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Studies on Seven-membered Ring Compounds. XXXV.[1] Ring Closure of γ-Cycloheptatrienyl-substituted α,β-Unsaturated Carbonyl Compounds to Benzocycloheptene Derivatives

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Ring closure reactions of γ-cycloheptatrienyl-substituted α,β-unsaturated carbonyl compounds by acid were examined. Treatment of 2-methyl-4-(2,4,6-cycloheptatrien-4-yl)-2-pentenal (II) with hydrobromic acid at room temperature in acetic acid afforded 1,3-dimethyl- (III) and 2,4-dimethyl-5*H*-benzocycloheptene (IV) accompanied by the production of 1,3,8-trimethylnaphthalene (V). On the ring closure of 5-(2,4,6-cycloheptatrien-4-yl)-3-hexen-2-one (VIII) by a similar procedure, 1,4-dimethyl-5*H*-benzocycloheptene (IX), 1,4,5-trimethylnaphthalene (X), and 1,4,6-trimethylnaphthalene (XI) were isolated.

Previously, 4-(2,4,6-cycloheptatrien-1-yl)-2-butenal derivatives were prepared by the reaction of 7-ethoxy-1,3,5-cycloheptatriene with aldehyde enamies in the presence of acetic acid through a one step introduction of the four–carbon chain into the seven-membered ring.[1] In the present work, the ring closure reaction of this class of compounds, γ-cycloheptatrienyl-substituted α,β-unsaturated carbonyl derivatives, was undertaken. Several papers have been published concerning the ring closure reaction between a carbonyl group and a double bond; however, examples involving the participation of the double bond of the cycloheptatriene ring in such a ring closure reaction have not yet been reported in the literature. If the double bond of cycloheptatriene ring is capable to undergoing such a ring closure reaction, a new route for the preparation of seven-membered ring compounds fused to another carbon ring(s) would be expected by the cyclization of cycloheptatrienes substituted with a carbon chain carrying a proper functional group, and the formation of benzocycloheptene derivatives would be anticipated in the present ring closure of γ-cycloheptatrienyl-substituted α,β-unsaturated carbonyl compounds. The present work was also intended to serve as a model for subsequent attempts to prepare azulenes by the ring closure of cycloheptatriene derivatives having a three–carbon side chain.

A preliminary attempt to directly cyclize 2-methyl-4-(2,4,6-cycloheptatrien-1-yl)-2-pentenal (I), which was previously obtained by the reaction between 7-ethoxy-1,3,5-cycloheptatriene and propionaldehyde enamine,[1] with hydrobromic acid in acetic acid was unsuccessful, and resulted in the cleavage of the side chain to produce tropylium cation. A similar cleavage of the side chain of (2,4,6-cycloheptatrien-1-yl)-2-propanone by acid had been reported by Conrow.[3] To avoid this side chain fragmentation, thermal isomerization of I to its double bond isomer was undertaken and a mixture of I and 2-methyl-4-(2,4,6-cycloheptatrien-4-yl)-2-pentenal (II) in an approximate ratio of 1:3 was obtained on heating of I at 140° for seventy hours. Stirring of the resulting mixture of isomers in acetic acid containing hydrobromic acid at room temperature afforded an oily product, whose analytical gas chromatogram showed four peaks in a ratio of about 1:11:4:4, in order of increasing retention times. The preparative gas chromatography of this product accomplished the isolation of two components corresponding to the second and third peaks; however, the isolation of the

1) Part XXXIV: T. Watanabe and N. Soma, *Chem. Pharm. Bull.* (Tokyo), **18**, 1604 (1970).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo, 140, Japan.*
3) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

