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Stereoselective Construction of the *cis*-Hydrindan System by Intramolecular Diels–Alder Reaction

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cis-9b-Cyano-3a-methyl-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene derivatives (**14**, **20**) were synthesized stereoselectively *via* the intramolecular Diels–Alder reaction of 1,2-dihydrobenzocyclobutenes (**11**, **19**). The *cis* stereochemistry in the cycloadducts was confirmed by nuclear Overhauser effect (NOE) experiments. Examination of CPK molecular models revealed that the stereoselectivity of the transformations could be attributed to a predominance of the endo conformer (*e.g.* **12**) in the transition state. Moreover, the stereochemical outcome of the decyanation of **14** by dissolving metal reduction is also considered.

Keywords——stereoselective synthesis; *cis*-hydrindan system; intramolecular Diels–Alder reaction; 1,2-dihydrobenzocyclobutene; dissolving metal reduction; nuclear Overhauser effect experiment

In connection with our preliminary studies directed towards the total synthesis of natural products by intramolecular Diels–Alder reaction using 1,2-dihydrobenzocyclobutenes,[1] we reported[2] that the thermolysis of the 1-cyanobenzocyclobutene derivative (**1**) and the substrate (**3**) without a cyano group at the C-1 position gave the *cis*-fused (**2**) and the *trans*-fused (**4**) product, respectively, in a stereoselective manner. This stereoselectivity was found to be dependent upon the presence of a cyano group at the C-1 position of the 1,2-dihydrobenzocyclobutene. However, the reason for this striking difference in the stereochemical outcome has not yet been fully elucidated.

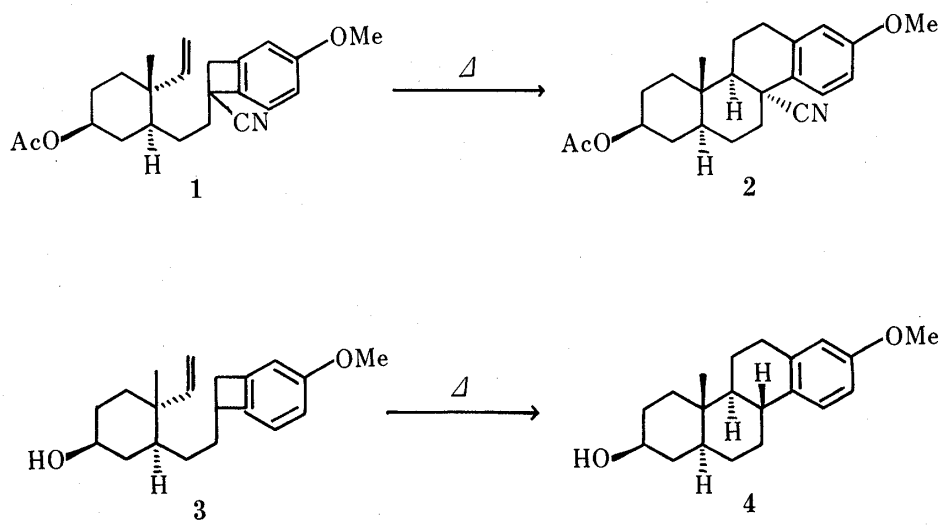
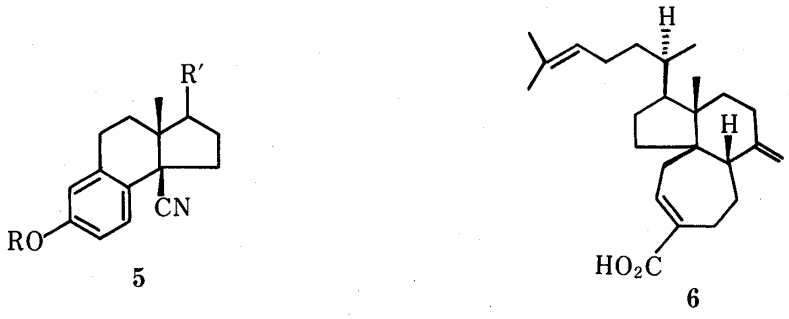


Chart 1

Since most of the cases reported so far[3] were in the construction of a 6/6-fused ring system, we became interested in the stereoselectivity for the construction of a 5/6-fused tricyclic ring system, particularly the stereocontrolled synthesis of a *cis*-hydrindan derivative (**5**) which, after appropriate manipulation, could be functionalized not only at the aromatic ring but also at the angular cyano group to generate potential precursors for some natural products such as gascardic acid (**6**).[4]



5 6

Fig. 1

The substrate for thermolysis was prepared from 1-cyano-1,2-dihydro-4-methoxybenzocyclobutene[3a] (**7**). Alkylation of **7** with the bromoacetal (**8**) in the presence of sodium amide, followed by acid hydrolysis, gave the aldehyde (**10**) which was then reacted with isopropenylmagnesium bromide to afford **11** as an inseparable diastereomeric mixture in 57.6% yield from **7**.

