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A Novel and Stereoselective Synthesis of (*E*)-1-Acylbutadienes from 1-Chloroalkyl Phenyl Sulfoxides and 4-(Phenylthio)butanal through α,β -Epoxy Sulfoxides¹⁾

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The alkylation of 4-(phenylthio)butanal with 1-chloroalkyl phenyl sulfoxides gave chlorohydrins, which were treated with excess thiophenolate in *tert*-butanol to afford α,δ -bis(phenylthio)ketones in good overall yield. On treatment with *m*-chloroperbenzoic acid followed by pyrolysis in refluxing toluene, the bis(phenylthio)ketones gave 1-acylbutadienes in moderate yield with high *E*-stereoselectivity.

Keywords— α,β -epoxy sulfoxide; sulfoxide; acylbutadiene; butadiene; acyl anion; vinyl cation

α,β -Unsaturated carbonyl compounds are quite useful in various synthetic reactions such as the Diels–Alder reaction²⁾ and Michael-type reactions.³⁾ Further addition of an unsaturation to the α,β -unsaturated carbonyl compounds gives straight dienone-type compounds, which show more interesting chemical properties. Recently, these compounds were used in the synthesis of alkenylpyrroles and indoles.⁴⁾ Several useful methods for the synthesis of straight dienone-type carbonyl compounds have been reported so far⁵⁾; however, extensive development of new synthetic procedures is desirable in this area of chemistry.

Recently, we have reported a new and versatile procedure for synthesizing several α,β -unsaturated carbonyl compounds with carbon homologation through α,β -epoxy sulfoxides.⁶⁾ In the course of studies on the new synthetic method for unsaturated carbonyl compounds

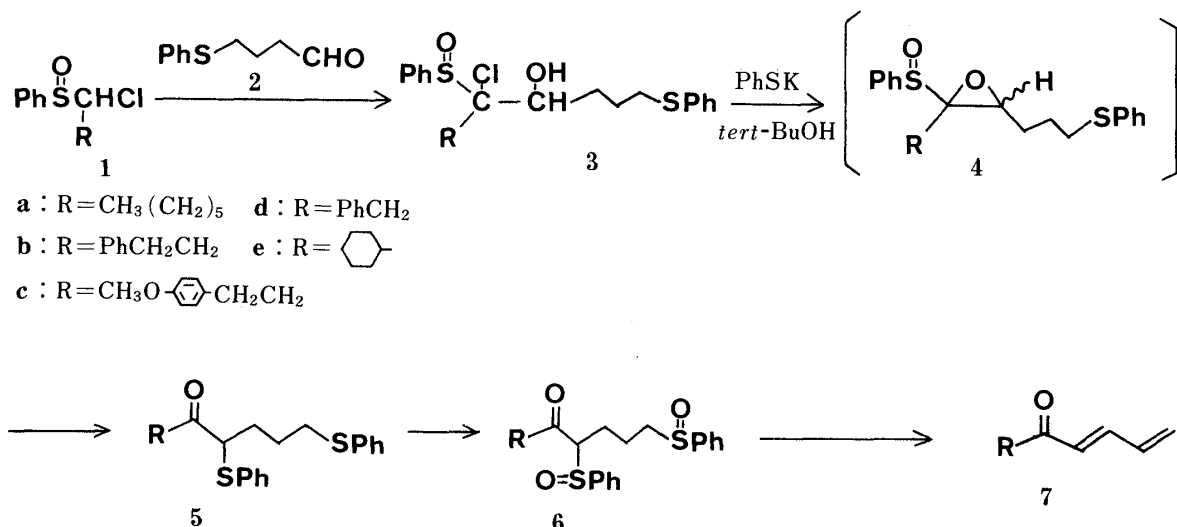


Chart 1

through α,β -epoxy sulfoxides, a new and efficient procedure for a stereoselective synthesis of (*E*)-1-acylbutadienes (**7**) from 1-chloroalkyl phenyl sulfoxides (**1**) and 4-(phenylthio)butanal (**2**)⁷ through α,β -epoxy sulfoxides (**4**) was found. The procedure is summarized in Chart 1.

