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Arylation of Olefins by Arylazo Aryl Sulfones under Palladium(0) Catalysis[1)]

Nobumasa KAMIGATA,* Akira SATOH, Tetsuya KONDOH, and Masayuki KAMEYAMA
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

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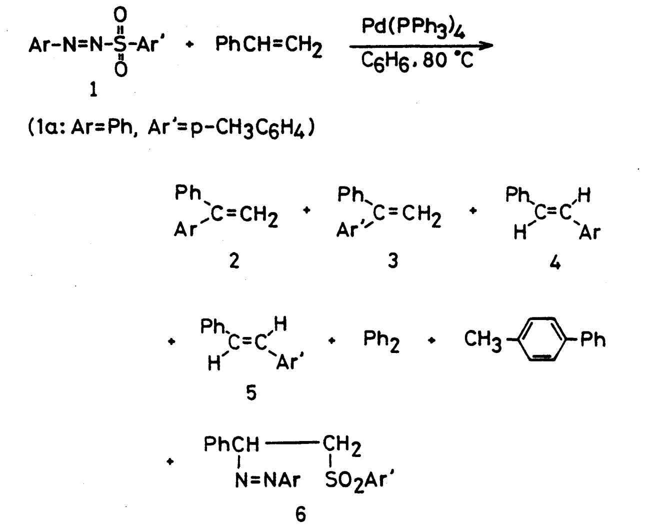
The palladium(0)-catalyzed reaction of arylazo aryl sulfones with olefins in benzene at 80 °C gave aryl-substituted olefins in good yield. Diarylpalladium(II) species was proposed as an intermediate in this reaction.

The arylation of unsaturated compounds by arenediazonium salts with copper salt catalysis was first disclosed by Meerwein et al.[2)] The Meerwein arylation is a useful synthetic procedure, because of the availability of a variety of arylamines and good product yield. However, it generally requires the olefins to be activated by an electron-withdrawing group, such as carbonyl, cyano, aryl, vinyl, ethynyl or chloro group. Doyle et al. reported a modified Meerwein arylation with significant yield improvement by the use of free arylamines and alkyl nitrite in place of arenediazonium salts.[3)] However, the limitation of olefinic compounds still remains. Arylpalladium reagents obtained from aryl halides or arylmercurials have been utilized extensively for arylation of olefins,[4)] and the arylation is known to be free from the requirement for activation in the olefinic substance. Recently, Kikukawa et al. reported a novel arylation of olefins by arenediazonium salts[5)] or *N*-nitroso-*N*-arylacetamides[6)] in the presence of a catalytic amount of palladium(0). In a preliminary paper we reported that arylazo aryl sulfones react with styrene in the presence of tetrakis(triphenylphosphine)palladium(0) as a catalyst under mild conditions to give (*E*)-1-aryl-2-phenylethene and 1-aryl-1-phenylethene in good yields.[7)] We give here a full account for the palladium(0)-catalyzed arylation of olefins by arylazo aryl sulfones.

Results and Discussion

Dropwise addition of phenylazo *p*-tolyl sulfone (**1a**) in benzene to a stirred solution of styrene and tetrakis(triphenylphosphine)palladium(0) in benzene resulted in evolution of nitrogen. TLC analysis showed that the crude products are separated in roughly two spots, and these components were separated by column chromatography. The products of the former fraction were determined as 1,1-diphenylethylene (**2**) 10%, 1-phenyl-1-(*p*-tolyl)ethylene (**3**) 10%, (*E*)-stilbene (**4**) 32%, (*E*)-1-phenyl-2-(*p*-tolyl)ethylene (**5**) 32%, biphenyl 1%, and 4-methylbiphenyl 1%. The latter fraction was recrystallized from ethanol to give pale yellow crystals which were identified as 2-phenyl-2-(phenylazo)ethyl *p*-tolyl sulfone (**6a**) (yield, 21%). The products **2**—**6** seem to be formed by the catalytic reaction of **1a** by the palladium(0) complex since the thermal reaction of **1** with styrene without catalyst is known not to form such arylated compounds **2**—**6** but to form an aryl radical as an intermediate which acts as an initiator for the polymerization of styrene.[8)] The other transition metal catalysts such as $Pd(OAc)_2$, $Pd(dba)_2$, $PdCl_2$, $RhCl(PPh_3)_3$, and $RuCl_2(PPh_3)_3$ have showed little catalytic effect for the arylation of styrene by **1a**. It is interesting to note that both phenyl and *p*-tolyl groups of **1a** are arylated at the *α*- and *β*-position of styrene in almost equal amount to give **2** or **3**, and **4** or **5**, respectively.



