An Oxidative Rearrangement of 6-Phenylbicyclo[3.2.0]heptan-6-ol to 1,1′-Biphenyl-Carbaldehydes: A Mechanistic Study

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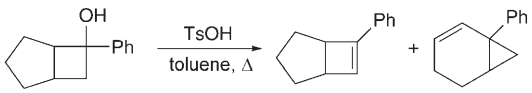
Acid-catalyzed rearrangement of 6-phenylbicyclo[3.2.0]heptan-6-ol gave 1,1′-biphenyl and 1,1′-biphenyl-carbaldehydes in small amounts as well as the expected rearrangement products. A detailed study of the reaction mechanism revealed that the conversion occurs *via* an oxidative process through the consecutive formation of cycloheptadienes, cycloheptatrienes, and 1,1′-biphenyls. The acid-catalyzed rearrangement of 6-phenylbicyclo[3.2.0]hept-2-en-6-ols gave 1- and 2-phenylcycloheptatrienes directly, from which 1,1′-biphenyl and 1,1′-biphenyl-carbaldehydes were obtained by oxidation.

Introduction. – As known, a common way of generating alkenes is acid-catalyzed dehydration of alcohols. In general, many of the dehydration reactions produce alkenes. On the other hand, during dehydration reactions, further rearrangements may occur to give more stabilized carbocations, and such cascade rearrangements are found in the synthesis of biological molecules such as terpenes [1].

In our previous studies, we synthesized some strained cyclic allenes and used many cyclic alkenes produced by the acid-catalyzed dehydration of alcohols [2]. Recently, *Algi* and *Balci* [3] prepared 6-phenylbicyclo[3.2.0]hept-6-ene (**2**) by dehydration of 6-phenylbicyclo[3.2.0]heptan-6-ol (**1**) (*Scheme 1*), from which they synthesized many fluoro- or bromo-substituted indane derivatives by the addition of halocarbenes.

Scheme 1



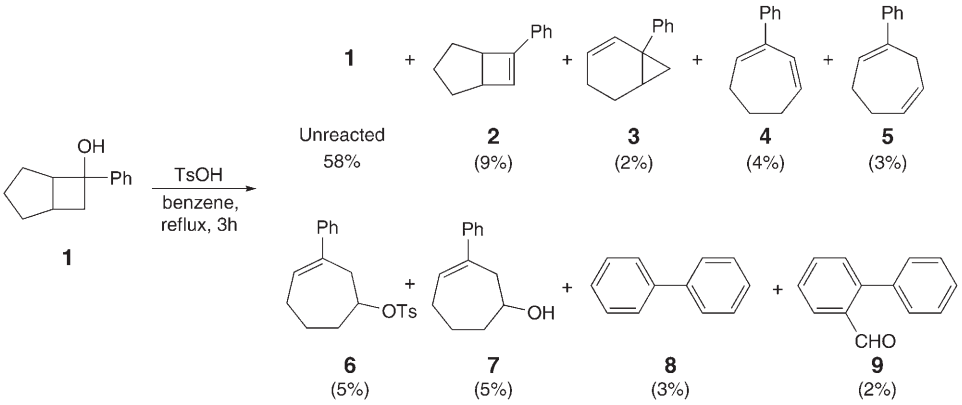
1 **2** **3**

In our ongoing project on strained allenes, we required alkene **2**. For the acid-catalyzed dehydration of **1**, without using a *Dean–Stark* trap to remove the formed H_2O when we refluxed **1** in benzene in the presence of TsOH, we saw surprising results and isolated many rearranged products. In this paper, we present the products and discuss their formation mechanisms.

Results and Discussion. – We performed the dehydration of **1** in the presence of TsOH in refluxing benzene (*ca.* 80°). The carbocationic rearrangement of **1**, followed by chromatography, gave eight products together with unreacted **1**: 6-phenybicyclo[3.2.0]hept-6-ene (**2**), 1-phenylbicyclo[4.1.0]hept-2-ene (**3**), 2-phenylcyclohepta-

1,3-diene (**4**), 2-phenylcyclohepta-1,4-diene (**5**), 3-phenylcyclohept-3-en-1-yl 4-methylbenzenesulfonate (**6**), 3-phenylcyclohept-3-en-1-ol (**7**), 1,1′-biphenyl (**8**), and 1,1′-biphenyl-2-carbaldehyde (**9**) (*Scheme 2*).

Scheme 2

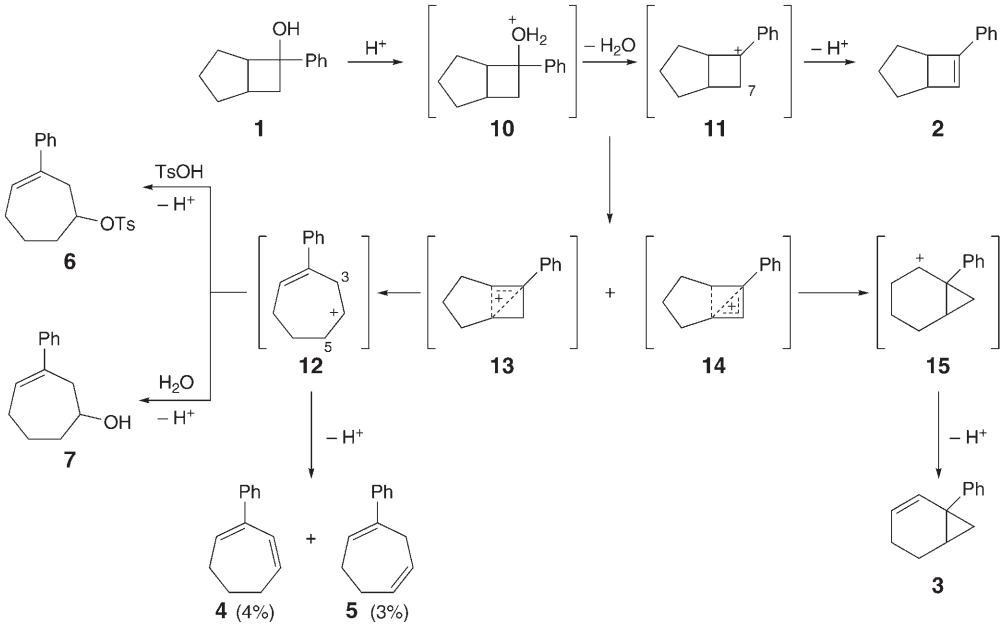


The structures of the products were determined on the basis of spectral data and their comparison with published data. As compounds **2** [3], **3** [3], **4** [4], **5** [5], **6** [6], **7** [6], **8** [7], and **9** [8] are known in the literature, they were readily identified. In addition, the structure of tosylate **6** was confirmed *via* its chemical transformation by treatment with ^{t}BuOK to afford the 1,3-diene **4**.