other components was not successful because of lack of material and decomposition under the conditions used in the preparative chromatography. The main reaction product showing the above second peak was collected as an colorless oil, which did not exhibit any carbonyl or hydroxyl absorption in the infrared (IR) spectrum, and its ultraviolet (UV) spectrum showed absorption similar to that of 5*H*-benzocycloheptene with an absorption maximum at 279 mμ. These spectroscopic data suggested the expected ring closure reaction of II to dimethylbenzocycloheptene had taken place, and the elemental analytical values agreed with the composition, $C_{13}H_{14}$. However, the nuclear magnetic resonance (NMR) spectrum exhibited complicated absorptions not interpretable as a single dimethylbenzocycloheptene and indicated that this product was an isomeric mixture of two dimethyl-5*H*-benzocycloheptenes. Thus, in the spectrum, two kinds of doublet arising from methylene protons of the cycloheptatriene ring appeared at 7.14 (J=6.7 cps) and 7.10 τ (J=6.2 cps) with an intensity ratio of about 3:2. The appearance of these absorptions due to methylene protons as the doublets definitely locates the methylene groups at C-5. Based on the presumption that two methyl groups of the both benzocycloheptene isomers would be located at the *meta* positions of the fused benzene ring, which was formed by the ring closure of the side chain of II, this mixture was deduced as a mixture consisting of 1,3-dimethyl- (III) and 2,4-dimethyl-5*H*-benzocycloheptene (IV). The NMR spectral absorptions in the olefinic region of the mixture also were completely interpretable in terms of a mixture of III and IV. However, which compound, III or IV, is the major component of the mixture remained undecided.

The other product collected by preparative gas chromatography as colorless crystals, mp 45—46.5°, showed elemental analytical values of the same composition, $C_{13}H_{14}$, as III and IV. The UV spectrum exhibited an absorption characteristic of naphthalene derivatives, and the NMR spectrum indicated the presence of three methyl groups and five aromatic hydrogens. Consequently, the structure of this product was presumed to be a trimethylnaphthalene. With respect to the position of three methyl groups, two groups were deduced as being situated at the 1- and 3-positions because one benzene ring of the naphthalene also was built up by the ring closure of the side chain of II as in the case of the formation of III and IV. The comparison of the melting point of the product with those of the reported trimethylnaphthalenes having methyl groups at the 1,3-positions suggested the product as being either 1,3,5- or 1,3,8-trimethylnaphthalene; the melting point of the former had been reported as 47° and the latter, as 48°.[4] This suggestion was supported by the NMR spectrum, which showed, in the aromatic proton region, two broad singlets at 2.95 and 2.49 τ (1H each), and complex of multiplets at around 2.80 (2H) and 2.30 τ (1H) indicative of the presence of three adjacent protons. Triple resonance at 7.37 and 7.53 τ, in the methyl proton region, simplified the above two broad singlets at 2.95 and 2.49 τ, respectively, into a doublet (J=1.7 cps) and a doublet of doublets (J=1.7 and 1.0 cps), allowing the assignment of the structure of the product not as 1,3,5- but 1,3,8-trimethylnaphthalene (V). Namely, the above results are interpretable by assuming that the singlets at 2.95 and 2.49 τ are due to H-4 and due to H-2, respectively, of V, the coupling of 1.0 cps being considered as originating between H-8 and H-4.

In order to further confirm the above ring closure reaction, cyclization of 5-(2,4,6-cycloheptatrien-4-yl)-3-hexen-2-one (VIII) was next examined. In this case, the complication of the formation of two isomeric benzocycloheptenes as observed with II should be avoidable, and the production of a single benzocycloheptene derivative, 1,4-dimethyl-5*H*-benzocycloheptene (IX) was anticipated. The ketone, 5-(2,4,6-cycloheptatrien-1-yl)-3-hexen-2-one (VII), was prepared by condensation of 2-(2,4,6-cycloheptatrien-1-yl)propionaldehyde (VI) with acetone, and subsequent thermal isomerization at 170° for 2.5 hours gave a mixture of VIII and unchanged VII in an approximate ratio of 3:2. The structure of VII was confirmed by satisfactory analytical values, $\nu_{C=O}$ at 1675 cm^{-1} in the IR spectrum, and NMR spectrum in-

4) I.M. Heilbron and D.G. Wilkinson, *J. Chem. Soc.*, **1930**, 2537.