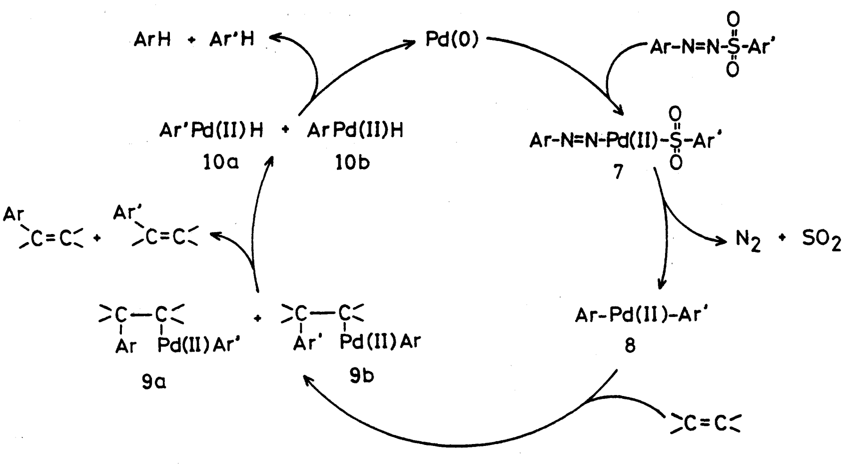
Similarly, the reactions of *p*-tolylazo phenyl sulfone (**1b**), phenylazo phenyl sulfone (**1c**), and *p*-tolylazo *p*-tolyl sulfone (**1d**) with styrene were carried out in the presence of tetrakis(triphenylphosphine)palladium(0) in benzene solution under nitrogen at 80 °C. The results are summarized in Table 1. It is noteworthy that the yields of the products **2**, **3**, **4**, and **5** were almost the same both in the reactions of **1a** and **1b**, respectively. The result suggests that a common reactive intermediate is formed from either reaction of **1a** and **1b** by the palladium(0) catalysis, and the Ar and Ar′ groups of the intermediate have the same reactivity. When the Ar and Ar′ groups of the azosulfone **1** are the same (Entries 3 and 4), the products are simplified.

These reactions may be accounted for by the oxidative addition of arylazo aryl sulfone to palladium(0) catalyst giving Ar-N=N-Pd(II)-SO_2-Ar′ (**7**), which splits off nitrogen and sulfur dioxide to form a diarylpalladium(II) complex, Ar-Pd(II)-Ar′ (**8**). The reactive intermediate **8** adds to an olefin giving adducts **9a** and **9b** which afford arylated olefin **2**—**5** and Ar′-Pd(II)-H (**10a**) or Ar-Pd(II)-H (**10b**). The reductive elimination of arenes (ArH and Ar′H) from **10** follows,

Table 1. Reaction of Arylazo Aryl Sulfones with Styrene Catalyzed by Tetrakis(triphenylphosphine)palladium(0) in Benzene at 80 °C[a)]

	Ar and Ar′ in **1**		Product, Yield[b)]/%					
	Ar	Ar′	**2**	**3**	**4**	**5**	**6**	Biaryls
1a	C_6H_5	p-$CH_3C_6H_4$	10	10	32	32	21	c
1b	p-$CH_3C_6H_4$	C_6H_5	11	12	33	32	22	c
1c	C_6H_5	C_6H_5	17	—	56	—	32	d
1d	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	—	15	—	49	35	e

a) The reactions were performed by addition of arylazo aryl sulfone (2.0 mmol) in benzene (8.0 cm^3) to a stirred solution of styrene (10 mmol) and $Pd(PPh_3)_4$ (0.02 mmol) in benzene (2.0 cm^3) under nitrogen at 80 °C for 2 h. b) The yield was determined by GC analysis based on the arylazo aryl sulfone used. c) Biphenyl (1%) and 4-methylbiphenyl (1%) were formed. d) Biphenyl (2%) was formed. e) 4-Methylbiphenyl (2%) and 4,4′-dimethylbiphenyl (4%) were formed.