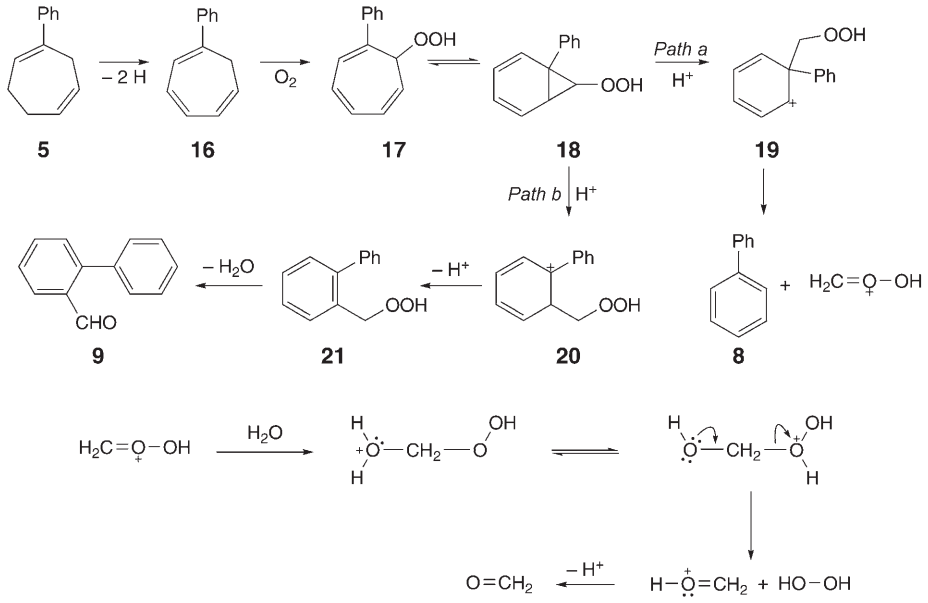
The formation of compounds **2**–**7** may be explained as shown in *Scheme 3*. Protonation of **1** gives (6-phenylbicyclo[3.2.0]hept-6-yl)onium (**10**), which converts to carbocation **11** by loss of H_2O. Deprotonation at C(7) in **11** gives alkene **2**. Cations **13** and **14** are formed by the ring-opening of **11**. Deprotonation of **15** affords alkene **3**. Deprotonation at C(3) or C(5) of cation **12** yields dienes **4** and **5**, respectively. In addition, carbocation **12** can undergo nucleophilic attack by TsOH to give tosylate **6** or by H_2O to yield alcohol **7**.

The formation of compounds **8** and **9** may be explained as shown in *Scheme 4*. We assume that the 1-phenylcyclohepta-1,3,5-triene (**16**) is formed by dehydrogenation of 1,3-dienes **4** and/or **5** in the reaction medium or during chromatography. In a previous study, *Manukov* and *Bazhina* [9] reported the auto-oxidation of 1,4,4- and 1,5,5-trimethylcyclohept-1-enes. We assume that cycloheptatriene systems may be auto-oxidized as cycloheptene systems because of the presence of the more conjugated double bonds and allylic CH_2 unit. Thus, an insertion of O_2 into an allylic H–C bond of 1-phenylcyclohepta-1,3,5-triene (**16**) may yield hydroperoxide **17**. It is well known that the cycloheptatriene unit is in equilibrium with its valence isomer norcaradiene [10]. The cyclopropane ring in the norcaradiene **18** may be cleaved in two different ways, *a* and *b*. In the case of *Path a*, the intermediate **19** is formed, and removal of HCHO gives 1,1′-biphenyl (**8**). The intermediate **20** formed in the case of *Path b* converts to intermediate **21** by deprotonation. Removal of H_2O from **21** yields biphenyl-2-carbaldehyde (**9**).

Scheme 3



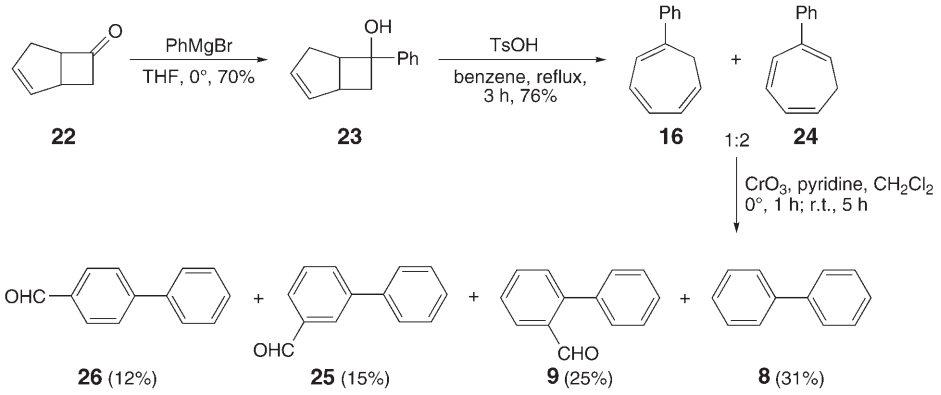
Scheme 4



To reveal the role of air O_2, 2-phenylcyclohepta-1,3-diene (**4**) was treated with silica gel. While a solution of **4** in benzene and/or hexane in the presence of silica gel under N_2 did not show any change, the similar mixture of **4** under air O_2 started to decompose after one week. From these experiments, we concluded that auto-oxidation of the cycloheptadiene systems is possible.

