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Friedel–Crafts Transannular Alkylation of Benzene with (*Z*, *Z*)-1,5-Cyclooctadiene: Reassignment of Two Phenylbicyclooctanes by ^{13}C NMR Spectroscopy and Separate Preparation

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Our previous structure assignment of two phenylbicyclooctanes obtained in Friedel–Crafts transannular alkylation of benzene with (Z,Z)-1,5-cyclooctadiene has been reinvestigated and partly corrected on the basis of ^{13}C NMR spectral data, a separate preparation of an authentic sample, and MM3 calculation. The compounds assigned previously to *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane and *exo*-3-phenylbicyclo[3.2.1]octane among six products should be assigned to 1-phenyl-*cis*-bicyclo[3.3.0]octane and *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane, respectively, showing that almost all products have bicyclo[3.3.0]octane framework. A new preparative method for an authentic 1-phenyl-*cis*-bicyclo[3.3.0]octane and MM3 calculations of all products are also presented.

We have reported Friedel–Crafts transannular alkylation of aromatic compounds with non-conjugated cyclic dienes catalyzed by mineral acids and several Lewis acid metal chlorides[1a] and also by cation-exchanged clays[1b] in which we assigned the structure of six products obtained from (Z,Z)-1,5-cyclooctadiene (1,5-COD) and benzene as *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (**1**), *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (**2**), *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (**3**), *exo*-3-phenylbicyclo[3.2.1]octane (**4**, tentative), *endo*-3-phenylbicyclo[3.2.1]octane (**5**, tentative), and *endo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (**6**). Among these six compounds, authentic samples for **2**, **3**, **5**, and **6** have been prepared separately by applying and/or modifying the known methods, while the structure of the two compounds **1** and **4** has been assigned as such mainly on the basis of ^{1}H and ^{13}C NMR spectral data. However, Professor M. A. Minton's suggestion[2] and our own reinvestigation by ^{13}C NMR spectroscopy, separate preparation of an authentic sample, and MM3 calculation led us to conclude that **1** and **4** should be assigned to 1-phenyl-*cis*-bicyclo[3.3.0]octane (**1′**) and *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (**1**), respectively.

Results and Discussion

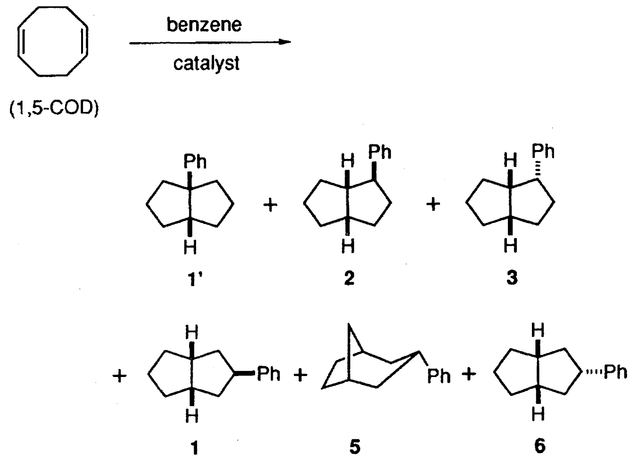
Friedel–Crafts transannular alkylation of benzene with (Z,Z)-1,5-cyclooctadiene (1,5-COD) was tried again on a scale double that of the reported one. The yields and the product ratio were almost identical with the reported data (see Experimental part). This time, each compound assigned previously as **1** and **4** was isolated in a pure form, respectively, by recycling preparative high performance liquid chromatography (HPLC). Each structure was characterized by ^{13}C NMR spectra by comparison of their chemical shifts with the calculated shifts using the observed chemical shifts of *cis*-bicyclo[3.3.0]octane[3] and bicyclo[3.2.1]octane[4] as well as the substituent effect of phenyl group, +17, +7, and −2 ppm for α, β, and γ carbons (Table 1),[5] the spectra of which clearly showed a symmetrical structure in both compounds. Careful analyses of these data showed that the compounds **1** and **4** should be assigned to 1-phenyl-*cis*-bicyclo[3.3.0]octane (**1′**) and *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (**1**), respectively. The interunit relationship determined by 2-dimensional ^{1}H–^{1}H (400 MHz) and ^{1}H (400 MHz)–^{13}C (100 MHz) correlated NMR spectroscopy (COSY) also supported their structures. The chemical shifts of **1** were quite similar to those of the corresponding *endo*-isomer **6**. The correct structure assignment of the products in this transannular alkylation is shown in Scheme 1 where the compounds **1** and **4** assigned formerly are replaced by **1′** and **1**, respectively.

