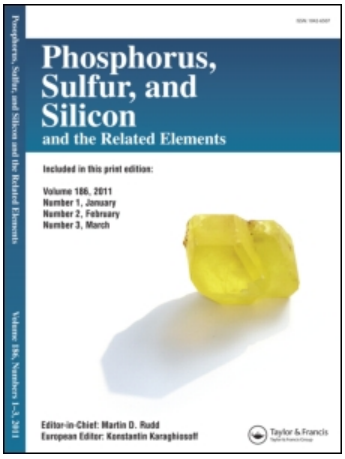

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Reactions of Arylazo Aryl Sulfones with α,β-Unsaturated Esters and Ketones Catalyzed by Palladium(O) Complex

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REACTIONS OF ARYLAZO ARYL SULFONES WITH α,β-UNSATURATED ESTERS AND KETONES CATALYZED BY PALLADIUM(0) COMPLEX[1]

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The palladium(0) catalyzed reactions of arylazo aryl sulfones (**1**) with α,β-unsaturated esters in benzene give aryl-substituted esters as major products and hydroarylated esters as minor products. The reactions of **1** with acyclic α,β-unsaturated ketones give considerable amounts of hydroarylated ketones and aryl-substituted ketones under similar conditions, whereas the reactions of **1** with cyclic α,β-unsaturated ketones afforded selectively hydroarylated compounds and no formation of aryl-substituted ketones was found. A plausible reaction mechanism is proposed.

Key words: Arylazo aryl sulfones; palladium(0) catalyst; arylation; α,β-unsaturated carbonyl compounds; diarylpalladium(II) intermediate; catalytic cycle.

Recently, much attention has been paid to the palladium catalyzed substitution reaction of vinylic hydrogen by aryl and vinyl halides.[2] Kikukawa *et al.* have first demonstrated that arenediazonium salts react with olefins in the presence of palladium catalyst to give arylated olefins in high yields.[3] We previously reported that the reactions of arylazo aryl sulfones (**1**) with olefins catalyzed by tetrakis(triphenylphosphine)palladium(0) in benzene gave aryl-substituted olefins in good yields.[4] We found that the reactions of **1** with α,β-unsaturated esters and ketones catalyzed by palladium(0) complex give hydroarylated compounds as well as aryl-substituted compounds, and the results will be described herein.

RESULTS AND DISCUSSION

Dropwise addition of a solution of phenylazo phenyl sulfone (**1a**) in benzene to a stirred solution of ethyl acrylate (**2a**) and tetrakis(triphenylphosphine)-palladium(0) in benzene at 80°C resulted in evolution of nitrogen. The reaction mixture was subjected to silica-gel chromatography and gel permeation chromatography to give ethyl (E)-3-phenylpropenoate (**3a**) (53%), ethyl (Z)-3-phenylpropenoate (**4a**) (2%), ethyl 3-phenylpropanoate (**5a**) (2%), and biphenyl (4%). Similarly, the reactions of **1a**, *p*-tolylazo *p*-tolyl sulfone (**1b**), and *p*-methoxyphenylazo *p*-methoxyphenyl sulfone (**1c**) with **2a**, ethyl crotonate (**2b**),

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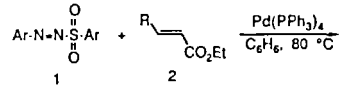
TABLE I

Reactions of Arylazo Aryl Sulfones with α,β-Unsaturated Esters

Entry	Ar in 1	R in 2	Products[a] (Yield/%)		
1	**1a** Ph	**2a** H	**3a** 53	**4a** 2	**5a** 2
2	**1b** *p*-Tol	**2a** H	**3b** 64	**4b** 4	**5b** 0
3	**1c** *p*-$MeOC_6H_4$	**2a** H	**3c** 24	**4c** 0	**5c** 2
4	**1a** Ph	**2b** Me	**3d** 38	**4d** 9	**5d** 3
5	**1b** *p*-Tol	**2b** Me	**3e** 56	**4e** 8	**5e** 8
6	**1c** *p*-$MeOC_6H_4$	**2b** Me	**3f** 33	**4f** 5	**5f** 2
7	**1a** Ph	**2c** Ph	**3g** 63[b]	—	**5g** 16
8	**1b** *p*-Tol	**2c** Ph	**3h** 52	**4h** 22	**5h** 15
9	**1c** *p*-$MeOC_6H_4$	**2c** Ph	**3i** 40	**4i** 20	**5i** 6

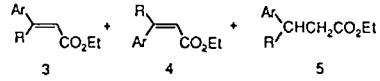
[a] Biaryls (ARPh and Ar_2) were formed in 3–7% yield in all cases.
[b] The yield includes the yield of 4 since the products 3 and 4 are the same in this case.