To gain more insight into the reaction mechanism and to explain the formation of biaryl systems, we decided to synthesize and oxidize 1-phenylcyclohepta-1,3,5-triene (**16**) itself. The addition of PhMgBr to **22** afforded 6-phenylbicyclo[3.2.0]hept-2-en-6-ol (**23**) (*Scheme 5*). The acid-catalyzed dehydration of alcohol **23** with TsOH in benzene at reflux temperature (*ca.* 80°) resulted in the formation of 1-phenylcyclohepta-1,3,5-triene (**16**) and 2-phenylcyclohepta-1,3,5-triene (**24**) in a ratio of 1:2, which was determined from the ^{1}H-NMR spectrum of the mixture (*Scheme 5*).

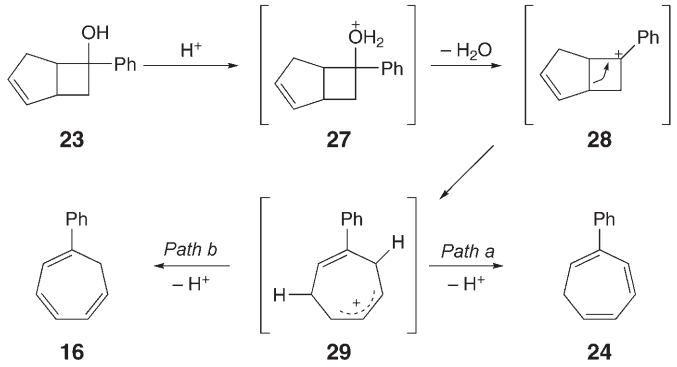
Scheme 5



Without separation, the structures of **16** and **24** were determined on the basis of spectral data and comparison with published data [11]. We determined that the mixture converts to the carbaldehydes **9**, **25**, and **26** on being exposed to air O_2 without solvent for *ca.* 7 days. The ^{1}H-NMR (400 MHz) spectrum of the product mixtures shows three aldehyde signals: 10.09, 10.06, and 9.92 ppm. The mixture was submitted to silica gel column chromatography and was separated into four known products: 1-phenylcyclohepta-1,3,5-triene (**16**) [11], 1,1′-biphenyl-2-carbaldehyde (**9**) [8], 1,1′-biphenyl-3-carbaldehyde (**25**) [12], and 1,1′-biphenyl-4-carbaldehyde (**26**) [13]. In addition, oxidation of the mixture of **16** and **24** with CrO_3/pyridine in CH_2Cl_2 at 0° gave four products: 1,1′-biphenyl (**8**), 1,1′-biphenyl-2-carbaldehyde (**9**), 1,1′-biphenyl-3-carbaldehyde (**25**) and 1,1′-biphenyl-4-carbaldehyde (**26**) (*Scheme 5*). The mixture of products was separated by silica gel column chromatography.

In a previous study, *Nee et al.* [14], investigated elimination reactions of 6-bicyclo[3.2.0]hept-2-enyl tosylates, and reported their conversion to cycloheptatrienes by hydrolysis. The formation of compounds **16** and **24** may be explained by a similar mechanism as shown in *Scheme 6*. Protonation of **23** gives (6-phenylbicyclo[3.2.0]hept-2-en-6-yl)oxonium (**27**), which converts to carbocation **28** by loss of H_2O. Carbocation **28** is rearranged to cycloheptadienyl carbocation **29**, which is an allylic carbocation.

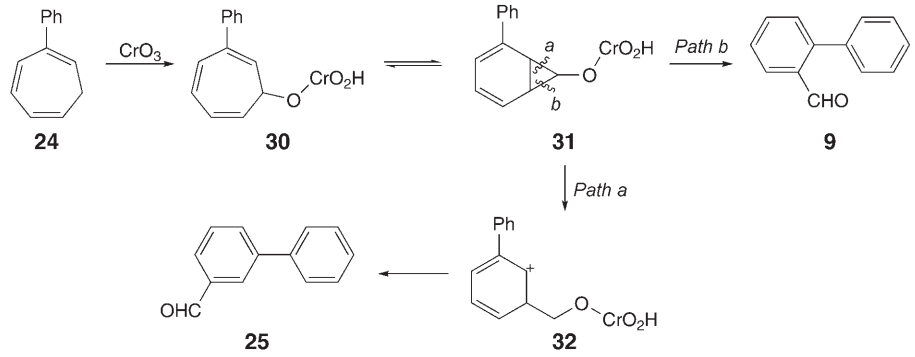
Scheme 6



While deprotonation at C(3) gives 2-phenylcyclohepta-1,3,5-triene (**24**), deprotonation at C(7) leads to 1-phenylcyclohepta-1,3,5-triene (**16**) (*Scheme 6*).

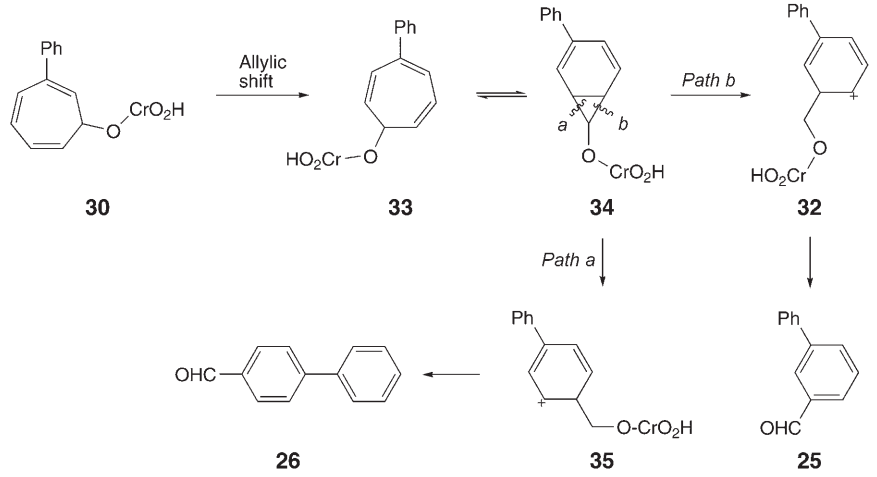
Müller and *Roček* [15] previously investigated the mechanism of chromic acid oxidation of cycloheptatriene. Recently, *Celik et al.* [16] synthesized diols using phenyliodine(III) bis(trifluoroacetate) and reported the smooth formation of benzaldehyde from the oxidation of cycloheptatriene. The formation of compounds **9** and **25** can be explained by a similar mechanism as shown in *Scheme 7*. The chromate (or hydroperoxide) **30** is in equilibrium with its valence isomer norcaradiene **31**, which converts to **25** *via* intermediate **32** (*Scheme 7*, *Path a*). In a similar way, *Path b* gives 1,1′-biphenyl-2-carbaldehyde (**9**).