Scheme 1.

and Pd(0) is regenerated (Scheme 1).

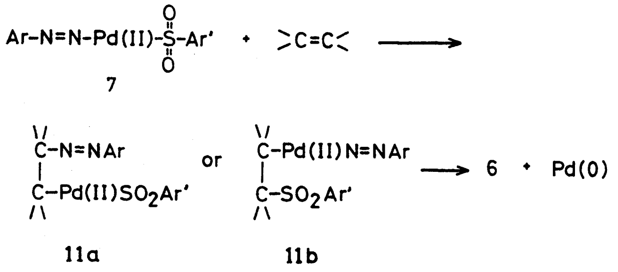
The diarylpalladium(II) species **8** successfully interprets the product ratio 2/3=1 and 4/5=1 both in the reaction of **1a** and **1b** since Ar and Ar′ groups in **8** are expected to have the same reactivity toward olefin and it is also to be expected that **10a** and **10b** will eliminate from **9a** and **9b** in the same rate, respectively. The formation of the diarylpalladium(II) species was supported by detection of biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl (Table 1) since these products are considered to be formed by the reductive elimination from **8** accompanying with regeneration of Pd(0) (Scheme 2).

$$\text{Ar-Pd(II)-Ar}' \longrightarrow \text{Ar-Ar}' + \text{Pd(0)}$$

Scheme 2.

The formation of arene (ArH and Ar′H) by the reductive elimination from **10** is difficult to detect when the aryl group of **1** is phenyl. Next, the reaction of p-methoxyphenylazo p-tolyl sulfone with styrene was carried out in the presence of the palladium(0) catalyst in benzene, and the formation of both anisole and toluene was found by GC-MS.

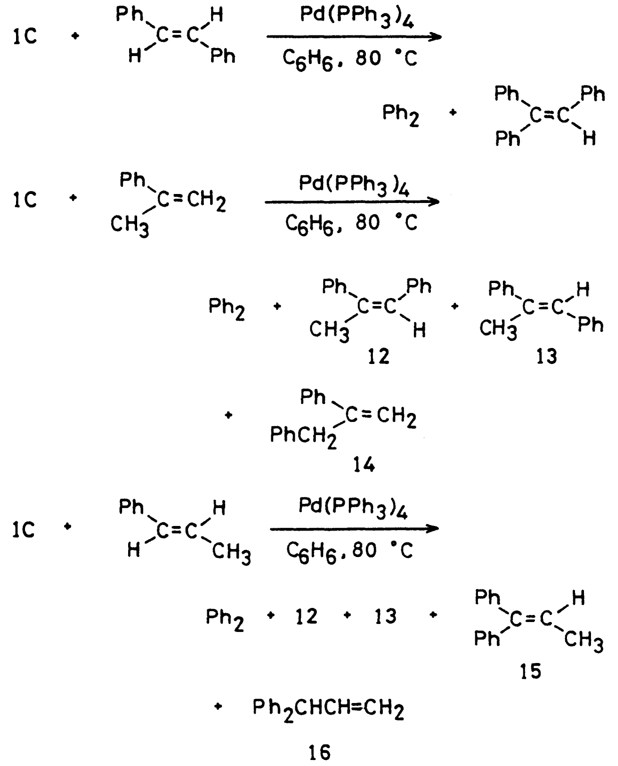
The formation of **6** is accounted for by the addition of arylazo(arylsulfonyl)palladium(II) species **7** (shown in Scheme 1) to olefin to give the adduct **11a** or **11b** which followed by the reductive elimination of **6** accompanying with regeneration of Pd(0) species (Scheme 3).



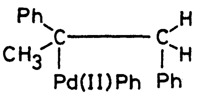
Scheme 3.

