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Polycyclic 2*H*-Pyran Derivatives by Intramolecular Hetero-*Diels-Alder* Reactions of α-Sulfur-Substituted α,β-Unsaturated Carbonyl Compounds

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Summary. Reaction of 1-(phenylsulfenyl)-, 1-(phenylsulfinyl)-, and 1-(phenylsulfonyl)-2- propanones as well as 2-(phenylsulfonyl)-acetophenone with 2-(3-methyl-2-butenyloxy)- and 2-((*E*)-3-phenyl-2-propenyloxy)-benzaldehydes yielded the corresponding *Knoevenagel* condensation products. The latter compounds underwent intramolecular cycloadditions affording *cis*-fused 2*H*-pyran derivatives as the major products.

Keywords. Intramolecular hetero-*Diels-Alder* reaction; Sulfides; Sulfoxides; Sulfones; 2*H*-Pyrans.

Introduction

Hetero-*Diels-Alder* reactions have attracted considerable attention from both synthetic and mechanistic points of view. Particularly, the reactions of enol ethers with α,β-unsaturated carbonyl compounds which can formally be treated as 1-oxa-1,3-butadienes have been utilized in the synthesis of 2*H*-pyran derivatives present in many natural products [1–4]. These reactions belong to the group of cycloadditions with inverse electron demand. It has been found that the presence of electron withdrawing groups at C-2 or C-3 in heterodiene system is necessary to lower the energy of the LUMO of the diene which then can more easily overlap with the HOMO of the dienophile. The heterodiene reaction can be performed inter- or intramolecularly.

In recent studies we have examined the influence of cyano, carbonyl, and ethoxycarbonyl groups at C-3 in 1-oxa-1,3-butadienes on the intramolecular hetero-*Diels-Alder* reaction [5]. In this study we demonstrate that sulfur containing substituents incorporated into 1-oxa-1,3-butadienes positively influence the results of the cycloaddition. To our knowledge there are only a few examples of hetero-*Diels-Alder* cycloadditions of α,β-unsaturated carbonyl compounds substituted by the phenylthio group reported in the literature [6–8]; all known examples concern intermolecular reactions.

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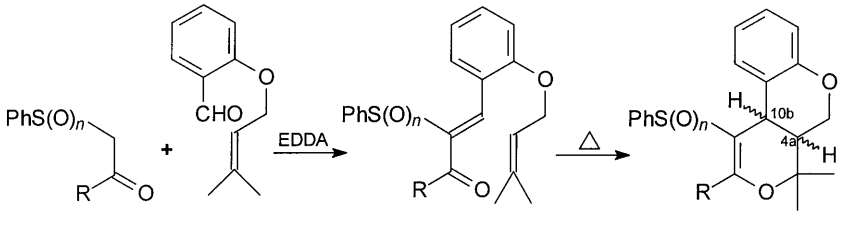
Results and Discussion

The aim of our studies was to investigate the intramolecular hetero-*Diels-Alder* reactions of α-sulfur-substituted α,β-unsaturated carbonyl compounds containing *o*-alkenyloxyaryl groups in position β. We wanted to compare the influence of the electron withdrawing groups phenylsulfenyl, phenylsulfinyl, and phenylsulfonyl on diastereoselectivity and yields. The influence of alkyl and aryl groups in the dienophile moieties was also taken into account.

The active methylene compounds applied as substrates were 1-(phenylsulfenyl)-2-propanone (**1**, [9], sulfide), 1-(phenylsulfinyl)-2-propanone (**2**, [9], sulfoxide), 1-(phenylsulfonyl)-2-propanone (**3**, [10], sulfone), and 2-(phenylsulfonyl)-acetophenone (**4**, sulfone). The second reagents were aldehydes containing 2-(3-methyl-2-butenyloxy) (**5**) and 2-((*E*)-3-phenyl-2-propenyloxy) (**6**) groups [11] in the neighbouring position to the carbonyl function. In cycloadditions, these groups should act as dienophiles. Compounds **1**–**4** were condensed with aldehydes **5** and **6** yielding the *Knoevenagel* condensation products which in turn underwent intramolecular hetero-*Diels-Alder* reactions.

The reaction of sulfide **1** with aldehyde **5** gave rise to the formation of **7** in good yield (73%). The intramolecular hetero-*Diels-Alder* cycloaddition of **7** afforded **8** as a mixture of *cis*- and *trans*-annulated cycloadducts (Scheme 1). The ratio of the two diastereoisomers (9:1) in the crude product was determined by ^{1}H NMR spectroscopy. The configuration of the *cis*- and *trans*-annulated compounds was deduced from the chemical shift values and coupling constants of two vicinal protons attached to C-4a and C-10b. The stereochemical assignments were confirmed by two-dimensional NMR spectra (COSY, ROESY). In the ^{1}H NMR spectrum of *cis*-**8** recorded at low sample concentration (0.009 mol/dm^3), the proton at C-4a appeared as ddd at $\delta = 2.17$ ppm with coupling constants of 11.45, 3.9, and 5.1 Hz. The value of 5.1 Hz refers to the coupling of 4a-H with the proton at C-10b and indicates their *cis* arrangement [12]. The resonance of the proton at C-10b was observed as qdd at $\delta = 3.63$ ppm with coupling constants of 5.1, 1.9, and 1.75 Hz. $^5J = 1.9$ Hz refers to the coupling of 10b-H with the protons of the methyl group at position C-2 (d, 1.95 Hz). 10b-H couples to the *pseudo*-equatorial proton at position 5 with $^4J = 1.75$ Hz. The same value ^4J was found considering the signal of 5-H$_{eq}$ (ddd, $\delta = 4.40$ ppm, $^2J = 11.0$ Hz, $^3J = 3.95$ Hz, $^4J = 1.75$ Hz). 5-H$_{eq}$ and 10b-H must



