51 (1H, d, J= 15.2 Hz) and 5.53 (1H, d, J= 15.2 Hz)]; 6.32 (1H, s, C<u>H</u>Ph); 7.14-7.35 (5H, m, aromatic protons). <sup>13</sup>C-NMR: 13.9, 25.7, 29.7, 34.1, 40.3, 98.2, 126.0, 126.1, 126.2, 126.6, 128.0, 128.5, 133.8, 134.3, 140.7; MS (m/e %): 240 (M<sup>+</sup>,10), 211, (4), 171 (60), 155 (17), 141 (17), 128 (42), 115 (30), 91 (100), 77 (13), 55 (13), 41 (42).

### 4-(methyl)methyliden-1,7-diphenyl-1,6-heptadiene (10)

<sup>1</sup>H-NMR: 1.87 (3H, d, J = 6.8 Hz, methyl); 2.92 (2H, d, J = 7.1 Hz, allylic CH<sub>2</sub>); 2.97 (2H, d, J = 6.8 Hz, allylic CH<sub>2</sub>); 5.42 (1H, q, J = 6.8 Hz, C<u>H</u>Me); 6.11-6.28 (2H, m, C<u>H</u>=CHPh); 6.38 (1H, d, J= 15.8 Hz, CH=C<u>H</u>Ph); 6.39 (1H, d, J = 15.8 Hz, CH=C<u>H</u>Ph); 7.10-7.45 (10H, m, aromatic protons), MS (m/e %) (M<sup>+</sup>, 274), 205 (42), 183 (69), 155 (79), 115 (79), 91 (100), 77 (21), 65 (15).

(1E, 4E) and (1Z, 4E) 1,5-diphenylpentadiene (11).

The mixture of both isomers, obtained in ca. 70:30 ratio, was analyzed as deuterochloroform solution by <sup>1</sup>H-NMR.

<sup>1</sup>H-NMR: 3.14 (0.6H, tt, J= 6.6, 1.3 Hz, CH<sub>2</sub>, due to E-E isomer); 3.24 (1.4H, ddt, J= 7.7, 6.2, 1.6 Hz, CH<sub>2</sub>, due to E-Z isomer); 5.60 (0.7H, dt, J= 11.5, 7.7 Hz, CH=CHPh, due to E-Z isomer); 6.31 (0.6H, dt, J= 15.9, 6.6 Hz, CH=CHPh, due to E-E isomer); 6.32 (0.7H, dt, J= 15.9, 6.2 Hz, CH=CHPh, due to E-Z isomer); 6.49 (0.6H, d, J= 15.9 Hz, CH=CHPh, due to E-E isomer); 6.50 (0.7H, d, J= 15.9 Hz, CH=CHPh, due to E-Z isomer); 6.59 (0.7H, d, J= 11.5 Hz, CH=CHPh, due to E-Z isomer); 7.20-7.50 (10H, m, aromatic protons).

### (Z) and (E)-1-phenyl-1,4-pentadiene (12).

The mixture of both isomers, obtained in ca. 55:45 ratio, was analyzed as deuterochloroform solution as above.

<sup>1</sup>H-NMR: 2.96 (0.90H, tq, J= 6.6, 1.5 Hz, allylic CH<sub>2</sub>, due to E isomer); 3.06 (1.1H, ddq, J= 7.6, 6.0, 1.6 Hz, allylic CH<sub>2</sub>, due to Z isomer); 5.03-5.08 (1H, m, CH=C<u>H<sub>2</sub></u>); 5.11 (0.45H, dq, J= 17.1, 1.7 Hz, CH=C<u>H<sub>2</sub></u>, due to E isomer); 5.12 (0.55H, dq, J= 17.2, 1.8 Hz, CH=C<u>H<sub>2</sub></u>, due to Z isomer); 5.70 (0.55, dt, J= 11.6, 7.6 Hz, C<u>H</u>=CHPh, due to Z isomer); 5.85-5.96 (1H, m, C<u>H</u>=CH<sub>2</sub>); 6.23 (0.45H, dt, J= 15.8, 6.6 Hz, C<u>H</u>=CHPh, due to E isomer); 6.41 (0.45H, d, J= 15.8 Hz, CH=C<u>H</u>Ph, due to E isomer); 6.52 (0.55H, d, J= 11.6 Hz, CH=C<u>H</u>Ph, due to Z isomer); 7.20-7.45 (5H, m, aromatic protons).

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