Scheme 7



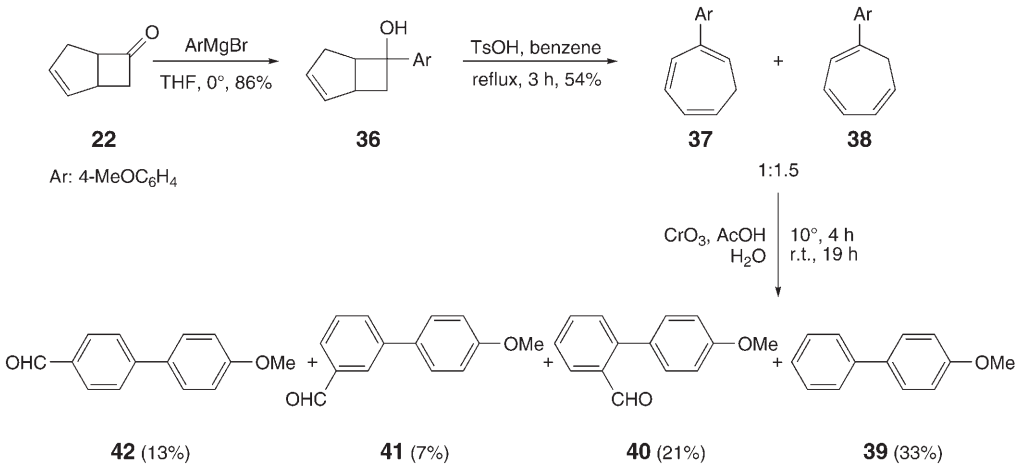
It is well known that in many allylic oxidations with Cr(VI) reagents, an 'allylic shift' occurs during the oxidation [17]. The formation of 1,1′-biphenyl-4-carbaldehyde (**26**) may be explained by a similar process. The chromate (or hydroperoxide) derivative **30** undergoes an allylic shift to form chromate **33**, which is in equilibrium with its valence isomer norcaradiene **34**. The norcaradiene isomer **34** yields 1,1′-biphenyl-4-carbaldehyde (**26**) *via* intermediate **35** (*Path a*). In a similar way, intermediate **32** may convert to 1,1′-biphenyl-3-carbaldehyde (**25**; *Path b*, *Scheme 8*).

Scheme 8



We wondered how the conversion proceeds in another phenyl-substituted cycloheptatriene system. Therefore, we prepared 2-(4-methoxyphenyl)- [18] and 1-(4-methoxyphenyl)cyclohepta-1,3,5-triene (**37** and **38**, resp.) [18] by acid-catalyzed rearrangement of **36**. Without separation, the structures of **37** and **38** were elucidated on the basis of spectral data given in the literature [18]. We determined that compound **37** converts to the carbaldehydes **40** – **42** with the effect of air O_2 within *ca.* 10 days. In a similar way, oxidation of the mixture of **37** and **38** with CrO_3/pyridine in CH_2Cl_2 gave 4-methoxy-1,1′-biphenyl (**39**) [7], and the known carbaldehydes 4′-methoxy-1,1′-biphenyl-2-carbaldehyde (**40**) [8][19], 4′-methoxy-1,1′-biphenyl-3-carbaldehyde (**41**) [20], and 4′-methoxy-1,1′-biphenyl-4-carbaldehyde (**42**) [21] (*Scheme 9*).

Scheme 9



Conclusions. – In this paper, we elucidated the formation mechanism of 1,1′-biphenyls and 1,1′-biphenyl-carbaldehydes from the acid-catalyzed rearrangement of 6-phenylbicyclo[3.2.0]heptan-6-ol and 6-phenylbicyclo[3.2.0]hept-2-en-6-ol. Moreover, for the first time we described an alternative synthetic method for the preparation of 1- and 2-phenylcyclohepta-1,3,5-triene by acid-catalyzed rearrangement of 6-arylbicyclo[3.2.0]hept-2-en-6-ols.

Experimental Part

General. cis-Bicyclo[3.2.0]hept-2-en-6-one was purchased from *Merck*. Column chromatography (CC): silica gel (60–230 mesh, *Merck*). M.p.: *Electrothermal 9100* apparatus. IR Spectra: *Jasco FT/IR-430* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Varian Mercury-400* and *Bruker AC-400* instruments; as internal standards Me_4Si (δ 0.00) for ^{1}H-NMR and $CDCl_3$ (δ 77.0) for ^{13}C-NMR spectroscopy; δ in ppm, J in Hz. Elemental analyses: *LECO CHNS 932* elemental analyzer.

6-Phenylbicyclo[3.2.0]heptan-6-ol (**1**). The alcohol **1** was prepared as described in [22]. Yield 77%. Colorless liquid [6]. IR (film on KBr): 3421, 3058, 3027, 2948, 2852, 1646, 1635, 1446, 1132, 1068. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.52–7.50 (*m*, 2 arom. H); 7.35–7.32 (*m*, 2 arom. H); 7.24–7.20 (*m*, 1 arom. H); 2.94–2.90 (*m*, H–C(5)); 2.64–2.58 (*m*, 2 H); 2.08–2.05 (*m*, CH, OH); 1.96–1.76 (*m*, 3 H); 1.60–1.49 (*m*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.2; 128.4; 126.6; 124.4; 72.8; 51.0; 41.6; 32.8; 31.4; 26.8; 26.0. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [6].