1: *n* = 0, *R* = CH_3 **5**
2: *n* = 1, *R* = CH_3
3: *n* = 2, *R* = CH_3
4: *n* = 2, *R* = Ph

7: *n* = 0, *R* = CH_3 **8**: *n* = 0, *R* = CH_3, *cis/trans* = 9:1
9: *n* = 1, *R* = CH_3 **10**: *n* = 1, *R* = CH_3, *cis/trans* = 2.5:1
11: *n* = 2, *R* = CH_3 **12**: *n* = 2, *R* = CH_3, *cis/trans* = 6.5:1
13: *n* = 2, *R* = Ph **14**: *n* = 2, *R* = Ph, *cis/trans* >100:1

Scheme 1

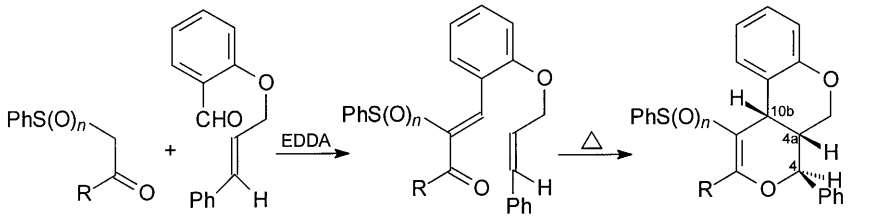
be in *cis*-configuration, and 10b-H is oriented *pseudo*-equatorially; thus, 4a-H adopts a *pseudo*-axial position. In the COSY and ROESY spectra of *cis*-**8** there are cross peaks correlating 10b-H with the protons of 2-CH_3 and 5-H_{eq}. Since we managed to isolate only pure *cis*-**8** by column chromatography, the configuration of *trans*-**8** was determined from the ^{1}H NMR spectrum of a mixture. In this case, the proton at C-10b was a doublet at $\delta = 3.35$ ppm displaying a large coupling constant of 11.3 Hz.

The reactions of sulfoxide **2** (racemic mixture) and sulfone **3** with aldehyde **5** yielded products **9** and **11** (Scheme 1). Heating of **9** and **11** in toluene afforded the expected cycloadducts **10** and **12** as a mixture of *cis*- and *trans*-annulated pyrans. The stereochemistry of the *cis*-fused pyrans (major amount) was confirmed by ^{1}H NMR spectroscopic analysis. For *cis*-**10** and *cis*-**12**, the signals of the protons at C-4a appeared as ddd at $\delta = 2.05$–2.09 ppm with coupling constants of 11.7, 2.1 Hz and 4.65 Hz (*cis*-**10**) or 8.3, 5.2, and 5.2 Hz (*cis*-**12**). The coupling constants $^3J = 4.65$ Hz (*cis*-**10**) and $^3J = 5.2$ Hz (*cis*-**12**) indicate that 4a-H and 10b-H are in *cis*-configuration. The signals for 10b-H of **10** and **12** at $\delta = 4.19$–4.24 ppm are broad. The configurations of the *trans*-annulated diastereoisomers **10** and **12** were deduced from the ^{1}H NMR spectra of a mixture of the crude products. For *trans*-**10**, the proton at C-10b was a doublet at 4.02 ppm with a large coupling constant of 11.4 Hz. For *trans*-**12**, the corresponding data are d, 3.67 ppm, and 10.0 Hz.

The condensation of sulfone **4** with aldehyde **5** furnished the *Knoevenagel* educt **13**; heating of **13** in toluene yielded the *cis*-annulated cycloadduct **14** as the sole product (Scheme 1). Its ^{1}H NMR spectrum displayed the signal of the proton at C-10b as a doublet at $\delta = 4.58$ ppm with $^3J = 5.4$ Hz. The proton 4a-H resonated as ddd at $\delta = 2.27$ ppm with coupling constants of 5.3, 10.9, and 5.3 Hz.

Next we investigated the reactions of compounds **1**–**4** with aldehyde **6** containing the (*E*)-3-phenyl-2-propenyloxy moiety (Scheme 2). The condensations involved the formation of products **15**, **17**, **19**, and **21**. Heating of these compounds in boiling xylene resulted in formation of the *Diels-Alder* cycloadducts **16**, **18**, **20**, and **22** as the sole products out of four possible diastereoisomers.

