TRANSFORMATION OF (ISOCHROMAN-1-YL)METHYLKETONES TO NAPHTHALENE DERIVATIVES

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Abstract —— Treatment of (isochroman-1-yl)methylketones (2c-h) with potassium *tert*-butoxide gave different naphthalene derivatives (5-14) via novel ring transformation, depending on the presence or absence and the nature of the substituents adjacent to the carbonyl group in 2.

We[1] previously reported that ethyl 2-(isochroman-1-yl)acetoacetate (2a) or diethyl (isochroman-1-yl)malonate (2b), prepared by the reaction of 1-ethoxyisochroman (1) with ethyl acetoacetate or diethyl malonate, undergo ring transformation on heating with potassium *tert*-butoxide or sodium ethoxide, yielding ethyl dihydro-2-naphthoate. As an extension of the previous work, we now wish to report the ring transformation of (isochroman-1-yl)methylketones (2c-h) having substituents (R^1 and R^2) at the α and α' positions of the carbonyl group. Compounds 2c-h were prepared by the reaction of 1 with the corresponding ketone. For example, 1 on treatment with acetophenone at 40-50°C in the presence of boron trifluoride etherate gave α-(isochroman-1-yl)acetophenone (2c) in 65% yield. Ring transformation of 2c-h was performed by heating a benzene solution of 2c-h at 50-60°C in the presence of potassium *tert*-butoxide. The products obtained are classified into A (compounds 3-8) and B (compounds 9-14) groups according to their formation-mechanism discussed later on. Moreover, which type of products are mainly obtained is correlated to the presence or absence and the nature of substituents at α and α' positions of the carbonyl group in 2.

Thus, 2c (R^1=Ph, R^2=H), with no α-substituent, gave mainly A group of compounds, α-phenyl-2-naphthalenemethanol[2] (5c, 11%) and 2'-benzonaphthone[3] (7c, 33%),

accompanied with a trace of B group of compound, 3-phenyl-1,2-dihydronaphthalene [4] (10c, 1%). Similarly, 1-(isochroman-1-yl)-3,3-dimethyl-2-butanone (2d) (R^1=*tert*-Bu, R^2=H) afforded mainly A group of compounds, 2,2-dimethyl-1-(2-naphthyl)propan-2-ol (5d,7%), 2,2-dimethyl-1-(1,2-dihydronaphthalen-2-yl)-1-propanone (6d, 6%), 2'-pivalonaphthone[5] (7d, 16%), and 2,2-dimethyl-1-(1,2,3,4-tetrahydronaphthalen-2-yl)-1-propanone (8d, 8%), accompanied with a minor amount of B group of compound, 3-*tert*-butyl-1,2-dihydronaphthalene (10d, 5%).

