CHEMICAL & PHARMACEUTICAL BULLETIN

Vol. 19, No. 11 November 1971

Regular Articles

[Chem. Pharm. Bull. 19(11)2215—2221(1971)]

UDC 547.913.5.057

Studies on Seven-membered Ring Compounds. XXXVI.[1] Synthesis of Azulene Derivatives by Ring Closure of β-Cycloheptatrienyl-substituted Carbonyl Compounds

Taiichiro Watanabe and Nobuo Soma

Central Research Laboratories, Sankyo Co., Ltd.[2]

(Received December 4, 1970)

Treatment of 2-phenyl-3-(2,4,6-cycloheptatrien-1-yl)propionaldehyde ethylene acetal (III) with stannic chloride in benzene followed by dehydrogenation with sulfur afforded 2-phenylazulene (V) and 1-(2-hydroxyethyloxy)-2-phenylazulene (VI). Benz[a]azulene (XV) was obtained along with anthracene (XVI) when 2-(2,4,6-cycloheptatrien-1-yl)-benzaldehyde (XII) or its ethylene acetal (XI) was treated with stannic chloride in benzene or with hydrogen bromide in acetic acid.

In a previous paper,[1] it was demonstrated that γ-cycloheptatrienyl-substituted α,β-unsaturated carbonyl compounds such as 5-(2,4,6-cycloheptatrien-1-yl)-3-hexen-2-one underwent a ring closure reaction to give 5H-benzocycloheptene derivatives when treated with acid. As an extension of this ring closure reaction, we intended, in the present work, to prepare azulene derivatives by the ring closure of β-cycloheptatrienyl substituted carbonyl compounds. Several methods for the preparation of azulene derivatives have been reported[3]; however, examples involving the formation of the azulene five-membered ring by the cyclization of the carbon chain attached to a cycloheptatriene nucleus have not yet been reported in the literature.

First, synthesis of 2-phenylazulene (V) starting from 2-(2,4,6-cycloheptatrien-1-yl)-acetophenone (I), which was conveniently prepared in a previous work[4] by the reaction between tropylium fluoroborate and morpholine enamine of acetophenone, was undertaken. The Wittig reaction of I with (methoxymethylene)triphenylphosphorane in ether gave a mixture of *cis* and *trans* isomers of 1-methoxy-2-phenyl-3-(2,4,6-cycloheptatrien-1-yl)-1-propene (II). The nuclear magnetic resonance (NMR) spectrum of this isomeric mixture included two different methoxyl signals at 6.37 and 6.43 τ in an approximate ratio of 3:2, and the absorptions attributable to the methylene and vinyl protons of the side chain also appeared as two sets of doublets (7.07 and 7.37 τ, J=8.0 cps each) and two broad singlets (3.69 and 3.95 τ) respectively. Attempts to hydrolyze II to the free aldehyde, 3-(2,4,6-cyclohepta-

1) Part XXXV: T. Watanabe, I. Kawamoto and N. Soma, *Chem. Pharm. Bull.* (Tokyo), **18**, 2087 (1970).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo, 140, Japan.*
3) See, for instance, W. Keller-Schierlein and E. Heilbronner, "Non-Benzenoid Aromatic Compounds," ed. by D. Ginsburg, Interscience Publishers, Inc., New York, 1959, p. 277.
4) T. Watanabe and N. Soma, *Chem. Pharm. Bull.* (Tokyo), **18**, 1595 (1970).

NII-Electronic Library Service

trien-1-yl)-2-phenylpropionaldehyde, were unsuccessful, and furnished an unidetified viscous oily product; however, direct conversion of II to the cyclic ethylene acetal (III) was effected by refluxing II with ethylene glycol in benzene using *p*-toluenesulfonic acid as the catalyst. The structure of III was suppoted by the NMR spectrum, which showed no methoxyl signal, but exhibited a new singlet (6.29 τ, 4H) and doublet (5.10 τ, 1H, J=3.8 cps) attributable, respectively, to the methylene and methyne protons of the ethylene acetal moiety. Treatment of III with stannic chloride in benzene at room temperature afforded an oily product, which had the molecular formula $C_{18}H_{20}O_2$. The infrared (IR) spectrum of this product