The relative configurations of the hydrogen atoms of the three chirality centers C-4, C-4a, and C-10b of these compounds were established on the basis of their ^{1}H NMR spectra. The protons at C-10b appeared as doublets at $\delta = 3.59$–4.85 ppm with small coupling constants of 4.0–4.7 Hz. From these values it can be deduced



1: $n = 0$, $R = CH_3$ **6**
2: $n = 1$, $R = CH_3$
3: $n = 2$, $R = CH_3$
4: $n = 2$, $R = Ph$

15: $n = 0$, $R = CH_3$
17: $n = 1$, $R = CH_3$
19: $n = 2$, $R = CH_3$
21: $n = 2$, $R = Ph$

16: $n = 0$, $R = CH_3$
18: $n = 1$, $R = CH_3$
20: $n = 2$, $R = CH_3$
22: $n = 2$, $R = Ph$

Scheme 2

Table 1. Reaction conditions, yields, and diastereoisomeric ratios of cycloadducts

Substrate	Cycloadduct	Reaction conditions (h/°C)	Yield/%	Ratio of *cis*:*trans*
7	*cis*-**8**/*trans*-**8**	20/111	55	9:1
9	*cis*-**10**/*trans*-**10**	10/111	60	2.5:1
11	*cis*-**12**/*trans*-**12**	15/111	58	6.5:1
13	*cis*-**14**	15/111	57	> 100:1
15	*cis*-**16**	24/136	62	> 100:1
17	*cis*-**18**	15/136	65	> 100:1
19	*cis*-**20**	20/136	60	> 100:1
21	*cis*-**22**	20/136	60	> 100:1

that compounds **16**, **18**, **20**, and **22** are *cis*-annulated. The signals of the protons at C-4 were doublets at $\delta = 5.05$–5.23 ppm with large coupling constants (8.7–11.2 Hz). This indicates *trans*-configuration of the two vicinal protons C4-H and C4a-H. The results of the reactions leading to the cycloadducts obtained are summarized in Table 1.

In conclusion, the reactions of activated methylene compounds with aromatic 2-alkenyloxy aldehydes afford in the first step α,β-unsaturated carbonyl compounds which subsequently undergo intramolecular hetero-*Diels-Alder* cycloadditions upon heating. Generally, the *cis*-diastereoisomer or a mixture of *cis*- and *trans*-products in which the *cis*-product predominates are obtained. The intermediate α,β-unsaturated carbonyl compounds may exist as (*E*) or (*Z*) isomers. Their ^{1}H NMR spectra indicated that they were the single isomers, the signals of the vinyl protons in the α,β-unsaturated systems appearing as singlets of intensity 1. Their chemical shift values suggest that these compounds are the (*Z*)-isomers [12].

A decrease of the diastereoselectivity of the reactions of the intermediate products **7**, **11**, and **9** possessing the PhS, $PhSO_2$, and PhSO groups was observed in this order, whereas the reactivity increased. No significant difference comparing the reactivity of compounds **7**, **9**, **11**, and **13** possessing methyl groups attached to the terminal dienophile with that of the analogous compound **15**, **17**, **19**, and **21** containing phenyl groups at the same position was observed. In contrast, we noticed a large difference in diastereoselectivity, the reactions of the latter compounds, leading exclusive to the *cis*-cycloadducts.

Experimental

Melting points: Boetius hot stage apparatus; IR spectra: Bruker IFS 48, KBr pellets or film; NMR spectra: Bruker AMX 500 (^{1}H: 500.14 MHz, ^{13}C: 125.77 MHz), $CDCl_3$, *TMS* as an internal standard, ^{13}C signal assignments: DEPT, XHCORR; mass spectra: Finningan Mat 95 (70 eV); microanalyses: Euro EA 3000 Elemental Analyzer, their results were in satisfactory agreement with the calculated values.

1-(Phenylsulfenyl)-2-propanone (**1**) and 1-(phenylsulfinyl)-2-propanone (**2**) were obtained according to Ref. [9]. The preparation of 1-(phenylsulfonyl)-2-propanone (**3**) is described in Ref. [10], 2-(phenylsulfonyl)-acetophenone (**4**) was purchased from Aldrich. 2-(3-Methyl-2-butenyloxy)-

benzaldehyde (**5**) and 2-((*E*)-3-phenyl-2-propenyloxy)-benzaldehyde (**6**) were obtained according to Ref. [11].

Reaction of compounds **1–4** *with 2-alkenyloxybenzaldehydes* **5** and **6**

To a solution of compounds **1–4** (0.01 mol) in 20 cm^3 of dry CH_3CN, aldehydes **5** or **6** (0.01 mol) and 60 mg ethylene diammonium diacetate (*EDDA*) were added. The solution was stirred for several hours and left at room temperature. The progress of the reactions was monitored by TLC. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using petrol ether and *t*-butyl-methyl ether (1:2) as eluent. Crystallization from a mixture of petrol ether and *t*-butyl-methyl ether (3:1) afforded the condensation products.

4-(2-(3-Methyl-2-butenyloxy)-phenyl)-3-phenylsulfenyl-3-buten-2-one (**7**; $C_{21}H_{22}O_2S$)

Pale yellow oil; 73%; IR (film): $\nu = 3061$, 2967, 2860 (CH), 1687 (C=O), 1599 (C=C) cm^{-1}; ^1H NMR ($CDCl_3, \delta$): 1.75 (d, J(2″-H,3″-CH_3) = 1.1 Hz, 3H, 3″-CH_3), 1.79 (d, J(2″-H,3″-CH_3) = 1.35 Hz, 3H, 3″-CH_3), 2.36 (s, 3H, $COCH_3$), 4.58 (d, J(2″-H,1″-H) = 6.5 Hz, 2H, 1″-H), 5.49 (m, 1H, 2″-H), 6.82–7.93 (m, 9H, CH_{arom}), 8.29 (s, 1H, 4-H) ppm; MS: m/z (%) = 338.1 (24, $M^{+\cdot}$), 270.1 (49, M-$C_5H_9^{+\cdot}$), 255.0 (63, [M-C_5H_7O]$^{+\cdot}$), 218.0 (26, M-C_6H_5, $CH_3CO^{+\cdot}$), 161.1 (69, $C_6H_4OC_5H_9^{+\cdot}$), 110.0 (39, C_6H_5S, $H^{+\cdot}$), 69.1 (100, $C_5H_9^{+\cdot}$).

