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# Friedel–Crafts Transannular Alkylation of Aromatic Compounds with Nonconjugated Cyclic Dienes

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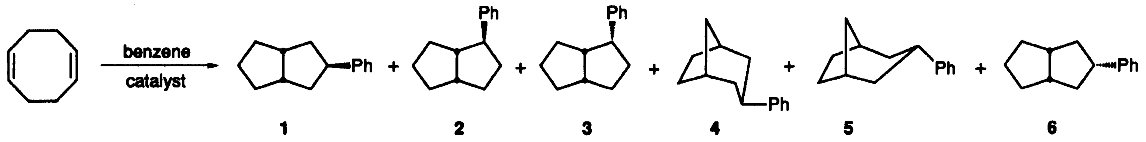
Friedel–Crafts transannular alkylation of aromatic compounds with nonconjugated cyclic dienes such as (*Z,Z*)-1,5-cyclooctadiene (1,5-COD), bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), and 1,4-cyclohexadiene was studied. The five to six isomers of phenylbicyclooctanes were produced in the alkylation of benzene with 1,5-COD in the presence of either Brönsted acid or Lewis acid as the catalyst. The isomer ratios depended on the nature and the amount of catalyst, the reaction time, and the reaction temperature. In the $AlCl_3$-catalyzed reaction of 1,5-COD with toluene it was disclosed that an initial *para*-rich isomer distribution of the products shifted to a *meta*-rich one in a prolonged reaction. With norbornadiene a transannular cyclized compounds was obtained, while with 1,4-cyclohexadiene no transannular cyclization was observed.

It has been well-known that (*Z, Z*)-1,5-cyclooctadiene (abbreviated to 1,5-COD) reacted with several electrophilic reagents to form *cis*-bicyclo[3.3.0]octane and/or bicyclo[3.2.1]octane derivatives by a transannular cyclization.[1)] Alkenes are the well-known alkylating reagents for Friedel–Crafts alkylation of aromatic compounds, but only two reports[2)] have so far appeared on the alkylation accompanied by a transannular cyclization and yet the products had not been precisely and correctly identified in those reports. As one of the series of our studies on transannular cyclization of 1,5-COD,[3,4)] we describe here the result of Friedel–Crafts alkylation of benzene with 1,5-COD in detail together with that of some related reactions.

## Results and Discussion

**Friedel–Crafts Transannular Alkylation of Benzene with 1,5-COD.** The reaction of 1,5-COD with benzene, which was used as the reactant as well as the solvent, was conducted smoothly to produce the five to six phenylbicyclooctanes (**1**—**6**) in the presence of some mole equivalents of either Brönsted acid or Lewis acid relative to 1,5-COD (Scheme 1, Tables 1 and 2). The isomer ratios were dependent on the nature and the amount of catalyst, the reaction time, and the reaction temperature. The use of concd $H_2SO_4$ and $CF_3SO_3H$ (1 mol equiv to 1,5-COD) gave the mixture mainly consisting of the compounds **1**, **2**, and **4** in good yields. The reactions did not proceed with phosphoric and hydrochloric acid even at reflux temperature, or with an excess of hydrogen chloride gas. As shown in Table 2 the use of 1 mol equiv of Lewis acid (relative to 1,5-COD) except for $AlCl_3$ gave mixtures consisting of nearly equal amounts of the compounds **1**—**4**; with $AlCl_3$ the compounds **2** and **4** became major and, further, the formation of **6** was observed. The reaction did not proceed with Lewis acids such as $ZnCl_2$, $TeCl_4$, and $LnCl_4$[5)] (Ln=Dy, La, and Yb) as the catalyst. Since $AlCl_3$ and $MoCl_5$ were revealed to be the active Lewis acid catalysts to afford good yields of the products, we carried out these reactions under several reaction conditions (Table 2). In the $AlCl_3$-catalyzed reactions, it was disclosed that the product yield as well as the isomer ratio was dependent on the amount of catalyst, the reaction time, and the reaction temperature. With the increase of the amount of the catalyst, the compounds **1** and **3** decreased and the compound **6** was formed. As a result, the main products became **2**, **4**, and **6**. Also with extending the time and with raising the temperature the compound **1** decreased remarkably and the compound **6** was formed. These results may suggest that the initial products isomerized partly to thermodynamically more stable compounds. In a prolonged reaction the isolated yields of the compounds **1**—**6** decreased because of the formation of some decomposition products such as *cis*-bicyclo[3.3.0]octane and some high molecular weight compounds (MW>600, GC/MS analysis). On the other hand, the $MoCl_5$-catalyzed reactions, which produced the compounds **1**—**4**, were not affected so much by the change of above described conditions, only the results by the change of the temperature being shown in Table 2. In this case the formation of **6** was not observed at all.

Although bicyclo[3.3.0]octanes **2** and **3** are the known compounds and could be synthesized separately as authentic samples by combining four literature methods (Scheme 2),[6)] the compounds **1**, **4**, **5**, and **6** are new, in which **6** was prepared by similar methods for the preparation of **2** and **3** as shown in Scheme 2. The compound **1** was isolated in a pure form and its structure was elucidated. On the other hand, as to **4** and **5**, although the framework of 3-phenylbicyclo[3.2.1]octane was confirmed from the separate synthesis of **5** shown in Scheme 2,[7)] the precise structure assignment (*endo*-isomer or *exo*-isomer) is still obscure and might be reversed. The compound **4** (*exo*-isomer; tentatively assigned) was isolated as a mixture with the compound **6** and its $^{13}$C NMR spectrum and mass spectrum (GC/MS) are quite similar to those of **5** (*endo*-isomer; tentatively assigned).