and ethyl cinnamate (**2c**) were carried out in the presence of the palladium(0) complex to give aryl substituted compounds **3** and **4** as major products and hydroarylated compounds **5** as minor products. It is of interest that the hydroarylation giving **5** was observed in the present reaction, whereas no such product was found in the reaction of **1** with olefin.[4] The results are summarized in Table I. The reactions were little affected by other transition metal catalysts such as tris(dibenzilideneacetone)dipalladium(0), dichlorobis-(triphenylphosphine)-palladium(II), dichlorobis(benzonitrile)palladium(II), dichlorobis(acetonitrile)-palladium(II), palladium(II) acetate, palladium(II) chloride, dichlorobis(triphenyl-phosphine)nickel(II), chlorotris(triphenylphosphine)rhodium(I), and dichlorotris-(triphenylphosphine)ruthenium(II).



1 2

1a: Ar = Ph 2a: R = H
1b: Ar = p-Tol 2b: R = CH_3
1c: Ar = p-$CH_3OC_6H_4$ 2c: R = Ph



3 4 5

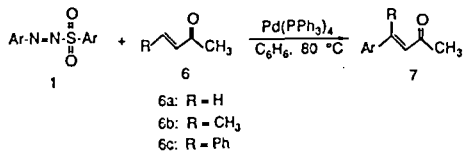
The reactions of **1** with acyclic α,β-unsaturated ketones were also carried out in the presence of a catalytic amount of palladium(0) complex. The results are summarized in Table II. When **1a** was reacted with 3-buten-2-one, phenyl substituted and hydrophenylated compounds were formed in comparable amounts; namely, 4-phenyl-3-buten-2-one (**7a**) (53%) was obtained together with 4-phenyl-2-butanone (**8a**) (44%). Moreover, in the case of the reaction of **1a** or **1b** with 4-phenyl-3-buten-2-one (**6c**) the aryl-substituted compounds (**7e**) or (**7f**) were formed in small amounts only, while the hydroarylated compounds (**8e**) or (**8f**) were obtained as the major products. In the reaction of **1** with α,β-unsaturated ketones, arylsulfonyl-substituted compound (**9**) and hydroarylsul-fonylated compound (**10**) were formed as well as **7** and **8**.

TABLE II

Reactions of Arylazo Aryl Sulfones with Acyclic α,β-Unsaturated Ketones

Entry	Ar in 1	R in 6	Products[a] (Yield/%)					
10	Ph	H	**7a** 53	**8a** 44	**9a** 0	**10a** 0		
11	*p*-Tol	H	**7b** 53	**8b** 31	**9b** 0	**10b** 13		
12	Ph	Me	**7c** 6	**8c** 6	**9c** 0	**10c** 36		
13	*p*-Tol	Me	**7d** 6	**8d** 15	**9d** 0	**10d** 22		
14	Ph	Ph	**7e** 1	**8e** 58	**9e** 8	**10e** 14		
15	*p*-Tol	Ph	**7f** 1	**8f** 38	**9f** 6	**10f** 6		

[a] Biaryls (ArPh and Ar_2) were formed in 4–7% yield in all cases.



The reaction of **1** with cyclic α,β-unsaturated ketones (**11**) under similar conditions afforded only hydroarylated compounds (**12**). Formation of an aryl substituted compound was not detected. The results are summarized in Table III.

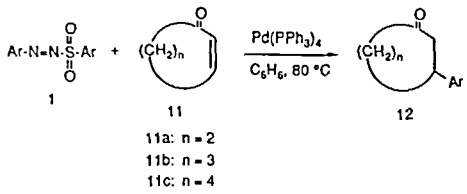


TABLE III

Reactions of Arylazo Aryl Sulfones with 2-Cycloenones

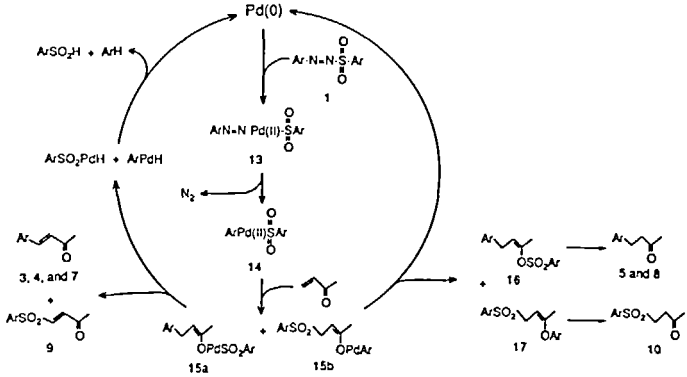
Entry	Ar in 1	n in 11	Product[a] (Yield/%)
16	Ph	2	**12a** 54
17	*p*-Tol	2	**12b** 54
18	*p*-$MeOC_6H_4$	2	**12c** 19
19	Ph	3	**12d** 22
20	*p*-Tol	3	**12e** 42
21	*p*-$MeOc_6H_4$	3	**12f** 25
22	Ph	4	**12g** 27
23	*p*-Tol	4	**12h** 42
24[b]	*p*-$MeOC_6H_4$	4	**12i** 33