4-(2-(3-Methyl-2-butenyloxy)-phenyl)-3-phenylsulfinyl-3-buten-2-one (**9**; $C_{21}H_{22}O_3S$)

Pale yellow oil; 75%; IR (film): $\nu = 3067$, 2973, 2929 (CH), 1674 (C=O), 1599 (C=C) 1053 (S=O) cm^{-1}; ^1H NMR ($CDCl_3, \delta$): 1.74 (d, J(2″-H,3″-CH_3) = 1.1 Hz, 3H, 3″-CH_3), 1.78 (d, J(2″-H,3″-CH_3) = 1.35 Hz, 3H, 3″-CH_3), 1.79 (s, 3H, $COCH_3$), 4.57 (d, J(2″-H,1″-H) = 6.5 Hz, 2H, 1″-H), 5.44 (m, 1H, 2″-H), 6.93–7.76 (m, 9H, CH_{arom}), 7.83 (s, 1H, 4-H) ppm; MS: m/z (%) = 161.0 (14, $C_6H_4OC_5H_9^{+\cdot}$), 117.1 (18, M-C_5H_9, CH_3CO, $C_6H_5SO^{+\cdot}$), 69.1 (100, $C_5H_9^{+\cdot}$).

4-(2-(3-Methyl-2-butenyloxy)-phenyl)-3-phenylsulfonyl-3-buten-2-one (**11**; $C_{21}H_{22}O_4S$)

Pale yellow oil; 72%; IR (film): $\nu = 3067$, 2973, 2916 (CH), 1699 (C=O), 1599 (C=C) 1316, 1153 (S=O) cm^{-1}; ^1H NMR ($CDCl_3, \delta$): 1.74 (d, J(2″-H,3″-CH_3) = 1.1 Hz, 3H, 3″-CH_3), 1.78 (d, J(2″-H,3″-CH_3) = 1.35 Hz, 3H, 3″-CH_3), 2.21 (s, 3H, $COCH_3$), 4.60 (d, J(2″-H,1″-H) = 6.5 Hz, 2H, 1″-H), 5.44 (m, 1H, 2″-H), 6.90–7.93 (m, 9H, CH_{arom}), 8.24 (s, 1H, 4-H) ppm; MS: m/z (%) = 370.0 (1, $M^{+\cdot}$), 286.9 (9, M-$C_5H_8O^{+\cdot}$), 122.0 (90), 69.0 (100, $C_5H_9^{+\cdot}$).

3-(2-(3-Methyl-2-butenyloxy)-phenyl)-1-phenyl-2-phenylsulfonyl-2-propen-1-one (**13**; $C_{26}H_{24}O_4S$)

Pale yellow oil; 70%; IR (film): $\nu = 3067$, 2973, 2923 (CH), 1664 (C=O), 1598 (C=C) 1315, 1149 (S=O) cm^{-1}; ^1H NMR ($CDCl_3, \delta$): 1.75 (d, J(2″-H,3″-CH_3) = 1.1 Hz, 3H, 3″-CH_3), 1.81 (d, J(2″-H,3″-CH_3) = 1.35 Hz, 3H, 3″-CH_3), 4.56 (d, J(2″-H,1″-H) = 6.4 Hz, 2H, 1″-H), 5.43 (m, 1H, 2″-H), 6.59–7.99 (m, 14H, CH_{arom}), 8.48 (s, 1H, 3-H) ppm; MS: m/z (%) = 432.2 (1, $M^{+\cdot}$), 364.1 (8, M-$C_5H_8^{+\cdot}$), 287.1 (13, M-C_5H_8, $C_6H_5^{+\cdot}$), 223.1 (100, M-C_5H_8, $C_6H_5SO_2^{+\cdot}$), 105.0 (38, $C_6H_5CO^{+\cdot}$), 69.0 (17, $C_5H_9^{+\cdot}$).

4-(2-((E)-(3-Phenyl-2-propenyloxy))-phenyl)-3-phenylsulfenyl-3-buten-2-one (**15**; $C_{25}H_{22}O_2S$)

Pale yellow oil; 75%; IR (film): $\nu = 3058$, 2916, 2866 (CH), 1681 (C=O), 1596 (C=C) cm^{-1}; ^1H NMR ($CDCl_3, \delta$): 2.38 (s, 3H, $COCH_3$), 4.79 (d, J(2″-H,1″-H) = 5.7 Hz, 2H, 1″-H), 6.44 (dt, J(1″-

H,2″-H) = 5.6 Hz, *J*(3″-H,2″-H) = 16.0 Hz, 1H, 2″-H), 6.77 (d, *J*(2″-H,3″-H) = 16 Hz, 1H, 3″-H), 6.95–7.95 (m, 14H, CH_{arom}), 8.37 (s, 1H, 4-H) ppm; MS: *m/z* (%) = 386.1 (8.6, $M^{+\cdot}$), 254.1 (13, M-$C_6H_5C_3H_3O^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$), 91.1 (14.5), 77.0 (13, $C_6H_5^{+\cdot}$), 43.0 (23, $CH_3CO^{+\cdot}$).