Scheme 1.

Table 1. Product Yield and Ratio in Protonic Acid-Catalyzed Friedel–Crafts Transannular Alkylation of Benzene with 1,5-COD[a)]

| Catalyst (mmol) | Isolated yield / %[b)] | Product ratio / %[c)] | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| concd $H_2SO_4$ (2) | 7 | 46 | 20 | 15 | 17 | 2 | 0 |
| concd $H_2SO_4$ (10) | 26 | 45 | 22 | 15 | 16 | 2 | 0 |
| concd $H_2SO_4$ (20)[d)] | 55 | 58 | 21 | 3 | 16 | 2 | 0 |
| $CF_3SO_3H$ (20) | 79 | 28 | 38 | 8 | 24 | 2 | 0 |
| concd $H_2SO_4/H_3PO_4$ (10/10) | 13 | 66 | 16 | 2 | 13 | 3 | 0 |

a) 1,5-COD (20 mmol) and benzene (50 cm$^3$) at 25 °C for 3 h. b) Based on 1,5-COD. c) GLC area ratio. d) Reaction time, 2 h.

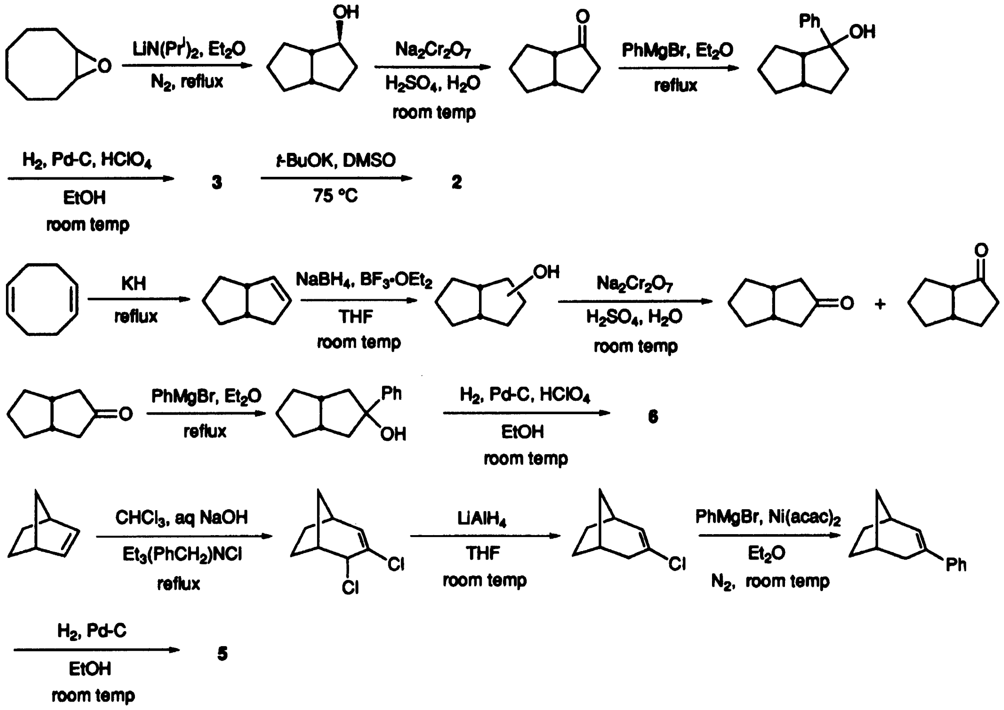
Table 2. Product Yield and Ratio in Lewis Acid-Catalyzed Friedel–Crafts Transannular Alkylation of Benzene with 1,5-COD[a)]

| Catalyst | (mmol) | Conditions | | Isolated | Product ratio/%[c)] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Time/h | Temp/°C | yield/%[b)] | 1 | 2 | 3 | 4 | 5 | 6 |
| $AlCl_3$ | 2 | 3 | 25 | 75 | 21 | 40 | 14 | 25 | Tr. | Tr. |
| $AlCl_3$ | 10 | 3 | 25 | 60 | 2 | 47 | 6 | 23 | 2 | 20 |
| $AlCl_3$ | 20 | 3 | 25 | 63 | 3 | 48 | 6 | 22 | 1 | 20 |
| $AlCl_3$ | 10 | 0.25 | 25 | 67 | 24 | 33 | 19 | 23 | 1 | 0 |
| $AlCl_3$ | 10 | 0.5 | 25 | 81 | 4 | 55 | 12 | 22 | 1 | 6 |
| $AlCl_3$ | 10 | 48 | 25 | 56 | Tr. | 49 | 19 | 16 | 4 | 12 |
| $AlCl_3$ | 10 | 3 | 5 | 68 | 12 | 39 | 21 | 28 | Tr. | 0 |
| $AlCl_3$ | 10 | 3 | Reflux | 62 | Tr. | 42 | 16 | 21 | 4 | 16 |
| $MoCl_5$ | 10 | 3 | 0 | 63 | 30 | 34 | 13 | 23 | Tr. | 0 |
| $MoCl_5$ | 10 | 3 | 25 | 60 | 31 | 32 | 14 | 22 | 1 | 0 |
| $MoCl_5$ | 10 | 3 | Reflux | 55 | 47 | 24 | 11 | 16 | Tr. | 0 |
| $SnCl_4$ | 20 | 24 | 25 | 10 | 17 | 34 | 20 | 28 | 1 | 0 |
| $TiCl_4$ | 20 | 5 | 25 | 17 | 11 | 28 | 40 | 21 | Tr. | 0 |
| $BF_3 \cdot OEt_2$ | 20 | 5 | 25 | 43 | 20 | 26 | 33 | 20 | 1 | 0 |
| $FeCl_3$ | 20 | 3 | 25 | 58 | 38 | 29 | 13 | 20 | Tr. | 0 |
| $SbCl_5$ | 20 | 3 | 25 | 43 | 42 | 29 | 11 | 18 | Tr. | 0 |