Thermolysis of **11** was carried out by heating in *o*-dichlorobenzene at 180 °C for 8 h under an atmosphere of argon to afford the tricyclic adducts (**14**) and (**15**), both epimeric mixtures at C-9b in a 13:1 ratio in 69.8% yield. The structures of the adducts (**14**, **15**) were tentatively assigned on the basis of the nuclear magnetic resonance (NMR) signals due to the C-3a methyl protons. The methyl protons in the adduct (**14**) are in an environment which causes them to be deshielded by the cyano group at C-9b and their signal appears at the relatively lowfield location of δ 1.23, while the methyl protons of **15** are within the shielding cone of the aromatic ring and their signal appears at the relatively highfield position of δ 0.67. The stereoselectivity of the cycloaddition was considered to arise as follows. Examination of CPK molecular models of the *o*-quinodimethane transition states ($T_1^{\neq}$, $T_2^{\neq}$) reveals that severe repulsion develops between the methyl and the *o*-quinodimethane ring, both of which are forced to close by the interaction of the cyano group and the olefinic proton (Ha), in **13** ($T_2^{\neq}$), whereas this type of interaction is absent in **12** ($T_1^{\neq}$). This interaction may be the cause of the stereoselectivity realized in the intramolecular cycloaddition of **11**.

The stereochemical assignment in the major adduct (**14**) could be confirmed by an nuclear Overhauser effect (NOE) experiment. Thus, the cyanide (**14**) was reduced with diisobutylaluminum hydride (DIBAH) to the aldehyde (**16**) which was then converted to the ketoacetal (**18**) by successive acetalization and pyridinium dichromate (PDC) oxidation. In the NMR spectrum of **18**, irradiation of the C-3a methyl proton gave a 12.3% NOE enhancement of the C-9b acetal methine proton. This result established not only the relative configuration of the two chiral centers in **18** but also that of the methyl and the cyano group in **14** as unambiguously *cis*.

In order to confirm the mechanistic interpretation of the stereoselectivity and to improve the yield of the cycloaddition, the thermolysis of the enone (**19**), readily available by Swern oxidation of the alcohol (**11**), was examined. On heating of the enone (**19**) in *o*-dichlorobenzene at 160 °C for 5 h, the adducts (**20**) and (**21**) were obtained in a 13:1 ratio in 83.7% yield. The structure of the major isomer (**20**) was confirmed by comparison with the