4-(2-((E)-(3-Phenyl-2-propenyloxy))-phenyl)-3-phenylsulfinyl-3-buten-2-one (**17**; $C_{25}H_{22}O_3S$)

Pale yellow crystals; 77%; m.p.: 95°C; IR (KBr): ν = 3080, 3005, 2854 (CH), 1668 (C=O), 1618 (C=C), 1053 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 1.81 (s, 3H, $COCH_3$), 4.76 (d, *J*(2″-H,1″-H) = 5.7 Hz, 2H, 1″-H), 6.37 (dt, *J*(1″-H,2″-H) = 5.7 Hz, *J*(3″-H,2″-H) = 16.0 Hz, 1H, 2″-H), 7.0 (d, *J*(2″-H,3″-H) = 16.0 Hz, 1H, 3″-H), 6.96–7.73 (m, 14H, CH_{arom}), 7.90 (s, 1H, 4-H) ppm; ^{13}C NMR ($CDCl_3, \delta$): 30.35 (C-1), 69.24 (C-1″), 112.50, 121.05, 123.67, 125.75, 126.67, 128.06, 128.64, 129.18, 130.85, 131.42, 131.55, 133.07, 133.36, 136,00 (C-3, C-4, C-2″, C-3″, C_{arom}), 152.50 (C-2) ppm; MS: *m/z* (%) = 403.3 (4, M + $H^{+\cdot}$), 385.3 (75, M-$OH^{+\cdot}$), 276.2 (23, M-$C_6H_5SO, H^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$).

4-(2-((E)-(3-Phenyl-2-propenyloxy))-phenyl)-3-phenylsulfonyl-3-buten-2-one (**19**; $C_{25}H_{22}O_4S$)

Pale yellow crystals; 75%; m.p.: 98°C; IR (KBr): ν = 3054, 3035, 2862 (CH), 1693 (C=O), 1598 (C=C), 1308, 1144 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 2.21 (s, 3H, $COCH_3$), 4.75 (d, *J*(2″-H,1″-H) = 5.6 Hz, 2H, 1″-H), 6.35 (dt, *J*(1″-H,2″-H) = 5.6 Hz, *J*(3″-H,2″-H) = 16.0 Hz, 1H, 2″-H), 6.74 (d, *J*(2″-H,3″-H) = 16.0 Hz, 1H, 3″-H), 6.85–7.93 (m, 14H, CH_{arom}), 8.31 (s, 1H, 4-H) ppm; MS: *m/z* (%) = 418.1 (2, $M^{+\cdot}$), 276.1 (3, M-$C_6H_5SO_2, H^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$), 91.1 (14), 77.0 (10.5, $C_6H_5^{+\cdot}$).

1-Phenyl-3-(2-((E)-(3-phenyl-2-propenyloxy))-phenyl)-2-phenylsulfonyl-2-propen-1-on (**21**; $C_{30}H_{24}O_4S$)

Pale yellow crystals; 80%; m.p.: 126°C; IR (KBr): ν = 3081, 3058, 2858 (CH), 1657 (C=O), 1596 (C=C), 1306, 1144 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 4.73 (d, *J*(2″-H,1″-H) = 5.6 Hz, 2H, 1″-H), 6.36 (dt, *J*(1″-H,2″-H) = 5.6 Hz, *J*(3″-H, 2″-H) = 16.0 Hz, 1H, 2″-H), 6.74 (d, *J*(2″-H,3″-H) = 16.0 Hz, 1H, 3″-H), 6.64–7.94 (m, 19H, CH_{arom}), 8.53 (s, 1H, 3-H) ppm; ^{13}C NMR ($CDCl_3, \delta$): 68.99 (C-1″), 112.40, 120.73, 121.23, 123.57, 126.67, 128.07, 128.54, 128.58, 128.65, 128.97, 129.66, 130.61, 132.62, 133.14, 133.42, 133.97, 135.91, 136.22, 138.01, 138.95, 140.36, 157.14 (C_{arom}), 192.07 (C-1) ppm; MS: *m/z* (%) = 480.2 (1, $M^{+\cdot}$), 338.1 (9.5, M-$C_6H_5SO_2, H^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$), 105.0 (12, $C_6H_5CO^{+\cdot}$), 77.0 (10, $C_6H_5^{+\cdot}$).

General procedure for the synthesis of cycloadducts **8**, **10**, **12**, **14**, **16**, **18**, **20**, *and* **22**

A solution of 5 mmol of the α,β-unsaturated carbonyl compounds **7**, **9**, **11**, **13**, **15**, **17**, **19**, or **21** in 10 cm^3 anhydrous toluene or xylene was refluxed for 10–24 h. The progress of the reactions was monitored by TLC. The solvent was evaporated, and the mixture was separated and purified by column chromatography on silica gel using petrol ether and *t*-butyl-methyl ether (1:1 or 2:1) as eluent. Recrystallization from a mixture of petrol ether and *t*-butyl-methyl ether (3:1) gave colourless crystals.