The preparation of an authentic sample of **1′** was attempted by the reported method[6] by treating *cis*-bicyclo[3.3.0]octane-1-carboxylic acid[7] with thionyl chloride followed by addition of benzene in the presence of $AlCl_3$ at reflux temperature. However, the expected **1′** was not produced at all and, instead, phenylbicyclooctanes [**2**, **3**, **1**, **5**, and **6**; 10% isolated yield (**2** : **3** : **1** : **5** : **6**=11 : 22 : 8 : 27 : 32)] and four isomeric *cis*-bicyclo[3.3.0]oct-1-yl phenyl ketones (4% isolated yield) were obtained. On the other hand, when *cis*-bicyclo[3.3.0]octane-1-carbonyl chloride was isolated and treated with benzene in the presence of $AlCl_3$ at lower temperature for shorter time, phenylbicyclooctanes [**1′**, **2**, and **5**; 6% isolated yield (**1′** : **2** : **5** = 84 : 7 : 9)] and four isomeric *cis*-bicyclo[3.3.0]oct-1-yl phenyl ketones (23% isolated yield) were

Table 1. The Observed ^{13}C NMR Chemical Shifts and the Calculated Shifts of the Compounds Having a Bicyclooctane Framework

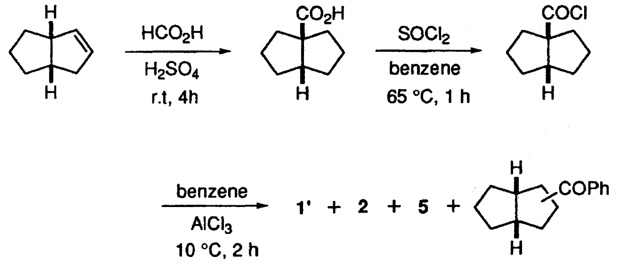
Compound	Chemical shift / ppm							
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1′	58.7	42.6	25.8	35.2	49.4	35.2	25.8	42.6
1	42.8	41.5	43.3	41.5	42.8	35.2	27.5	35.2
6	43.2	42.4	47.2	42.4	43.2	33.3	25.0	33.3
cis-Bicyclo[3.3.0]octane[a]	43.4	34.3	26.4	34.3	43.4	34.3	26.4	34.3
1-Phenyl-*cis*-bicyclo[3.3.0]octane[b] (**1′**)	60.4	41.3	24.4	32.3	50.4	32.3	24.4	41.3
3-Phenyl-*cis*-bicyclo[3.3.0]octane[b] (**1** and **6**)	41.4	41.3	43.4	41.3	41.4	34.3	26.4	34.3
2	51.9	53.6	36.4	33.8	43.6	33.9	25.1	32.3
3	48.0	48.7	27.4[c]	32.6[c]	42.7	35.7	27.4	29.6
2-Phenyl-*cis*-bicyclo[3.3.0]octane[b] (**2** and **3**)	50.4	51.3	33.4	32.3	41.4	34.3	26.4	32.3
5 (tentative)	32.3	40.0	34.3	40.0	32.3	33.1	33.1	31.7
Bicyclo[3.2.1]octane[d]	35.2	32.8	19.1	32.8	35.2	28.9	28.9	39.7
3-Phenylbicyclo[3.2.1]octane[b] (**5**)	33.2	39.8	36.1	39.8	33.2	28.9	28.9	39.7
8-Phenylbicyclo[3.2.1]octane[b]	42.2	30.8	19.1	30.8	42.2	26.9	26.9	56.7

a) Ref. 3. b) Calculated from the observed chemical shifts of *cis*-bicyclo[3.3.0]octane[3] and bicyclo[3.2.1]octane[4] for solutions in $CDCl_3$ with Me_4Si as an internal standard and the substituent effects of a phenyl group.[5] c) The assignment might be reversed. d) Ref. 4.