Rearrangement of 6-Phenylbicyclo[3.2.0]heptan-6-ol (**1**) *in the Presence of TsOH.* To a stirred soln. of **1** (4.30 g, 22.8 mmol) in 50 ml of benzene was added 4-methylbenzenesulfonic acid (TsOH) (0.30 g, 1.7 mmol), followed by refluxing for 3 h. The mixture was washed with H_2O (3×30 ml) and dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed on silica gel, eluting with hexane. The products are listed in the order of fractions from CC.

1,1′-Biphenyl (**8**). 0.10 g (3%). Needles. M.p. 69–71° ([7]: 68–71°). IR (KBr): 3056, 3031, 2927, 1479, 1427. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55–7.52 (br. *d*, $J = 7.3$, 4 H); 7.40–7.36 (br. *t*, $J = 7.3$, 4 H); 7.31–7.27 (br. *t*, $J = 7.3$, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.2; 128.8; 127.2; 127.2. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [7].

6-Phenylbicyclo[3.2.0]hept-6-ene (**2**) [3]. 0.35 g (9%). Colorless liquid. IR (KBr): 3062, 2956, 2871, 1683, 1637, 1448. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.19–7.09 (*m*, 5 arom. H); 5.96 (*m*, 1 olefinic H); 3.35–3.33 (*m*, H–C(5)); 3.00–2.98 (*m*, H–C(1)); 1.65–1.12 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 146.3; 134.2; 128.6; 128.1; 127.5; 124.9; 46.3; 44.1; 26.9; 26.4; 23.9. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [3].

3-Phenylcyclohept-3-en-1-yl 4-Methylbenzenesulfonate (**6**) [6]. 0.30 g (4%). Colorless crystals. M.p. 42–43°. IR (KBr): 3077, 3023, 2940, 2856, 1594, 1353, 1189, 1174, 1095, 902, 763, 665, 557. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.76–7.74 (br. *d*, $J = 7.3$, *AA′* part of *AA′BB′* system, 2 arom. H); 7.26–7.24 (br. *d*, $J = 7.3$, *BB′* part of *AA′BB′* system, 2 arom. H); 7.18–7.16 (*m*, 3 arom. H); 7.04–7.02 (*m*, 2 arom. H); 6.13 (br. *t*, $J = 6.9$, 1 olefinic H); 4.49–4.42 (*ddt*, $J = 10.3, 3.7, 1.9$, H–C(1)); 2.93–2.87 (*dd*, $J = 14.2, 11.2$, *A* part of *AB* system, 1 H of CH_2(2)); 2.73–2.70 (br. *d*, $J = 14.2$, *B* part of *AB* system, 1 H of CH_2(2)); 2.32 (*s*, Me); 2.29–2.08 (*m*, 3 H); 1.98–1.85 (*m*, 1 H); 1.75–1.68 (*m*, 1 H); 1.44–1.32 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 144.6; 143.2; 137.4; 134.2; 132.6; 129.8; 128.2; 127.8; 126.8; 125.6; 80.2; 38.8; 38.6; 27.6; 24.0; 21.8. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [6].

2-Phenylcyclohepta-1,3-diene (**4**) [4]. 0.16 g (4%). Colorless liquid. IR (film on KBr): 3052, 2920, 2849, 1655, 1628, 1540, 1479, 1455, 720, 676. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.25 (*m*, 4 arom. H); 7.24–7.18 (*m*, 1 H); 6.15 (*t*, $J = 6.3$, 1 H); 6.10–6.01 (*m*, 2 H); 2.32–2.27 (*m*, 2 H); 2.27–2.16 (*m*, 2 H); 1.64–1.54 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.2; 137.8; 133.8; 128.8; 128.4; 128.2; 126.8; 126.6; 30.2; 30.0; 29.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [4].

2-Phenylcyclohepta-1,4-diene (**5**) [5]. 0.12 g (3%). Colorless liquid. IR (film on KBr): 3054, 2923, 2852, 1652, 1635, 1558, 1488, 1457, 750, 696. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.24 (*m*, 5 arom. H); 6.09 (*t*, $J = 6.8$, H–C(1)); 5.73–5.69 (*m*, H–C(4), H–C(5)); 3.29–3.23 (br. *d*, $J = 4.0$, 2 H); 2.48 (*dd*, $J = 12.6$,

6.8, 2 H); 2.28–2.23 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.9; 131.2; 128.9; 128.6; 127.4; 127.0; 126.6; 126.0; 30.9; 29.9; 26.4.

1-Phenylbicyclo[4.1.0]hept-2-ene (**3**) [3]. 80 mg (2%). Colorless liquid. IR (film on KBr): 3060, 2928, 2860, 1657, 1639, 1560, 1488, 1457, 755, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.24–7.18 (*m*, 4 arom. H); 7.15–7.05 (*m*, 1 arom. H); 6.06 (*dd*, *J* = 10.0, 2.1, H–C(2)); 5.48 (*ddd*, *J* = 10.0, 6.7, 2.1, H–C(3)); 2.10–1.99 (*m*, 2 H); 1.82–1.70 (*m*, 2 H); 1.50–1.44 (*m*, 1 H); 1.27 (*dd*, *J* = 8.7, 4.9, H–C(7)); 1.10–1.06 (br. *t*, *J* = 4.9, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 146.8; 133.6; 128.8; 127.4; 126.1; 123.3; 25.7; 24.4; 20.8; 19.5; 18.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in the literature [3].

The elution in CC was continued with hexane/$CHCl_3$ 7:3.

3-Phenylcyclohept-3-en-1-ol (**7**) [6]. 215 mg (5%). Colorless crystals. M.p. 63–64° ([6]: 79°). IR (KBr): 3380, 3073, 3027, 2921, 2836, 1596, 1457, 1440, 1307, 1029, 852, 755, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33–7.29 (*m*, 2 arom. H); 7.27–7.24 (*m*, 2 arom. H); 7.21–7.15 (*m*, 1 arom. H); 6.17 (*t*, *J* = 6.9, 1 olefinic H); 3.81 (*ddt*, *J* = 8.9, 3.3, 2.2, H–C(1)); 2.87 (*dd*, *J* = 14.5, 9.2, *A* part of *AB* system, 1 H of CH_2(2)); 2.78 (*dt*, *J* = 14.5, 1.8, *B* part of *AB* system, 1 H of CH_2(2)); 2.25–2.19 (*m*, 2 H); 2.12–2.06 (*m*, 1 H); 1.84–1.77 (*m*, 1 H); 1.76–1.64 (*m*, 1 H); 1.60 (br. *s*, –OH, 1 H); 1.48–1.43 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 144.4; 138.8; 132.0; 128.2; 126.6; 125.8; 68.4; 41.4; 41.2; 28.2; 23.4. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [6].