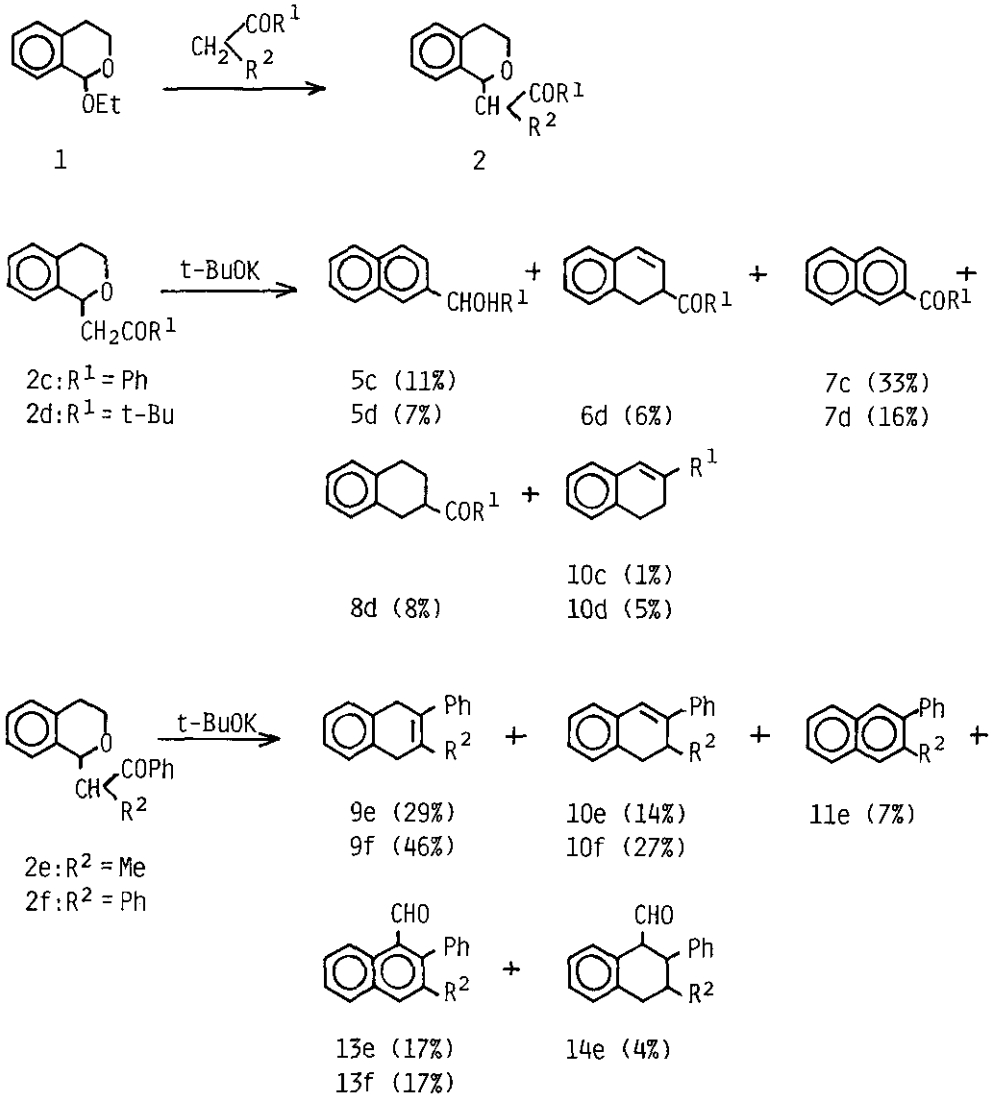

Chart 1

Secondly, 2-(isochroman-1-yl)propiophenone (2e) (R^1=Ph, R^2=Me), with α-methyl substituent, gave B group of compounds, 2-methyl-3-phenyl-1,4-dihydronaphthalene (9e, 29%), 2-methyl-3-phenyl-1,2-dihydronaphthalene (10e, 14%), 2-methyl-3-phenylnaphthalene[6] (11e, 7%), 3-methyl-2-phenyl-1-naphthalenecarbaldehyde (13e, 17%), and 3-methyl-2-phenyl-1,2,3,4-tetrahydro-1-naphthalenecarbaldehyde (14e, 4%). Similarly, α-(isochroman-1-yl)deoxybenzoin (2f), with R^1=R^2=Ph, gave B group of compounds, 2,3-diphenyl-1,4-dihydronaphthalene (9f, 46%), 2,3-diphenyl-1,2-dihydronaphthalene[7] (10f, 27%), and 2,3-diphenyl-1-naphthalenecarbaldehyde (13f, 17%).

Finally, isochroman derivatives (2g,h) having a cyclic ketone gave both A and B groups of compounds. Namely, 2-(isochroman-1-yl)-1-tetralone (2g) gave A group of compounds, *erythro*-3'-hydroxy-2,2'-spirobi(1,2,3,4-tetrahydronaphthalen)-1-one (*erythro*-3g, 24%), its *threo*-isomer (*threo*-3g, 13%), and 1,3'-dihydroxy-