The alkylation of 4-(phenylthio)butanal (**2**) with 1-chloroheptyl phenyl sulfoxide (**1a**) by using lithium diisopropylamide (LDA) as a base gave chlorohydrins (**3a-L**,⁸) 30%; **3a-P**,⁸) 50%). Treatment of these chlorohydrins (**3a**) with 30% aq. KOH or potassium *tert*-butoxide in *tert*-butanol/tetrahydrofuran (THF) at room temperature gave low yields of the desired α,β -epoxy sulfoxides (**4a**). This result implied the unstable nature of the α,β -epoxy sulfoxides (**4a**). To overcome this problem, the chlorohydrin (**3a-P**) was treated with base in the presence of the nucleophile, potassium thiophenolate (2.2 eq), at room temperature for 10 min. In this reaction the resulting **4a** quickly reacted with thiophenolate^{6b,9}) to afford the desired 1,4-

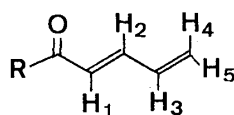
TABLE I. Preparation of 1-Acylbutadienes from 1-(Phenylthio)butanal and 1-Chloroalkyl Phenyl Sulfoxides through α,β -Epoxy Sulfoxides

	1 (R)	Yield (%) ^{a)}			(E)-1-Acylbutadiene (7)	
		3	5	6		
1a	Hexyl	L 30 P 50	69 75	59		64
1b	Phenethyl	L 44 P 49	67 80	39		51
1c	4-Methoxyphenethyl	L 32 P 33	65 87	55		40
1d	Benzyl	L 29 P 56	46 58	59		47
1e	Cyclohexyl	L 34 P 53	65 81	50		65

a) Isolated yield after silica gel column chromatography.

TABLE II. Coupling Constants of Vinylic Protons of 1-Acylbutadienes (7)

		Coupling constants (Hz)				
7 (R)		$J_{H_1H_2}$	$J_{H_2H_3}$	$J_{H_3H_4}$	$J_{H_3H_5}$	$J_{H_4H_5}$
7a	Hexyl	15.6	11.0	16.9	10.0	1.5
7b	Phenethyl	15.7	10.8	16.2	9.9	1.4
7c	4-Methoxyphenethyl	15.6	10.8	16.9	10.1	1.4
7d	Benzyl	16.5	10.4	17.0	9.9	1.7
7e	Cyclohexyl	16.1	10.7	16.1	10.7	1.5



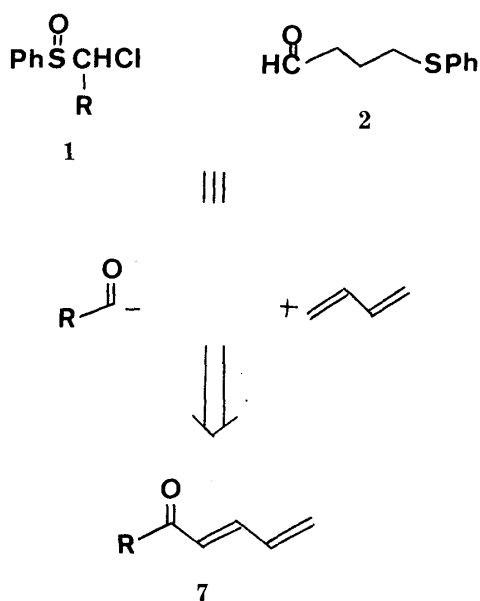


Fig. 1

bis(phenylthio)-5-undecanone (**5a**) in 75% yield. The two diastereomers of the chlorohydrin (**3a**) showed almost the same reactivity toward thiophenolate to afford the bis(phenylthio)ketone (**5a**).

Oxidation of the sulfur groups of **5a** with *m*-chloroperbenzoic acid (*m*-CPBA) gave the isomeric mixture of sulfoxides (**6a**) in 59% yield. Pyrolysis of the sulfoxides (**6a**) in refluxing toluene under an N_2 atmosphere for 45 min followed by silica gel column chromatography afforded the expected 1,3-undecadien-5-one (**7a**)^{5d} in 64% yield as a single product. The results of the preparation of 1-acylbutadienes through α,β -epoxy sulfoxides are summarized in Table I.

The stereochemistry of the dienes (**7**) was established by careful analyses of the 400 MHz $^1\text{H-NMR}$ spectra of **7** as shown in Table II. The values observed for the vicinal coupling constants of vinyl protons ($J_{\text{H}_1-\text{H}_2}$; $J = 15.6\text{--}16.5\text{ Hz}$) were characteristic of *trans* double bonds.