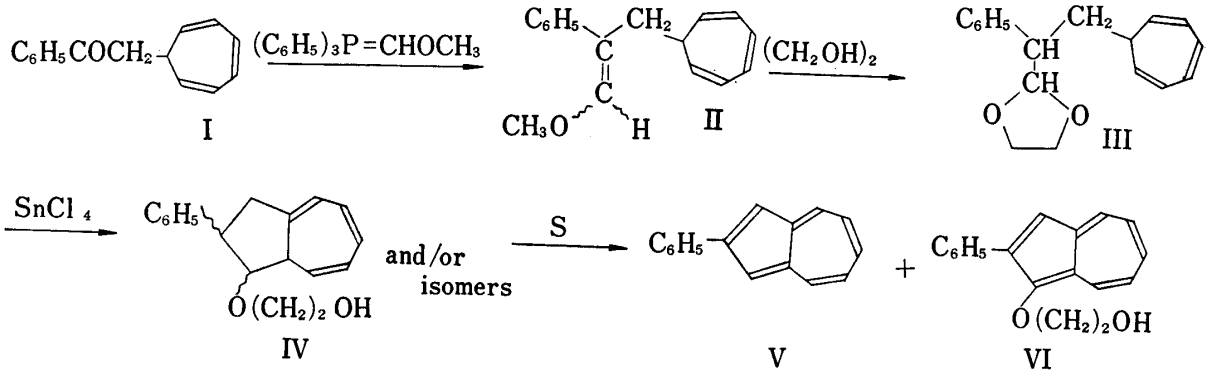


Chart 1

exhibited ν_{OH} at 3497 cm^{-1}, and the NMR spectrum indicated the presence of a 1,7-disubstituted 1,3,5-cycloheptatriene structure with two multiplets at around 3.52 and 3.90 τ (2H each) and a doublet of doublets (1H, J=10.0 and 4.0 cps) at 4.86 τ. These results obviously demonstrated that the expected ring closure of III had occurred and permitted the assignment of the structure of the product as either 1-(2-hydroxyethyloxy)-2-phenyl-1,2,3,8a-tetrahydroazulene (IV) or its 1,2,3,3a-tetrahydroisomer. However, definitive data which would distinguish between these two possible structures and information concerning the stereochemistry of the product was not obtained from the NMR spectrum owing to the complexity of the methylene and methyne signals. Heating of this oily product in triethylene glycol dimethyl ether with sulfur at 210—230° for three hours afforded after chromatography of the reaction mixture two highly colored crystalline products, blue (mp 230°) and green (mp 88—89°) crystals. The blue crystalline product showed no ν_{OH} in the IR spectrum and was determined to be the anticipated 2-phenylazulene (V) by the molecular formula $C_{16}H_{12}$ and comparison of the melting point and the ultraviolet (UV) spectrum with those reported in the literature.[5] The green crystals which showed ν_{OH} at 3410 cm^{-1} were deduced as being 1-(2-hydroxyethyloxy)-2-phenylazulene (VI) on the basis of the UV spectral resemblance to V and the mass spectrum, which showed the molecular ion peak at *m/e* 264 and a fragmentation peak at *m/e* 209, $C_{16}H_{11}O^+$, indicative of the presence of a phenylazulenyloxy moiety.

An attempt to extend the above cyclization reaction to a β-cycloheptatrienyl-substituted α,β-unsaturated carbonyl compound and produce an azulene without such a dehydrogenation process as required in the preparation of V from III was unsuccessful. When 1,1-diethoxy-3-(2,4,6-cycloheptatrien-1-yl)-2-propene (IX) was treated with stannic chloride in a manner similar to that for III, the reaction mixture exhibited deep violet color suggestive of the formation of the expected azulene; however, the color faded on the treatment of the mixture with water and an unidentified viscous oil was only product isolated. Treatment of IX with hydrobromic acid in acetic acid under the conditions similar to those used previously in the ring closure of a 4-(cycloheptatrienyl)-2-pentenal derivative to furnish a benzo-

5) Pl. A. Plattner, R. Sandrin and J. Wyss, *Helv. Chim. Acta*, **29**, 1604 (1946); Pl. A. Plattner, A. Fürst, M. Gordon and K. Zimmermann, *ibid.*, **33**, 1910 (1950).

NII-Electronic Library Service

cycloheptene[1] was also examined without success, giving a black powder. The unsaturated aldehyde acetal (IX) used in these reactions was obtained by catalytic hydrogenation of 1,1-diethoxy-3-(2,4,6-cycloheptatrien-1-yl)-2-propyne (VIII), which was prepared by the reaction between 7-ethoxy-1,3,5-cycloheptatriene (VII) and the Grignard reagent of 1,1-diethoxy-2-propyne. The structure of VIII was confirmed by satisfactory analytical values, $\nu_{C\equiv C}$ at 2247 cm^{-1} in the IR spectrum, and the NMR spectrum, which included the methyne, methylene, and methyl resonances of the acetal group at 4.82, 6.39, and 8.80 τ respectively and indicated the persence of the 7-substituted 1,3,5-cycloheptatrienyl structure with multiplets at 3.37 (2H), 3.87 (2H), 4.69 (2H), and 7.50 τ (1H). The structural assignment of IX was based on the molecular ion peak at *m/e* 220 in the mass spectrum, $\nu_{C=C}$ at 1660 cm^{-1} in the IR spectrum, and the NMR spectrum wherein two olefinic proton signals of the side chain appeared at around 4.07 and 4.49 τ overlapping with the absorptions due to olefinic protons of the cycloheptatrinen ring.