The regioselectivity for the arylation of styrene by **1** is different from that of the related arylation of styrene by N-nitroso-N-arylacetamide under palladium(0) reported by Kikukawa et al.[6)] They obtained the arylation products at the α- and β-position of styrene in the ratio of 5 : 95. On the other hand, in our case, the ratio of the arylation at the α- and β-position of styrene is 1 : 3. These differences may be attributed to the difference of the reductive-eliminating group from the adduct.

The reactions of **1c** with (E)-stilbene, 2-phenylpropene, and (*E*)-1-phenylpropene in the presence of a catalytic amount of the palladium(0) catalyst in benzene were also carried out at 80 °C for 2 h. The reaction of **1c** with (*E*)-stilbene gave biphenyl 6% and triphenylethylene 44%. The reaction of **1c** with 2-phenylpropene afforded biphenyl 7%, (*Z*)-1,2-diphenylpropene (**12**) 6%, (*E*)-1,2-diphenylpropene (**13**) 30%, and 2,3-diphenylpropene (**14**) 35%. The reaction of **1c** with (*E*)-1-phenylpropene formed biphenyl 11%, **12** 4%, **13** 25%, 1,1-diphenylpropene (**15**) 20%, and 3,3-diphenylpropene (**16**) 7%.



The formation of the compounds **12**—**16** is accounted for by the reaction of the diphenylpalladium(II) species, formed from **1c** and Pd(0), with 2-phenylpropene or (*E*)-1-phenylpropene giving the adduct **17** and **18** or **19**, respectively. The PhPd group can eliminate with all possible *β*-hydrogen from this intermediate: **17** affords **12**, **13**, and **14**; similarly, **18** affords **12** and **13**; and **19** affords **15** and **16**.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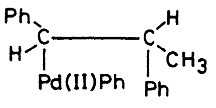
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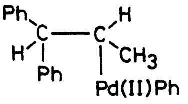
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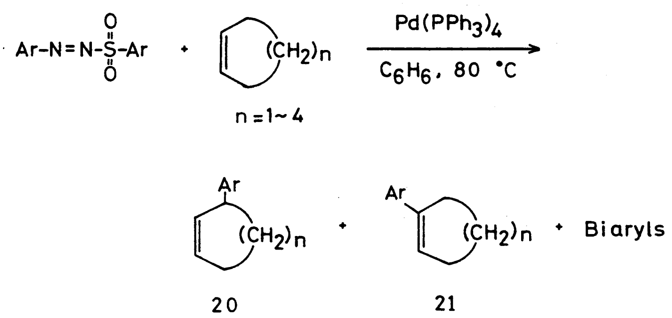
The palladium(0)-catalyzed arylation of cycloalkenes with **1** is also carried out under similar conditions. The results are summarized in Table 2. In this case, 3-arylcycloalkene **20** and 1-arylcycloalkene **21** were obtained in good yield with minor by-products, biaryls; although alicyclic olefins are known to be poor substrates in the Meerwein arylation.[2] It is of interest that 1-arylcyclopentene was formed in a little higher yield than 3-arylcyclopentene in each of the reactions of arylazo aryl sulfone with cyclopentene. The isomer distribution of the arylation products obtained here were considerably different from those of related phenylation of cyclopentene by aniline and *t*-butyl nitrite catalyzed by bis(dibenzylideneacetone)palladium(0).[5e] Whereas, the reaction of arylazo aryl sulfone with cyclohexene, cycloheptene, and cyclooctene afforded 3-arylcyclohexene, 3-arylcycloheptene,

Table 2. Reaction of Arylazo Aryl Sulfones with Cycloalkenes Catalyzed by Tetrakis(triphenylphosphine)palladium(0) in Benzene at 80 °C[a]