[a] Biaryls (ArPh and Ar_2) were formed in 3–10% yield in all cases.

[b] 3-(*p*-Methoxyphenylsulfonyl) cycloheptanone (**13i**) was isolated in 13% yield.

The hydroarylation did not take place in the palladium(0) catalyzed reaction of **1** with alkenes; the aryl-substitution reaction was the only one observed.[4] We proposed diarylpalladium(II) species, ArPd(II)Ar′, as an intermediate in the reaction of **1** with olefins which is formed by an oxidative addition of **1** to palladium(0) giving $ArN_2Pd(II)SO_2Ar'$ and subsequent extrusion of nitrogen and sulfur dioxide.[4]

The plausible mechanism of the reaction of **1** with α,β-unsaturated ketones and esters is shown in the Scheme 1. Oxidative addition of **1** to palladium(0) giving arylazo(arylsulfonyl)palladium(II) species (**13**) which only split off nitrogen and do not lose sulfur dioxide under the reaction conditions to form aryl(arylsulfonyl)palladium(II) species (**14**). 1,4-Addition of the intermediate **14** to α,β-unsaturated compounds gives the adduct **15a** or **15b** where elimination occur in two ways. One is the 1,4-elimination of $ArSO_2Pd(II)H$ and ArPd(II)H from **15a** and **15b** to yield **3**, **4** or **7**, and **9**, respectively. By the subsequent reductive elimination of $ArSO_2H$ and ArH from $ArSO_2Pd(II)H$ and ArPd(II)H, respectively, with the Pd(0) species being regenerated a catalytic cycle is achieved. The second reaction path way is that in which the Pd(0) species is regenerated directly from **15a** and **15b**, with formation of enol sulfonyl ethers **16** and enol ethers **17**, respectively. These ethers are hydrolyzed during work-up step to give **5** and **8**, and **10**, respectively. Thus, we consider that the difference of the reaction of **1** between alkene and α,β-unsaturated carbonyl compound is that diaryl-palladium(II) species, ArPd(II)Ar′, represent the intermediate in the reaction with alkene, whereas, aryl(arylsulfonyl)palladium(II) species (**14**) are the intermediates in the reaction involving α,β-unsaturated carbonyl compound. The intermediate **14** will be more reactive than diarylpalladium(II) species toward α,β-unsaturated carbonyl compounds since the electron density of the palladium atom of **14** is less than that of diarylpalladium(II) caused by the strong electron withdrawing sulfonyl group and hence the palladium atom in **14** attacks more easily the oxygen atom of α,β-unsaturated carbonyl compounds before losing sulfur dioxide. To clarify the participation of the intermediate **16** and **17** the reaction mixture of **1a** with **6c** in the presence of the palladium(II) catalyst was quenched with deuterium oxide. The formation of 3-deuterio-4,4-diphenyl-2-butanone and 3-deuterio-4-phenyl-4-phenylsulfonyl-2-butanone were observed by



Scheme 1

Mass and ^{1}H NMR spectroscopy. The results supported the reaction pathway via **16** and **17** of the Scheme 1. It is not clear at the present time why the product distributions are so much different in the palladium(0) catalyzed reactions of **1** with α,β-unsaturated esters, acyclic α,β-unsaturated ketones, and cyclic α,β-unsaturated ketones.

EXPERIMENTAL

Measurements. Melting points and boiling points are uncorrected. IR spectra were determined on a Hitachi Model 260–10 spectrometer with samples as either neat liquids or KBr disks. ^{1}H NMR spectra were recorded at 60 MHz by using a JEOL JNM-PMX 60 SI spectrometer with Me_4Si as an internal standard in $CDCl_3$. ^{13}C NMR were examined at 90 MHz by using a JEOL JNM-FX 90Q system operating at 22.49 MHz in the Fourier Transform mode. The technique of INEPT (3/4 J) was employed to assign methine carbons. Mass spectra were determined with a JEOL JMS-DX 300 mass spectrometer with JEOL JMA-5000 Mass Data System at an ionizing voltage of 20–70 eV. Gas chromatography was carried out with a Hitachi Model 163 and 263–30 gas chromatograph (FID) using a 1 m column packed with 10% SE–30, and quantitatively analyzed by internal standard method using acetophenone, benzophenone, diphenylmethane, tetradecane, tridecane or undecane. The gel permeation chromatography was performed by using a JAI LC-08 liquid chromatograph with a JAIGEL 1 H column ($20\phi \times 600$ mm $\times$ 2) using chloroform as an eluent.