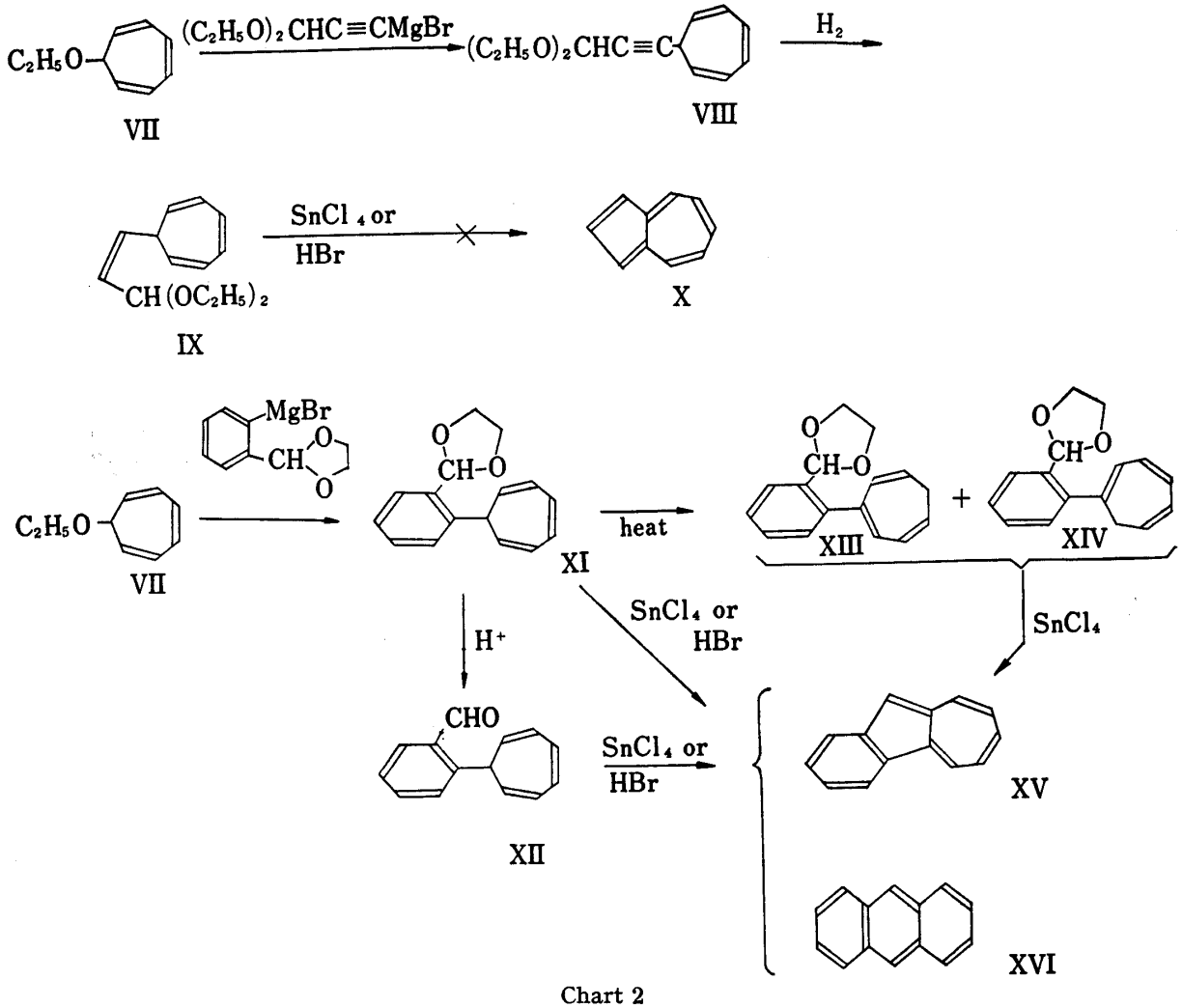


Chart 2

A plausible reason for the failure of IX to cyclize may be that the double bond of the side chain rapidly isomerized to the trans form before the carbonium ion produced on the side chain could undergo the expected ring closure reaction. This consideration led us to examine the ring closure reaction of cycloheptatrienylbenzaldehyde derivatives, in which such double bond isomerization as conceived in the case of IX can not take place, thus the formation of benzazulenes would be expected. The ethylene acetal (XI) of 2-(2,4,6-cycloheptatrien-1-yl)-benzaldehyde (XII) was prepared by the reaction of VII with the Grignard reagent of 2-bromo-