n in cycloalkene	Ar in ArN_2SO_2Ar	Product, Yield[b]/%					
		3-Aryl-cycloalkene		1-Aryl-cycloalkene		ArPh	ArAr
1	C_6H_5	**20a**	18	**21a**	26	—	9
1	*p*-$CH_3C_6H_4$	**20b**	23	**21a**	41	5	4
1	*p*-$CH_3OC_6H_4$	**20c**	20	**21c**	23	3	2
2	C_6H_5	**20d**	61	**21d**	4	—	8
2	*p*-$CH_3C_6H_4$	**20e**	42	**21e**	2	8	0
2	*p*-$CH_3OC_6H_4$	**20f**	33	**21f**	1	7	1
3	C_6H_5	**20g**	62	**21g**	1	—	11
3	*p*-$CH_3C_6H_4$	**20h**	89	**21h**	0	0	10
3	*p*-$CH_3OC_6H_4$	**20i**	41	**21i**	Trace	9	1
3	*p*-ClC_6H_4	**20j**	37	**21j**	1	11	0
4	C_6H_5	**20k**	67	**21k**	6	—	8
4	*p*-$CH_3C_6H_4$	**20l**	66	**21l**	Trace	3	8
4	*p*-$CH_3OC_6H_4$	**20m**	76	**21m**	5	3	1
4	*p*-ClC_6H_4	**20n**	78	**21n**	0	5	0

a) The reactions were carried out by addition of arylazo aryl sulfone (2.0 mmol) in benzene (8.0 cm^3) to a stirred solution of cycloalkene (10.0 mmol) and $Pd(PPh_3)_4$ (0.02 mmol) in benzene (2.0 cm^3) under nitrogen at 80 °C for 24 h. b) The yield was determined by GC analysis based on the arylazo aryl sulfone employed.

and 3-arylcyclooctene, respectively, as the major arylation product, the corresponding 1-arylcycloalkene was obtained in much lower yield to zero, although the reason is not clear at the present time.



Experimental

Measurement. Melting points and boiling points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrophotometer with samples as either neat liquids or in KBr disks. ^{1}H NMR spectra were recorded at 60 MHz by using a JNM-PMX 60 SI spectrometer with Me_4Si as an internal standard in $CDCl_3$. Mass spectra were determined with a JEOL JMS-DX300 mass spectrometer with JEOL JMA-5000 Mass Data System at an ionizing voltage of 20—70 eV. Gas chromatography was carried out with Hitachi Models 163 and 263-30 gas chromatographs (FID) using a 1 m column packed with 10% SE-30. The gel permeation chromatography was performed by using a JAI LC-08 liquid chromatograph with a JAIGEL-1H column (20 ϕ×600 mm×2, chloroform as eluent).

Materials. All solvents were distilled and stored under nitrogen. Palladium chloride of Wako Chemicals was used without further purification. Tetrakis(triphenylphosphine)-palladium(0),[9] palladium acetate(II),[10] bis(dibenzylideneacetone)palladium(0),[11] chlorotris(triphenylphosphine)rhodium(I),[12] and dichlorotris(triphenylphosphine)ruthenium-(II),[13] were prepared by the method described in the literature. Phenylazo *p*-tolyl sulfone (**1a**), *p*-tolylazo phenyl sulfone (**1b**), phenylazo phenyl sulfone (**1c**), *p*-tolylazo *p*-tolyl sulfone (**1d**), *p*-methoxyphenylazo *p*-methoxyphenyl sulfone (**1e**), and *p*-chlorophenylazo *p*-chlorophenyl sulfone (**1f**) were prepared by the published procedures.[14] Styrene, 2-phenylpropene, (*E*)-1-phenylpropene, cyclopentene, cyclohexene, cycloheptene, cyclooctene of Tokyo Kasei Chemicals were purified by distillation under nitrogen prior to use.

General Procedure for the Reaction of Arylazo Aryl Sulfone with Styrenes. A solution containing arylazo aryl sulfone (2.0 mmol) in benzene (5.0 cm^3) was added dropwise to a stirred solution containing styrene or a styrene derivative (10 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.02 mmol) in benzene (2.0 cm^3) heated at 80 °C under nitrogen over a period of 30 min, and the mixture was further stirred for 2 h. The crude reaction mixture was chromatographed on silica gel using hexane–ethyl acetate as eluent. The stereo- and regioisomers of the arylation products were isolated by GC. The structure of biphenyl, 4-methylbiphenyl, 4,4′-dimethylbiphenyl, 1,1-diphenylethylene (**2**), 1-phenyl-1-(*p*-tolyl)ethylene (**3**), (*E*)-stilbene (**4**), (*E*)-1-phenyl-2-(*p*-tolyl)ethylene (**5**), triphenylethylene (**11**), (*Z*)-1,2-diphenylpropene (**12**), (*E*)-1,2-diphenylpropene (**13**), 2,3-diphenylpropene (**14**), 1,1-diphenylpropene (**15**), and 3,3-diphenylpropene (**16**) were identified by comparison of their retention times of GC; IR, ^{1}H NMR, and GC mass spectra with those of authentic samples. The adducts **6** were isolated as the corresponding [1,3]sigmatropic hydrogen shifted isomer, and the structure was determined by the following spectroscopic data.