Materials All solvents were distilled and stored under nitrogen. Tetrakis(triphenylphosphine)palladium(0) was prepared by the method described previously.[5] Phenylazo phenyl sulfone (mp 75–76°C (decomp.); lit. mp 76–77°C (decomp.)),[6] p-tolylazo *p*-tolyl sulfone (mp 95–96°C (decomp.); lit. mp 96–97°C (decomp.)),[6] and *p*-methoxyphenylazo *p*-methoxyphenyl sulfone (mp 111–112°C (decomp.)) were prepared according to the published procedures.

General procedure for the Reaction of Arylazo Aryl Sulfones (**1**) *with* α,β*-Unsaturated Ketones and Esters.* To a stirred solution containing the α,β-unsaturated compound (10.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.02 mmol) in benzene (2.0 ml) heated at 80°C was added a solution containing the arylazo aryl sulfone (2.0 mmol) in benzene (5.0 ml) under nitrogen over a period of 30 min, and the mixture was further stirred for 2 h. The crude reaction mixture was subjected to an elution chromatography on silica-gel by using hexane-ethyl acetate as an eluent. The stereo- and regioisomers of the arylation products were isolated by gel permeation chromatography. Their structures were determined on the basis of their spectroscopic data.

Ethyl (E)-3-phenylpropenoate[7] (**3a**). IR (neat) 1715 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (3H, t, J = 7.0 Hz), 4.18 (2H, q, J = 7.0 Hz), 6.32 (1H, d, J = 16.0 Hz), 7.13–7.43 (5H, m), and 7.58 (1H, d, J = 16.0 Hz): MS, *m/z* 176 (M^+), 148, and 131.

Ethyl (E)-3-(p-tolyl)propenoate[8] (**3b**). IR (neat) 1715 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (3H, t, J = 7.0 Hz), 2.32 (3H, s), 4.22 (2H, q, J = 7.0 Hz), 6.28 (1H, d, J = 16.0 Hz), 7.07 (2H, d, J = 9.0 Hz), 7.32 (2H, d, J = 9.0 Hz), and 7.58 (1H, d, J = 16.0 Hz); MS, *m/z* 190 (M^+), 162, and 145.

Ethyl (E)-(p-methoxyphenyl)propenoate (**3c**). mp 47–48°C (48–50°C);[9] IR (neat) 1700 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (3H, t, J = 7.0 Hz), 3.75 (3H, s), 4.18 (2H, q, J = 7.0 Hz), 6.25 (1H, d, J = 16.0 Hz), 6.82 (2H, d, J = 9.0 Hz), 7.38 (2H, d, J = 9.0 Hz), and 7.57 (1H, d, J = 16.0 Hz).

Ethyl (E)-3-phenyl-2-butenoate[7] (**3d**). IR (neat) 1715 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, J = 7.0 Hz), 2.52 (3H, s), 4.17 (2H, q, J = 7.0 Hz), 6.07 (1H, s), and 6.87–7.62 (5H, m); MS, *m/z* 190 (M^+), 161, and 145.

Ethyl (E)-3-(p-tolyl)-2-butenoate[10] (**3e**). IR (neat) 1710 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (3H, t, J = 7.0 Hz), 2.32 (3H, s), 2.53 (3H, s), 4.15 (2H, q, J = 7.0 Hz), 6.03 (1H, s), 7.07 (2H, d, J = 7.2 Hz), and 7.23 (2H (2H, d, J = 7.2 Hz); MS, *m/z* 204 (M^+) and 159.

Ethyl (E)-3-(p-methoxyphenyl)-2-butenoate[11] (**3f**). IR (neat) 1710 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (3H, t, J = 7.0 Hz), 2.50 (3H, s), 3.73 (3H, s), 4.12 (2H, q, J = 7.0 Hz), 6.03 (1H, s), 6.77 (2H, d, J = 9.0 Hz), and 7.32 (2H, d, J = 9.0 Hz); MS, *m/z* 220 (M^+), 191, and 175.