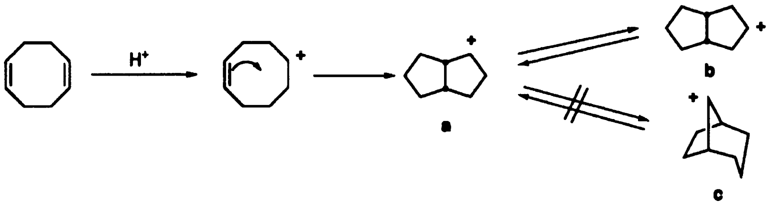
a) 1,5-COD (20 mmol) and benzene (50 cm$^3$). b) Based on 1,5-COD. c) GLC area ratio.

A trace amount of *cis*-bicyclo[3.3.0]octane was produced even when a mixture of 1,5-COD, $AlCl_3$, and nitrobenzene was stirred at 25 °C for 4 h, while *cis*-bicyclo[3.3.0]oct-2-ene was produced in 1% yield by treating 1,5-COD with $AlCl_3$ at 25 °C for 24 h. These results suggest that the initially produced electrophile is probably a *cis*-bicyclo[3.3.0]octyl cation **a** as shown in Scheme 3. The cation **a** may isomerize to the cations **b** and **c** by a 1,2-hydride shift and the Wagner–Meerwein rearrangement, respectively. Out of three cations, the cations **a** and **b** electrophilically attack benzene to produce the compounds **1**—**3**. In the so far known electrophilic transannular cyclizations, 2-substituted *cis*-bicyclo[3.3.0]octanes and 8-substituted bicyclo[3.2.1]octanes were mainly produced.[1)] Therefore, the formation of 2-phenyl-*cis*-bicyclo[3.3.0]octanes and 8-phenylbicyclo[3.2.1]octanes was expected. In this transannular alkylation, 2-phenyl-*cis*-bicyclo[3.3.0]octanes (**2** and **3**) were produced, but 8-phenylbicyclo[3.2.1]octanes were not produced at all, and instead 3-phenyl-*cis*-bicyclo-[3.3.0]octanes (**1** and **6**) as well as 3-phenylbicyclo-[3.2.1]octanes (**4** and **5**) were obtained. The reaction pathway for **4** and **5** is not yet clear. The compound **6**, which was formed only with $AlCl_3$ under forced conditions, was surely derived from **1**—**5** by isomerization probably via hydride abstraction with $AlCl_3$. We confirmed separately that the treatment of **1** with $AlCl_3$ in benzene at 25 °C for 3 h afforded a mixture of **1**—**6**.

In order to obtain information concerning the thermodynamic stabilities of these isomers, their heats of

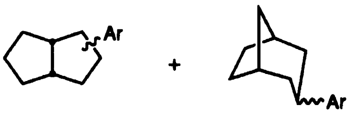


Scheme 2.



Scheme 3.

formation were calculated by the AM1 method.[8] The heats of formation of the compounds **1**, **2**, **3**, **4**, and **5** relative to that of the compound **6** (0.00 kcal mol$^{-1}$, 1 cal=4.184 J) were 0.03, 0.96, 3.37, 4.89, and 7.68 kcal mol$^{-1}$, respectively. This result shows that *endo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (**6**) is thermodynamically the most stable isomer. It is also in good agreement with the observation that **3** isomerized to **2** by the treatment with *t*-BuOK in DMSO (Scheme 2),[6c] while **6** did not isomerize to **1** by similar treatment.



**7a** : Ar = tolyl
**7b** : Ar = methoxyphenyl
**7c** : Ar = fluorophenyl
**7d** : Ar = *t*-butylphenyl
**7e** : Ar = 2,5-dimethylphenyl
**7f** : Ar = mesityl

Chart 1.

**Alkylation of Various Aromatic Compounds with 1,5-COD.** Toluene, anisole, fluorobenzene, *t*-butylbenzene, *p*-xylene, and mesitylene were used as reactants for reactions with 1,5-COD catalyzed by either concd $H_2SO_4$ (1 mol equiv to 1,5-COD) or $AlCl_3$ (1/2 mol equiv). As a result, tolylbicyclooctanes (**7a**), (methoxyphenyl)bicyclooctanes (**7b**), (fluorophenyl)bicyclooctanes (**7c**), (*t*-butylphenyl)bicyclooctanes (**7d**), (2,5-dimethylphenyl)bicyclooctanes (**7e**), and mesitylbicyclooctanes (**7f**) were obtained as a mixture of 3—11 isomers, respectively (Chart 1, Table 3). In contrast to the $AlCl_3$-catalyzed case, alkylation with $H_2SO_4$ catalyst always produced one major product, the structure of which was assumed to be *exo*-3-aryl-*cis*-bicyclo[3.3.0]octanes by comparison of mass spectrum pattern with that of **1**. The spectrum showed many peaks, while the spectra of compounds other than *exo*-3-aryl-*cis*-bicyclo[3.3.0]octanes were generally quite simple and showed the base peak assignable to the corresponding styrenes. Unfortunately, any compounds in these isomers could not be isolated in a pure form by column chromatography, vacuum distillation, or preparative gas chromatography.