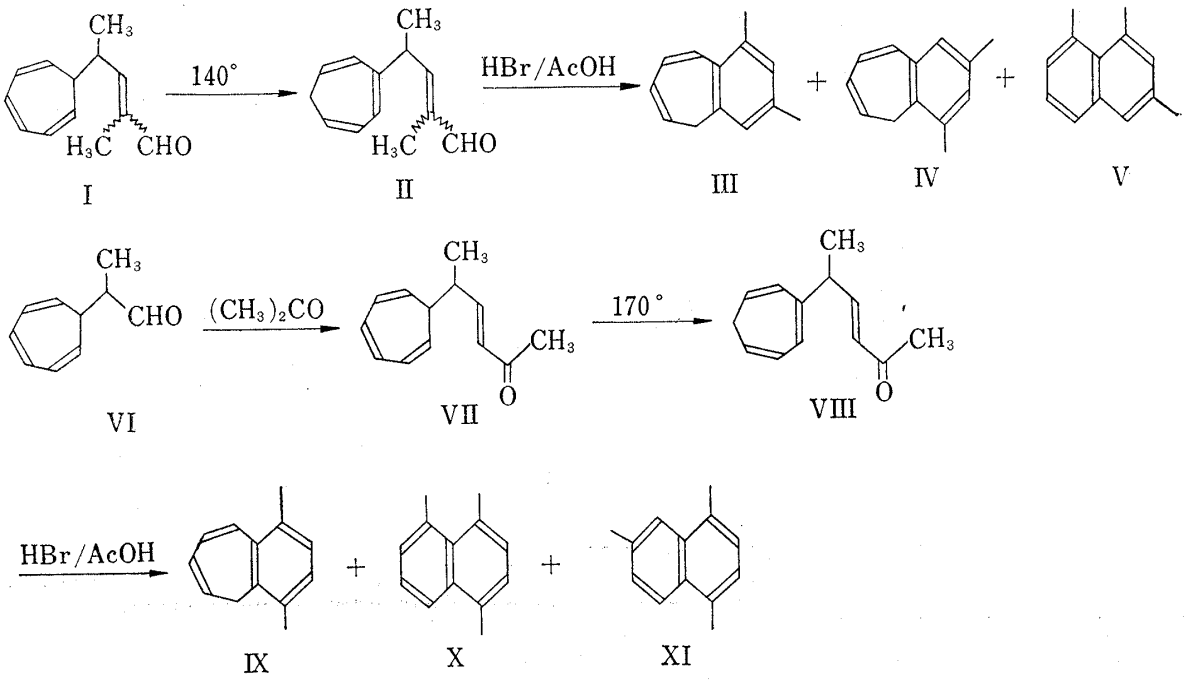

Chart 1

dicative of the presence of two methyl groups and a 7-substituted 1,3,5-cycloheptatriene ring. The geometry on the side chain double bond of VIII was designated as *trans* by the magnitude of the coupling constant, 16 cps, between H-3 (3.94 τ) and H-4 (3.27 τ). Acid treatment of the mixture of VII and VIII similar to that for II gave, after preparative gas chromatography of the reaction mixture, the expected product, IX, along with two minor products, an oily and a crystalline (mp 60—61°) trimethylnaphthalenes. The crystalline naphthalene was designated as 1,4,5-trimethylnaphthalene (X), which corresponded to V isolated on the ring closure of II, by the comparison of the melting point with the reported value and the consistency of its NMR spectral absorptions with the structure. The spectrum showed a singlet (2H) assignable to H-2 and H-3 at 2.99 τ and complicated multiplets at around 2.27 (1H) and 2.82 τ (2H) indicative of the presence of adjacent three aromatic protons. The structure of another oily trimethylnaphthalene was presumed as 1,4,6-trimethylnaphthalene (XI), since two methyl groups of this naphthalene also were deduced as being *para* on the benzene ring having arisen from the side chain of VIII. This was confirmed by the NMR spectrum wherein the H-2 and H-3 displayed, as in X, a superimposing singlet at 3.02 τ and the signals assignable to H-5, H-7, and H-8 were, respectively, observed as a fine splitting singlet at 2.39 τ, a doublet of doublets at 2.81 τ (J=8.5 and 2.0 cps), and a doublet at 2.27 τ (J=8.5 cps). Structure of IX was supported by the UV spectral similarity to 5*H*-benzocycloheptene, and the NMR spectrum, which included a doublet (J=7.0 cps) at 7.18 τ due to the methylene protons of the cycloheptatriene moiety and two doublets at 3.02 and 3.22 τ (J=8.0 cps, 1H each) indicative of the presence of two adjacent aromatic protons. Moreover, the structure of IX was proved by the following alternative synthesis. The product obtained by Wolff–Kishner reduction of 4-(2,5-dimethylbenzoyl)butyric acid (XII),[5] 5-(2,5-dimethylphenyl)valeric acid (XIII), was cyclized to 1,4-dimethyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (XIV) by being heated in polyphosphoric acid. Compound XIV was brominated to 6-bromo-1,4-dimethyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (XV) and heating of XV in dimethylformamide with lithium chloride afforded 1,4-dimethyl-8,9-dihydro-5*H*-benzocycloheptene-5-one (XVI), which