Ethyl 3-(p-methoxyphenyl)butanoate (**5f**). IR (neat) 1730 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (3H, t, J = 7.0 Hz), 1.27 (3H, d, J = 7.0 Hz), 2.52 (2H, d, J = 7.0 Hz), 3.03–3.46 (1H, m), 3.77 (3H, s),

4.08 (2H, q, J = 7.0 Hz), 6.77 (2H, d, J = 9.0 Hz), and 7.12 (2H, d, J = 9.0 Hz); MS, *m/z* 222 (M^+); HRMS, *m/z* 222.1269 ($C_{13}H_{18}O_3$ requires 222.1256).

Ethyl 3,3-diphenylpropenoate[12] (**3g**). IR (neat) 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (3H, t, J = 7.0 Hz), 3.98 (2H, q, J = 7.0 Hz), 6.13–6.32 (1H, m), and 6.97–7.40 (10H, m); MS, *m/z* 252 (M^+), 223, and 207.

Ethyl 3,3-diphenylpropanoate[13] (**5g**). IR (neat) 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (3H, t, J = 7.0 Hz), 3.00 (2H, d, J = 7.8 Hz), 4.00 (2H, q, J = 7.0 Hz), 4.52 (1H, t, J = 7.8 Hz), and 7.17 (10H, s); MS, *m/z* 254 (M^+) and 225.

Ethyl (E)-3-phenyl-3-(p-tolyl)propenoate (**3h**). IR (neat) 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (3H, t, J = 7.0 Hz), 2.30 (3H, s), 4.00 (2H, q, J = 7.0 Hz), 6.27 (1H, s), and 6.73–7.63 (9H, m); MS, *m/z* 266 (M^+), 237, and 221; HRMS, *m/z* 266.1342 ($C_{18}H_{18}O_2$ requires 266.1307).

Ethyl (Z)-3-phenyl-3-(p-tolyl)propenoate (**4h**). IR (neat) 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (3H, t, J = 7.0 Hz), 2.37 (3H, s), 4.03 (2H, q, J = 7.0 Hz), 6.25 (1H, s), and 6.82–7.57 (9H, m); MS, *m/z* 266 (M^+), 237, and 221; HRMS, *m/z* 266.1336 ($C_{18}H_{18}O_2$ requires 266.1307).

Ethyl 3-phenyl-3-(p-tolyl)-propanoate (**5h**). IR (neat) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (3H, t, J = 7.0 Hz), 2.27 (3H, s), 3.00 (2H, d, J = 7.8 Hz), 3.98 (2H, q, J = 7.0 Hz), 4.47 (1H, t, J = 7.8 Hz), 6.98 (4H, m), and 7.15 (5H, s); MS, *m/z* 268 (M^+); HRMS, *m/z* 268.1443 ($C_{18}H_{20}O_2$ requires 268.1463).

Ethyl (E)-3-(p-methoxyphenyl)-3-phenyl-propenoate (**3i**). IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (3H, t, J = 7.0 Hz), 3.70 (3H, s), 4.00 (2H, q, J = 7.0 Hz), 6.28 (1H, s), 6.77 (2H, d, J = 9.0 Hz), 7.18 (2H, d, J = 9.0 Hz), and 7.25 (5H, s); MS, *m/z* 282 (M^+), 253, and 237; HRMS, *m/z* 282.1255 ($C_{18}H_{18}O_3$ requires 282.1256).

Ethyl (Z)-3-(p-methoxyphenyl)-3-phenylpropenoate (**4i**). IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (3H, t, J = 7.0 Hz), 3.75 (3H, s), 4.05 (2H, q, J = 7.0 Hz), 6.23 (1H, s), 6.83 (2H, d, J = 9.0 Hz), 7.26 (2H, d, J = 9.0 Hz), and 7.27 (5H, s); MS, *m/z* 282 (M^+), 253, and 237; HRMS, *m/z* 282.1243 ($C_{18}H_{18}O_3$ requires 282.1256).

Ethyl 3-(p-methoxyphenyl)-3-phenylpropanoate (**5i**). IR (neat) 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (3H, t, J = 7.0 Hz), 2.98 (2H, d, J = 7.8 Hz), 3.72 (3H, s), 4.03 (2H, q, J = 7.0 Hz), 4.48 (1H, t, J = 7.8 Hz), 6.77 (2H, d, J = 9.0 Hz), 7.18 (5H, s), and 7.33 (2H, d, J = 9.0 Hz); MS, *m/z* 284 (M^+) and 255; HRMS, *m/z* 284.1413 ($C_{13}H_{20}O_3$ requires 284.1412).