Products obtained in the $AlCl_3$-catalyzed alkylation of toluene isomerized to reach an equilibrium isomeric

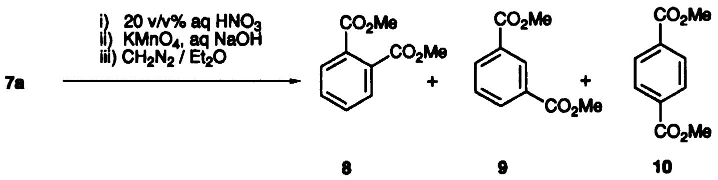
Table 3. Product Yield and Number of Isomers in $AlCl_3$ or $H_2SO_4$-Catalyzed Friedel–Crafts Transannular Alkylation of Substituted Benzenes with 1,5-CODa)

| ArH | Catalyst | Isolated yield/%b) | Number of isomers |
|---|---|---|---|
| Benzene | $H_2SO_4$ | 55 | 5e) |
| Toluene | $H_2SO_4$ | 50 | 8f) |
| Anisole | $H_2SO_4$ | 4 | 11 |
| Fluorobenzene | $H_2SO_4$ | 23 | 9g) |
| *t*-Butylbenzene | $H_2SO_4$ | 40 | 8h) |
| *p*-Xylene | $H_2SO_4$ | 31 | 3i) |
| Mesitylene | $H_2SO_4$ | 20 | 3j) |
| Benzene | $AlCl_3$ | 60 | 6 |
| Toluene | $AlCl_3$ | 92 | 8 |
| Toluenec) | $AlCl_3$ | 35 | 8 |
| Anisole | $AlCl_3$ | 68 | 8 |
| Fluorobenzene | $AlCl_3$ | 53 | 6 |
| *t*-Butylbenzened) | $AlCl_3$ | 8 | 5 |
| *p*-Xylene | $AlCl_3$ | 44 | 3 |
| Mesitylene | $AlCl_3$ | 66 | 3 |

a) 1,5-COD (20 mmol), ArH (50 cm$^3$), $AlCl_3$ (10 mmol) or concd $H_2SO_4$ (20 mmol) at 25 °C for 3h. b) Based on 1,5-COD. c) Reaction time, 72 h. d) Reaction time, 24 h. e) A major isomer (percentages in the mixture by GLC) *exo*-3-phenyl-*cis*-bicyclo[3.3.0]octane (55%). f) *exo*-3-(*p*-Tolyl)-*cis*-bicyclo[3.3.0]octane (69%). g) *exo*-3-(*p*-Fluorophenyl)-*cis*-bicyclo[3.3.0]octane (56%). h) *exo*-3-(*p*-*t*-Butylphenyl)-*cis*-bicyclo[3.3.0]octane (69%). i) *exo*-3-(2,5-Dimethylphenyl)-*cis*-bicyclo[3.3.0]octane (56%). j) *exo*-3-Mesityl-*cis*-bicyclo[3.3.0]octane (70%).

mixture within 24 h. Separate preparation of each isomer of **7a** was unsuccessful except for *endo*-2-(*p*-tolyl)-*cis*-bicyclo[3.3.0]octane.6) Therefore, the ratio of *ortho*-, *meta*-, and *para*-isomers in the products **7a** from toluene was determined after oxidation by the following method. The compounds **7a** were treated successively with nitric acid, $KMnO_4$, and diazomethane to produce a mixture of methyl esters of benzenedicarboxylic acids (**8**—**10**) (Scheme 4, see Experimental part). The ratio of **8**:**9**:**10** is related to the isomer distribution of *ortho*-, *meta*-, and *para*- in **7a**. Typical results of oxidation of several mixtures together with those of the separately prepared *endo*-2-(*p*-tolyl)-*cis*-bicyclo[3.3.0]-octane were shown in Table 4. The isomers in the products obtained under the condition of $AlCl_3$ catalyst at 25 °C for 3 h were revealed to be *para*-rich (Run 3), while those under the condition of $AlCl_3$ catalyst at 25 °C for 72 h were *meta*-rich (Run 4). The ratio observed in the latter case, namely, *ortho*-: *meta*-: *para*- =trace:65:35, was nearly the same as a thermodynamic equilibrium ratio of *t*-butylmethylbenzene.9) The alkylation under the $H_2SO_4$-catalyzed condition showed much higher *para*-orientation (Run 2). These results led to the conclusion that alkylation occurred predominantly at the *para*-position, irrespective of the formation of the [3.3.0]- or [3.2.1]-system, followed by an isomerization to *meta*-isomer in the $AlCl_3$-catalyzed reaction. Yur'ev et al.2b) reported similar transannular cyclization of 1,5-COD with toluene catalyzed by the system of $WCl_6$, $EtAlCl_2$, and ethanol (olefin metathesis catalyst) at room temperature and concluded that the resulting tolylbicyclooctanes were consisted of only *meta*-isomer from the result of oxidation with concd $HNO_3$ to produce dimethyl isophthalate (**9**). Although they did not show any detailed oxidation conditions, it seems probable that the isomerization to the thermodynamically stable *meta*-isomer occurred during the oxidation treatment. In contrast, our oxidation conditions were very mild and the isomerization did not occur as clarified from the oxidation product of authentic *endo*-2-(*p*-tolyl)-*cis*-bicyclo[3.3.0]octane (Run 1). Therefore, we are sure that our results reflect the correct *ortho*-/*meta*-/*para*- distribution in the products of transannular cyclization of 1,5-COD with toluene under several conditions.