5) C.L. Anderson, W.J. Horton, F.E. Walker, and M.R. Weiler, *J. Am. Chem. Soc.*, **77**, 598 (1955).

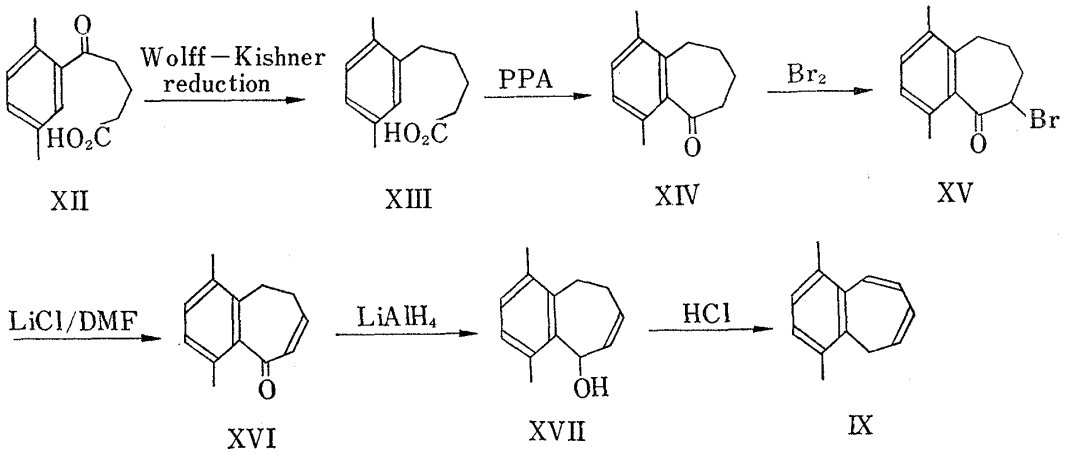

Chart 2

was reduced with lithium aluminum hydride to give 1,4-dimethyl-5-hydroxy-8,9-dihydro-5*H*-benzocycloheptene (XVII). Treatment of XVII with hydrogen chloride gave the desired IX, which was identical with the product obtained the ring closure of VIII.

From above results, it was demonstrated that γ-(2,4,6-cycloheptatrien-4-yl)substituted α,β-unsaturated carbonyl compounds underwent ring closure to afford 5*H*-benzocycloheptene derivatives when treated with an acid, accompanied by the formation of naphthalene derivatives. The side chain of these cycloheptatrienyl-substituted carbonyl compounds can cyclize either at the C-4 or at C-2 position of the cycloheptatriene ring; the ring closure of VIII at the C-4 would produce intermediate, A, while that at C-2, intermediate B. Deprotonation and dehydration on intermediate A will afford benzocycloheptene isomers C and/or D, and the formation of isomer, C, D, and/or E, will be anticipated from intermediate B. Double bond isomerization of these benzocycloheptenes could furnish the 5*H*-benzocycloheptene derivative, IX, actually isolated. The formation of IX *via* 1,4-dimethyl-7*H*-benzocycloheptene seems to be not preferable considering Bartelli's report[6] wherein the major product of acid treatment