(E)-4-Phenyl-3-buten-2-one[14] (**7a**). IR (neat) 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (3H, s), 6.63 (1H, d, J = 16.0 Hz), 7.10–7.65 (5H, m), and 7.43 (1H, d, J = 16.0 Hz); MS, *m/z* 146 (M^+), 131, and 103.

4-Phenyl-2-butanone[15] (**8a**). IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (3H, s), 2.70–2.92 (4H, m), and 7.17 (5H, s); MS, *m/z* 147 (M^+), 133, and 105.

(E)-4-(p-Tolyl)-3-buten-2-one[16] (**7b**). IR (neat) 1665 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (6H, s), 6.52 (1H, d, J = 16.0 Hz), 7.07 (2H, d, J = 8.5 Hz), 7.27 (2H, d, J = 8.5 Hz), and 7.37 (1H, d, J = 16.0 Hz); MS, *m/z* 160 (M^+), 145, and 117.

4-(p-Tolyl)-2-butanone[17] (**8b**). IR (neat) 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08 (3H, s), 2.27 (3H, s), 2.65–2.88 (4H, m), and 6.95 (4H, s); MS, *m/z* 162 (M^+), 147, and 119.

4-(p-Tolylsulfonyl)-2-butanone (**10b**). IR (neat) 1730 (C=O), 1325 and 1155 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (3H, s), 2.46 (3H, s), 2.91 (2H, t, J = 6.8 Hz), 3.36 (2H, t, J = 6.8 Hz), 7.38 (2H, d, J = 8.2 Hz), and 7.79 (2H, d, J = 8.2 Hz); MS, *m/z* 226 (M^+), 198, 156, and 91; HRMS, *m/z* 226.0665 ($C_{11}H_{14}O_3S$ requires 226.0663).

(E)-4-Phenyl-3-pentene-2-one[18] (**7c**). IR (neat) 1675 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (3H, s), 2.47 (3H, s), 6.34 (1H, s), and 7.10–7.52 (5H, m); MS, *m/z* 160 (M^+), 159, 145, 117, 115, and 91.

4-Phenyl-2-pentanone[19] (**8c**). IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (3H, d, J =

7.2 Hz), 2.05 (3H, s), 2.65 (1H, d, J = 8.0 Hz), 2.67 (1H, d, J = 6.0 Hz), 3.28 (1H, ddq, J = 8.0, 7.2, and 6.0 Hz), and 7.12 (5H, s); MS, *m/z* 162 (M^+), 147, and 119.

4-Phenylsulfonyl-2-pentanone (**10c**). mp 48–49°C; IR (neat) 1725 (C=O), 1310 and 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3H, d, J = 6.2 Hz), 2.13 (3H, s), 2.54 (1H, dd, J = 17.8 and 9.4 Hz), 3.16 (1H, dd, J = 17.8 and 3.6 Hz), 3.59–3.93 (1H, m), and 7.24–7.98 (5H, m); MS, *m/z* 227 ($M^+ + 1$), 226 (M^+), 184, and 142; HRMS, *m/z* 226.0668 ($C_{11}H_{14}O_3S$ requires 226.0663).

(E)-4-(p-Tolyl)-3-penten-2-one[20] (**7d**). IR (neat) 1685 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (3H, s), 2.35 (3H, s), 2.52 (3H, s), 6.40–6.53 (1H, m), 7.15 (2H, d, J = 8.6 Hz), and 7.32 (2H, d, J = 8.6 Hz); MS, *m/z* 174 (M^+), 173, 159, and 131.

4-(p-Tolyl)-2-pentanone[21] (**8d**). IR (neat) 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3H, d, J = 7.2 Hz), 2.03 (3H, s), 2.28 (3H, s), 2.62 (1H, d, J = 8.0 Hz), 2.65 (1H, d, J = 6.0 Hz), 3.23 (1H, ddq, J = 8.0, 7.2, and 6.0 Hz), and 6.98 (4H, m); MS, *m/z* 176 (M^+), 161, and 133.

4-(p-Tolylsulfonyl)-2-pentanone (**10d**). mp (decomp.) 64.5–65.5°C; IR (KBr) 1715 (C=O), 1305, 1290, and 1145 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3H, d, J = 6.8 Hz), 2.16 (3H, s), 2.43 (3H, s), 2.53 (1H, dd, J = 17.6 and 9.4 Hz), 3.15 (1H, dd, J = 17.6 and 3.6 Hz), 3.42–3.92 (1H, m), 7.29 (2H, d, J = 8.2 Hz), and 7.68 (2H, d, J = 8.2 Hz); MS, *m/z* 240 (M^+), 198, and 156; HRMS, *m/z* 240,0803 ($C_{12}H_{16}O_3S$ requires 240.0820).