**Reactions of Benzene with Nonconjugated Cyclic Dienes.** Some other nonconjugated cyclic dienes were also subjected to react with benzene in the presence of $AlCl_3$ (1/2 mol equiv to diene) or concd $H_2SO_4$ (1 mol equiv). Benzene was alkylated with bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) in the presence of $AlCl_3$ (1/2 mol equiv) at 25 °C for 30 min to produce a tricyclic compound **11** in 36% yield. In a prolonged reaction the compound **11** disappeared gradually, while a bicyclic compound, *endo*-2-phenylnorbornane (**12**) appeared, and after 24 h only **12** was obtained in 21% yield (Scheme 5). The *exo*-isomer of **12** was not formed. We confirmed separately that **11** was converted solely to **12** in benzene in the presence of $AlCl_3$ catalyst at 25 °C for 1.6 h in 33% yield. The reaction pathway shown in Scheme 5 may be conceivable for this reaction. Namely, the diene was attacked

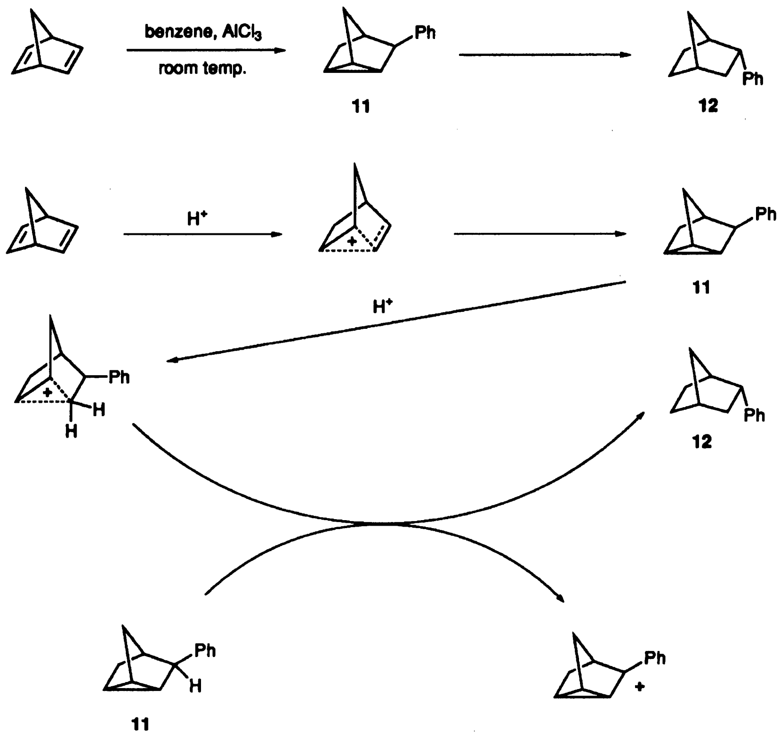


Scheme 4.

Table 4. Oxidation of **7a**[a)]

| Run | Reactant | GLC yield/%[b)] | Product ratio/% | | |
|---|---|---|---|---|---|
| | | | **8** | **9** | **10** |
| 1 | *endo*-2-(*p*-Tolyl)-*cis*-bicyclo[3.3.0]octane | 82 | Tr. | Tr. | >99 |
| 2 | **7a**[c)] | 59 | 1 | 19 | 80 |
| 3 | **7a**[d)] | 80 | 5 | 38 | 57 |
| 4 | **7a**[e)] | 73 | Tr. | 65 | 35 |

a) For conditions see experimental part. b) Based on the reactant. c) Products obtained under the condition of 1 mol equiv of concd $H_2SO_4$ (to 1,5-COD) at 25 °C for 3h. d) Products obtained under the condition of 1/2 mol equiv of $AlCl_3$ at 25 °C for 3h. e) Products obtained under the condition of 1/2 mol equiv of $AlCl_3$ at 25 °C for 72h.



Scheme 5.

first by a proton to produce a nonclassical carbocation. The electrophilic attack of the cation upon benzene produced the transannular product **11**. The compound **11** was attacked by a proton to give another carbocation in which an intermolecular hydride transfer occurred to induce the cleavage of the carbon–carbon bond leading to **12**.

From the reaction of 1,4-cyclohexadiene with benzene in the presence of $AlCl_3$ catalyst, cyclohexylbenzene (**13**) was produced in 23% yield together with a small amount of **14** and **15** (Chart 2). Any transannular cyclized products were not obtained.

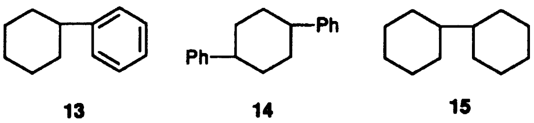


Chart 2.

## Experimental

FT-IR spectra (thin film for liquids) were recorded on a Shimadzu FTIR-8100 spectrophotometer equipped with a

DR-8000 data processing system. $^1$H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer for solutions in $CDCl_3$. $^{13}$C NMR spectra were recorded on JEOL GSX-270 (67.8 MHz) and JEOL FX-100 (25.0 MHz) spectrometers for solutions in $CDCl_3$. Mass spectra were measured on a Shimadzu QP-2000 mass spectrometer equipped with a Shimadzu GC-14A gas-liquid chromatography. The ionizing voltage was 70 eV for all compounds. GLC analyses were performed on a Hitachi 163 instrument (2 m×3 mm stainless steel column packed with 10% Apiezon-M on Neopak 1A) and a Shimadzu GC-14A instrument (25 m Hicap-CBP10-S25-050 capillary column) with flame-ionization detectors and $N_2$ as carrier gas. Preparative gas chromatographies were carried out on a Shimadzu GC-3AH instrument on a 10% Apiezon-L on Chromosorb WAW column. Column chromatography on $SiO_2$ was performed with Wakogel C-200 [hexane and hexane–ethyl acetate (9:1) as eluents]. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