2-Phenyl-2-(phenylhydrazono)ethyl *p*-Tolyl Sulfone: Mp 179—180 °C; IR (KBr) 3340, 1310, and 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s), 4.58 (2H, s), 7.21 (2H, d, *J*=7.8 Hz), 7.24 (10H, s), 7.75 (2H, d, *J*=7.8 Hz), and 9.35 (1H, s); MS, *m/z* 364 (M^+); HRMS, *m/z* 364.1258 ($C_{21}H_{20}O_2N_2S$ requires 364.1245). This compound is easily converted to **6a** by treating with an acid. 2-Phenyl-2-(phenylazo)ethyl *p*-tolyl sulfone (**6a**): mp 139—140 °C; IR (KBr) 1450, 1310, and 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s), 3.5—3.9 (1H, m), 4.2—4.6 (1H, m), 5.3—5.6 (1H, m), 7.10 (2H, d, *J*=7.8 Hz), 7.25 (5H, s), 7.38 (5H, s), and 7.64 (2H, d, *J*=7.8 Hz); MS, *m/z* 364 (M^+); HRMS, *m/z* 364.1242 ($C_{21}H_{20}O_2N_2S$ requires 364.1245).

2-Phenyl-2-(*p*-tolylhydrazono)ethyl Phenyl Sulfone (Isomer of 6b): Mp 170—171 °C; IR (KBr) 3340, 1300, and 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.31 (3H, s), 4.61 (2H, s), 7.2—7.8 (14H, m), and 9.36 (1H, s); MS, *m/z* 364 (M^+); HRMS, *m/z* 364.1239 ($C_{21}H_{20}O_2N_2S$ requires 364.1245).

2-Phenyl-2-(phenylhydrazono)ethyl Phenyl Sulfone (Isomer of 6c): Mp 153—154 °C; IR (KBr) 3350, 1300, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.65 (2H, s), 7.2—8.0 (15H, m), and 9.40 (1H, s); MS, *m/z* 350 (M^+); HRMS, *m/z* 350.1119 ($C_{20}H_{18}O_2N_2S$ requires 350.1089).

2-Phenyl-2-(*p*-tolylhydrazono)ethyl *p*-Tolyl Sulfone (Isomer of 6d): Mp 172—173 °C; IR (KBr) 3340, 1300, and 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.31 (3H, s), 2.37 (3H, s), 4.60 (2H, s), 7.1—7.8 (13H, m), and 9.38 (1H, s); MS, *m/z* 378 (M^+); HRMS, *m/z* 378.1409 ($C_{22}H_{22}O_2N_2S$ requires 378.1402).

Arylation of Cycloalkenes. General Procedure. All procedures were carried out under nitrogen, although aerobic conditions also gave satisfactory results. To a stirred solution containing cycloalkene (10 mmol), tetrakis(triphenylphosphine)palladium(0) (0.02 mmol) in benzene (2.0 cm^3) heated at 80 °C was added dropwise a solution containing of arylazo aryl sulfone (2.0 mmol) in benzene (5.0 cm^3) over a period of 30 min, and the solution was further stirred for 24 h. The crude reaction mixture was subjected to elution chromatography on silica gel using hexane–ethyl acetate as eluent. The regioisomers of the arylation products **20** and **21** were isolated by gel permeation chromatography, and the structures were determined on the basis of their spectroscopic data.

3-Phenylcyclopentene[15] (20a): IR(neat) 2940, 2850, 1605, 1495, 1450, 755, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.53—2.90 (4H, m), 3.63—4.10 (1H, m), 5.63—6.02 (2H, m), and 7.12 (5H, m); MS, *m/z* 144 (M^+), 129, and 115.