NII-Electronic Library Service

benzaldehyde ethylene acetal. The structure of XI was supported by the satisfactory analytical values and the NMR spectrum, in which aromatic protons, methylene and methyne protons of the acetal moiety exhibited signals at 2.63 (4H), 6.13 (4H), 4.23 τ (1H) respectively and the presence of the cycloheptatriene ring was indicated by a triplet of triplets (1H) at 6.83 τ and three multiplets at 3.37, 3.82, and 4.72 τ (2H each). When XI was treated with stannic chloride in benzene, green crystals melting at 188°, $C_{14}H_{10}$, were isolated in about 10% yield after extraction of the reaction mixture with phosphoric acid. The crystals were confirmed as being the expected benz[a]azulene (XV) by the molecular formula and agreement of the melting point and IR spectrum with those of the authentic sample.[6] This formation of XV from XI was accompanied by a ring contraction of the seven-membered ring of XI: anthracene (XVI) was obtained in about 15% yield from the organic layer separated from the phosphoric acid extraction of the reaction mixture. Treatment of XI with hydrobromic acid in acetic acid afforded the same two products (XV and XVI). Moreover, the free aldehyde, XII, obtained by the hydrolysis of XI underwent a similar ring closure reaction giving XV and XVI, on being treated either with stannic chloride in benzene or with hydrogen bromide in acetic acid.

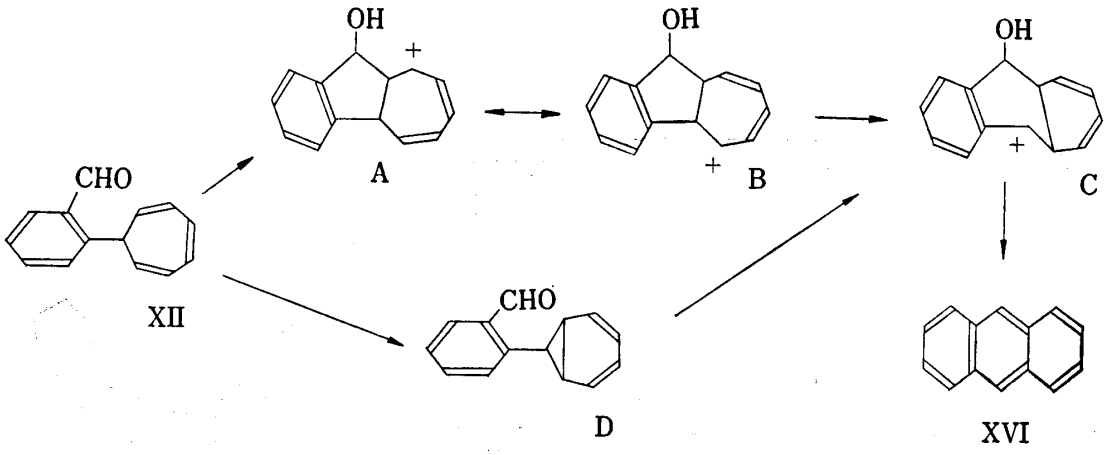
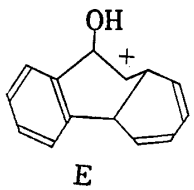


Chart 3

The formation of XVI from XII is explainable by a ring contraction of the cation B derived from a double bond shift of the initially formed cyclization intermediate A. Benzylic nature of the cation C seems to be advantageous for the exclusive ring contraction of B over that of A, which should, via an intermediate E, give rise to the formation of phenanthrene instead of the anthracene actually isolated. Isomerization of XII to the norcaradiene D and subsequent ring closure of the aldehyde side chain accompanied by ring opening of the cyclopropane ring also may afford XVI; however, we are rather suspicious of the isomerization of XII under the conditions used.



E

In connection with the production of anthracene from XI or XII, the ring closure of the double bond isomers of XI was also examined. Refluxing XI in xylene for 24 hours gave a mixture of 2-(2,4,6-cycloheptatrien-4-yl)- (XIII) and 2-(2,4,6-cycloheptatrien-2-yl)-benzaldehyde ethylene acetal (XIV) in an approximate ratio of 1:1 as determined by the NMR spectrum wherein absorptions due to methylene protons of the seven-membered ring of XIII and XIV appeared, respectively, as a triplet (J=6.5 cps) at 7.65 τ and a doublet (J=7.0 cps) at 7.53 τ. When this mixture was treated with stannic chloride in benzene, XV was obtained in a yield almost equal to that from XI; however, essentially no anthracene

6) E.K. Jensene, E.A.K. Eschenmoser and E. Heilbroner, *Helv. Chim. Acta*, **39**, 1051 (1956).