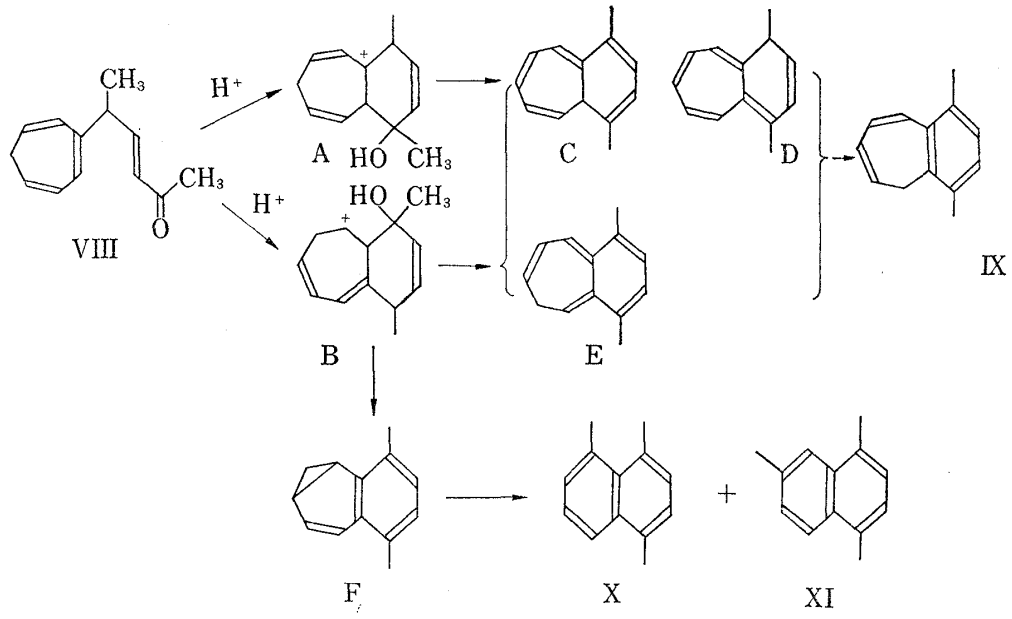

Chart 3

6) D.J. Bartelli and C.C. Ong, *J. Am. Chem. Soc.*, **87**, 3719 (1965).

of 5-hydroxy-7-methyl-6,7-dihydro-5*H*-benzocycloheptene was shown to be 7-methyl-7*H*-benzocycloheptene, the isomerization of which to the 5*H*-benzocycloheptene isomer being not described. Naphthalene formation from benzocycloheptene derivatives was excluded by the experiment wherein IX was treated with hydrobromic acid under the same conditions as used in the ring closure reaction wherein unchanged IX was recovered. One possible explanation for the formation of the two naphthalene derivatives, X and XI, from VIII involves the rearrangement of a benzonorcaradiene F derived from the above-mentioned cyclization intermediate B. The rupture of the cyclopropane ring can take place at either side of the methylene group, thus producing naphthalene bearing the third methyl group either at the α- or β-position.

Application of the present ring closure reaction of cycloheptatrienyl-substituted carbonyl compounds to the preparation of azulenes will be reported in the subsequent paper.

Experimental

Thermal Isomerization of 2-Methyl-4-(2,4,6-cycloheptatrien-1-yl)-2-pentenal (I) to 2-Methyl-4-(2,4,6-cycloheptatrien-4-yl)-2-pentenal (II)——In N_2 stream, 6.18 g of I was heated at 140° for 70 hr. Distillation of the resulting oil under reduced pressure gave 4.1 g of colorless oil (mixture of I and II in a ratio of about 1:3), bp 95—102° (0.35 mmHg). The NMR spectrum (CCl_4 solution) included the following absorptions: triplet (J=6.0 cps) at 7.80 τ ($C\underline{H}_2$ in the cycloheptatriene moiety of II), multiplet at 8.40 τ (C<u>H</u> in the cycloheptatriene moiety of I), multiplet at 6.40 τ (H-4 of II), multiplet at 7.02 τ (H-4 of I). The intensity ratio of the peak-3 to peak-4 was determined as 3:1.