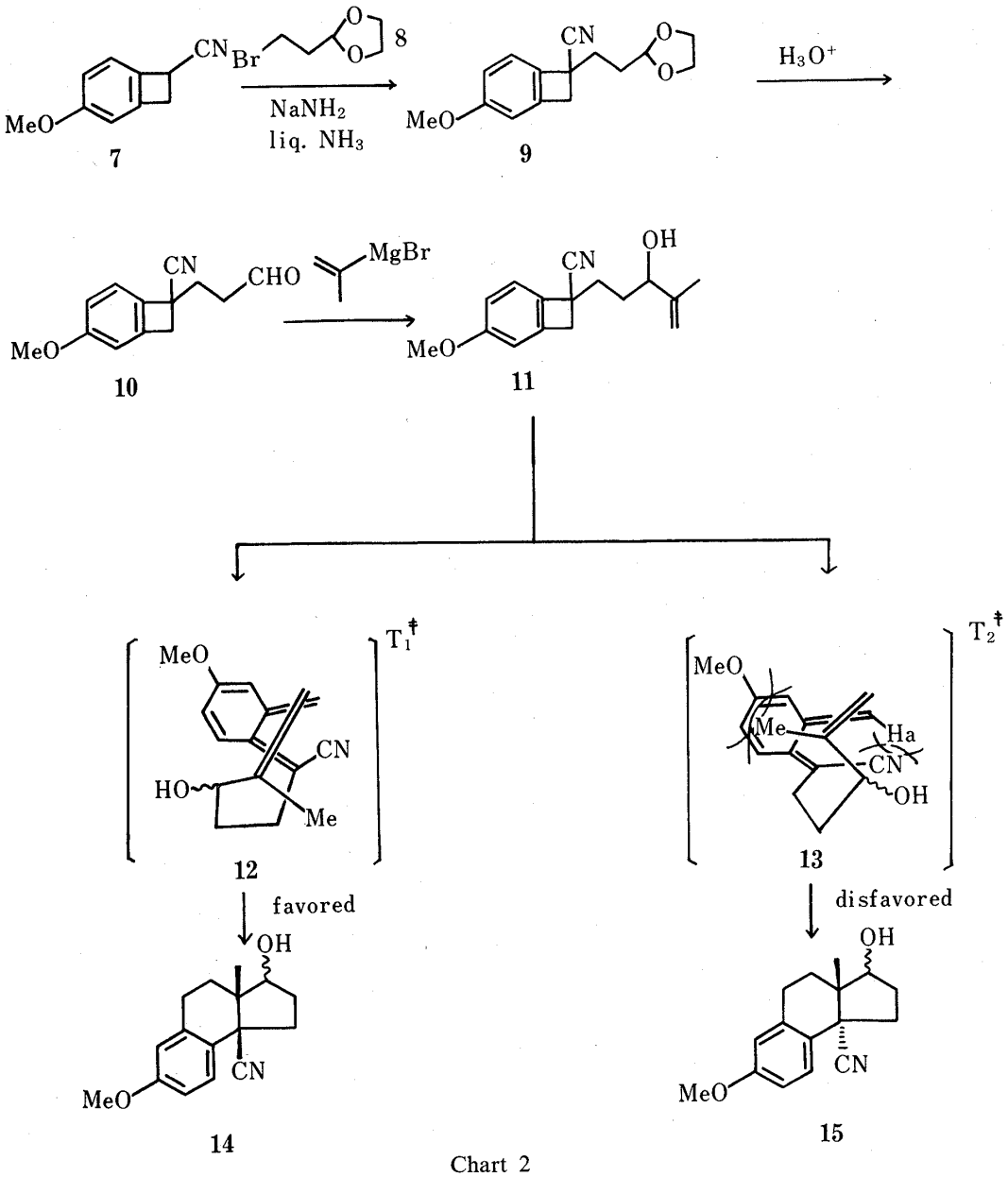


Chart 2

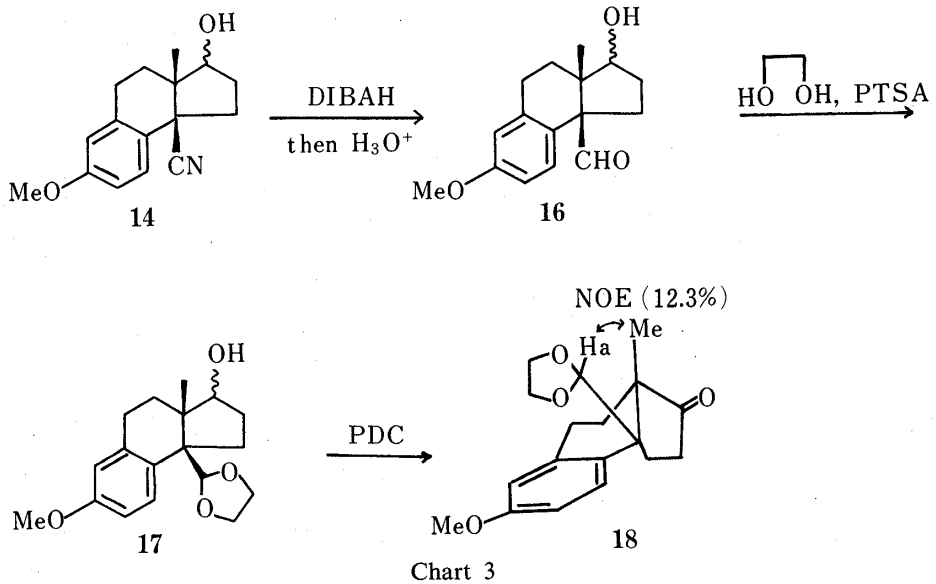


Chart 3

compound prepared by pyridinium chlorochromate (PCC) oxidation of **14**. As we expected, improvement of the yield of the thermolysis could be achieved by activation of the dienophile part, and the result supported the view that the severe steric interaction between the methyl and the *o*-quinodimethane ring in the transition state ($T_2^{\neq}$) caused the high stereoselectivity.