Though the yields are moderate, the overall simplicity and mildness of the operation are characteristic of this new and straightforward procedure, which should be useful for the synthesis of 1-acylbutadienes as well as other straight dienone-type unsaturated carbonyl compounds. It is interesting to note that in this procedure 1-chloroalkyl phenyl sulfoxides (**1**) and 4-(phenylthio)butanal (**2**) are the synthetic equivalents of an acyl anion and of a vinyl cation of butadiene, respectively, as shown in Fig. 1.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured directly on a KBr plate or KBr disks with a JASCO IR-810 spectrometer. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were measured in CDCl_3 solution with a JEOL FX-100 and GX-400 spectrometer using Me_4Si as an internal standard. Electron impact mass spectra (MS) were obtained on a Hitachi M-80B double focusing spectrometer at 70 eV by direct insertion. Silica gel C-200 (Wako Pure Chemical Industries) containing 2% fluorescence reagent 254 and quartz column were used for column chromatography and the products having ultraviolet (UV) absorption were detected by UV irradiation.

General Procedure for the Preparation of α,δ -Bis(phenylthio)-ketones (5a–e**)**—The synthesis of 1,4-bis(phenylthio)-5-undecanone (**5a**) is described as an example. A solution of 1-chloroheptyl phenyl sulfoxide (**1a**; 2 mmol) in 1 ml of dry THF was added dropwise through a syringe to a solution of LDA (2.1 mmol) in dry THF (4 ml) at -70°C under N_2 with stirring. The solution was stirred at -70°C for 10 min and then a solution of 4-(phenylthio)butanal (**2**; 2.2 mmol) in 1 ml of dry THF was added and the reaction mixture was stirred for 10 min. The reaction was quenched with sat. aq. NH_4Cl and the whole was extracted with benzene. The products were separated

by silica gel column chromatography (hexane:AcOEt=10:1) to give **3a-L** and **3a-P** in 30% and 50% yields, respectively. **3a-L**: Colorless oil. IR (neat): 3375 (OH), 1035 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 0.92 (3H, t, $J=6$ Hz), 1.12–2.30 (14H, m), 2.60–3.04 (2H, m), 3.68–3.98 (1H, m), 4.89 (1H, s), 7.09–7.86 (10H, m). MS m/z (%): 312 ($[\text{M}-\text{PhSOH}]^+$, 1), 180 (9), 126 (100).

3a-P: Colorless oil. IR (neat): 3400 (OH), 1045 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 0.90 (3H, t, $J=6$ Hz), 1.04–2.12 (14H, m), 2.68–3.12 (3H, m), 3.56–3.84 (1H, m), 7.08–7.92 (10H, m). MS m/z (%): 312 ($[\text{M}-\text{PhSOH}]^+$, 12), 277 (69), 186 (22), 136 (62), 125 (85), 97 (21), 78 (100).

A solution of **3a-P** (2.35 mmol) in THF was added to a mixture of PhSH (5.17 mmol) and *tert*-BuOK (5.17 mmol) in *tert*-BuOH (20 ml) at room temperature, and the mixture was stirred for 10 min. The reaction mixture was neutralized with NH_4Cl and the solvents were evaporated off. The residue was extracted with benzene and the extract was washed with 10% aq. NaOH followed by sat. aq. NH_4Cl , and then dried over Na_2SO_4 . The product was purified by silica gel column chromatography (hexane:AcOEt=50:1) to give **5a** as a colorless oil in 75% yield. IR (neat): 1710 (CO) cm^{-1} . $^1\text{H-NMR}$ δ : 0.87 (3H, t, $J=7$ Hz), 1.08–2.06 (12H, m), 2.44–2.68 (2H, m), 2.92 (2H, t, $J=6$ Hz), 3.60 (1H, t, $J=7$ Hz), 7.08–7.24 (10H, m). MS m/z (%): 386 (M^+ , 15), 277 ($[\text{M}-\text{PhS}]^+$, 70), 273 ($[\text{M}-\text{C}_6\text{H}_{13}\text{CO}]^+$, 73), 163 (100); Found: m/z 386.1764. Calcd for $\text{C}_{23}\text{H}_{30}\text{OS}_2$: M, 386.1791.