NII-Electronic Library Service

was isolated from the reaction mixture. This remarkable decrease of anthracene formation is consistent with the mechanism described above for the formation of XVI from XII because intermediates such as C can not be drawn in the case of the ring closure of XIII or XIV.

Experimental

1-Methoxy-2-phenyl-3-(2,4,6-cycloheptatrien-1-yl)-1-propene (II)——To an ice-cooled solution of phenyl lithium prepared from 0.24 g of metallic Li and 2.77 g of bromobenzene in 20 ml of ether 5.50 g of (methoxymethyl)triphenylphosphonium chloride was added dropwise with stirring under an nitrogen atmosphere. The mixture was heated under reflux for 5 min, then stirred 50 min at room temperature. To this was added a solution of 3.15 g of 2-(2,4,6-cycloheptatrien-1-yl)acetophenone (I) in 20 ml of ether with stirring and cooling in an ice-water-bath. The resulting mixture was heated under reflux for 1.5 hr and allowed to stand at room temperature overnight. The reaction mixture was filtered, the separated crystals were washed with ether and ether washings were combined with the filtrate. The ether solution, after being washed successively with H_2O, aqueous $NaHSO_3$, aqueous $NaHCO_3$, and H_2O, was dried over $MgSO_4$. This was concentrated to about 50 ml, 1.1 ml of 30% H_2O_2 was added dropwise with stirring, and the stirring was continued further for 30 min at room temperature. The mixture was washed successively with H_2O, aqueous $NaHSO_3$, aqueous $NaHCO_3$, and H_2O, and then dried over $MgSO_4$. The ether was evaporated, and a cyclohexane solution of the residue was passed through a column of 150 g of Al_2O_3. Evaporation of the cyclohexane from the eluate afforded 1.24 g of II as colorless oil. IR(liquid) cm^{-1}: 1652 (C=C), 1143 (C–O). Mass Spectrum: *m/e* 238 (M^+, $C_{17}H_{18}O$; 238). NMR(CCl_4)τ: 2.85(5H, multiplet), 3.52(2H, multiplet), 3.60—4.17(3H, multiplet including two broad singlets at 3.69 and 3.95 τ), 4.83(2H, multiplet), 6.37 (1.8H, singlet), 6.43 (1.2H, singlet), 7.07(1.2H, doublet, J=8.0 cps), 7.37(0.8H, doublet, J=8.0 cps), 8.28 (1H, multiplet).

3-(2,4,6-Cycloheptatrien-1-yl)-2-phenylpropionaldehyde Ethylene Acetal (III)——A mixture of 0.2 g of II, 0.1 g of ethylene glycol and 4 mg of *p*-toluenesulfonic acid in 30 ml of benzene was heated under reflux for 3 hr. After cooling, the benzene was evaporated, and the oily residue was chromatographed on alumina. Elution with cyclohexane gave 0.13 g of colorless oil. IR(liquid) cm^{-1}: 1142, 1103 (C–O). NMR(CCl_4)τ: 2.85(5H, singlet), 3.52(2H, multiplet), 4.00(2H, multiplet), 4.93(2H, multiplet), 5.10(1H, doublet, J=3.8 cps), 6.29(4H, singlet), 6.99(1H, doublet of triplets, J=3.8 and 10.0 cps), 7.90(2H, multiplet), 8.59(1H, multiplet). This oily product was used as the material for the ring closure reaction without further purification.

1-(2-Hydroxyethyloxy)-2-phenyltetrahydroazulene (IV)——A solution of 0.56 ml of $SnCl_4$ in 15 ml of benzene was added to a stirred solution of 0.39 g of III in 85 ml of the same solvent under cooling in an ice-water-bath, and the mixture was stirred at room temperature for 30 min. To the resulting solution was added 50 ml of 10% HCl, and the insoluble materials were removed by filtration through celite. The benzene layer was separated from the filtrate, washed with H_2O, and dried over $MgSO_4$. After benzene was evaporated, the residue was chromatographed on 40 g of silica gel. Elution with $CHCl_3$ gave 0.15 g of IV as colorless oil. Mass Spectrum: *m/e* 268.146 (M^+, $C_{18}H_{20}O_2$; 268.144). IR(liquid) cm^{-1}: 3497(OH), 1120, 1065(C–O). NMR(CCl_4)τ: 2.5—3.0(5H, multiplet), 3.52(2H, multiplet), 3.90(2H, multiplet), 4.86(1H, doublet of doublets, J=10.0 and 4.0 cps), 5.85(1H, doublet of doublets, J=9.0 and 6.0 cps), 6.2—8.0(9H, multiplet including a singlet at 6.45).