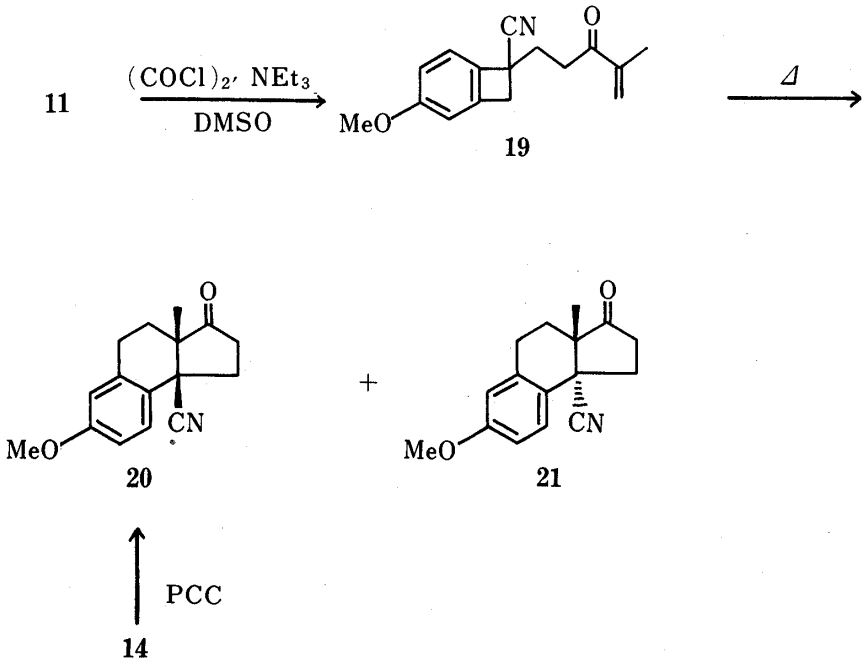


Chart 4

In contrast with **11**, it was reported[5] that the thermolysis of 1-(1,2-dihydro-4-methoxybenzocyclobuten-1-yl)-4-methyl-4-penten-3-ol (**22**) gave the adduct (**26**) stereoselectively as an epimeric mixture at C-3. We reexamined the NMR spectrum of the crude product, and confirmed that the cycloaddition did give two adducts (**25**) (δ 1.00 for C-3a Me) and (**26**) (δ 0.50) in a 1 : 4 ratio. Examination of CPK molecular models for the two conformers (**23**, **24**) in the transition state ($T_3^{\neq}$, $T_4^{\neq}$) shows a slight interaction among Ha, Hb and Hc (or –OH) in $T_3^{\neq}$, whereas this type of interaction and the methyl–*o*-quinodimethane interaction caused by the Ha–CN interaction in $T_2^{\neq}$ are absent in $T_4^{\neq}$. Therefore the 1 : 4 ratio of the adducts seems to reflect the slight difference in energy ($\Delta\Delta G^{\neq}$) between the transition states $T_3^{\neq}$ and $T_4^{\neq}$.

Finally, we investigated the decyanation[6] of the *cis*-hydrindan (**14**) by a dissolving metal reduction. It is interesting to compare the stereochemical outcome of this conversion with the case of *cis*-6/6 fused cyanides (**31**,[7] **33**[3e]), which give the *trans*-6/6 fused system (**32**, **34**) shown in Chart 6. Thus, the alcohol (**14**) was reacted with sodium in liquid ammonia in the presence of ethanol to afford a mixture of the decyanated alcohols (**25**, **26**) in 85% yield; these products were converted to the tricyclic ketones (**29**, **30**) in 69% yield in a 3 : 1 ratio (by NMR analysis). This stereoselectivity[8] could be rationalized by examining the conformation of the carbanion in the transition state ($T_5^{\neq}$, $T_6^{\neq}$). Of the two conformations where overlap of the carbanion sp^3 orbital with the adjacent *pi*-orbital of the aromatic ring is effective, the conformer (**28**) has a 1,3-diaxial interaction between C-1 β-H and C-3a methyl. Hence, the conformer **27** would be expected to be more stable than **28** and to serve as the precursor for the observed major product (**29**).

Thus, we were able to develop a highly stereoselective route to a tricyclic *cis*-hydrindan system with a C_1 unit (which might be convertible to other functional groups) at the C-9b position in a reasonable yield, and we carried out a mechanistic investigation of the