4,4-Diphenyl-3-buten-2-one[16,18] (**7e**). IR (neat) 1695 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (3H, s), 6.43 (1H, s), and 7.10–7.50 (10H, m); MS, *m/z* 222 (M^+), 207, and 179.

4,4-Diphenyl-2-butanone[19] (**8e**). IR (neat) 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (3H, s), 3.12 (2H, d, J = 7.5 Hz), 4.53 (1H, t, J = 7.5 Hz), and 7.10 (10H, s); MS, *m/z* 224 (M^+), 209, and 181.

4-Phenyl-4-phenylsulfonyl-3-buten-2-one (**9e**). IR (neat) 1675 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (3H, s), 7.08–7.79 (11H, m); MS, *m/z* 286 (M^+), 222, 145, and 131; HRMS, *m/z* 286.0613 ($C_{16}H_{14}O_3S$ requires 286.0663).

4-Phenyl-4-phenylsulfonyl-2-butanone (**10e**). mp 108–109°C; IR (KBr) 1715 (C=O), 1310 and 1155 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (3H, s), 3.22 (1H, dd, J = 17.6 and 8.4 Hz), 3.54 (1H, dd, J = 17.6 and 4.6 Hz), 4.69 (1H, dd, J = 8.4 and 4.6 Hz), and 6.77–7.69 (10H, m); MS, *m/z* 288 (M^+), 147, and 105; HRMS, *m/z* 288.0849 ($C_{16}H_{16}O_3S$ requires 288.0820).

4-Phenyl-4-(p-tolyl)-3-buten-2-one[23] (**7f**). MS, *m/z* 236 (M^+), 235, 221, and 193.

4-Phenyl-4-(p-tolyl)-2-butanone[24] (**8f**). IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00 (3H, s), 2.23 (3H, s), 3.10 (2H, d, J = 7.5 Hz), 4.52 (1H, t, J = 7.5 Hz), 7.00 (5H, s), and 7.15 (4H, m); MS, *m/z* 238 (M^+), 223, and 195.

4-Phenyl-4-(p-tolysulfonyl)-3-buten-2-one (**9f**). IR (neat) 1685 (C=O), 1330 and 1155 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (6H, s), 6.84–7.85 (6H, m), 6.86 (2H, d, J = 15.2 Hz), and 7.47 (2H, d, J = 15.2 Hz); MS, *m/z* 300 (M^+), 236, 145, 131, and 91; HRMS, *m/z* 300.0852 ($C_{17}H_{16}O_3S$ requires 300.0820).

4-Phenyl-4-(p-tolylsulfonyl)-2-butanone (**10f**). IR (neat) 1730 (C=O), 1320, 1310, and 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (3H, s), 2.39 (3H, s), 3.23 (1H, dd, J = 17.6 and 8.4 Hz), 3.56 (1H, dd, J = 17.6 and 4.6 Hz), 4.68 (1H, dd, J = 8.4 and 4.6 Hz), and 6.89–7.54 (9H, m); MS, *m/z* 303 ($M^+ + 1$), 302 (M^+), 147, 131, 119, 104, and 92; HRMS, *m/z* 302.1046 ($C_{17}H_{18}O_3S$ requires 302.0976).

3-Phenylcyclopentanone[21] (**12a**). IR (neat) 1745 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63–2.92 (6H, m), 3.30–3.72 (1H, m), and 7.15 (5H, s); ^{13}C NMR ($CDCl_3$) δ 31.18, 38.84, 42.26, 45.75, 126.70 (4C), 128.67, 143.16, and 218.04; MS, *m/z* 160 (M^+), 131, and 104.

3-(p-Tolyl)cyclopentanone[26] (**12b**). IR (neat) 1745 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58–2.90 (6H, m), 2.28 (3H, s), 3.02–3.65 (1H, m), and 7.00 (4H, m); ^{13}C NMR ($CDCl_3$) δ 20.90, 31.14, 38.73, 41.76, 45.79, 126.50 (2C), 129.24 (2C), 136.14, 140.08, and 218.00; MS, *m/z* 174 (M^+), 159, 145, and 131.

3-(p-Methoxyphenyl)cyclopentanone[27] (**12c**). IR (neat) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–2.98 (6H, m), 3.03–3.57 (1H, m), 3.75 (3H, s), 6.78 (2H, d, J = 9.0 Hz), and 7.07 (2H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 31.22, 38.73, 41.38, 45.86, 55.19, 113.99 (2C), 127.49 (2C), 135.08, 158.29, and 218.07; MS, *m/z* 190 (M^+), 161, and 147.