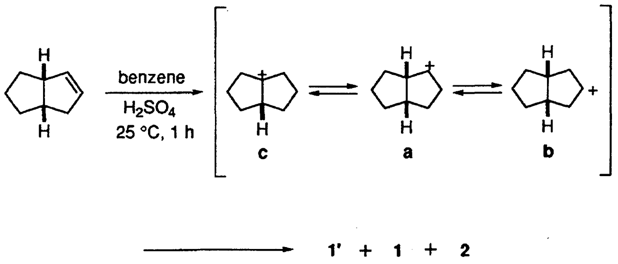


Scheme 1.

obtained (Experimental part) (Scheme 2). Here, the compound **1′** was isolated in a pure form by recycling HPLC as an oil.[8] The compound **1′** could also be synthesized as a mixture with **2** and **1** [71% isolated yield (**1′** : **2** : **1** = 56 : 26 : 18)] by treatment of benzene (50 cm^3) with *cis*-bicyclo[3.3.0]oct-2-ene (20.0 mmol) in the presence of concd H_2SO_4 (20.0 mmol) where a bicyclo[3.3.0]octyl cation (**c**)[9] might be favorably formed (Scheme 3).



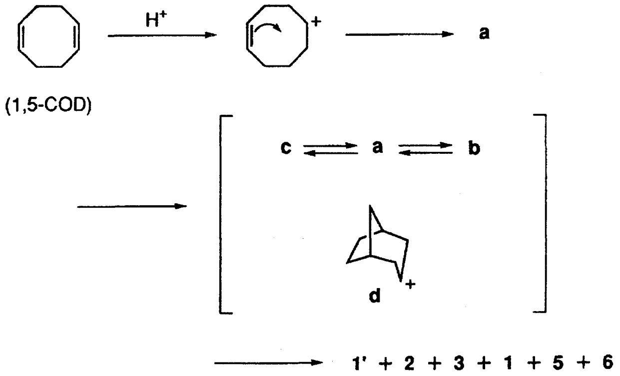
Scheme 2.



Scheme 3.

In this alkylation the initially produced electrophile is probably a bicyclo[3.3.0]octyl cation **a**, as shown in Scheme 4. The cation **a** may isomerize to the cations **b** and **c** by a 1,2-hydride shift and to the cation **d** by the skeletal rearrangement, respectively. Among the four cations, the cations **a**, **b**, and **c** attack benzene electrophilically to produce the compounds **2** and **3**, the compounds **1** and **6**, and the compound **1′**, respectively.

We have calculated the heats of formation of **1′**, **2**, **3**, **1**, **5**, and **6** by the AM1 method[10] in order to obtain some in-



Scheme 4.

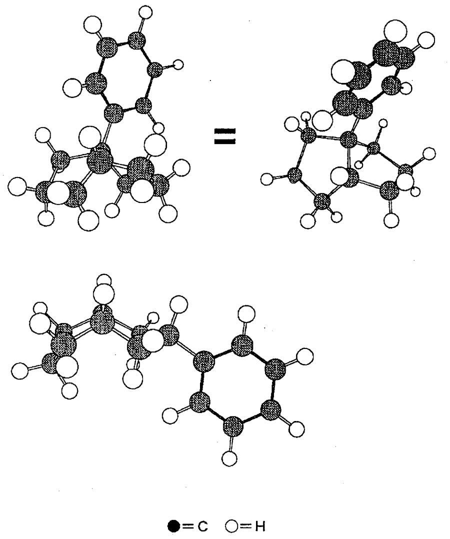


Fig. 1. The optimized structure of **1′** (the upper) and **6** (the lower) by MM3.