Dehydrogenation of IV: Formation of 2-Phenylazulene (V) and 1-(2-Hydroxylethyloxy)-2-phenylazulene (VI)——A mixture of 0.10 g of IV and 0.085 g of sulfur in 1.1 ml of triethylene glycol dimethyl ether was heated at 210—230° for 3 hr. Benzene and H_2O were added to the reaction mixture, and the benzene layer was separated, washed with H_2O, and dried over $MgSO_4$. The benzene was evaporated, and the remaining dark blue oil was chromatographed on 10 g of silica gel with benzene and then benzene–chloroform mixture (1:1) as the solvent. Evaporation of the benzene eluates left a dark blue, crystalline product, and this was chromatogaphed on alumina with benzene as the solvent giving 7 mg of V as blue crystals. The analytical sample, mp 230°, was purified by the preparative silica gel thin-layer chromatogaphy with cyclohexane–benzene mixture (1:1) followed by recrystallization from EtOH. Mass Spectrum: *m/e* 204.094 (M^+, $C_{16}H_{12}$; 204.094). UV $\lambda_{max}^{n\text{-hexane}}$ mμ (log ε): 240(4.12), 295(4.80), 306(4.82), 354(3.77), 370(4.07), 390(4.20), 572(2.53), 619(2.51), 675(2.12).

Fractions eluted from the above silica gel column with benzene–chloroform mixture were concentrated, and the remaining dark green crystals were purified by preparative thin-layer chromatography employing silica gel as adsorbent and benzene as developing solvent. Eluates from the green colored adsorbent were evaporated, the residue was dissolved in benzene, and the solution was extracted with 85% phosphoric acid. After addition of H_2O to the phosphoric acid layer, the mixture was extracted with benzene, and the benzene extract was washed with H_2O, then dried over $MgSO_4$. Evaporation of the benzene left VI as green crystals, mp 88—89°. Yield, 11 mg. Mass Spectrum: *m/e* 264.116 (M^+, $C_{18}H_{16}O_2$; 264.115). UV $\lambda_{max}^{n\text{-hexane}}$ mμ(log ε): 243(3.95), 302(4.56), 309(4.55), 358(3.55), 375(3.65), 392(3.67), 620(2.39), 670(2.37). IR (KBr) cm^{-1}: 3410(OH).

NII-Electronic Library Service

1,1-Diethoxy-3-(2,4,6-cycloheptatrien-1-yl)-2-propyne (VIII)——To a stirred solution of ethylmagnesium bromide prepared from 0.72 g of metallic Mg and 3.22 g of ethyl bromide in 10 ml of tetrahydrofuran was added a solution of 3.84 g of 1,1-diethoxy-2-propyne in 5 ml of the same solvent at −10°, and the mixture was stirred at room temperature for 1.5 hr. To this was added a solution of 4.08 g of 7-ethoxy-1,3,5-cycloheptatriene (VII) in 5 ml of tetrahydrofuran at 0—10°, and the mixture was heated at 60° with stirring for 20 min. After addition of 30 ml of saturated aqueous NH_4Cl solution, the reaction mixture was extracted with benzene, and the benzene layer was washed with H_2O and dried over $MgSO_4$. Removal of the benzene and distillation of the residue afforded 2.0 g of pale yellow oil, bp 85—93° (0.0014 mmHg). *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.27; H, 8.58. UV λ_{max}^{EtOH} mμ (log ε): 256.5(3.52). IR (liguid) cm^{-1}: 2247 (C≡C). NMR (CCl_4)τ: 3.37 (2H, multiplet), 3.87(2H, multiplet), 4.69(2H, multiplet), 4.82(1H, doublet, J=1.5 cps), 6.39(4H, multiplet), 7.50(1H, multiplet), 8.80(6H, triplet, J=7.0 cps).

1,1-Diethoxy-3-(2,4,6-cycloheptatrien-1-yl)-2-propene (IX)——A solution of 0.42 g of VIII in 5 ml of *n*-hexane containing 0.1 ml of quinoline was hydrogenated over 0.083 g of Lindler catalyst in the usual manner. After an uptake of 1.1 mole equivalent hydrogen, the catalyst was removed by filtration, and the *n*-hexane was evaporated. Distillation of the residue gave 0.3 g of pale yellow oil, bp 80—90° (bath temp) (0.0014 mmHg). IR (liquid) cm^{-1}: 1660(C=C). Mass Spectrum: *m/e* 220 (M^+, $C_{14}H_{20}O_2$: 220). NMR(CCl_4)τ: 3.37(2H, multiplet), 3.7—4.7 (4H, multiplet), 4.92(3H, multiplet), 6.55(4H, multiplet), 7.50(1H, multiplet), 8.89(6H, triplet, J=7.0 cps).