1,1′-Biphenyl-2-carbaldehyde (**9**) [8]. 80 mg (2%). Viscous oil. IR (film on KBr): 3060, 3027, 2923, 2850, 1473, 1454, 1691. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.92 (*d*, *J* = 0.7, CHO); 7.96 (*dd*, *J* = 7.8, 1.04, 1 H); 7.58 (*dt*, *J* = 7.8, 1.4, 1 H); 7.45–7.30 (*m*, 7 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 192.4; 146.0; 137.8; 133.8; 133.6; 130.8; 130.0; 128.4; 128.2; 127.8; 127.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [8].

The last fraction of CC contained unreacted starting material, alcohol **1** [3] (2.50 g).

6-Phenylbicyclo[3.2.0]hept-2-en-6-ol (**23**). To a stirred soln. of Mg (0.6 g, 25 mmol) in 25 ml of dry THF at r.t. was added bromobenzene (a few drops) and a small amount of I_2, and the mixture was stirred at a bath temp. of 65°. To this mixture, bromobenzene (3.14 g, 20 mmol) in 5 ml of THF was added during 1 h, and stirring was continued for 1 h at the same temp. The mixture was cooled to r.t., and bicyclo[3.2.0]hept-2-en-6-one (**22**) (1.5 g, 13 mmol) in 5 ml of THF was added, followed by stirring for 3 h. The mixture was extracted with Et_2O (2 × 50 ml). The combined org. extracts were washed with H_2O (100 ml) and dried ($MgSO_4$). Evaporation of the solvent (30°/20 Torr) gave **23** as a yellowish liquid. 2.40 g (93%). IR (film on KBr): 3459, 3048, 2921, 2850, 1604, 1594, 1494, 1446, 1348, 1228, 1070, 730, 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.39 (*m*, 2 arom. H); 7.32–7.28 (*m*, 2 arom. H); 7.20–7.16 (*m*, 2 arom. H); 5.92–5.88 (*m*, 2 olefinic H); 3.33–3.28 (br. *t*, *J* = 7.6, H–C(5)); 3.16–3.12 (*m*, H–C(1)); 2.93–2.87 (*ddd*, *J* = 12.3, 8.2, 0.9, H_{exo}–C(4)); 2.81–2.75 (*ddd*, *J* = 18.1, 3.5, 1.8, H_{endo}–C(7)); 2.48–2.41 (*ddd*, *J* = 18.1, 8.7, 1.6, H_{exo}–C(7)); 2.02–1.99 (*ddd*, *J* = 12.3, 3.4, 0.9, H_{endo}–C(4)); 1.60 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 147.4; 135.6; 132.9; 128.4; 126.8; 124.8; 76.8; 48.0; 44.6; 39.6; 32.9. Anal. calc. for $C_{13}H_{14}O$: C 83.83, H 7.58; found: C 83.79, H 7.60.

Rearrangement of 6-Phenylbicyclo[3.2.0]hept-2-en-6-ol (**23**) *in the Presence of TsOH.* The procedure described for **1** was applied to **23** to afford *1-phenylcyclohepta-1,3,5-triene* (**16**) and *2-phenylcyclohepta-1,3,5-triene* (**24**) in a ratio of 1:2 (total yield 76%). At this stage, the mixture could not be separated. After the mixture was exposed to air O_2 for 7 d, CC (30 g) eluting with hexane gave **16**, along with the oxidized products **9**, **25**, and **26**.

Data of **16** [23]. Colorless liquid. IR (film on KBr): 3056, 3027, 2971, 2931, 2886, 1598, 1482, 1446, 1159, 1031, 1008, 759, 738, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54–7.52 (*m*, 2 arom. H); 7.45–7.36 (*m*, 3 arom. H); 6.67 (*dd*, *J* = 11.1, 5.9, *A* part of *AB* system, H–C(3)); 6.58 (*dd*, *J* = 11.1, 5.4, *B* part of *AB* system, H–C(4)); 6.43 (*d*, *J* = 5.9, H–C(2)); 6.20 (*dd*, *J* = 9.2, 5.4, H–C(5)); 5.42 (*dd*, *J* = 9.2, 7.1, H–C(6)); 2.71–2.69 (*d*, *J* = 7.1, CH_2(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.2; 133.2; 130.8; 130.2; 128.4; 127.4; 127.2; 127.0; 122.8; 121.0; 31.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [23].

Oxidation of 1-Phenylcyclohepta-1,3,5-triene (**16**) *and 2-Phenylcyclohepta-1,3,5-triene* (**24**) *with CrO_3/Pyridine.* To a magnetically stirred soln. of CrO_3 (2.73 g, 27 mmol) in 20 ml of pyridine and 15 ml of CH_2Cl_2 cooled to 0° was added dropwise a soln. of the mixture of **16** and **24** (0.70 g, 4.2 mmol; ratio **16**/**24** 1:2, see above and *Scheme 5*) in 5 ml of CH_2Cl_2 over 5 min. This soln. was stirred for 2 h at the same

temp. and for an additional 6 h at r.t. The solvent (pyridine and CH_2Cl_2) was removed under reduced pressure. To the residue, 50 ml of CH_2Cl_2 was added and filtered to remove precipitated material. The extract was washed with 1M HCl soln. (10 ml) and H_2O (10 ml), and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to CC (60 g) eluting with hexane/$CHCl_3$ 8:2. The reaction products are described in the order of the CC fractions.

1,1′-Biphenyl (**8**) [7]. 0.20 g (31%).

1,1′-Biphenyl-2-carbaldehyde (**9**) [8]. 190 mg (25%). Viscous oil.