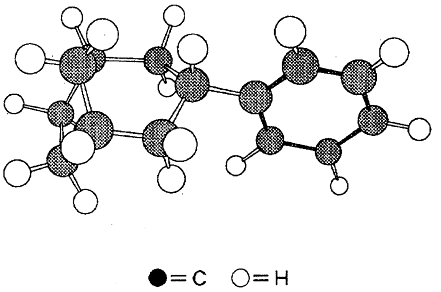


Fig. 2. The optimized structure of **5** by MM3.

formation concerning the thermodynamic stabilities of these isomers. The heat of formation of the compound **1′** was newly calculated and the heats of formation of **1′**, **2**, **3**, **1**, and **5** relative to **6** (0.00 kcal mol^{-1}, 1 cal = 4.184 J) were 5.01, 0.96, 3.37, 0.03, and 7.68 kcal mol^{-1}, respectively. This result shows that *endo*-3-phenyl-*cis*-bicyclo[3.3.0]octane **6** is again thermodynamically the most stable isomer. Furthermore, the heats of formation of **1′**, **2**, **3**, **1**, **5**, and **6** were also calculated by the MM3 method.[11] Those of **1′**, **2**, **3**, **1**, and **5** relative to **6** (0.00 kcal mol^{-1}) were 5.12, 0.77, 1.43, 0.21, and 5.40 kcal mol^{-1}, respectively, showing that the stability order of compounds as well as their values are not so much different from that obtained by AM1 method. The heats of formation reflect the steric energy in the molecule and the compounds **1′**, **3**, and **5** were suggested to have much higher steric energy. As can be seen from the structures of **1′** and **6** optimized by MM3 method (Fig. 1), the compound **1′** has a more twisted structure than **6**.[12] The compound **5** showed the large upfield shift of C-8 (Table 1) which may be caused by steric compression, namely the hydrogen–hydrogen electron repulsions[13] as can be seen from its optimized structure (a boat form) by MM3 method in Fig. 2. In addition, the compound **5** should be *endo*-3-phenylbicyclo[3.2.1]octane because it has been known that *endo*-3-methylbicyclo[3.2.1]octane showed the upfield shift of C-8, while *exo*-3-methylbicyclo[3.2.1]octane did not.[14] The optimized structures of **1**, **2**, and **3** are shown in Fig. 3.

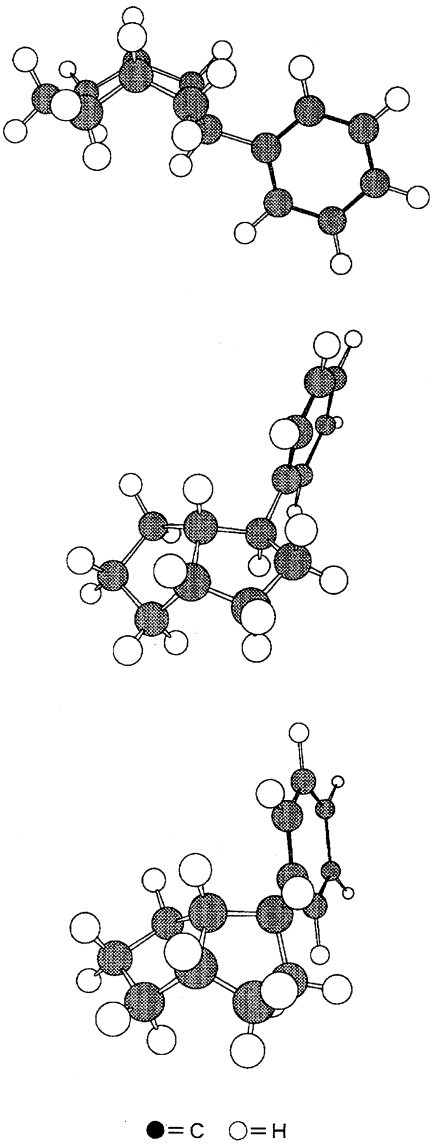


Fig. 3. The optimized structure of **1** (the upper), **2** (the middle), and **3** (the lower) by MM3.