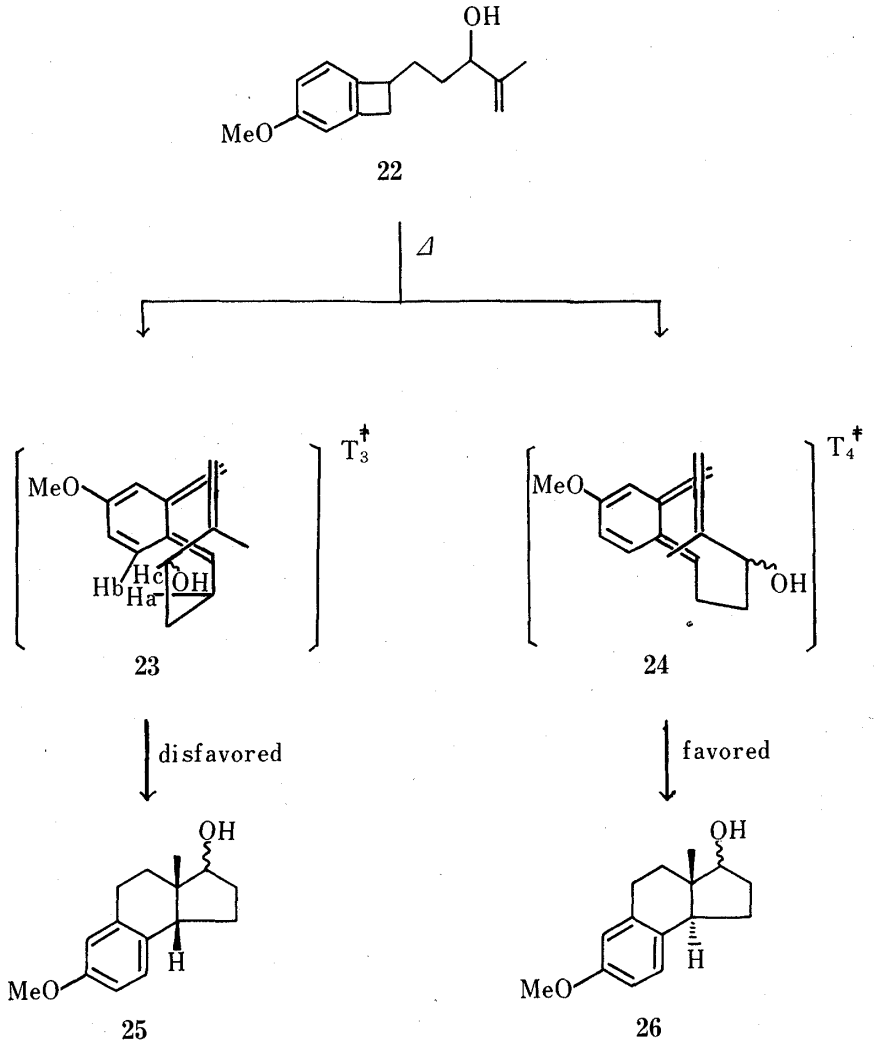


Chart 5

intramolecular cycloadditions. Moreover, it was clarified that the stereoselectivity in a dissolving metal reduction of **14** gave the reverse result compared with the cases of **31** and **33**.

Experimental

Melting points were determined on a Yanagimoto MP-22 apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 125 grating spectrophotometer and NMR spectra on a JEOL-PMX-60 or JEOL-PS-100 spectrometer using tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, m=multiplet. Ordinary mass spectra (MS) measured with a Hitachi M-52G instrument, while accurate MS were taken with a JEOL-TMS-01SG-2 spectrometer. All experiments were carried out under an atmosphere of dry argon or nitrogen.

3-(1-Cyano-1,2-dihydro-4-methoxybenzocyclobuten-1-yl)propanal (10)——A stirred solution of the acetal (**9**)[5] (1 g) in acetone (30 ml) was treated with 10% HCl (15 ml) at room temperature. The mixture was stirred at the same temperature for 48 h, then the solvents were removed under reduced pressure. The residue was extracted with benzene and the extract was washed with sat. NaCl solution, then dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was chromatographed on silica gel with benzene–AcOEt (5 : 1 v/v) as an eluent to give the aldehyde (**10**) (0.8 g, 96%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2230 (C≡N), 1720 (C=O). NMR ($CDCl_3$) δ: 3.01 (1H, d, J=14 Hz, ArC$\underset{\underline{H}}{\overset{\underline{H}}{<}}$), 3.53 (1H, d, J=14 Hz, ArC$\underset{\underline{H}}{\overset{\underline{H}}{<}}$), 3.66 (3H, s, $-OC\underline{H}_3$), 6.59—7.08 (3H, m, ArH), 9.68 (1H, s, $-C\underline{H}O$). MS m/z: 215 (M^+). High resolution MS (m/z): Calcd for $C_{13}H_{13}NO_2$: 215.0915. Found: 215.0930.

1-(1-Cyano-1,2-dihydro-4-methoxybenzocyclobuten-1-yl)-4-methyl-4-penten-3-ol (11)——A solution of the aldehyde (**10**) (7.7 g) in dry tetrahydrofuran (THF) (40 ml) was added dropwise at room temperature to a stirred