1,1′-Biphenyl-3-carbaldehyde (**25**) [12]. 110 mg (15%). M.p. 44–46° ([12]: Viscous oil). IR (film on KBr): 3060, 2848, 2751, 1473, 1454, 1691. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.09 (*s*, CHO); 8.37 (*s*, H–C(2)); 8.11–8.10 (*m*, H–C(5)); 7.65–7.39 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 192.6; 142.4; 141.8; 140.2; 133.4; 129.8; 129.1; 128.8; 128.2; 128.1; 127.4. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in the literature [12].

1,1′-Biphenyl-4-carbaldehyde (**26**) [13]. 90 mg (12%). Colorless crystals. M.p. 57–59° ([24]: 58–59°). IR (KBr): 3031, 2825, 2732, 1486, 1450, 1698. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.06 (*s*, CHO); 8.06 (*d*, J = 8.1, 2 H); 7.96 (*d*, J = 8.1, 2 H); 7.76 (*d*, J = 7.4, 2 H); 7.55 (*t*, J = 7.4, 2 H); 7.50–7.45 (*t*, J = 7.4, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 193.5; 146.7; 139.6; 135.9; 131.0; 129.9; 129.4; 128.2; 127.9. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in the literature [13].

6-(4-Methoxyphenyl)bicyclo[3.2.0]hept-2-en-6-ol (**36**). The procedure described for the preparation of **23** was applied by using 4-methoxyphenyl bromide to afford **36** in a yield of 86% (yellowish liquid). IR (film on KBr): 3480, 3046, 2958, 2931, 2836, 1610, 1511, 1488, 1247, 1178, 1031, 827, 727, 601. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41, 6.92 (*AA′BB′* system, J = 8.7, 4 arom. H); 5.98 (*m*, 2 olefinic H); 3.84 (*s*, MeO); 3.38–3.36 (br. *t*, J = 7.6, H–C(5)); 3.26–3.17 (*m*, H–C(1)); 2.93–2.96 (*ddd*, J = 11.9, 8.2, 0.8, H_{exo}–C(4)); 2.94–2.84 (*ddd*, J = 18.1, 1.8, H_{endo}–C(7)); 2.57–2.54 (*ddd*, J = 18.1, 8.7, 1.8, H_{exo}–C(7)); 2.12–2.07 (*ddd*, J = 11.9, 3.4, 0.8, H_{endo}–C(4)); 1.60 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 158.2; 139.8; 135.6; 132.9; 126.0; 113.6; 76.4; 55.4; 47.8; 44.4; 39.6; 32.9. Anal. calc. for $C_{14}H_{16}O_2$: C 77.75, H 7.46; found: C 77.78, H 7.43.

Rearrangement of 6-Phenylbicyclo[3.2.0]hept-2-en-6-ol (**36**) *in the Presence of TsOH.* The reaction was performed as described for **1** to give *2-(4-methoxyphenyl)cyclohepta-1,3,5-triene* (**37**) [18] and *1-(4-methoxyphenyl)cyclohepta-1,3,5-triene* (**38**) [18] in a ratio of 1:1.5 (total yield 54%). At this stage, the mixture could not be separated. After the mixture was exposed to air O_2 for 7 d, CC eluting with hexane gave (**38**), along with the oxidized products **40**–**42**.

Data of **38** [18]. Colorless solid. M.p. 58°. IR (KBr): 3004, 2956, 2933, 2906, 2834, 1604, 1508, 1488, 1284, 1247, 1180, 1037, 829, 705. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.53, 6.95 (*AA′BB′* system, J = 8.8, 4 arom. H); 6.78 (*dd*, J = 11.0, 6.0, *A* part of *AB* system, H–C(3)); 6.68 (*dd*, J = 11.0, 5.5, *B* part of *AB* system, H–C(4)); 6.52 (*d*, J = 6.0, H–C(2)); 6.36 (*dd*, J = 9.2, 5.5, H–C(5)); 5.53 (*dd*, J = 9.2, 7.2, H–C(6)); 3.87 (*s*, MeO); 2.84 (*d*, J = 7.2, CH_2(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.1; 133.6; 132.4; 131.1; 129.6; 128.8; 127.1; 121.4; 120.67; 113.8; 55.4; 31.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [18].

Oxidation of **37** *and* **38** *with CrO_3/Pyridine.* The procedure described for the oxidation of the mixture **16**/**24** was applied to the mixture **37**/**38**. The mixture was submitted to CC eluting with hexane/$CHCl_3$ 8:2. The reaction products are listed in the order of the fractions of CC.

4-Methoxy-1,1′-biphenyl (**39**) [7]. 33%. Needles. M.p. 85–88° ([25]: 86°). IR (KBr): 3031, 3000, 2960, 2935, 2834, 1288, 1270, 1249, 833, 688. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.58–7.53 (*m*, 4 H); 7.45–7.41 (br. *t*, J = 7.3, 2 H); 7.34–7.32 (br. *t*, J = 7.3, 1 H); 7.01–6.98 (*dt*, J = 9.15, 2.2, 2 H); 3.86 (*s*, MeO). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.4; 141.1; 134.0; 128.9; 128.4; 127.0; 126.9; 114.4; 55.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [7].

4′-Methoxy-1,1′-biphenyl-2-carbaldehyde (**40**) [8][19]. 21%. Needles. M.p. 39–42° ([19]: colorless oil). IR (KBr): 3068, 3029, 2956, 2939, 2908, 2838, 1685, 1598, 1295, 1251, 1184, 1031, 819, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.99 (*s*, CHO); 8.01–7.99 (br. *d*, J = 7.7, H–C(3)); 7.63–7.59 (*dt*, J = 7.7, 1.1, H–C(5)); 7.47–7.42 (*m*, H–C(6)); 7.31–7.29 (*m*, H–C(4)); 7.26–7.25 (br. *d*, J = 8.6, *AA′* part of *AA′BB′* system, H–C(2′), H–C(6′)); 7.02–7.00 (br. *d*, J = 8.6, *BB′* part of *AA′BB′* system, H–C(3′), H–C(5′)); 3.86 (*s*, MeO). ^{13}C-NMR (100 MHz, $CDCl_3$): 192.9; 159.9; 145.8; 133.9; 133.8; 131.6; 131.1; 130.2; 127.8; 127.6; 114.2; 55.6. ^{1}H- and ^{13}C-NMR spectra are in good agreement with the data given in [8].