1-Phenyl-4,7-bis(phenylthio)-3-heptanone (5b)—Chlorohydrin (**3b-L**): Colorless oil. IR (neat): 3360 (OH), 1050 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.24–3.44 (10H, m), 3.76–4.00 (1H, m), 4.28–4.92 (1H, m), 7.00–8.00 (15H, m). MS m/z (%): 332 ($[\text{M}-\text{PhSOH}]^+$, 3), 297 (3), 136 (7), 126 (62), 109 (27), 91 (100). **3b-P**: Colorless crystals. mp 108–110 °C (AcOEt–hexane). IR (KBr): 3400 (OH), 1040 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.40–1.68 (7H, m), 1.72–2.16 (4H, m), 3.48–3.80 (1H, m), 7.08–7.92 (15H, m). MS m/z (%): 332 ($[\text{M}-\text{PhSOH}]^+$, 3), 297 (11), 126 (65), 109 (47), 78 (100); Found: C, 65.41; H, 5.88; S, 13.89%. Calcd for $\text{C}_{25}\text{H}_{27}\text{ClO}_2\text{S}_2$: C, 65.40; H, 5.94; S, 13.97%.

5b: Colorless oil. IR (neat): 1710 (CO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.36–2.04 (4H, m), 2.40–3.60 (7H, m), 6.90–7.44 (15H, m). MS m/z (%): 406 (M^+ , 18), 297 ($[\text{M}-\text{PhS}]^+$, 75), 273 ($[\text{M}-\text{PhCH}_2\text{CH}_2\text{CO}]^+$, 72), 163 (95), 123 (94), 91 (100); Found: m/z 406.1384. Calcd for $\text{C}_{25}\text{H}_{26}\text{OS}_2$: M, 406.1345.

1-(4-Methoxyphenyl)-4,7-bis(phenylthio)-3-heptanone (5c)—Chlorohydrin (**3c-L**): Colorless oil. IR (neat): 3370 (OH), 1035 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.20–2.36 (11H, m), 3.80 (3H, s), 4.10–4.96 (1H, m), 6.68–7.96 (14H, m). MS m/z (%): 362 ($[\text{M}-\text{PhSOH}]^+$, 2), 182 (23), 147 (48), 121 (100). **3c-P**: Colorless crystals. mp 102–104 °C (AcOEt–hexane). IR (KBr): 3340 (OH), 1035 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.28–3.10 (11H, m), 3.48–3.88 (1H, m), 3.78 (3H, s), 6.76–7.92 (14H, m). MS m/z (%): 362 ($[\text{M}-\text{PhSOH}]^+$, 11), 344 (52), 199 (62), 121 (100); Found: C, 63.87; H, 5.89; S, 13.01%. Calcd for $\text{C}_{26}\text{H}_{29}\text{ClO}_3\text{S}_2$: C, 63.84; H, 5.99; S, 13.11%.

5c: Colorless oil. IR (neat): 1705 (CO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.40–1.96 (4H, m), 2.48–3.26 (6H, m), 3.51 (1H, t, $J=7$ Hz), 3.76 (3H, s), 6.68–7.46 (14H, m). MS m/z (%): 436 (M^+ , 13), 327 ($[\text{M}-\text{PhS}]^+$, 34), 273 ($[\text{M}-\text{MeOC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}]^+$, 39), 163 (56), 121 (100); Found: m/z 436.1513. Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_2\text{S}_2$: M, 436.1497.

1-Phenyl-3,6-bis(phenylthio)-2-hexanone (5d)—Chlorohydrin (**3d-L**): Colorless oil. IR (neat): 3360 (OH), 1020 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.28–2.14 (4H, m), 2.85 (2H, t, $J=6$ Hz), 3.36 (1H, d, $J=15$ Hz), 3.80–4.04 (1H, m), 4.15 (1H, d, $J=15$ Hz), 5.22 (1H, s), 7.04–7.88 (15H, m). MS m/z (%): 318 ($[\text{M}-\text{PhSOH}]^+$, 4), 283 (28), 126 (60), 109 (45), 78 (100). **3d-P**: Colorless crystals. mp 108–110 °C (AcOEt–hexane). IR (KBr): 3400 (OH), 1040 cm^{-1} . $^1\text{H-NMR}$ δ : 1.20–2.52 (6H, m), 2.72–3.16 (2H, m), 3.32 (1H, d, $J=15$ Hz), 3.54 (1H, d, $J=15$ Hz), 7.08–7.88 (15H, m). MS m/z (%): 318 ($[\text{M}-\text{PhSOH}]^+$, 9), 283 (95), 173 (47), 136 (60), 125 (79), 109 (73), 77 (100); Found: C, 64.91; H, 5.66; S, 14.44%. Calcd for $\text{C}_{24}\text{H}_{25}\text{ClO}_2\text{S}_2$: C, 64.76; H, 5.67; S, 14.41%.