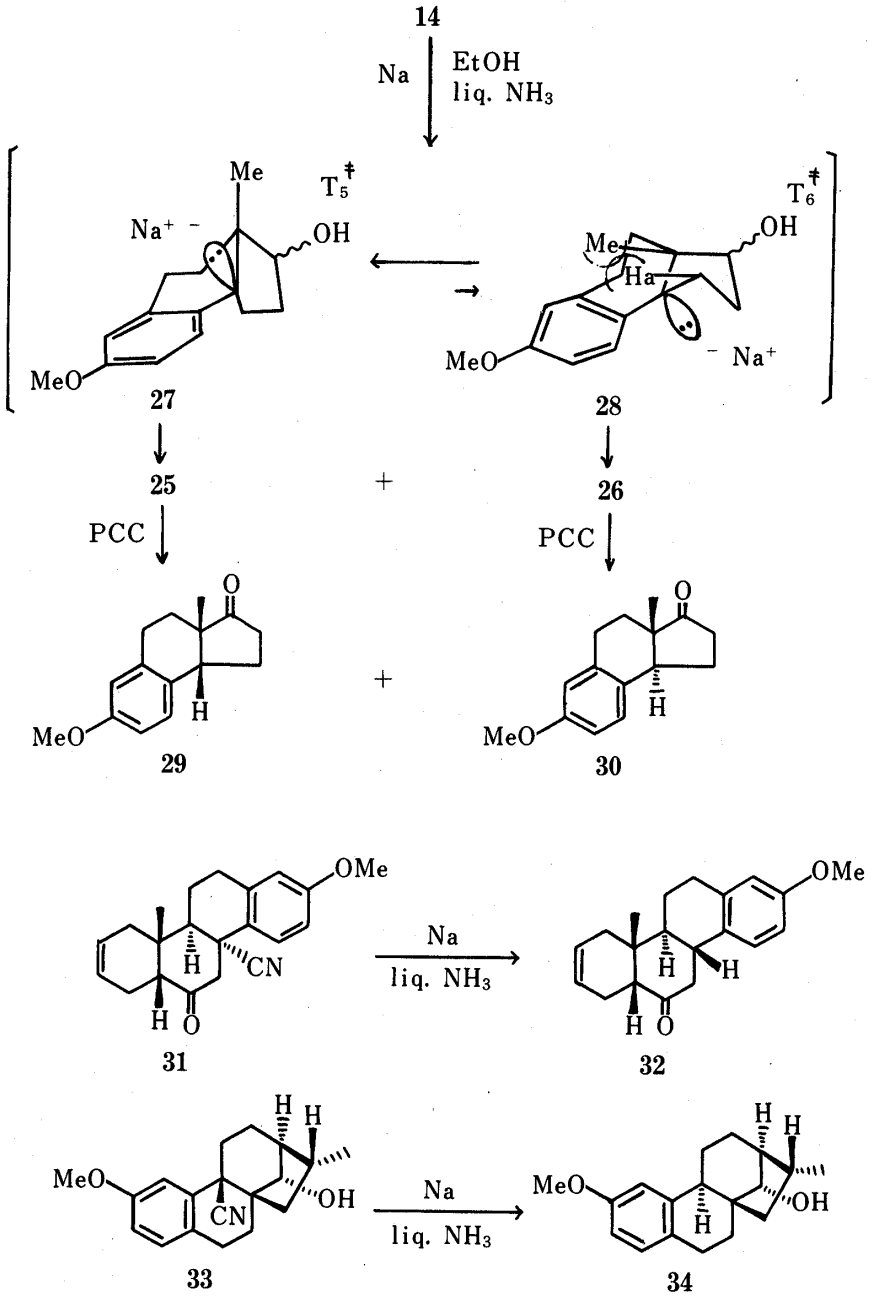


Chart 6

solution of isopropenylmagnesium bromide [prepared from isopropenyl bromide (6.5 g) and Mg (1.5 g)] in dry THF (140 ml). After 1 h, sat. NH_4Cl solution was added and the whole was extracted with benzene. The extract was washed with sat. NaCl solution, then dried over Na_2SO_4, and the solvent was removed. The residue was chromatographed on silica gel with benzene–AcOEt (5 : 1, v/v) as an eluent to give the alcohol (**11**) (6.9 g, 75%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 2200 (C≡N). NMR (CCl_4) δ: 1.71 (3H, s, >C=C<^{CH_3}), 3.15 (1H, d, J=14 Hz, ArC<$^{H}_{H}$) 3.61 (1H, d, J=14 Hz, ArC<$^{H}_{H}$), 3.73 (3H, s, $-OCH_3$), 4.78, 4.90 (each 1H, s, olefinic H), 6.63—7.13 (3H, m, ArH). MS m/z: 257 (M^+). High resolution MS (m/z): Calcd for $C_{16}H_{19}NO_2$: 257.1414. Found: 257.1414. *Anal.* Calcd for $C_{16}H_{19}NO_2 \cdot 1/4H_2O$: C, 73.39; H, 7.50; N, 5.34. Found: C, 73.27; H, 7.27; N, 4.97.

Thermolysis of 11——A solution of **11** (127 mg) in dry *o*-dichlorobenzene (13 ml) was heated with stirring at 180 °C for 8 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel with benzene–AcOEt (4 : 1, v/v) as an eluent to give the tricyclic *cis*-hydrindan (**14**) (83.5 mg, 65%) as a reddish oil, which was an inseparable epimeric mixture at C-3. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 2200 (C≡N). NMR ($CDCl_3$) δ: 1.23 (3H, s, $-CH_3$), 3.71 (3H, s, $-OCH_3$), 6.43—7.35 (3H, m, ArH). MS m/z: 257 (M^+). High resolution MS (m/z): Calcd for $C_{16}H_{19}NO_2$:

257.1414. Found: 257.1400. *Anal.* Calcd for $C_{16}H_{19}NO_2 \cdot 1/8H_2O$: C, 74.03; H, 7.47; N, 5.39. Found: C, 73.74; H, 7.43; N, 5.25. From the later eluate, the *trans*-isomer (**15**) (6.1 mg, 4.8%), an inseparable epimeric mixture at C-3, was collected as a reddish oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 2200 (C≡N). NMR ($CDCl_3$) δ: 0.67 (3H, s, $-CH_3$), 3.70 (3H, s, $-OCH_3$), 6.43—7.35 (3H, m, ArH). MS *m/z*: 257 (M^+). High resolution MS (*m/z*): Calcd for $C_{16}H_{19}NO_2$: 257.1414. Found: 257.1392.