Although we assumed one major product in the reaction of other aromatic compounds such as toluene, fluorobenzene, *t*-butylbenzene, xylene, and mesitylene with 1,5-COD in the presence of concd H_2SO_4 as *exo*- 3-aryl-*cis*-bicyclo[3.3.0]-octanes,[1a] we should also assume it to be 1-aryl-*cis*-bicyclo-[3.3.0]octanes by comparison of mass spectrum pattern with that of **1′**.

Experimental

FT-IR spectra (thin film for liquids) were recorded on Shimadzu FTIR-8100 spectrophotometer equipped with a DR-8000 data processing system and Nicolet Impact-400D spectrophotometer equipped with a data processing system. Some abbreviations are listed as follows: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. NMR spectra were recorded on JEOL EX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) and JEOL GSX-270 (^{1}H, 270 MHz) spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. The coupling constants (*J*) are given in Hz. Some abbreviations are listed as follows: s, singlet; d, doublet; t, triplet; quint, quintet; m, multiplet. Mass spectra were measured on Shimadzu QP-5000S mass spectrometer equipped with a Shimadzu GC-17 gas-liquid chromatograph (30 m×0.254 mm, 0.25 μm film thickness, J&W Scientific fused silica capillary column DB-1). Electron-impact (EI) method was used for ionization and the ionizing voltage was 70 eV for all compounds. GLC analyses were performed on a Shimadzu GC-14A instrument (25 m×0.33 mm, 5.0 μm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with flame-ionization detectors and helium as carrier gas. Recycling preparative high performance liquid chromatography (HPLC) was performed on a JAI LC-908-G30 instrument (600 mm×20 mm×2, JAIGEL-1H and JAIGEL-2H dual styrene polymer columns) equipped with ultraviolet (UV) and refractive-index (RI) detector and $CHCl_3$ as eluent. Column chromatography on SiO_2 was performed with Wakogel® C-300 [hexane, hexane–ethyl acetate (9 : 1), and ethyl acetate as eluents].

All commercially available organic and inorganic compounds were used without further purification. Authentic samples of **2**, **3**, **5**, and **6** for GLC determination were synthesized by the previously reported methods.[1a)] The compound **1′**,[6)] and the compound **1**,[1a)] bicyclo[3.3.0]oct-2-ene,[7a)] *cis*-bicyclo[3.3.0]octane-1-carboxylic acid,[7b)] *cis*-bicyclo[3.3.0]octane-1-carbonyl chloride,[6)] and *cis*-bicyclo[3.3.0]oct-1-yl phenyl ketones[6)] are known compounds. Some data which had already been published were shown again for convenience.