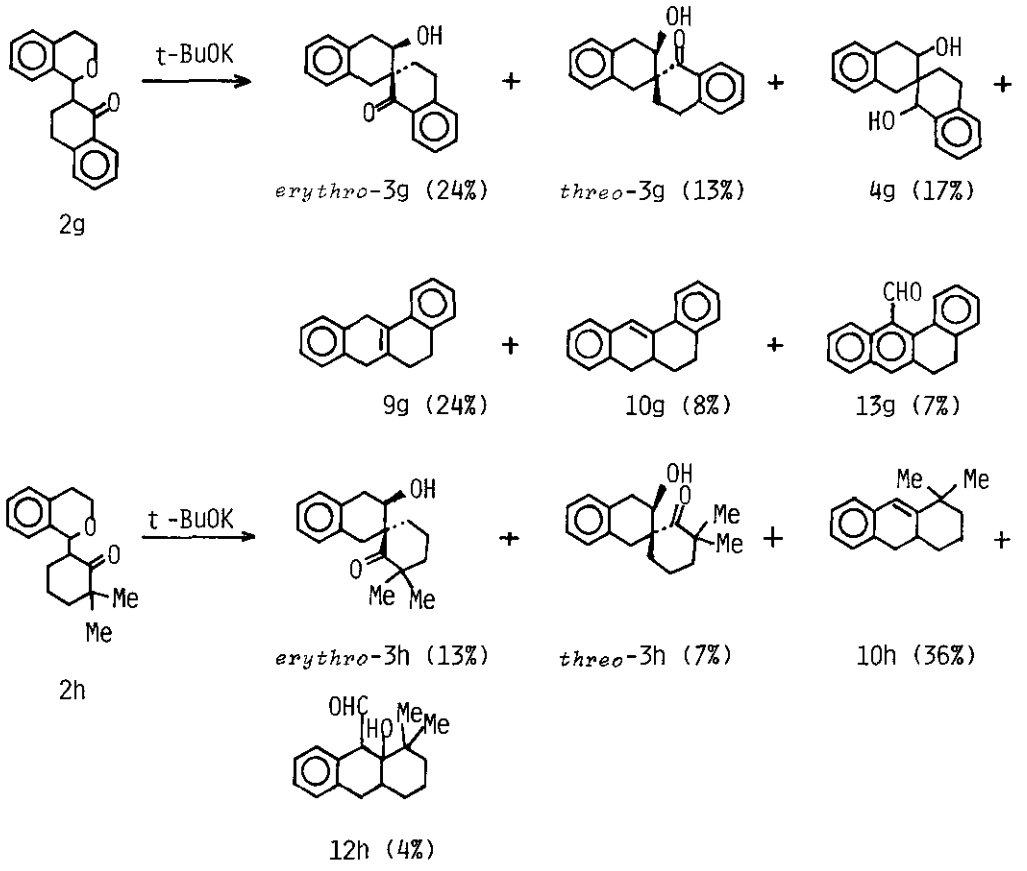

Chart 2

2,2'-spirobi(1,2,3,4-tetrahydronaphthalene) (4g, 17%), accompanied with B group of compounds, 5,6,7,12-tetrahydrobenz[a]anthracene (9g, 24%), 5,6,6a,7-tetrahydrobenz[a]anthracene (10g, 8%), and 5,6-dihydro-12-benz[a]anthracenecarbaldehyde (13g, 7%). Assignment of the stereochemistry of 3g was based on a comparison of chemical shift due to their C_3,-protons. In the NMR spectrum, the signal of *erythro*-3g was observed at δ 4.3-4.5 ppm as a multiplet, while that of *threo*-3g appeared at δ 4.6-5.0 ppm, to be attributed to the deshielding effect of the carbonyl group, as a multiplet. Similarly, 2,2-dimethyl-6-(isochroman-1-yl)cyclohexanone (2h) gave A group of compounds, *erythro*-3'-hydroxy-3,3-dimethylspiro[cyclohexane-1,2'-(1',2',3',4'-tetrahydronaphthalene)]-2-one (*erythro*-3h, 13%) and its *threo*-isomer (*threo*-3h, 7%), accompanied with B group of compounds, 1,1-dimethyl-1,2,3,4,4a,10-hexahydroanthracene (10h, 36%) and 9a-hydroxy-1,1-dimethyl-1,2,3,4,4a,10-hexahydro-9-anthracenecarbaldehyde (12h, 4%).