(4aRS,10bSR)-4a, 10b-Dihydro-2,4,4-trimethyl-1-phenylsulfenyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**8**; $C_{21}H_{22}O_2S$)

Colourless crystals; 49.5%; m.p.: 146°C; IR (KBr): ν = 3073, 2986, 2860 (CH), 1611 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 1.43 (s, 3H, 4-CH_3), 1.47 (s, 3H, 4-CH_3), 2.11 (d, *J*(10b-H,2-CH_3) = 1.95 Hz, 3H, 2-CH_3), 2.17 (ddd, *J*(10b-H, 4a-H) = 5.1 Hz, *J*(5-H_{ax},4a-H) = 11.45 Hz, *J*(5-H_{eq},4a-H) = 3.9 Hz, 1H, 4a-H), 3.63 (ddq, *J*(4a-H, 10b-H) = 5.1 Hz, *J*(2-CH_3, 10b-H) = 1.9 Hz, *J*(5-H_{eq}, 10b-H) = 1.75 Hz, 1H, 10b-H), 3.98 (dd, *J*(4a-H, 5-H_{ax}) = 11.5 Hz, J_{gem} = 11.0 Hz, 1H, 5-H_{ax}), 4.40 (ddd,

J(4a-H, 5-H$_{eq}$) = 3.95 Hz, J_{gem} = 11.0 Hz, J(10b-H, 5-H$_{eq}$) = 1.75 Hz, 1H, 5-H$_{eq}$), 6.68–7.24 (m, 9H, CH$_{arom}$) ppm; ^{13}C NMR ($CDCl_3$, δ): 19.77 (2-CH_3), 25.85 (4-CH_3), 26.29 (4-CH_3), 34.75 (C-10b), 38.37 (4a-H), 63.27 (C-5), 75.02 (C-4), 99.41 (C-1), 115.65, 118.92, 121.10, 124.60, 125.71, 128.08, 128.68, 133.68, 138.61, 153.65(C$_{arom}$), 157.86 (C-2) ppm; MS: m/z (%) = 338.1 (100, $M^{+\cdot}$), 270.1 (39, M-$C_5H_8^{+\cdot}$), 255.1 (80, M-$C_5H_7O^{+\cdot}$), 161.1 (86, $C_6H_4OC_5H_9^{+\cdot}$).

(4aRS, 10bSR)-4a,10b-Dihydro-2,4,4-trimethyl-1-phenylsulfinyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**10**; $C_{21}H_{22}O_3S$)

Colourless crystals; 43%; m.p.: 182°C; IR (KBr): ν = 3055, 2979, 2898 (CH), 1605 (C=C), 1036 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.40 (s, 3H, 4-CH_3), 1.48 (s, 3H, 4-CH_3), 2.05 (ddd, J(10b-H, 4a-H) = 4.65 Hz, J(5-H$_{ax}$, 4a-H) = 11.7 Hz, J(5-H$_{eq}$,4a-H) = 2.1 Hz, 1H, 4a-H), 2.24 (d, J(10b-H,2-CH_3) = 1.8 Hz, 3H, 2-CH_3), 3.89 (t, J(4a-H, 5-H$_{ax}$) = 11.3 Hz, J_{gem} = 11.3 Hz, 1H, 5-H$_{ax}$), 4.24 (br, 1H, 10b-H), 4.31 (ddd, J(4a-H, 5-H$_{eq}$) = 4.5 Hz, J_{gem} = 11.0 Hz, J(10b-H, 5-H$_{eq}$) = 1.7 Hz, 1H, 5-H$_{eq}$), 6.18–7.59 (m, 9H, CH$_{arom}$) ppm; ^{13}C NMR ($CDCl_3$, δ): 19.40 (2-CH_3), 25.64 (4-CH_3), 26.61 (4-CH_3), 31.23 (C-10b), 37.70 (C-4a), 63.20 (C-5), 77.26 (C-4), 112.67 (C-1), 115.08, 119.07, 119.19, 123.59, 128.12, 128.78, 134.42, 143.49, 153.29, 153.29(C$_{arom}$), 157.97 (C-2) ppm; MS: m/z (%) = 354.2 (4, $M^{+\cdot}$), 337.2 (100, M-$OH^{+\cdot}$), 228.2 (14, M-$C_6H_5SO, H^{+\cdot}$), 185.1 (16).

(4aRS,10bSR)-4a,10b-Dihydro-2,4,4-trimethyl-1-phenylsulfonyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**12**; $C_{21}H_{22}O_4S$)