General Procedure for Friedel–Crafts Transannular Alkylation of Benzene with (Z,Z)-1,5-Cyclooctadiene (1,5-COD) in the Presence of Concd H_2SO_4 or $AlCl_3$. A mixture of benzene (100 cm^3) and concd H_2SO_4 (3.92 g, 40 mmol) or anhydrous $AlCl_3$ powder (5.33 g, 40 mmol) was stirred magnetically at 25 °C for 15 min. To the mixture was added dropwise 1,5-COD (4.33 g, 40.0 mmol); the resulting mixture was stirred at 25 °C for 3 h. The reaction mixture was poured into ice water (100 cm^3). The organic layer was separated, washed with water (3×50 cm^3), and dried over anhydrous Na_2SO_4. Removal of benzene and unreacted 1,5-COD under reduced pressure left a brown oil, which was distilled under reduced pressure to give a pale yellow colored mixture of products [3.21 g, 17.2 mmol, 43% isolated yield (**1′** : **2** : **3** : **1** : **5** : **6** = 51 : 25 : 5 : 17 : 2 : 0) in the case of concd H_2SO_4; 4.66 g, 25.0 mmol, 63% isolated yield (**1′** : **2** : **3** : **1** : **5** : **6** = 2 : 43 : 9 : 23 : 2 : 21) in the case of $AlCl_3$]. Some of them were isolated in a pure form by recycling preparative HPLC. For example, a part of the mixture (100.0 mg, 0.54 mmol) which was obtained by the reaction with H_2SO_4 catalyst was treated with recycling preparative HPLC to afford 1-phenyl-*cis*-bicyclo[3.3.0]octane (**1′**, 21.4 mg, 0.11 mmol, 21% isolated yield): a colorless oil; IR 3087 (w), 3058 (w), 3027 (w), 2946 (vs), 2863 (s), 1599 (w), 1493 (m), 1476 (w), 1460 (w, sh), 1451 (m), 1445 (m), 1032 (w), 903 (w), 760 (m), 754 (m), and 698 (vs) cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.42$ (2H, dtd, $J = 12.7$, 6.4, 4.4 Hz, 4,6-CH), 1.59 (2H, d quint, $J = 12.7$, 6.4 Hz, 3,7-CH), 1.67 (2H, d quint, $J = 12.7$, 6.4 Hz, 3,7-CH), 1.83 (2H, dt, $J = 12.7$, 6.4 Hz, 2,8-CH), 1.88 (2H, dt, $J = 12.7$, 6.4 Hz, 2,8-CH), 1.95 (2H, ddt, $J = 12.7$, 8.8, 6.4 Hz, 4,6-CH), 2.71 (1H, tt, $J = 8.8$, 4.4 Hz, 5-CH), 7.14 (1H, t, $J = 7.1$ Hz, ArH), 7.27 (2H, d, $J = 8.3$ Hz, ArH), and 7.31 (2H, dd, $J = 8.3$, 7.1 Hz, ArH); ^{13}C NMR (100 MHz) $\delta = 25.8$ (t, 2×C), 35.2 (t, 2×C), 42.6 (t, 2×C), 49.4 (d), 58.7 (s), 125.1 (d), 126.2 (d, 2×C), 128.0 (d, 2×C), and 152.2 (s); MS *m/z* 186 (M^+; 66%), 157 (63), 143 (100), 129 (78), 115 (60), 104 (65), 91 (53), 77 (30), 65 (16), 51 (25), and 41 (45). Found: C, 90.00; H, 9.81%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%.

For another example, a part of the mixture (900.0 mg, 4.83 mmol) which was obtained by the reaction with $AlCl_3$ catalyst was treated with recycling preparative HPLC to afford *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (**2**, 520.0 mg, 2.79 mmol, 58% isolated yield) and *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (**1**, 62.5 mg, 0.34 mmol, 7% isolated yield). *exo*-3-Phenyl-*cis*-bicyclo[3.3.0]octane **1**: a colorless oil; ^{1}H NMR (400 MHz) $\delta = 1.18$—1.27 (2H, m, 6,8-CH), 1.31—1.41 (1H, m, 7-CH), 1.64—1.73 (1H, m, 7-CH), 1.74—1.80 (4H, m, 2,4-CH_2), 1.87—1.96 (2H, m, 6,8-CH), 2.50—2.60 (2H, m, 1,5-CH), 3.08 (1H, tt, $J = 9.3$, 8.3 Hz, 3-CH), and 7.14—7.30 (5H, m, ArH); ^{13}C NMR (100 MHz) $\delta = 27.5$ (t), 35.2 (t, 2×C), 41.5 (t, 2×C), 42.8 (d,2×C), 43.3 (d), 125.7 (d), 127.2 (d, 2×C), 128.2 (d, 2×C), and 145.2 (s). Found: C, 90.47; H, 9.94%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%.