3-Phenylcyclohexanone[28] (**12d**). IR (neat) 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–3.28 (9H, m) and 7.15 (5H, s); ^{13}C NMR ($CDCl_3$) δ 25.49, 32.85, 41.20, 44.76, 48.93, 126.54 (2C), 125.70 (2C), 128.67, 144.37, and 210.68; MS, *m/z* 174 (M^+), 146, and 131.

3-(p-Tolyl)cyclohexanone[29] (**12e**). IR (neat) 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–3.35 (9H, m), 2.33 (3H, s), and 6.89–7.28 (4H, m); ^{13}C NMR ($CDCl_3$) δ 20.90, 25.45, 32.89, 41.16, 44.34, 48.97, 126.35 (2C), 129.31 (2C), 136.14, 141.45, and 210.79; MS, *m/z* 188 (M^+) and 145.

3-(p-Methoxyphenyl)cyclohexanone[30] (**12f**). IR (neat) 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–3.25 (9H, m), 3.72 (3H, s), 6.73 (2H, d, J = 9.0 Hz), and 7.00 (2H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 25.45, 33.04, 41.08, 43.96, 49.20, 55.27, 114.06 (2C), 127.42 (2C), 136.59, 158.29, and 210,79; MS, *m/z* 204 (M^+) and 161.

3-Phenylcycloheptanone[31] (**12g**). IR (neat) 1705 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22–3.28 (11H, m) and 7.10 (5H, s); ^{13}C NMR ($CDCl_3$) δ 24.20, 29.28, 39.22, 42.79, 43.93, 51.29, 126.25 (2C), 126.32 (2C), 128.67, 146.95, and 213.11; MS, *m/z* 188 (M^+), 159, and 145.

3-(p-Tolyl)cycloheptanone[32] (**12h**). IR (neat) 1705 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13–3.10 (11H, m), 2.27 (3H, m), and 6.82–7.25 (4H, m); ^{13}C NMR ($CDCl_3$) δ 20.90, 24.16, 29.17, 39.18, 42.29, 43.89, 51.32, 126.28 (2C), 129.24 (2C), 135.76, 143.95, and 213.14; MS, *m/z* 202 (M^+), 187, 173, and 159.

3-(p-Methoxyphenyl)cycloheptanone (**12i**). mp 45–46°C (lit. mp 45–46°C)[32]; IR (KBr) 1690 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02–3.17 (11H, m), 3.77 (3H, s), 6.77 (2H, d, J = 9.0 Hz), and 7.07 (2H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 24.20, 29.21, 39.37, 41.95, 43.93, 51.51, 55.23, 114.03 (2C), 127.30 (2C), 139.14, 158.10, and 213.26; MS, *m/z* 218 (M^+) and 176.

3-(p-Methoxyphenylsulfonyl)cycloheptanone (**13i**). IR (neat) 1710 (C=O), 1320 and 1140 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–3.34(11H, m), 3.83 (3H, s), 6.93 (2H, d, J = 9.0 Hz), and 7.68 (2H, d, J = 9.0 Hz); MS, *m/z* 282 (M^+), 264, 216, 171, and 111; HRMS, *m/z* 282.0940 ($C_{14}H_{18}O_4S$ requires 282.0925).

Quenching Study of the Reaction Mixture of **1a** *with* **6c** *by Deuterium Oxide.* Deuterium oxide was added to the reaction mixture of **1a** with **6c** and stirred at room temperature for 2 h. The organic layer was subjected to the gel permeation chromatography to give 3-deuterio-4,4-diphenyl-2-butanone and 3-deuterio-4-phenyl-4-phenyl-sulfonyl-2-butanone.

3-Deuterio-4,4-diphenyl-2-butanone. ^1H NMR ($CDCl_3$) δ 2.02 (3H, s), 3.14 (1H, d, J = 7.5 Hz), 4.52 (1H, d, J = 7.5 Hz), and 7.11 (10H, s); MS, *m/z* 225 (M^+); HRMS, *m/z* 225.1258 ($C_{16}H_{15}DO$ requires 225.1264).

3-Deuterio-4-phenyl-4-phenylsulfonyl-2-butanone. ^1H NMR ($CDCl_3$) δ 2.13 (3H, s), 3.24 and 3.52 (1H, dd, J = 8.4 and 4.6 Hz), 4.65 (1H, dd, J = 8.4 and 4.8 Hz), and 6.75–7.68 (10H, m), MS, *m/z* 289 (M^+); HRMS, *m/z* 289.0875 ($C_{16}H_{15}DO_3S$ requires 289.0883).

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