An Attempt to Prepare Azule (X) by the Reaction of IX with $SnCl_4$——To a solution of 0.4 g of IX in 70 ml of benzene was added 1.1 g of $SnCl_4$ dissolved in 20 ml of the same solvent with stirring and cooling in an ice-bath. The mixture assumed a deep violet color. After stirring for 45 min at room temperature 30 ml of 10% HCl was added to the mixture, when the violet color disappeared. The benzene layer was separated, washed with H_2O, and dried over $MgSO_4$. Removal of the benzene left 0.14 g of brown viscous sirup, which exhibited $\nu_{c=o}$ at 1690 cm^{-1}. By thin-layer chromatography of this product, the presence of azulene was not detected.

2-(2,4,6-Cycloheptatrien-1-yl)benzaldehyde Ethylene Acetal (XI)——A mixture of 73.1 g of *o*-bromobenzaldehyde, 27.5 g of ethylene glycol, and 1.0 g of *p*-toluenesulfonic acid in 800 ml of benzene was refluxed for 4 hr, during which time water formed was removed by azeotropic distillation with benzene. Fractional distillation of the reaction mixture under reduced pressure gave 43.7 g of *o*-bromobenzaldehyde ethylene acetal, bp 126—127°(5 mmHg). *Anal.* Calcd. for $C_9H_9O_2Br$: C, 47.18; H, 3.96; Br, 34.89. Found: C, 46.93; H, 4.03; Br, 35.17. NMR(CCl_4)τ: 2.3—3.0(4H, multiplet), 4.02(1H, singlet), 6.05(4H, multiplet).

From 4.58 g of the above-mentioned acetal and 0.48 g of Mg, the Grignard reagent was prepared by the usual procedure in 45 ml of tetrahydrofuran. To this solution was added 2.71 g of 7-ethoxy-1,3,5-cycloheptatriene (VII) dissolved in 20 ml of tetrahydrofuran with stirring and cooling in an ice-bath. The mixture was heated under reflux for 2 hr. The tetrahydrofuran was evaporated, the resude was dissolved in benzene, and 50 ml of 3% $NaHCO_3$ was added with stirring. After filtration of the mixture through celite, the benzene layer was separated from the filtrate, washed with 3% $NaHCO_3$, and dried over $MaSO_4$. Removal of the benzene followed by distillation of the residue gave 1.6 g of pale yellow oil, bp 152—157° (0.05 mmHg). *Anal.* Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.87; H, 6.70. IR (liquid) cm^{-1}: 1116, 1073 (C-O). UV λ_{max}^{EtOH} mμ(log ε): 261.5(3.52). NMR (CCl_4)τ: 2.63 (4H, multiplet), 3.37 (2H, multiplet), 3.85 (2H, multiplet), 4.23 (1H, singlet), 4.72 (2H, multiplet), 6.13 (4H, multiplet), 6.83 (1H, triplet of triplets, J=7.0 and 1.0 cps).

Thermal Isomerization of XI to 2-(2,4,6-Cycloheptatriene-4-yl)-(XIII) and 2-(2,4,6-Cycloheptatrien-2-yl)-benzaldehyde Ethylene Acetal (XIV)——A solution of 4.9 g of XI in 40 ml of xylene was refluxed for 24 hr, during which time the triplet of triplets at 6.83τ due to XI disappeared gradually; on inspection of the NMR spectrum of the reaction mixture, a doublet (J=7.0 cps) and a triplet (J=6.5 cps) apperead, instead,at 7.35 and 7.65 τ, respectively. Fractional distillation of the reaction mixture gave 3.0 g of colorless oil, bp 140—155° (bath temp.) (0.08 mmHg). The following NMR spectrum indicated the product to be a mixture of XIII and XIV in a ratio of 1: 1. NMR(CCl_4)τ: 2.67 (4H, multiplet), 3.40 (1.5H, multiplet), 3.79 (2H, multiplet), 4.57 (2.5H, multiplet), 6.05 (4H, multiplet), 7.35 (1H, doublet, J=7.0 cps), 7.65 (1H, triplet, J= 6.5 cps).