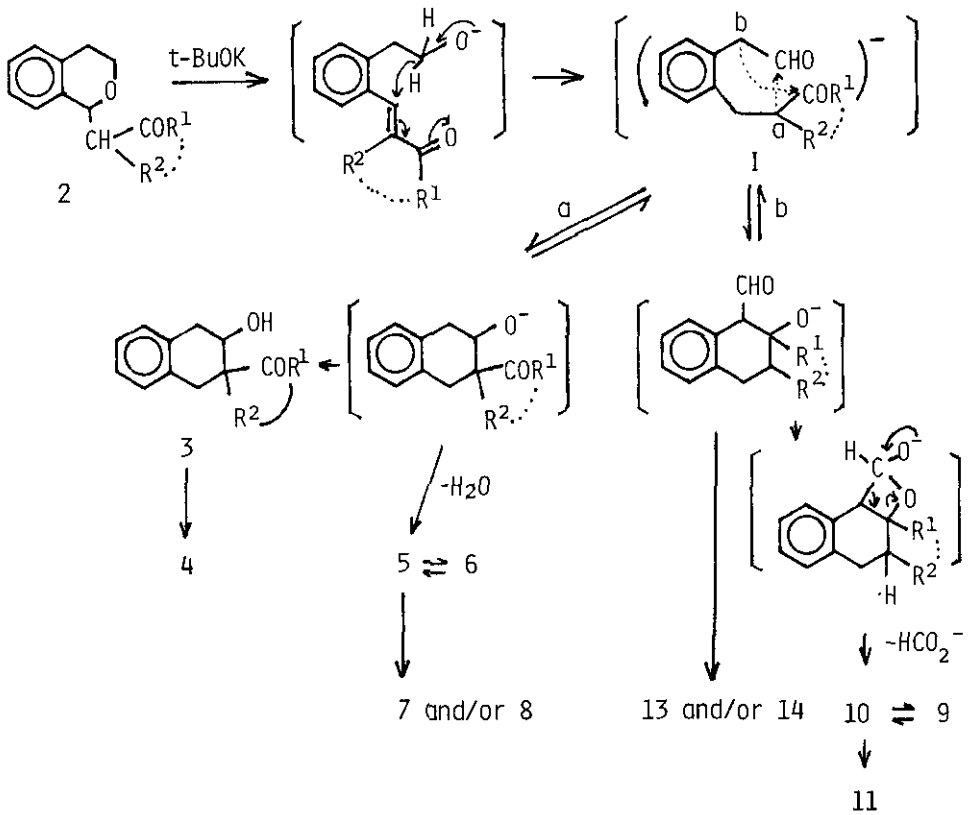

Chart 3

A possible mechanism[8] for the ring transformation of 2 is illustrated in Chart 3. Ring opening of isochroman followed by intramolecular hydride transfer gives a reactive formyl intermediate I. This intermediate cyclizes through two distinct pathway, a and b. It appears logical that A group of compounds, 4-8, represent the products of intramolecular aldol reaction through path a, while B group of compounds, 9-14, represent the products of the reaction through path b. The presence or absence and the nature of substituents at the α and α' positions of the carbonyl group in 2 have a substantial effect on a pathway of recyclization of formyl intermediate I.

The ring transformation of 2g,h having a cyclic ketone to 3g,h are useful for the synthesis of spiro compounds and an attempt to synthesize spiroketones (3) from 2 having a various cyclic ketones are now in progress.

EXPERIMENTAL

Melting points (determined on a Yanagimoto micromelting point apparatus) are uncorrected. NMR spectra of the compounds except 9e and 10e were obtained on a Hitachi R-24 spectrometer at 60 MHz with tetramethylsilane as an internal standard. Those of 9e and 10e were obtained on a JEOL GX-400 spectrometer at 400 MHz. Gas chromatogaphic-mass (GC-MS) spectra were recorded on a Shimadzu LKB-9000 spectrometer and infrared (IR) spectra on a JASCO A-102 spectrometer.