All commercially available organic and inorganic compounds were used without further purification except for the solvent which was distilled before use. Authentic samples of **2**, **3**, and *cis*-bicyclo[3.3.0]oct-2-ene for GLC determination were synthesized by the literature methods as shown in Scheme 2.$^{6)}$ New compounds **5** (tentative), **6**, and *endo*-2-(*p*-tolyl)-*cis*-bicyclo[3.3.0]octane were similarly prepared from 3-phenylbicyclo[3.2.1]oct-2-ene,$^{7)}$ bicyclo[3.3.0]octan-3-one, and bicyclo[3.3.0]octan-2-one, respectively, as will be described below. *cis*-Bicyclo[3.3.0]octane is a known compound and identified by mass spectrum (GC/MS).$^{10)}$ The compounds **8**, **9**, and **10** were prepared by treatment of the corresponding commercial acids with diazomethane.$^{11)}$ An authentic sample of **11** was synthesized by the literature method.$^{12)}$ The compounds **13** and **15** were commercially available. The compound **14** is a known compound and identified by $^{13}$C NMR spectral data.$^{13)}$

***exo*-2-Phenyl-*cis*-bicyclo[3.3.0]octane (2).** A colorless oil isolated by column chromatography. $^{13}$C NMR $\delta=25.1$ (t), 32.3 (t), 33.8 (t), 33.9 (t), 36.4 (t), 43.6 (d), 51.9 (d), 53.6 (d), 125.7 (d), 127.3 (d), 128.2 (d), and 145.9 (s); MS *m/z* (rel intensity) 186 ($M^+$; 11), 117 (6), 104 (100), 91 (8), 67 (8), and 41 (5). (Found: C, 90.35; H, 9.74%).

***endo*-2-Phenyl-*cis*-bicyclo[3.3.0]octane (3).** A colorless oil isolated by column chromatography. $^{13}$C NMR $\delta=27.4$ (t), 27.4 (t), 29.6 (t), 32.6 (t), 35.8 (t), 42.7 (t), 48.0 (d), 48.7 (d), 125.4 (d), 127.9 (d), 127.9 (d), and 143.4 (s); MS *m/z* (rel intensity) 186 ($M^+$; 10), 117 (6), 104 (100), 91 (8), 67 (11), and 41 (9). (Found: C, 90.39; H, 9.92%).

***endo*-3-Phenylbicyclo[3.2.1]octane (5) (tentative).** A mixture of 3-phenylbicyclo[3.2.1]oct-2-ene$^{7)}$ (1.93 g, 10.5 mmol), 5% Pd–C (106 mg), and ethanol (35 cm$^3$) was stirred under hydrogen (1 atm) at room temperature until the uptake of hydrogen was complete. After filtration of the catalyst, the filtrate was concentrated to produce a colorless oil. The oil was purified by column chromatography on $SiO_2$ using hexane as eluent to give colorless needle-like crystals of **5** (1.63 g, 8.74 mmol, yield 83%). Mp 42.0—42.5 °C, bp 91.5 °C (2 mmHg, 1 mmHg=133.322 Pa); IR 3025 (w), 2926 (vs), 2855 (s), 1597 (w), 1493 (m), 1451 (m), 752 (s), and 698 (vs) cm$^{-1}$; $^1$H NMR $\delta=1.04$—2.30 (12H, m), 2.70—2.84 (1H, m), and 7.12—7.32 (5H, m); $^{13}$C NMR $\delta=31.7$ (t), 32.3 (d), 33.1 (t), 34.3 (d), 40.0 (t), 125.6 (d), 127.4 (d), 128.1 (d), and 147.4 (s); MS *m/z* (rel intensity) 186 ($M^+$; 26), 104 (100), 91 (41), 81 (31), 67 (21), and 41 (32). (Found: C, 90.55; H, 9.92%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%).

***endo*-3-Phenyl-*cis*-bicyclo[3.3.0]octane (6).** A mixture of magnesium (200 mg, 8.23 mmol) and bromobenzene (760 mg, 4.84 mmol) was subjected to reflux in diethyl ether (25 cm$^3$) for a while. To the mixture was added dropwise *cis*-bicyclo[3.3.0]octan-3-one$^{6b)}$ (464 mg, 3.74 mmol) and the mixture was stirred magnetically at reflux temperature for 15 min. After it had been cooled, the mixture was treated with saturated aq $NH_4Cl$ (20 cm$^3$) and then the ethereal layer was separated. The water layer was extracted with diethyl ether (2×20 cm$^3$). The combined ethereal layer was washed with saturated aq $NaHCO_3$ (15 cm$^3$) and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a pale yellow oil (380 mg). A mixture of the oil (380 mg), 10% Pd–C (100 mg), 35% perchloric acid (0.15 cm$^3$), and ethanol (10 cm$^3$) was stirred under hydrogen (1 atm) at room temperature until the uptake of hydrogen was complete. After filtration of the catalyst, the filtrate was added with water (50 cm$^3$) and then extracted with diethyl ether (3×25 cm$^3$). The ether extract was washed with saturated aq $NaHCO_3$ (20 cm$^3$), dried over $MgSO_4$, and evaporated to leave a pale yellow oil. The oil was purified by column chromatography on $SiO_2$ using hexane as eluent to give a colorless oil of **6** (340 mg, 1.83 mmol, yield 43%) which contained a small amount of **1** (**6**:**1**=96:4). IR 3083 (w), 3061 (w), 3029 (w), 2942 (vs), 2861 (s), 1603 (w), 1493 (m), 1468 (w), 1458 (w), 1447 (m), 1032 (w), 754 (s), and 698 (vs) cm$^{-1}$; $^1$H NMR $\delta=1.23$ (2H, td, $J=12.4$, 9.1 Hz), 1.39—1.63 (6H, m), 2.18—2.30 (2H, m), 2.54 (2H, s, br), 2.83—2.97 (1H, m), and 7.12—7.30 (5H, m); $^{13}$C NMR $\delta=25.0$ (t), 33.3 (t), 42.4 (t), 43.2 (d), 47.2 (d), 125.8 (d), 126.9 (d), 128.2 (d), and 144.8 (s); MS *m/z* (rel intensity) 186 ($M^+$; 25), 104 (100), 91 (25), 82 (20), 67 (23), and 41 (22). (Found: C, 90.39; H, 9.89%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%).