2-(2,4,6-Cycloheptarien-1-yl)benzaldehyde (XII)——A mixture of 10.1 g of XI, 150 ml of dioxane, and 37.5 ml of 10% aqueous oxalic acid solution was refluxed for 2 hr. The reaction mixture was concentrated, and the residue was dissolved in benzene. The benzene solution, after being washed with H_2O and dried over $MgSO_4$, was evaporated, and the residue was chromatographed on 60 g of silica gel. Elution with cyclohexane-benzene mixture (1: 1) furnished 7.4 g of an oily product (7.4 g), whose fractional distillation under reduced pressure gave 4.5 g of XII, bp 124—144° (bath temp.) (0.1 mmHg). IR(liquid) cm^{-1}: 2850, 2750, 1693. NMR (CCl_4)τ: 0.11 (1H, singlet), 2.33 (4H, multiplet), 3.32 (2H, multiplet), 3.77 (2H, multiplet), 4.67 (2H, multiplet), 6.35 (1H, triplet, J=6.0 cps). The 2.4-Dinitrophenylhydrazone: mp 200°. *Anal.* Calcd. for $C_{20}H_{16}O_4N_4$: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.52; H, 4.37; N, 14.99.

Formation of Benz[a]azulene (XV) and Anthracene (XVI) from XI——(i) with $SnCl_4$: To a stirred solution of 0.44 g of XI in 80 ml of benzene was added dropwise a solution of 0.9 ml of $SnCl_4$ in 20 ml of benzene under cooling in an ice-water-bath. The stirring was further continued for 30 min at room temperature,

NII-Electronic Library Service

10% HCl was added, and the mixture was filtered through celite. The benzene layer was separated, washed with H_2O, and dried over $MgSO_4$. Removal of the benzene left a dark crystalline mass, which was chromatographed on silica gel employing cyclohexane as the solvent. The eluates were evaporated, the residue was dissolved in benzene, and the benzene solution was extracted with 85% H_3PO_4. After H_2O was added to the H_3PO_4 solution, the mixture was extracted with benzene. Evaporation of the benzene gave 28 mg of crude XV. The analytical sample, mp 188°, was obtained after sublimation under reduced pressure followed by recrystallization from EtOH. *Anal.* Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 93.93; H, 5.79. The infrared, ultraviolet, and visible spectra were identical with those of XV reported by Jensene.[6]

The benzene layer separated from the H_3PO_4 layer on the above-mentioned extraction of the reaction mixture was washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from EtOH to white crystals, mp 215—217°. Yield, 51 mg. *Anal.* Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.49; H, 5.70. The IR spectrum was identical with that of authentic XVI.

(ii) with HBr: A solution of 0.2 g of XI in 5g of AcOH was added dropwise to a mixture of 3.4 g of 47% HBr and 20 g of AcOH with stirring and cooling in an ice–water–bath. The solution was allowed to stand at room temperature for 24 hr. The reaction mixture, after being diluted with H_2O, was extracted with benzene. Treatment of the benzene extract in a manner similar to that described in (i) furnished 15 mg of XV and 43 mg of XVI.

Formation of XV and XVI from XII——(i) with $SnCl_4$: A solution of 0.5 ml of $SnCl_4$ in 10 ml of benzene was added to a solution of 0.225 g of XII in 40 ml of the same solvent with stirring and cooling in an ice–water–bath. The mixture was allowed to stand at room temperature for 30 min and treated in a manner similar to that described for the reaction of XI with $SnCl_4$. From the H_3PO_4 solution, 31 mg of XV was obtained and the benzene layer gave 40 mg of XVI.

(ii) with HBr: Treatment of 0.32 g of XII with 6.0 g of 47% HBr in 35 ml of AcOH in a manner similar to that for the reaction of XI with HBr gave 46 mg of XV and 111 mg of XVI.

Treatment of a Mixture of XIII and XIV with $SnCl_4$: Formation of XV——To a stirred solution of 0.436 g of a mixture of XIII and XIV (1: 1) in 75 ml of benzene was added dropwise a solution of 0.9 ml of $SnCl_4$ in 20 ml of benzene under cooling in an ice–water–bath. After the addition was completed, the mixture was stirred for 30 min at room temperature, and treated in a manner similar to that described for the reaction of XI with $SnCl_4$. From the H_3PO_4 extract, 38 mg of XV was obtained. Evaporation of the benzene layer left 78 mg of an unidentified oily product, XVI being not isolated.

Acknowledgement The authors express their gratitude to Dr. T. Nozoe for his interest in this work. They are also indebted to Dr. G. Sunagawa, Director of this Laboratories, and Dr. I. Iwai for encouragement through the course of this work.

7) B.K. Jensden, E.A. Eschenmoser, and E. Heilbroner, *Helv. Chim. Acta*, 39, 1051, (1956).

NII-Electronic Library Service