General Procedure for the Preparation of (Isochroman-1-yl)methylketones (2c-h) Typical example; α-(Isochroman-1-yl)acetophenone (2c): A solution of 1-ethoxyisochroman (15 g, 84 mmol), acetophenone (12 g, 101 mmol), and $BF_3 \cdot Et_2O$ (3 ml) in dry benzene (15 ml) was heated at 40°C for 1 h in a N_2 atmosphere, poured into ice-water, and extracted with Et_2O. The Et_2O layer was washed with sat. $KHCO_3$ solution, dried, and concentrated. The residue was distilled under reduced pressure to give 13.8 g (65%) of 2c, bp 153-155°C (0.02 mmHg), mp 43-45°C (from hexane). *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.01; H, 6.39. IR (Nujol): 1680 cm^{-1}(CO). NMR ($CDCl_3$) δ: 2.46-3.10 (2H, m, 4'-H), 3.16-3.46 (2H, m, CH_2CO), 3.51-4.43 (2H, m, 3'-H), 5.41 (1H, t, *J*=6 Hz, 1'-H), 7.15 (4H, s, ArH), 7.26-7.68 (3H, m, ArH), 7.79-8.18 (2H, m, ArH). MS *m/e*: 252 (M^+). 2d: Yield, 54%, mp 56-57°C (from Et_2O). *Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.71; H, 8.70. IR (Nujol) 1700 cm^{-1} (CO). NMR

($CDCl_3$) δ: 1.20 (9H, s, Me x 3), 2.50-3.50 (4H, m, 1-H_2 and 4'-H_2), 3.65-4.30 (2H, m, 3'-H_2), 5.20-5.55 (1H, m, 1'-H), 7.20 (4H, s, ArH). MS *m/e*: 232 (M^+). 2e: Yield, 51%; mp 93-94°C (from MeOH). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17, H, 6.81. Found: C, 81.00; H, 6.79. IR (Nujol): 1680 cm^{-1} (CO). NMR ($CDCl_3$) δ: 1.09 (3H, d, *J*=7 Hz, Me), 5.20-5.42 (1H, m, 1'-H). MS *m/e*: 266 (M^+). 2f: Yield, 73%; mp 127-128°C (from MeOH). *Anal.* Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.87; H, 6.16. IR (Nujol): 1665 cm^{-1} (CO). NMR ($CDCl_3$) δ: 4.91-5.22 (1H, m, α-H), 5.57-5.95 (1H, m, 1'-H), 7.00-7.60 (12H, m, ArH), 7.70-8.15 (2H, m, ArH). MS *m/e*: 328 (M^+). 2g: Yield, ; mp 122-123°C (from Et_2O). *Anal.* Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.85; H, 6.49. IR (Nujol): 1660 cm^{-1} (CO). NMR ($CDCl_3$) δ: 5.68-5.90 (1H, m, 1'-H), 6.68-7.58 (7H, m, ArH), 8.21 (1H, dd, *J*=7 and 2 Hz, ArH). MS *m/e*: 278 (M^+). 2h: Yield, 59%; bp 130-140°C (0.01 mmHg), a viscous oil. *Anal.* Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.94, H, 8.76. IR (Neat): 1710 cm^{-1} (CO). NMR (CCl_4) δ: 1.14 (3H, s, Me), 1.21 (3H, s, Me), 1.40-3.10 (9H, m, cyclohexane-H and 4'-H_2), 3.41-4.41 (2H, m, 3'-H_2), 5.35-5.45 (1H, m, 1'-H), 7.16 (4H, m, ArH).

Reaction of 2c with *tert*-BuOK

tert-BuOK (3.2 g, 29 mmol) was added to a solution of 2c (6 g, 24 mmol) in dry benzene (140 ml), then the mixture was stirred at 50-60°C for 2 h in a N_2 atmosphere, poured into ice-water, and extracted with Et_2O. The Et_2O layer was washed with H_2O, dried, and concentrated. The residue was chromatographed on silica gel with petr. ether-AcOEt (30:1) to give succesively 0.058 g of a mixture[9] of 3-phenyl-1,2-dihydronaphthalene[4] (10c) and 2-phenylnaphthalene[4], 1.8 g (33%) of 2'-*benzonaphthone* (7c), mp 80-81°C (Lit.[3] mp 82°C), and 0.584 g (11%) of α-phenyl-2-naphthalenemethanol (5c), mp 85-86°C (Lit.[2] mp 82-83°C).