***endo*-2-(*p*-Tolyl)-*cis*-bicyclo[3.3.0]octane.** A colorless oil (yield 64%) prepared by the methods similar to those for **2** (Scheme 2) using *p*-tolylmagnesium bromide. IR 2900 (s), 2700 (m), 1510 (m), 1450 (m), 810 (m), and 790 (m) cm$^{-1}$; $^1$H NMR $\delta=1.10$—2.00 (10H, m,), 2.30—2.80 (3H, m), 2.30 (3H, s), and 7.10—7.20 (4H, m); $^{13}$C NMR $\delta=21.0$ (q), 27.5 (t), 27.5 (t), 29.7 (t), 32.6 (t), 35.8 (t), 42.6 (d), 48.0 (d), 48.2 (d), 127.7 (d), 128.5 (d), 134.6 (s), and 140.2 (s); MS *m/z* (rel intensity) 200 ($M^+$; 12), 131 (10), 118 (100), 105 (7), 91 (8), 79 (4), 67 (8), 53 (2), and 41 (7). (Found: C, 90.04; H, 10.16%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%).

**3-Phenyltricyclo[2.2.1.0$^{2,6}$]heptane (11).**$^{12)}$ A colorless oil isolated by vacuum distillation, bp 80.5—81.0 °C (2 mmHg); IR 3061 (m), 3027 (m), 2944 (vs), 2869 (vs), 1603 (m), 1497 (s), 1449 (s), 1304 (m), 1032 (m), 810 (s), 737 (s), and 698 (s) cm$^{-1}$; $^1$H NMR $\delta=1.04$ (1H, d, $J=10.6$ Hz), 1.18—1.31 (4H, m), 1.39 (1H, d, $J=10.2$ Hz), 1.52 (1H, d, $J=10.2$ Hz), 1.94 (1H, s), 2.82 (1H, s), and 7.14—7.29 (5H, m); $^{13}$C NMR $\delta=10.2$ (d), 11.5 (d), 13.6 (d), 28.8 (t), 34.7 (t), 36.0 (d), 49.5 (d), 125.7 (d), 127.8 (d), 127.8 (d), and 142.5 (s). (Found: C, 91.64; H, 8.45%).

**General Procedure of Friedel–Crafts Transannular Alkylation of Aromatic Compounds.** A mixture of aromatic compound (50 cm$^3$) and an acid (2—20 mmol; either protonic acid or Lewis acid) was stirred magnetically at 25 °C for 15 min. To the mixture was added dropwise 1,5-COD (2.16 g, 20.0 mmol) and the resulting mixture was stirred at 25 °C for an appropriate time by monitoring with GLC. The reaction mixture was washed with water (3×20 cm$^3$) and dried over anhydrous $MgSO_4$. Removal of aromatic compound and unreacted 1,5-COD under reduced pressure left a brown oil, which was subjected to column chromatography on $SiO_2$ [hexane; then hexane–ethyl acetate (9 : 1)] to give a mixture of products. Some of them were isolated in a pure form by preparative GLC. Some physical and spectral data of the compounds **1**, **4**, **7**, and **12** are as follows.

***exo*-3-Phenyl-*cis*-bicyclo[3.3.0]octane (1).** A colorless oil isolated by preparative GLC; 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 $\delta$=1.36—2.02 (12H, m), 2.65—2.76 (1H, m), and 7.10—7.35 (5H, m); $^{13}$C NMR $\delta$=25.8 (t), 35.2 (t), 42.5 (t), 49.4 (d), 58.7 (d), 125.0 (d), 126.1 (d), 128.0 (d), and 152.1 (s); MS $m/z$ (rel intensity) 186 ($M^+$; 80), 157 (75), 143 (100), 129 (87), 115 (55), 104 (65), 91 (66), 77 (28), 67 (21), and 41 (31). (Found: C, 90.04; H, 9.75%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%).

***exo*-3-Phenylbicyclo[3.2.1]octane (4) (tentative).** A colorless oil isolated as a mixture with **6** by preparative GLC (**6**:**4**=1 : 1). The structure of **4** was tentatively assigned as a stereoisomer (*exo*-) of compound **5** from $^{13}$C NMR data together with mass spectral data. $^{13}$C NMR $\delta$=27.5 (t), 35.1 (t), 41.4 (t), 42.8 (d), 43.2 (d), 125.8 (d), 127.2 (d), 128.1 (d), and 145.2 (s); MS $m/z$ (rel intensity) 186 ($M^+$; 24), 104 (100), 91 (28), and 67 (22). (Found for a mixture of **4** and **6**: C, 90.55; H, 9.92%. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%).