Ring Closure of 2-Methyl-4-(2,4,6-cycloheptatrien-4-yl)-2-pentenal (II): Formation of 1,3-Dimethyl- (III), 2,4-Dimethyl-5H-benzocycloheptene (IV), and 1,3,8-Trimethylnaphthalene (V)——A solution of 15.3 g of a mixture of II and I (II:I=about 3:1), obtained above by thermal isomerization of I, in 170 ml of AcOH was added dropwise into an ice-cooled solution of 261 g of 47% aqueous HBr in 1500 g of AcOH. The mixture was allowed to stand overnight at room temperature, H_2O was added, and the mixture was extracted with ether. The ether extract was washed with H_2O, and dried over $MgSO_4$. After evaporation of the solvents, the remaining oily product was chromatographed on Al_2O_3 with cyclohexane as the eluent giving 8.9 g of colorless oil, whose gas chromatographic analysis on a SE-30 column showed four peaks in a ratio of 1:11:4:4 in the order of increasing retention times. The second and third peak components were collected by the preparative gas chromatography. The component from peak-2 (mixture of III and IV) gave the following data. *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.50; H, 8.40. UV λ_{max}^{EtOH} mμ (log ε): 278 (3.91). NMR of the major component of the mixture (C_6D_6) τ: 7.85 (3H, singlet), 7.81 (3H, singlet), 7.10 (2H, doublet, J=6.2 cps), 4.35 (1H, doublet of triplets, J=10.0 and 6.2 cps), 4.02 (1H, doublet of doublets, J=10.0 and 5.0 cps), 3.61 (1H, doublet of doublets, J=5.0 and 11.5 cps), 3.32 (1H, singlet), 3.27 (1H, singlet), 2.95 (1H, doublet, J=11.5 cps). NMR of the minor component of the mixture (C_6D_6) τ: 7.85 (3H, singlet), 7.83 (3H, singlet), 7.14 (2H, doublet, J=6.2 cps), 4.35 (1H, doublet of triplets, J=10.0 and 6.2 cps), 3.97 (1H, doublet of doublets, J=10.0 and 5.0 cps), 3.61 (1H, doublet of doublets, J=5.0 and 11.5 cps), 3.10 (2H, singlet), 2.95 (1H, doublet, J=11.5 cps). The intensity ratio of the doublet at 7.10 τ to that at 7.14 τ was calculated as 3:2. The product showing the third peak on the above gas chromatographic analysis (V) was collected as colorless crystals, mp 45—46.5°. *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.47; H, 8.25. UV λ_{max}^{EtOH} mμ (log ε): 230.5 (5.03), 287 (3.90), 318 (2.74), 323.5 (2.75). NMR (CCl_4) τ: 7.53 (3H, singlet), 7.37 (6H, singlet), 2.95 (1H, broad singlet), 2.80 (2H, multiplet), 2.49 (1H, broad singlet), 2.30 (1H, multiplet).

5-(2,4,6-Cycloheptatrien-1-yl)-3-hexen-2-one (VII)——Twelve grams of NaOH in a mixture of 420 ml of H_2O and 360 ml of acetone was added to a solution of 12.0 g of 2-(1,3,5-cycloheptatrien-7-yl) propionaldehyde (VI) in 60 ml of acetone under cooling with ice-water. The mixture was allowed to stand overnight under N_2 at room temperature, and poured into a mixture of H_2O and benzene with stirring. The benzene layer was separated, washed with H_2O, and dried over $MgSO_4$. After evaporation of the solvents, the remaining oily product was distilled under reduced pressure giving 5.5 g of a pale yellow oil, bp 108—111° (0.9 mmHg). IR (liquid) cm^{-1}: 1675 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 251 (3.45), 374 (4.30). NMR (CCl_4) τ: 3.27 (1H, doublet of doublets, J=16.0 and 7.7 cps), 3.35 (2H, multiplet), 3.82 (2H, multiplet), 3.94 (1H, doublet, J=16.0 cps), 4.80 (2H, multiplet), 7.40 (1H, multiplet), 7.83 (3H, singlet), 8.37 (1H, multiplet), 8.80 (3H, doublet, J=7.0 cps). 2,4-Dinitrophenylhydrazone: mp 137—139°. *Anal.* Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 61.94; H, 5.63; N, 15.15.

Thermal Isomerization of 5-(2,4,6-Cycloheptatrien-1-yl)-3-hexen-2-one (VII) to 5-(2,4,6-Cycloheptatrien-4-yl)-3-hexen-2-one (VIII)——In a N_2 stream, 7.30 g of VII was heated at 170° for 2.5 hr. The resulting oil, after being chromatographed on Al_2O_3 with cyclohexane as the eluent, was distilled under reduced pressure

giving 2.2 g of a mixture of VII and VIII as a colorless oil, bp 100—107° (0.05 mmHg). The NMR spectrum (CCl_4) included the following absorptions: multiplet at 8.37 τ (C<u>H</u> of cycloheptatriene moiety of VII), triplet (J=7.0 cps) at 7.79 τ (C<u>H</u>$_2$ of cycloheptatriene moiety of VIII), doublet (J=6.8 cps) at 8.80 τ (C_5–C<u>H</u>$_3$ of VII), doublet (J=6.8 cps) at 8.68 τ (C_5–C<u>H</u>$_3$ of VIII). The intensity ratio of the above third peak to the last was calculated as 2:3.