3-(*p*-Tolyl)cyclopentene (20b): A colorless oil; IR (neat) 3060, 2930, 2855, 1615, 1515, 820, and 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.52—2.85 (4H, m), 2.28 (3H, s), 3.62—4.08 (1H, m), 5.58—6.08 (2H, m), 6.82—7.23 (4H, m); MS, *m/z* 158 (M^+), 143, and 128; HRMS, *m/z* 158.1098 ($C_{12}H_{14}$ requires 158.1095).

3-(*p*-Methoxyphenyl)cyclopentene (20c): A colorless oil; IR (neat) 2960, 2910, 2850, 1615, 1515, 1250, 830, and 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.45—2.87 (4H, m), 3.30—4.98 (1H, m), 3.65 (3H, s), 5.43—5.97 (2H, m), 6.65 (2H, d, *J*=9.0

Hz), and 6.95 (2H, d, J=9.0 Hz); MS, m/z 174 (M^+) and 159; HRMS, m/z 174.1046 ($C_{12}H_{14}O$ requires 174.1044).

3-Phenylcyclohexene[16] (20d): IR (neat) 3030, 2930, 1610, 1500, 1460, 765, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.70—3.05 (6H, m), 3.13—3.60 (1H, m), 5.40—6.30 (2H, m), and 7.13 (5H, s); MS, m/z 158 (M^+), 143, and 129.

3-(*p*-Tolyl)cyclohexene (20e): A colorless oil; IR(neat) 3030, 2920, 1515, 1435, and 825 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.22—3.02 (6H, m), 2.27 (3H, s), 3.10—3.50 (1H, m), 5.43—5.83 (2H, m), and 6.83—7.23 (4H, m); MS, m/z 172 (M^+), 157, and 144; HRMS, m/z 172.1250 ($C_{13}H_{16}$ requires 172.1252).

3-(*p*-Methoxyphenyl)cyclohexene (20f): A colorless oil; IR (neat) 3060, 2970, 1635, 1530, 1260, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90—3.03 (6H, m), 3.27 (1H, m), 3.72 (3H, m), 5.35—5.98 (2H, m), 6.72 (2H, d, J=9.0 Hz), and 7.05 (2H, d, J=9.0 Hz); MS, m/z 188 (M^+), 173, and 160; HRMS, m/z 188.1208 ($C_{13}H_{16}O$ requires 188.1201).

3-Phenylcycloheptene[17] (20g): IR (neat) 3040, 2940, 2860, 1610, 1500, 1450, 760, and 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.10—3.00 (8H, m), 3.23—3.77 (1H, m), 5.50—6.15 (2H, m), and 7.17 (5H, s); MS, m/z 172 (M^+), 157, 144, and 130.

3-(*p*-Tolyl)cycloheptene (20h): A colorless oil; IR (neat) 3010, 2925, 2855, 1510, 1440 and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87—2.95 (8H, m), 2.25 (3H, s), 3.17—3.72 (1H, m), 5.47—6.05 (2H, m), and 6.98 (4H, m); MS, m/z 186 (M^+), 171, and 158; HRMS, m/z 186.1417 ($C_{14}H_{18}$ requires 186.1408).

3-(*p*-Methoxyphenyl)cycloheptene (20i): A colorless oil; IR(neat) 2930, 1615, 1520, 1245, 1040, and 825 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.83—3.03 (8H, m), 3.42 (1H, m), 3.70 (3H, s), 5.60—5.93 (2H, m), 6.68 (2H, d, J=9.0 Hz), and 7.02 (2H, d, J=9.0 Hz); MS, m/z 202 (M^+), 187, and 173; HRMS, m/z 202.1336 ($C_{14}H_{18}O$ requires 202.1357).

3-(*p*-Chlorophenyl)cycloheptene (20j): A colorless oil; IR (neat) 2925, 1600, 1495, 1095, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.82—3.00 (8H, m), 3.25—3.65 (1H, m), 5.63—5.93 (2H, m), and 6.90—7.35 (4H, m); MS, m/z 206 (M^+) 191, 178, and 171; HRMS, m/z 206.0845 ($C_{13}H_{15}Cl$ requires 206.0862).