Colourless crystals; 50%; m.p.: 162°C; IR (KBr): ν = 3067, 2973, 2929 (CH), 1592 (C=C), 1297, 1147 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.25 (s, 3H, 4-CH_3), 1.44 (s, 3H, 4-CH_3), 2.09 (ddd, J(10b-H, 4a-H) = 5.2 Hz, J(5-H$_{ax}$, 4a-H) = 8.2 Hz, J(5-H$_{eq}$,4a-H) = 5.2 Hz, 1H, 4a-H), 2.33 (d, J(10b-H, 2-CH_3) = 1.8 Hz, 3H, 2-CH_3), 4.02 (dd, J(4a-H, 5-H$_{ax}$) = 8.3 Hz, J_{gem} = 11.3 Hz, 1H, 5-H$_{ax}$), 4.19 (br, 1H, 10b-H), 4.30 (ddd, J(4a-H, 5-H$_{eq}$) = 5.5 Hz, J_{gem} = 11.3 Hz, J(10b-H, 5-H$_{eq}$) = 0.8 Hz, 1H, 5-H$_{eq}$), 6.40–7.56 (m, 9H, CH$_{arom}$) ppm; ^{13}C NMR ($CDCl_3$, δ): 20.77 (2-CH_3), 24.96 (4-CH_3), 26.81 (4-CH_3), 33.08 (C-10b), 39.16 (C-4a), 64.32 (C-5), 77.95 (C-4), 111.31 (C-1), 115.53, 120.29, 121.49, 125.65, 128.38, 128.61, 131.60, 132.77, 143.39, 154.15(C$_{arom}$), 163.22 (C-2) ppm; MS: m/z (%) = 370.1 (40, $M^{+\cdot}$), 228.1 (100, M-$C_6H_5SO_2, H^{+\cdot}$), 213.1 (51, M-$C_6H_5SO, H, CH_3^{+\cdot}$), 185.1 (76).

(4aRS,10bSR)-4a,10b-Dihydro-4,4-dimethyl-2-phenyl-1-phenylsulfonyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**14**; $C_{26}H_{24}O_4S$)

Colourless crystals; 57%; m.p.: 202°C; IR (KBr): ν = 3061, 2973, 2885 (CH), 1613 (C=C), 1286, 1149 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.28 (s, 3H, 4-CH_3), 1.56 (s, 3H, 4-CH_3), 2.27 (ddd, J(10b-H, 4a-H) = 5.3 Hz, J(5-H$_{ax}$, 4a-H) = 10.9 Hz, J(5-H$_{eq}$, 4a-H) = 5.3 Hz, 1H, 4a-H), 4.30 (dd, J(4a-H, 5-H$_{ax}$) = 10.0 Hz, J_{gem} = 11.6 Hz, 1H, 5-H$_{ax}$), 4.48 (dd, J(4a-H, 5-H$_{eq}$) = 5.1 Hz, J_{gem} = 11.6 Hz, 1H, 5-H$_{eq}$), 4.58 (d, J(4a-H, 10b-H) = 5.4 Hz, 1H, 10b-H), 6.68–7.83 (m, 14H, CH$_{arom}$) ppm; ^{13}C NMR ($CDCl_3$, δ): 24.72 (4-CH_3), 27.19 (4-CH_3), 33.32 (C-10b), 39.75 (C-4a), 64.68 (C-5), 79.45 (C-4), 115.79 (C-1), 115.95, 120.98, 121.90, 126.64, 127.62, 128.03, 128.55, 129.51, 129.56, 131.57, 131.87, 134.73, 143.45, 154.21(C$_{arom}$), 162.98 (C-2) ppm; MS: m/z (%) = 432.2 (11, $M^{+\cdot}$), 290.1 (100, M-$C_6H_5SO_2, H^{+\cdot}$), 222.1 (24, M-$C_6H_5SO_2, C_5H_9^{+\cdot}$), 185.1 (13, M-$C_6H_5SO_2, H, C_6H_5CO^{+\cdot}$), 105.0 (37, $C_6H_5CO^{+\cdot}$) 69.0 (9, $C_5H_9^{+\cdot}$).

(4RS,4aSR,10bRS)-4a,10b-Dihydro-2-methyl-4-phenyl-1-phenylsulfenyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**16**; $C_{25}H_{22}O_2S$)

Colourless crystals; 62%; m.p.: 150°C; IR (KBr): ν = 3067, 2998, 2885 (CH), 1630, 1579 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.21 (d, J(10b-H, 2-CH_3) = 0.85 Hz, 3H, 2-CH_3), 2.43 (m, 1H,

4a-H), 4.59 (br, d, J(4a-H, 10b-H) = 4.7 Hz, 1H, 10b-H), 3.92 (dd, J(4a-H, 5-H) = 4.3 Hz, J_{gem} = 11.3 Hz, 1H, 5-H), 4.07 (dd, J(4a-H, 5-H) = 2.3 Hz, J_{gem} = 11.3 Hz, 1H, 5-H), 5.10 (d, J(4a-H, 4-H) = 8.7 Hz, 1H, 4-H), 6.80–7.91 (m, 14H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3, \delta$): 18.90 (2-CH_3), 34.98 (C-10b), 38.19 (C-4a), 65.68 (C-5), 76.29 (C-4), 100.32 (C-1), 116.77, 120.65, 124.09, 125.08, 126.09, 126.73, 127.82, 128.39, 128.68, 129.01, 130.34, 137.53, 138.98, 153.01(C_{arom}), 160.02 (C-2) ppm; MS: m/z (%) = 386.2 (51.5, $M^{+\cdot}$), 254.1 (26, M-$C_6H_5C_3H_3O^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$), 91.1 (14), 43.0 (22, $CH_3CO^{+\cdot}$).