9bβ-Formyl-3aβ-methyl-3-hydroxy-7-methoxy-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene (16)——DIBAH (1.48 ml of a 25% hexane solution) was added dropwise to a stirred solution of **14** (223 mg) in dry toluene (2.4 ml) at −78 °C. The resulting mixture was stirred at −78 °C for 1 h and at room temperature for 1 h. Then the reaction was quenched with sat. NH_4Cl solution and the mixture was filtered with the aid of celite. Removal of the solvent gave a residue, which was chromatographed on silica gel using benzene–AcOEt (4 : 1, v/v) as an eluent to give the aldehyde (**16**) (84 mg, 62%) as a colorless oil, which was an inseparable epimeric mixture at C-3. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1720 (HC=O). NMR ($CDCl_3$) δ: 0.99 (1.2H, s, $-CH_3$), 1.05 (1.8H, s, $-CH_3$), 3.67 (3H, s, $-OCH_3$), 6.48—6.63 (3H, m, ArH), 9.32 (1H, s, $-CHO$). MS *m/z*: 260 (M^+). *Anal.* Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.76; H, 7.87.

9bβ-(1,1-Ethylenedioxymethyl)-3aβ-methyl-3-hydroxy-7-methoxy-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene (17)——A solution of **16** (85 mg) and ethylene glycol (79 mg) in benzene (3 ml) was refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA) for 12 h with a Dean–Stark apparatus. The mixture was washed with sat. $NaHCO_3$ solution and sat. NaCl solution, then dried over Na_2SO_4. Removal of the solvent gave a residue, which was chromatographed on silica gel with benzene–AcOEt (2 : 1, v/v) as an eluent to give the acetal (**17**) (67 mg, 85%) as a colorless oil, which was an inseparable epimeric mixture at C-3. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH). NMR ($CDCl_3$) δ: 1.03 (1.2H, s, $-CH_3$), 1.17 (1.8H, s, $-CH_3$), 3.70 (3H, s, $-CH_3$), 4.87 (0.6H, s, $-CH\langle^{O}_{O}\rangle$), 5.02(0.4H, s, $-CH\langle^{O}_{O}\rangle$), 6.43—7.71 (3H, m, ArH). MS *m/z*: 304 (M^+). High resolution MS (*m/z*): Calcd for $C_{18}H_{24}O_4$: 304.1674. Found: 304.1676. *Anal.* Calcd for $C_{18}H_{24}O_4 \cdot 1/4H_2O$: C, 68.98; H, 7.40. Found: C, 69.22; H, 7.86.

9bβ-(1,1-Ethylenedioxymethyl)-3aβ-methyl-3-oxo-7-methoxy-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene (18)——A suspension of the alcohol (**17**) (63 mg) and PDC (77 mg) in CH_2Cl_2 (0.5 ml) was stirred at room temperature for 12 h. After addition of Florisil, the reaction mixture was filtered by using celite and the solvent was removed. The residue was then chromatographed on silica gel with benzene–AcOEt (10 : 1, v/v) as an eluent to give the ketoacetal (**18**) (52 mg, 83%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (C=O). NMR (CCl_4) δ: 1.06 (3H, s, $-CH_3$), 4.95 (1H, s, $-CH\langle^{O}_{O}\rangle$), 6.29—7.51 (3H, m, ArH). MS *m/z*: 302 (M^+). High resolution MS (*m/z*): Calcd for $C_{18}H_{22}O_4$: 302.1518. Found: 302.1498. *Anal.* Calcd for $C_{18}H_{22}O_4 \cdot 1/4H_2O$: C, 70.45; H, 7.23. Found: C, 70.46; H, 7.18.