Reaction of 2d with *tert*-BuOK

A mixture of 2d (1 g, 4.3 mmol), *tert*-BuOK (0.58 g, 5.2 mmol), and dry benzene (30 ml) was treated in the same way as described for 2c. The residue from the extract was chromatographed on silica gel with petr. ether-AcOEt (30:1) to give 0.041 g (5%) of 3-*tert*-butyl-1,2-dihydronaphthalene (10d) as an oil. *Anal.* Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.95, H, 9.58. NMR (CCl_4) δ: 1.13 (9H, s, Me x 3), 2.05-2.92 (4H, m, 1-H_2 and 2-H_2), 6.28 (1H, s, 4-H), 7.01 (4H, s, ArH). The second fraction gave 0.274 g of a mixture[10] in the ratio of 10:5:4 of 2'-pivalonaphthone (7d, 16%), 2,2-dimethyl-1-(1,2,3,4-tetrahydronaph-

thalene-2-yl)-1-propanone (8d, 8%), and 2,2-dimethyl-1-(1,2-dihydronaphthalene-2-yl)-1-propanone (6d, 6%). NMR (CCl_4) δ: 6d: 1.31 (9H x 4/19, s, CMe_3), 2.30-3.25 (4H x 4/19, m, 1-H_2 and 2-H_2), 7.15 (5H x 4/19, s, 4-H and ArH). 7d: 1.48 (9H x 10/19, s, CMe_3), 7.40-8.05 (6H x 10/19, m, ArH), 8.20-8.34 (1H x 10/19, m, ArH). 8d: 1.18 (9H x 5/19, s, CMe_3), 2.30-3.25 (7H x 5/19, m, 1-H_2, 2-H, 3-H_2, and 4-H_2), 7.01 (4H x 5/19, s, ArH). GC-MS *m/e*: 6d, 214 (M^+); 7d, 212 (M^+); 8d, 216 (M^+). The mixture of 6d, 7d, and 8d was crystallized from MeOH-H_2O to give 7d, mp 54-55°C, [Lit.[5] bp 181-183°C (15 mmHg), mp 66°C]. The third fraction gave 0.06 g (7%) of 2,2-dimethyl-1-(2-naphthyl)propan-2-ol (5d) as a viscous oil. IR (Neat): 3450 cm^{-1} (OH). NMR (CCl_4) δ: 0.93 (9H, s, CMe_3), 2.25 (1H, br, OH), 4.32 (1H, s, CHOH), 7.20-7.95 (7H, m, ArH). MS *m/e* : 214 (M^+).

Reaction of 2e with *tert*-BuOK

A mixture of 2e (6 g, 23 mmol), *tert*-BuOK (3 g, 27 mmol), and dry benzene (150 ml) was stirred at 50-60°C for 7 h and treated in the same way as described for 2c. The residue from the extract was chromatographed on silica gel with petr. ether-AcOEt (16:1) to give 2.46 g of a mixture[11] in the ratio of 4:2:1 of 2-methyl-3-phenyl-1,4-dihydronaphthalene (9e, 29%), 2-methyl-3-phenyl-1,2-dihydronaphthalene (10e, 14%), and 2-methyl-3-phenylnaphthalene[6] (11e, 7%). NMR (CCl_4) δ: 9e: 1.74 (3H x 4/7, s, Me), 3.19-3.77 (4H x 4/7, m, 1-H_2 and 4-H_2), 7.00-7.90 (9H x 4/7, m, ArH). 10e: 1.00 (3H x 2/7, d, J=7 Hz, Me), 2.70-3.19 (3H x 2/7, m, 1-H_2 and 2-H), 7.00-7.90 (10H x 2/7, m, 4-H and ArH). 11e: 2.40 (3H x 1/7, s, Me), 7.00-7.90 (11H x 1/7, m, ArH). GC-MS *m/e*: 9e, 220 (M^+); 10e, 220 (M^+); 11e, 218 (M^+). The second fraction gave 1.2 g of a mixture in the ratio of 4:1 of 3-methyl-2-phenyl-1-naphthalenecarbaldehyde (13e, 17%) and 3-methyl-2-phenyl-1,2,3,4-tetrahydro-1-naphthalenecarbaldehyde (14e, 4%). NMR (CCl_4) δ: 13e: 2.20 (3H x 4/5, s, Me), 7.00-7.95 (9H x 4/5, m, ArH), 9.32 (1H x 4/5, d, J=4 Hz, 8-H), 10.10 (1H x 4/5, s, CHO). 14e: 0.89 (3H x 1/5, d, J=6 Hz, Me), 7.00-7.65 (8H x 1/5, m, ArH), 7.90-8.05 (1H x 1/5, m, 8-H), 9.78 (1H x 1/5, s, CHO). GC-MS *m/e*: 13e, 246 (M^+); 14e, 250 (M^+).