(4RS,4aSR,10bRS)-4a,10b-Dihydro-2-methyl-4-phenyl-1-phenylsulfinyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**18**; $C_{25}H_{22}O_3S$)

Colourless crystals; 65%; m.p.: 172°C; IR (KBr): ν = 3061, 2961, 2892 (CH), 1630, (C=C), 1031 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 2.23 (m, 1H, 4a-H), 2.38 (s, 3H, 2-CH_3), 3.89 (dd, J(4a-H, 5-H) = 3.3 Hz, J_{gem} = 11.4 Hz, 1H, 5-H), 4.23 (dd, J(4a-H, 5-H) = 2.6 Hz, J_{gem} = 11.5 Hz, 1H, 5-H), 4.30 (d, J(4a-H, 10b-H) = 4.0 Hz, 1H, 10b-H), 5.05 (d, J(4a-H, 4-H) = 9.9 Hz, 1H, 4-H), 5.96–7.65 (m, 14H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3, \delta$): 18.74 (2-CH_3), 27.59 (C-10b), 37.83 (C-4a), 65.81 (C-5), 77.68 (C-4), 115.67 (C-1), 116.35, 120.25, 122.64, 124.66, 126.85, 127.85, 128.71, 128.76, 129.30, 130.44, 130.63, 138.44, 144.43, 153.24(C_{arom}), 160.78 (C-2) ppm; MS: m/z (%) = 402.2 (2, $M^{+\cdot}$), 385.2 (100, M-$OH^{+\cdot}$), 276.2 (13, M-$C_6H_5SO, H^{+\cdot}$), 117.1 (46, $C_6H_5C_3H_4^{+\cdot}$).

(4RS,4aSR,10bRS)-4a,10b-Dihydro-2-methyl-4-phenyl-1-phenylsulfonyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**20**; $C_{25}H_{22}O_4S$)

Colourless crystals; 60%; m.p.: 153°C; IR (KBr): ν = 3066, 2920, 2882 (CH), 1615 (C=C), 1290, 1147 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 2.05 (dddd, J(10b-H, 4a-H) = 4.5 Hz, J(4-H, 4a-H) = 11.1 Hz, J(5-H, 4a-H) = 2.1 Hz, J(5-H, 4a-H) = 2.1 Hz, 1H, 4a-H), 2.15 (s, 3H, 2-CH_3), 3.85 (dd, J(4a-H, 5-H) = 2.1 Hz, J_{gem} = 11.5 Hz, 1H, 5-H), 4.17 (dd, J(4a-H, 5-H) = 2.2 Hz, J_{gem} = 11.5 Hz, 1H, 5-H), 4.46 (d, J(4a-H, 10b-H) = 4.4 Hz, 1H, 10b-H), 5.06 (d, J(4a-H, 4-H) = 11.1 Hz, 1H, 4-H), 6.39–7.93 (m, 14H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3, \delta$): 19.56 (2-CH_3), 34.64 (C-10b), 36.69 (C-4a), 65.56 (C-5), 77.69 (C-4), 114.48 (C-1), 116.57, 121.64, 123.66, 126.44, 126.59, 127.06, 128.29, 128.70, 128.93, 129.13, 131.47, 132.59, 137.56, 144.08, 152.59(C_{arom}), 164.89 (C-2) ppm; MS: m/z (%) = 418.1 (14.5, $M^{+\cdot}$), 276.1 (22, M-$C_6H_5SO_2, H)^{+\cdot}$), 233.1 (13, M-$C_6H_5SO_2$, H, $CH_3CO^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$), 91.1 (23).

(4RS,4aSR,10bRS)-4a,10b-Dihydro-2,4-diphenyl-1-phenylsulfonyl-4H,5H-pyrano[3,4-c][1] benzopyran (*cis*-**22**; $C_{30}H_{24}O_4S$)

Colourless crystals; 60%; m.p.: 195°C; IR (KBr): ν = 3061, 2923, 2848 (CH), 1618, 1591 (C=C), 1335, 1147 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3, \delta$): 2.3 (m, 1H, 4a-H), 3.96 (dd, J(4a-H, 5-H) = 1.65 Hz, J_{gem} = 11.4 Hz, 1H, 5-H), 4.29 (dd, J(4a-H, 5-H) = 1.6 Hz, J_{gem} = 11.3 Hz, 1H, 5-H), 4.85 (d, J(4a-H, 10b-H) = 4.6 Hz, 1H, 10b-H), 5.23 (d, J(4a-H, 4-H) = 11.2 Hz, 1H, 4-H), 6.89–7.93 (m, 19H, CH_{arom}) ppm; ^{13}C NMR ($CDCl_3, \delta$): 24.67 (C-10b), 26.97 (C-4a), 65.62 (C-5), 77.83 (C-4), 116.74 (C-1), 117.87, 121.99, 123.74, 126.89, 127.06, 127.59, 128.25, 128.30, 128.74, 128.95, 129.63, 129.80, 131.36, 131.98, 133.24, 137.61, 143.09, 152.61(C_{arom}), 164.44 (C-2) ppm; MS: m/z (%) = 480.1 (17, $M^{+\cdot}$), 338.1 (80, M-$C_6H_5SO_2, H^{+\cdot}$), 233.1 (22, M-$C_6H_5SO_2$, H, $C_6H_5CO^{+\cdot}$), 206.1 (23.5, M-$C_6H_5SO_2, C_6H_5C_3H_4O^{+\cdot}$), 117.1 (100, $C_6H_5C_3H_4^{+\cdot}$), 105.0 (38.5, $C_6H_5CO^{+\cdot}$), 91.1 (21), 77.0 (24, $C_6H_5^{+\cdot}$).

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