1-(1-Cyano-1,2-dihydro-4-methoxybenzocyclobuten-1-yl)-4-methyl-4-penten-3-one (19)——A mixture of dimethyl sulfoxide (DMSO) (387 mg) and CH_2Cl_2 (1.6 mg) was added slowly to a stirred solution of oxalyl chloride (272 mg) in CH_2Cl_2 (8 ml) at −78 °C. Stirring was continued at the same temperature for 2 min, then a solution of the alcohol (**11**) (580 mg) in CH_2Cl_2 (3.2 ml) was added slowly. After 15 min, triethylamine (1.57 ml) was added and the whole was stirred at −78 °C for 5 min, then at room temperature for 10 min. The reaction mixture was then treated with H_2O and extracted with CH_2Cl_2. The extract was washed with sat. NaCl solution, dried over Na_2SO_4 and evaporated to give a residue, which was chromatographed on silica gel with benzene–AcOEt (100 : 4, v/v) as an eluent to give the enone (**19**) (465 mg, 80%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2210 (C≡N), 1670 (C=O). NMR ($CDCl_3$) δ 1.87 (3H, s, $-CH_3$), 3.73 (3H, s, $-OCH_3$), 5.74, 5.97 (each 1H, s, olefinic H), 6.66—7.10 (3H, m, ArH). MS *m/z*: 255 (M^+). High resolution MS (*m/z*): Calcd for $C_{16}H_{17}NO_2$: 255.1258. Found: 255.1231.

Thermolysis of 19——A solution of **19** (52 mg) in dry *o*-dichlorobenzene (6 ml) was heated with stirring at 160 °C for 5 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel with benzene–AcOEt (100 : 4, v/v) as an eluent to give the tricyclic *cis*-hydrindan (**20**) (40 mg, 77%) as colorless leaflets, mp 82—83 °C, after recrystallization from Et_2O–*n*-hexane. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2200 (C≡N), 1740 (C=O). NMR ($CDCl_3$) δ: 1.36 (3H, s, $-CH_3$), 3.85 (3H, s, $-OCH_3$), 6.51—6.90 (3H, m, ArH). MS *m/z*: 255 (M^+). High resolution MS (*m/z*): Calcd for $C_{16}H_{17}NO_2$: 255.1258. Found: 255.1273. *Anal.* Calcd for $C_{16}H_{17}NO_2 \cdot 1/8H_2O$: C, 74.61; H, 6.75; N, 5.44. Found: C, 74.53; H, 6.65; N, 4.99. From the later eluate, the *trans*-isomer (**21**) (3.5 mg, 6.7%) was collected as a pale yellow oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2200 (C≡N), 1740 (C=O). NMR ($CDCl_3$) δ: 0.71 (3H, s, $-CH_3$), 3.85 (3H, s, $-OCH_3$), 6.51—6.90 (3H, m, ArH). MS *m/z*: 255 (M^+). High resolution MS (*m/z*): Calcd for $C_{16}H_{17}NO_2$: 255.1258. Found: 255.1235.

PCC Oxidation of 14——A solution of the alcohol (**14**) (152 mg) in dry CH_2Cl_2 (1.5 ml) was added in a single portion to a stirred suspension of PCC (190 mg) in dry CH_2Cl_2 (2 ml) at room temperature. After 8 h, the reaction mixture was treated with Florisil and filtered with the aid of celite. The solvent was removed and the residue was chromatographed on silica gel with benzene–AcOEt (7 : 1, v/v) as an eluent to give the ketone (**20**) (123 mg, 82%), which was identical with the authentic sample prepared above.

Dissolving Metal Reduction of 14——Sodium (17 mg) and dry EtOH (1 ml) were added to a stirred solution of **14** (92 mg) in a mixture of liquid ammonia (5 ml) and dry THF (1 ml) at −78 °C. Stirring was continued at the same temperature for 2 h, then a large excess of EtOH (5 ml) was added and the solvent was removed. The residue was diluted with H_2O (5 ml), extracted with $CHCl_3$, washed with sat. NaCl solution, and dried over Na_2SO_4. After

removal of the solvent, the residue was chromatographed on silica gel with benzene–AcOEt (1 : 1, v/v) as an eluent to give a mixture of the alcohols (**25**) and (**26**) (71 mg, 85%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH). MS *m/z*: 232 (M^+). The mixture of the alcohols (**25**, **26**) (67 mg) was taken up in dry CH_2Cl_2 (0.6 ml) and the solution was then added in a single portion to a stirred suspension of PCC (120 mg) in dry CH_2Cl_2 (1.7 ml) at room temperature. The reaction mixture was treated with Florisil, and filtered with the aid of celite, then the solvent was removed. The residue was chromatographed on silica gel using benzene–AcOEt (2 : 1, v/v) as an eluent to give a mixture of the ketones (**29**) and (**30**) (43 mg, 69%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (C=O). NMR ($CDCl_3$) δ: 0.66 (0.7H, s, $-CH_3$), 1.04 (2.3H, s, $-CH_3$), 3.68 (3H, s, $-OCH_3$), 6.28—7.05 (3H, m, ArH). MS *m/z*: 230 (M^+). High resolution MS (*m/z*): Calcd for $C_{15}H_{18}O_2$: 230.1305. Found: 230.1270.

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