5d: Colorless oil. IR (neat): 1710 (CO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.40–2.00 (4H, m), 2.79 (2H, t, $J=7$ Hz), 3.65 (1H, t, $J=7$ Hz), 3.87 (2H, s), 7.03–7.48 (15H, m). MS m/z (%): 392 (M^+ , 13), 301 ($[\text{M}-\text{PhCH}_2]^+$, 15), 283 ($[\text{M}-\text{PhS}]^+$, 19), 273 (69), 250 (11), 199 (36), 163 (100); Found: m/z 392.1253. Calcd for $\text{C}_{24}\text{H}_{24}\text{OS}_2$: M, 392.1240.

1-Cyclohexyl-2,5-bis(phenylthio)-1-pentanone (5e)—Chlorohydrin (**3e-L**): Colorless oil. IR (neat): 3400 (OH), 1050 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.08–3.10 (18H, m), 3.96–4.88 (1H, m), 7.08–7.94 (10H, m). MS m/z (%): 310 ($[\text{M}-\text{PhSOH}]^+$, 8), 250 (10), 218 (51), 126 (100). **3e-P**: Colorless crystals. mp 98–100 °C (AcOEt–hexane). IR (KBr): 3320 (OH), 1025 (SO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.08–2.76 (16H, m), 2.80–3.12 (2H, m), 3.48–3.88 (1H, m), 7.08–7.88 (10H, m). MS m/z (%): 344 (9), 310 ($[\text{M}-\text{PhSOH}]^+$, 12), 136 (56), 109 (50), 78 (100); Found: C, 63.30; H, 6.70; S, 14.59%. Calcd for $\text{C}_{23}\text{H}_{29}\text{ClO}_2\text{S}_2$: C, 63.20; H, 6.70; S, 14.67%.

5e: Colorless oil. IR (neat): 1710 (CO) cm^{-1} . $^1\text{H-NMR}$ δ : 1.04–2.08 (14H, m), 2.48–2.80 (1H, m), 2.89 (1H, t, $J=7$ Hz), 3.65 (1H, t, $J=7$ Hz), 7.00–7.56 (10H, m). MS m/z (%): 384 (M^+ , 21), 273 ($[\text{M}-\text{C}_6\text{H}_{11}\text{CO}]^+$, 100), 163 (82); Found: m/z 384.1587. Calcd for $\text{C}_{23}\text{H}_{28}\text{OS}_2$: M, 384.1594.

General Procedure for the Preparation of 1-Acylbutadienes (7a–e)—The synthesis of 1,3-undecadien-5-one (**7a**) is described as an example. *m*-CPBA (2 mmol) was added to a solution of **5a** (1 mmol) in CH_2Cl_2 (10 ml) at –60 °C with stirring. The temperature of the reaction mixture was allowed to rise to –40 °C. The reaction mixture was diluted with CH_2Cl_2 and washed with 10% aq. NaOH followed by sat. aq. NH_4Cl and then dried over Na_2SO_4 . The product was purified by silica gel column chromatography (hexane:AcOEt=1:1) to give a diastereomeric mixture of 1,4-bis(phenylsulfinyl)-5-undecanone (**6a**) as a colorless oil in 59% yield. A solution of **6a** (0.27 mmol) in dry toluene (3 ml) was refluxed under N_2 for 45 min. Evaporation of the solvent gave the residue, which was purified by silica gel column chromatography (hexane:AcOEt=50:1) to give **7a** as a light yellow oil in 64% yield. IR (neat):

1690, 1670, 1620, 1595 cm^{-1} . $^1\text{H-NMR}$ δ : 0.89 (3H, t, $J=7$ Hz), 1.29—1.33 (6H, m), 1.58—1.64 (3H, m), 2.57 (2H, t, $J=8$ Hz), 5.53 (1H, dd, $J=1.5$, 10.0 Hz), 5.66 (1H, dd, $J=1.5$, 16.9 Hz), 6.19 (1H, d, $J=15.6$ Hz), 6.46 (1H, ddd, $J=10.0$, 11.0, 16.9 Hz), 7.14 (1H, dd, $J=11.0$, 15.6 Hz). MS m/z (%): 166 (M^+ , 2), 96 (100), 81 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$, 85); Found: m/z 166.1323. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: M, 166.1290.