Preparation of 1-Phenyl-*cis*-bicyclo[3.3.0]octane (1′). To concd H_2SO_4 (144 cm^3) were added dropwise formic acid (99%, 24 cm^3) and a mixture of bicyclo[3.3.0]oct-2-ene[7a)] (12.00 g, 110.9 mmol) and carbon tetrachloride (12 cm^3) in turn during 2 h with magnetic stirring at room temperature. The mixture was stirred for further 2 h at the temperature and then poured into ice water (200 cm^3). The mixture was extracted with CH_2Cl_2 (4×100 cm^3). The extract was dried over anhydrous Na_2SO_4 and concentrated. The resulting dark oil was diluted with CH_2Cl_2 (100 cm^3) and extracted with 1.67 M (1 M = 1 mol dm^{-3}) aqueous KOH (2×200 cm^3). The aqueous extract was washed with CH_2Cl_2 (100 cm^3), acidified with concd HCl (100 cm^3), and extracted with CH_2Cl_2 (2×100 cm^3). The extract was washed with water (100 cm^3) and dried over anhydrous Na_2SO_4. Removal of the solvent left a black liquid of *cis*-bicyclo[3.3.0]octane-1-carboxylic acid (6.05 g, 39.2 mmol, 35% isolated yield). ^{13}C NMR (100 MHz) $\delta = 26.3$ (t, 2×C), 34.1 (t, 2×C), 38.2 (t, 2×C), 49.7 (d), 59.7 (s), 185.7 (s).

To a solution of *cis*-bicyclo[3.3.0]octane-1-carboxylic acid (1.80 g, 11.7 mmol) and dry benzene (5 cm^3) was added $SOCl_2$ (6.27g, 52.7 mmol) dropwise at 5 °C with magnetic stirring. The mixture was heated at 65 °C for 1 h with magnetic stirring. After removing the solvent and unreacted $SOCl_2$ under reduced pressure, the resulting black tar was subjected to bulb-to-bulb distillation to afford a colorless liquid of *cis*-bicyclo[3.3.0]octane-1-carbonyl chloride [bp, 130 °C {1 mmHg (1 mmHg = 133.322 Pa)}, 1.11 g, 6.43 mmol, 55% isolated yield]. ^{13}C NMR (100 MHz) $\delta = 25.8$ (t, 2×C), 33.8 (t, 2×C), 38.7 (t, 2×C), 49.5 (d), 70.7 (s), and 179.7 (s).

To a solution of *cis*-bicyclo[3.3.0]octane-1-carbonyl chloride (1.00 g, 5.79 mmol) and dry benzene (10 cm^3) was added anhydrous $AlCl_3$ powder (772.0 mg, 5.79 mmol) at 0 °C with magnetic stirring. The mixture was stirred at 10 °C for 2 h and then poured into ice water (50 cm^3). The benzene layer was separated and the aqueous layer was extracted with ether (3×50 cm^3). The combined organic layer was washed with 1 M aqueous KOH and then water to remove the produced *cis*-bicyclo[3.3.0]octane-1-carboxylic acid and then dried over anhydrous Na_2SO_4. Removal of the solvent left a pale yellow oil which was subjected to column chromatography (Wakogel® C-300, eluents: hexane and hexane–ethyl acetate). The products were a colorless oil of phenylbicyclooctanes [63.9 mg, 0.34 mmol, 6% isolated yield (**1′** : **2** : **5** = 84 : 7 : 9), hexane as eluent] and a colorless oil of four isomeric *cis*-bicyclo[3.3.0]oct-1-yl phenyl ketones (285.3 mg, 1.33 mmol, 23% isolated yield, hexane–ethyl acetate (9 : 1) as the eluent]. *cis*-Bicyclo[3.3.0]oct-1-yl phenyl ketones: IR 1678 (s, $\nu_{C=O}$) cm^{-1}; MS *m/z* 214 (M^+; 22%) and 105 (100) for a major isomer. The compound **1′** was isolated in a pure form (40.7 mg, 0.22 mmol, 4% isolated yield) by recycling preparative HPLC and identified again by ^{13}C NMR spectroscopy and GC-MS.

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