**Tolylbicyclooctanes (7a).** A colorless oil isolated by vacuum distillation, bp 111.0—112.0 °C (2 mmHg); the major compound in the $H_2SO_4$-catalyzed reaction was supposed to be *exo*-3-(*p*-tolyl)-*cis*-bicyclo[3.3.0]octane by comparison of mass spectral pattern with that of **1**: MS $m/z$ (rel intensity) 200 ($M^+$; 100), 185 (40), 171 (92), 157 (90), 143 (88), 129 (62), 118 (57), 105 (55), 91 (43), 77 (21), 65 (25), and 39 (44). (Found: C, 89.86; H, 10.23%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%).

**(Methoxyphenyl)bicyclooctanes (7b).** A colorless oil isolated by vacuum distillation, bp 129.0—130.5 °C (2 mmHg) (Found: C, 83.01; H, 9.42; O, 7.68%. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32; O, 7.39%).

**(Fluorophenyl)bicyclooctanes (7c).** A pale yellow oil isolated by vacuum distillation, bp 100 °C (2 mmHg); the major compound in the $H_2SO_4$-catalyzed reaction was similarly supposed to be *exo*-3-(4-fluorophenyl)-*cis*-bicyclo[3.3.0]octane: MS $m/z$ (rel intensity) 204 ($M^+$; 65), 175 (86), 161 (100), 147 (87), 133 (49), 122 (41), 109 (69), 67 (26), and 41 (42). (Found: C, 82.57; H, 8.34%. Calcd for $C_{14}H_{17}F$: C, 82.31; H, 8.39%).

**(*t*-Butylphenyl)bicyclooctanes (7d).** A colorless oil isolated by vacuum distillation, bp 110.0—121.0 °C (2 mmHg); the major compound in the $H_2SO_4$-catalyzed reaction was similarly supposed to be *exo*-3-(4-*t*-butylphenyl)-*cis*-bicyclo[3.3.0]octane: MS $m/z$ (rel intensity) 242 ($M^+$; 34), 227 (100), 185 (98), 145 (35), 129 (22), 117 (45), 91 (23), 57 (51), and 41 (40). (Found: C, 89.32; H, 10.81%. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81%).

**(2,5-Dimethylphenyl)bicyclooctanes (7e).** A colorless oil isolated by vacuum distillation, bp 121.0—123.5 °C (2 mmHg); the major compound in the $H_2SO_4$-catalyzed reaction was similarly supposed to be *exo*-3-(2,5-dimethylphenyl)-*cis*-bicyclo[3.3.0]octane: MS $m/z$ (rel intensity) 214 ($M^+$; 100), 199 (61), 185 (51), 171 (98), 157 (88), 143 (81), 132 (74), 119 (44), 105 (32), 91 (43), 79 (46), and 41 (70). (Found: C, 89.89; H, 10.55%. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35%).

**Mesitylbicyclooctanes (7f).** A colorless oil isolated by vacuum distillation, bp 105.0—119.0 °C (2 mmHg); the major compound in the $H_2SO_4$-catalyzed reaction was similarly supposed to be *exo*-3-mesityl-*cis*-bicyclo[3.3.0]octane: MS $m/z$ (rel intensity) 228 ($M^+$; 35), 159 (62), 146 (100), 133 (55), and 41 (23). (Found: C, 89.52; H, 10.86%. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59%).

***endo*-2-Phenylbicyclo[2.2.1]heptane (12).** A colorless oil isolated by column chromatography, bp 82.5—83.5 °C (2 mmHg) [lit,[14] 71 °C (0.6 mmHg)]; IR 3085 (w), 3060 (w), 3027 (w), 2950 (vs), 2870 (s), 1601 (m), 1495 (m), 1478 (w), 1451 (m), 1308 (w), 1032 (w), 764 (m), 714 (w), and 698 (s) cm$^{-1}$; $^1$H NMR $\delta$=1.15—1.60 (8H, m), 1.96 (1H, tm, $J$=11.3 Hz), 2.30—2.41 (2H, m), 3.17—3.26 (1H, m), and 7.13—7.32 (5H, m); $^{13}$C NMR $\delta$=22.9 (t), 30.2 (t), 34.3 (t), 37.6 (d), 40.6 (t), 42.6 (d), 46.1 (d), 125.4 (d), 127.9 (d), 128.1 (d), and 143.6 (s); MS $m/z$ (rel intensity) 172 ($M^+$; 30), 104 (100), 92 (50), 81 (39), and 67 (31). (Found: C, 90.91; H, 9.40%).

**General Procedure for Oxidation of 7a.** Tolylbicyclooctanes (**7a**) (0.55 g, 2.75 mmol) were stirred magnetically with 20 v/v% aq $HNO_3$ (10 cm$^3$) at 85 °C for 96 h. After it had been cooled down to room temperature, the mixture was neutralized with 7 M (1 M=1 mol dm$^{-3}$) aq NaOH (6 cm$^3$) and stirred at the temperature for 30 min. The mixture was then added with $KMnO_4$ (2.16 g, 13.7 mmol) portionwise at 60 °C and it was stirred at 60 °C for 4 h. After it had been cooled down to room temperature, the mixture was added with ethanol (10 cm$^3$) and stirred until the complete decomposition of $KMnO_4$ to $MnO_2$. After filtering the precipitated dark brown solid and washing it with hot water (100 cm$^3$), the filtrate was acidified by concd $H_2SO_4$ (6 cm$^3$) and allowed to stand in a refrigerator for a day. A precipitated pale yellow powder was collected by filtration and the filtrate was extracted with diethyl ether (3×50 cm$^3$). Evaporation of the ether left a small amount of the yellow powder. Both powders were combined and treated with an ethereal solution of diazomethane[11] to give a mixture of **8**, **9**, and **10**, their yields being determined by GLC with biphenyl as an internal standard.

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