(E)-1-Phenyl-4,6-heptadien-3-one (7b)—Light yellow oil. IR (neat): 1690, 1670, 1625, 1595 cm^{-1} . $^1\text{H-NMR}$ δ : 2.86—2.98 (4H, m), 5.52 (1H, dd, $J=1.4$, 9.9 Hz), 5.63 (1H, dd, $J=1.4$, 16.2 Hz), 6.18 (1H, d, $J=15.7$ Hz), 6.44 (1H, ddd, $J=9.9$, 10.8, 16.2 Hz), 7.12 (1H, dd, $J=10.8$, 15.7 Hz). MS m/z (%): 186 (M^+ , 55), 159 (18), 105 ($[\text{M}-\text{C}_4\text{H}_5\text{CO}]^+$, 39), 95 ($[\text{M}-\text{PhCH}_2]^+$, 42), 91 ($[\text{M}-\text{C}_4\text{H}_5\text{COCH}_2]^+$, 56), 81 ($[\text{M}-\text{PhCH}_2\text{CH}_2]^+$, 100), 53 ($[\text{M}-\text{PhCH}_2\text{CH}_2\text{CO}]^+$, 67); Found: m/z 186.1024. Calcd for $\text{C}_{13}\text{H}_{14}\text{O}$: M, 186.1005.

(E)-1-(4-Methoxyphenyl)-4,6-heptadien-3-one (7c)—Light yellow oil. IR (neat): 1685, 1655, 1615, 1590 cm^{-1} . $^1\text{H-NMR}$ δ : 2.78—2.92 (4H, m), 3.78 (3H, s), 5.52 (1H, dd, $J=1.4$, 10.1 Hz), 5.63 (1H, dd, $J=1.4$, 16.9 Hz), 6.17 (1H, d, $J=15.6$ Hz), 6.44 (1H, ddd, $J=10.1$, 10.8, 16.9 Hz), 6.80—6.84 (2H, m), 7.08—7.15 (2H, m). MS m/z (%): 216 (M^+ , 32), 135 ($[\text{M}-\text{C}_4\text{H}_5\text{CO}]^+$, 11), 134 (16), 121 ($[\text{M}-\text{C}_4\text{H}_5\text{COCH}_2]^+$, 100), 81 ($[\text{M}-\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2]^+$, 22), 53 ($[\text{M}-\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}]^+$, 31); Found: m/z 216.1161. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: M, 216.1150.

(E)-1-Phenyl-3,5-hexadien-2-one (7d)—Light yellow oil. IR (neat): 1680, 1655, 1620, 1585 cm^{-1} . $^1\text{H-NMR}$ δ : 3.84 (2H, s), 5.54 (1H, dd, $J=1.7$, 9.9 Hz), 5.65 (1H, dd, $J=1.7$, 17.0 Hz), 6.23 (1H, d, $J=16.5$ Hz), 6.40 (1H, ddd, $J=9.9$, 10.4, 17.0 Hz), 7.17—7.66 (6H, m). MS m/z (%): 172 (M^+ , 15), 91 ($[\text{M}-\text{C}_4\text{H}_5\text{CO}]^+$, 20), 81 ($[\text{M}-\text{PhCH}_2]^+$, 100), 65 (10), 53 ($[\text{M}-\text{PhCH}_2\text{CO}]^+$, 45); Found: m/z 172.0895. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}$: M, 172.0903.

(E)-1-Cyclohexyl-2,4-pentadien-1-one (7e)—Light yellow oil. IR (neat): 1690, 1660, 1625, 1590 cm^{-1} . $^1\text{H-NMR}$ δ : 1.20—1.43 (5H, m), 1.68—1.85 (5H, m), 2.53—2.59 (1H, m), 5.25 (1H, dd, $J=1.5$, 10.7 Hz), 5.65 (1H, dd, $J=1.5$, 16.1 Hz), 6.26 (1H, d, $J=16.1$ Hz), 6.46 (1H, ddd, $J=10.7$, 10.7, 16.1 Hz), 7.17 (1H, dd, $J=10.7$, 16.1 Hz). MS m/z (%): 164 (M^+ , 21), 83 ($[\text{M}-\text{C}_4\text{H}_5\text{CO}]^+$, 22), 81 ($[\text{M}-\text{C}_6\text{H}_{11}]^+$, 100), 53 ($[\text{M}-\text{C}_6\text{H}_{11}\text{CO}]^+$, 38); Found: m/z 164.1212. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: M, 164.1224.

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