Ring Closure of 5-(2,4,6-Cycloheptatrien-4-yl)-3-hexen-2-one (VIII): Formation of 1,4-Dimethyl-5*H*-benzocycloheptene (IX), 1,4,5-Trimethylnaphthalene (X), and 1,4,6-Trimethylnaphthalene (XI)——The mixture of VII and VIII (5.5 g) obtained from the above thermal isomerization of VII, was dissolved in 60 ml of AcOH. This solution was added dropwise into an ice-cooled solution of 90 g of 47% aqueous HBr in 500 ml of AcOH, and the mixture was allowed to stand at room temperature for 40 hr. Similar treatment of the reaction mixture as described for the ring closure of II gave 1.8 g of an oily product, whose gas chromatographic analysis on a SE-30 column showed ten peaks in an intensity ratio of 2:3:5:35:9:9:3:3:24:7 in order of increasing retention times. The preparative gas chromatography of this oil gave the following three products. Compound IX, corresponding to the 4th peak, was collected as colorless oil. *Anal.* Calcd for $C_{14}H_{13}$: C, 91.71; H, 8.29. Found: C, 90.98; H, 8.28. UV λ_{max}^{EtOH} mμ (log ε): 230 (shoulder, 4.02), 276 (3.84). NMR (CCl_4) τ: 2.83 (1H, doublet, J=11.0 cps), 3.02 (1H, doublet, J=8.0 cps), 3.22 (1H, doublet, J=8.0 cps), 3.54 (1H, doublet of doublets, J=11.0 and 5.0 cps), 3.98 (1H, doublet of doublets, J=9.5 and 5.0 cps), 4.27 (1H, triplet of doublets, J=7.0 and 9.5 cps), 7.18 (2H, doublet, J=7.0 cps), 7.66 (3H, singlet), 7.68 (3H, singlet). Compound X corresponding to the 6th peak in the above gas chromatographic analysis was collected as colorless crystals, mp 60—61°. *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.50; H, 8.35. UV λ_{max}^{EtOH} mμ (log ε): 230.5 (4.86), 291 (3.91), 320 (shoulder, 2.97), 326 (3.10). NMR (CCl_4) τ: 2.27 (1H, multiplet), 2.82 (2H, multiplet), 2.99 (2H, singlet), 7.11 (3H, singlet), 7.15 (3H, singlet), 7.41 (3H, singlet). Compound XI, which appeared as the 5th peak in the gas chromatographic analysis, was collected as colorless oil. *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.35; H, 8.63. UV λ_{max}^{EtOH} mμ (log ε): 230 (4.71), 289 (3.77), 317 (shoulder, 2.79), 325 (2.91). NMR (CCl_4) τ: 2.27 (1H, doublet, J=8.5 cps), 2.39 (1H, broad singlet), 2.81 (1H, doublet of doublets, J=8.5 and 2.0 cps), 3.02 (2H, singlet), 7.46 (6H, singlet), 7.53 (3H, singlet).

5-(2,5-Dimethylphenyl)valeric Acid (XIII)——A mixture of 91 g of 4-(2,5-dimethylbenzoyl)butyric acid (XII),[5] 57 ml of 85% hydrazine hydrate, and 78 g of KOH in 528 ml of diethylene glycol was refluxed for 2 hr. The mixture was distilled until the liquid temperature reached 205°, and then heated for 4 hr at this temperature. The cooled reaction mixture was poured into 1.0 l of 10% aqueous HCl, and extracted with ether. Evaporation of the ether gave 80.7 g of viscous oil. IR (liquid) cm^{-1}: 1710 (C=O). This oily product was used for the ring closure reaction without further purification.