3-Phenylcyclooctene[15b,18] (20k): IR (neat) 3030, 2940, 2870, 1605, 1490, 1440, 750, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00—3.05 (10H, m), 3.47—4.03 (1H, m), 5.35—6.17 (2H, m), and 7.17 (5H, s); MS, m/z 186 (M^+), 171, and 158.

3-(*p*-Tolyl)cyclooctene (20l): A colorless oil; IR (neat) 3020, 2940, 2870, 1520, 1470, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92—2.95 (10H, m), 2.25 (3H, s), 3.23—3.95 (1H, m), 5.30—6.05 (1H, m), and 6.67—7.40 (4H, m); MS, m/z 200 (M^+), 185, and 172; HRMS, m/z 200.1568 ($C_{15}H_{20}$ requires 200.1565).

3-(*p*-Methoxyphenyl)cyclooctene (20m): A colorless oil; IR (neat) 2950, 1620, 1520, 1260, and 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.13—2.93 (11H, m), 3.68 (3H, s), 5.33—5.92 (2H, m), 6.70 (2H, d, J=9.0 Hz), and 7.00 (2H, d, J=9.0 Hz); MS, m/z 216 (M^+), 201, and 188; HRMS, m/z 216.1515 ($C_{15}H_{20}O$ requires 216.1514).

3-(*p*-Chlorophenyl)cyclooctene (20n): A colorless oil; IR (neat) 2930, 1490, 1095, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 0.73—3.00 (10H, m), 3.38—3.97 (1H, m), 5.25—6.07 (2H, m), and 6.85—7.37 (4H, m); MS, m/z 220 (M^+), 192, and 185; HRMS, m/z 220.1017 ($C_{14}H_{17}Cl$ requires 220.1019).

1-Phenylcyclopentene[19] (21a): IR (neat) 2940, 2850, 1605, 1495, 1450, 755, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.53—2.90 (6H, m), 6.02—6.28 (2H, m), and 7.12—7.57 (5H, m); MS, m/z 144 (M^+), 129, and 115.

1-(*p*-Tolyl)cyclopentene[17,19] (21b): IR(neat) 2970, 2940, 2870, 1510, and 805 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.62—2.93 (6H, m), 2.28 (3H, s), 5.92—6.23 (1H, m), 7.02 (2H, d, J=8.0 Hz), and 7.25 (2H, d, J=8.0 Hz); MS, m/z 158 (M^+), 143, and 128.

1-(*p*-Methoxyphenyl)cyclopentene (21c): Mp 84.5—85.5 °C (lit, mp 81 °C):[19] IR (KBr) 2960, 2850, 1610, 1515, 1260, 840, and 805 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.50—2.28 (6H, m), 3.78 (3H, s), 5.88—6.07 (1H, m), 6.73 (2H, d, J=9.0 Hz), and 7.27 (2H, d, J=9.0 Hz); MS, m/z 174 (M^+), and 159.

The following 1-arylcycloalkenes **21d—g** and **21i—m** were determined only by the retention times of GC and GC mass spectra comparing with those authentic samples since these products were formed in very low yield.

1-Phenylcyclohexene[16,18] (21d): MS, m/z 158 (M^+), 143, and 128.

1-(*p*-Tolyl)cyclohexene[20] (21e): MS, m/z 172 (M^+), 157, and 144.

1-(*p*-Methoxyphenyl)cyclohexene[20] (21f): MS, m/z 188 (M^+), 173, and 158.

1-Phenylcycloheptene[21] (21g): MS, m/z 172 (M^+), 157, 144, and 129.

1-(*p*-Methoxyphenyl)cycloheptene[17] (21i): MS, m/z 202 (M^+), 187, and 174.

1-(*p*-Chlorophenyl)cycloheptene (21j): A colorless oil; MS, m/z 206 (M^+), 191, 178, and 171; HRMS, m/z 206.0802 ($C_{13}H_{15}Cl$ requires 206.0862).

1-Phenylcyclooctene[15b,18] (21k): MS, m/z 186 (M^+), 171, and 158.

1-(*p*-Tolyl)cyclooctene[22] (21l): MS, m/z 200 (M^+), 185, and 172.

1-(*p*-Methoxyphenyl)cyclooctene[23] (21m): MS, m/z 216 (M^+) and 188.

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