4′-Methoxy-1,1′-biphenyl-4-carbaldehyde (**42**) [21]. 130 mg (13%). Colorless crystals. M.p. 81–84° ([21]: 104–106°). IR (KBr): 3002, 2956, 2927, 2852, 2834, 1606, 1508, 1488, 1245, 1180, 1033, 831, 759, 701. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.03 (*s*, CHO); 7.93–7.91 (br. *d*, *J* = 8.2, *AA′* part of *AA′BB′* system, H–C(3), H–C(5)); 7.72–7.70 (br. *d*, *J* = 8.2, *BB′* part of *AA′BB′* system, H–C(2), H–C(6)); 7.60–7.58 (br. *d*, *J* = 8.6, *AA′* part of *AA′BB′* system, H–C(2′), H–C(6′)); 7.02–6.99 (br. *d*, *J* = 8.6, *BB′* part of *AA′BB′* system, H–C(3′), H–C(5′)); 3.87 (*s*, MeO). ^{13}C-NMR (100 MHz, $CDCl_3$): 192.2; 160.4; 147.0; 134.9; 132.4; 130.6; 128.8; 127.2; 114.8; 55.6. The ^{1}H-NMR spectrum is in good agreement with the data given in [21].

4′-Methoxy-1,1′-biphenyl-3-carbaldehyde (**41**) [20]. 70 mg (7%). Colorless crystals. M.p. 50–53° ([20]: 52°). IR (KBr): 3027, 2964, 2940, 2910, 2840, 1681, 1598, 1295, 1257, 1186, 819, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.08 (*s*, CHO); 8.06 (*s*, H–C(2)); 7.83–7.80 (*m*, H–C(4), H–C(6)); 7.69 (*t*, *J* = 8.4, H–C(5)); 7.58–7.56 (br. *d*, *J* = 8.6, *AA′* part of *AA′BB′* system, H–C(2′), H–C(6′)); 7.02–7.00 (br. *d*, *J* = 8.6, *BB′* part of *AA′BB′* system, H–C(3′), H–C(5′)); 3.87 (*s*, MeO). ^{13}C-NMR (100 MHz, $CDCl_3$): 192.6; 160.6; 144.8; 132.8; 132.4; 129.6; 128.4; 128.4; 127.8; 114.6; 55.6. The ^{1}H-NMR spectrum is in agreement with the data given in the literature [20].

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REFERENCES

[1] L. M. Harwood, 'Polar Rearrangements', Oxford Science Publications, New York, 1995, pp. 18.
[2] M. Ceylan, Y. Budak, M. Ulukaya, M. B. Gurdere, E. Findik, *Turk. J. Chem*. **2006**, *30*, 663, and refs. cit. therein.
[3] F. Algi, M. Balci, *Arkivoc* **2006**, *Part 10*, 173.
[4] A. A. Kulkarni, S. T. Diver, *Org. Lett*. **2003**, *5*, 3463.
[5] Q. Yao, *Org. Lett*. **2002**, *4*, 427.
[6] M. Christl, E. Gerstner, R. Kemmer, G. Llewellyn, W. Bentley, *Chem. Ber*. **1994**, *127*, 367.
[7] S. D. Cho, H. K. Kim, H. S. Yim, M. R. Kim, J. K. Lee, J. J. Kim, Y. J. Yoon, *Tetrahedron* **2007**, *63*, 1345.
[8] J. A. Varela, D. Pena, B. Goldfuss, D. Denisenko, J. Kulhanek, K. Polborn, P. Knochel, *Chem.–Eur. J.* **2004**, *10*, 4252.
[9] E. N. Manukov, G. N. Bazhina, *Khim. Prir. Soedin.* **1990**, *4*, 540; *Chem. Abstr.* **1991**, *114*, 102413.
[10] M. Balci, *Turk. J. Chem*. **1992**, *16*, 42.
[11] K. Takahashi, T. Suzuki, H. Toda, K. Takase, S. Koseki, T. Nakajima, *J. Org. Chem*. **1987**, *52*, 2666.
[12] B. Tao, D. W. Boykin, *J. Org. Chem*. **2004**, *69*, 4330.
[13] B. C. Hong, H. C. Tseng, S. H. Chen, *Tetrahedron* **2007**, *63*, 2840.
[14] M. Nee, W. F. Gorham, J. D. J. Roberts, *Org. Chem*. **1981**, *46*, 1021.
[15] P. Müller, J. Roček, *J. Am. Chem. Soc*. **1974**, *96*, 2836.
[16] M. Celik, C. Alp, B. Coskun, M. S. Gultekin, M. Balci, *Tetrahedron Lett*. **2006**, *47*, 3659.
[17] W. G. Dauben, M. E. Lorber, D. S. Fullerton, *J. Org. Chem*. **1969**, *34*, 3587.
[18] W. Abraham, K. Buck, C. Csongar, E. Henke, D. Kreysig, *J. Prakt. Chem*. **1979**, *321*, 117.
[19] I. Ozdemir, S. Demir, B. Cetinkaya, *Tetrahedron* **2005**, *61*, 9791.
[20] M. Lourak, R. Vanderesse, Y. Fort, P. Caubere, *J. Org. Chem*. **1989**, *54*, 4844.
[21] A. H. A. Tinnemans, W. H. Laarhoven, *J. Am. Chem. Soc*. **1974**, *96*, 4611.
[22] K. B. Wiberg, W. F. Chen, *J. Am. Chem. Soc.* **1974**, *96*, 3900.
[23] T. Tezuka, M. Kimura, A. Sato, T. Mukai, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1120.
[24] B. E. Huff, T. M. Koenig, D. Mitchell, A. Staszak, *Org. Synth.* **1998**, *75*, 53.
[25] G. W. Kabalka, L. Wang, R. M. Pagni, C. M. Hair, V. Namboodiri, *Synthesis* **2003**, 217.

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