6,7,8,9-Tetrahydro-1,4-dimethyl-5H-benzocyclohepten-5-one (XIV)——A mixture of 13.0 g of XIII and 130 g of polyphosphoric acid was heated at 95° with stirring for 10 min. The cooled reaction mixture was poured into a mixture of 150 g of ice and H_2O and the mixture was extracted with ether. The ether extract was successively washed with 3% aqueous $NaHCO_3$ and H_2O, dried over Na_2SO_4, and the ether was evaporated. Distillation of the residual oily product gave 7.7 g of colorless viscous oil, bp 93—96° (0.08 mmHg). *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.58. Found: C, 82.63; H, 8.54. IR (liquid) cm^{-1}: 1690 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 251 (3.69), 292 (3.16). NMR (CCl_4) τ: 3.01 (1H, doublet, J=8.0 cps), 3.16 (1H, doublet, J=8.0 cps), 7.50 (4H, multiplet), 7.77 (3H, singlet), 7.82 (3H, singlet), 8.33 (4H, multiplet).

6-Bromo-1,4-dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one (XV)——A solution of 37.4 g of bromine in 50 ml of CCl_4 was added dropwise at −10° to a solution of 40 g of XIV in 450 ml of ether. The mixture was stirred at room temperature for 1 hr, successively washed with 3% aqueous $NaHCO_3$ and H_2O, and dried over $MgSO_4$. After evaporation of the solvents, the residue was recrystallized from petroleum ether giving colorless crystals, mp 60°. Yield, 35.6 g. *Anal.* Calcd. for $C_{13}H_{15}OBr$: C, 58.43; H, 5.67; Br, 29.91. Found: C, 58.80; H, 5.54; Br, 29.80. IR (Nujol) cm^{-1}: 1703 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 263 (3.46). NMR (CCl_4) τ: 2.91 (1H, doublet, J=8.0 cps), 3.08 (1H, doublet, J=8.0 cps), 5.50 (1H, doublet of doublets, J=7.0 and 4.0 cps), 7.30 (4H, multiplet), 7.71 (3H, singlet), 7.77 (3H, singlet), 8.10 (2H, multiplet).

1,4-Dimethyl-8,9-dihydro-5*H*-benzocycloheptene (XVI)——A mixture of 36.9 g of XV, 17.6 g of LiCl in 500 ml of dimethylformamide was refluxed in N_2 stream for 2 hr. The reaction mixture was diluted with 1.5 l of H_2O and extracted with ether. The ether was evaporated and the residue was distilled under reduced pressure giving 17.1 g of colorless liquid, bp 107—113° (0.2 mmHg). IR (liquid) cm^{-1}: 1660 (C=O). This oily product was reduced to XVII without further purification.

1,4-Dimethyl-5-hydroxy-8,9-dihydro-5*H*-benzocycloheptene (XVII)——A solution of 17.0 g of XVI in 30 ml of ether was added to a suspension of 2.0 g of $LiAlH_4$ in 300 ml of the same solvent. The mixture was refluxed with stirring for 2 hr. After excess $LiAlH_4$ was decomposed with H_2O, 300 ml of 20% aqueous NH_4Cl solution was added, and the mixture was stirred. The ether layer was separated, dried over $MgSO_4$, and the ether was evaporated. The residual crude product was purified by SiO_2–chromatography with benzene as the eluent followed by recrystallization from petroleum ether giving colorless crystals, mp 75—76°. Yield, 5.9 g. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.57. Found: C, 82.55; H, 8.58. IR (Nujol) cm^{-1}: 3289 (OH). UV λ_{max}^{EtOH} mμ (log ε): 250 (4.04).

1,4-Dimethyl-5*H*-benzocycloheptene (IX) from 1,4-Dimethyl-5-hydroxy-8,9-dihydro-5*H*-benzocycloheptene (XVII)——A solution of 2.65 g of XVII in 26 ml of anhydrous EtOH saturated with dry HCl was refluxed for 30 min. The reaction mixture was poured into 100 ml of H_2O and extracted with pentane. After the pentane was evaporated, the residual oily product was distilled under reduced pressure giving 1.55 g of colorless oil bp, 86—90° (0.05 mmHg), which was identified with IX obtained by the ring closure of VIII by the comparison of the absorption spectra. *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.80; H, 8.38.

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