Reaction of 2f with *tert*-BuOK

A mixture of 2f (6 g, 18 mmol), *tert*-BuOK (2.5 g, 22 mmol), and dry benzene (150 ml) was refluxed for 4.5 h and treated in the same manner as described for 2c. The residue from the extract was chromatographed on silica gel with petr. ether-AcOEt (16:1) to give 2.36 g (46%) of 2,3-diphenyl-1,4-dihydronaphthalene (9f), mp 82-83°C (from cyclohexane). *Anal.* calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43.

Found: C, 93.76; H, 6.32. NMR ($CDCl_3$) δ: 3.84 (4H, s, 1-H_2 and 4-H_2), 7.13 (10H, s, Ph x 2), 7.25 (4H, s, ArH). MS *m/e*: 282 (M^+). The second fraction gave 1.29 g (27%) of 2,3-diphenyl-1,2-dihydronaphthalene (10f), mp 118-119°C (Lit.[7] mp 119.5-120.5°C). The third fraction gave 0.975 g (17%) of 2,3-diphenyl-1-naphthalenecarbaldehyde (13f), mp 155-157°C (from cyclohexane). *Anal.* Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.58; H, 5.34. IR (Nujol): 1680 cm^{-1} (CO). NMR ($CDCl_3$) δ: 7.01-8.19 (14H, m, ArH), 9.21-9.45 (1H, m, 8-H), 10.20 (1H, s, CHO). MS *m/e*: 308 (M^+).

Reaction of 2g with *tert*-BuOK

A mixture of 2g (6 g, 22 mmol), *tert*-BuOK (2.9 g, 26 mmol), and dry benzene (150 ml) was stirred at 50-60°C for 3 h in a N_2 and treated in the same manner as described for 2c. The residue was crystallized from petr. ether-AcOEt (8:1) to give 1 g (17%) of 1,3'-dihydroxy-2,2'-spirobi(1,2,3,4-tetrahydronaphthalene) (4g), mp 241-245°C (from DMSO-H_2O). *Anal.* Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 80.97; H, 7.18 IR (Nujol): 3300 cm^{-1}(OH). NMR (pyridine-d_5) δ: 1.81-3.06 (8H, m, 3-H_2, 4-H_2, 1'-H_2, and 4'-H_2), 3.88-4.24 (1H, m, 3'-H), 4.81 (1H, s, 1-H), 5.03-5.42 (2H, br, OH x 2), 6.28-6.84 (8H, m, ArH).

The mother liquor was concentrated and the residue was chromatographed on silica gel with petr. ether-AcOEt (8:1) to give 1.61 g of a mixture[12] in the ratio of 2:1 of 5,6,7,12-tetrahydrobenz[a]anthracene (9g) and 5,6,6a,7-tetrahydrobenz[a]-anthracene (10g). NMR ($CDCl_3$) δ: 9g: 2.36 (2H x 3/4, t, J=8 Hz, 6-H_2), 2.85 (2H x 3/4, t, J=8 Hz, 5-H_2), 3.58 and 3.57 (each 1H x 3/4, each d, each J=6 Hz, 12-H_2), 3.78 (2H x 3/4, m, 7-H_2), 7.11-7.44 (7H x 3/4, m, ArH), 7.87 (1H x 3/4, d, J=8 Hz, ArH). 10g: 1.58-1.70 (2H x 1/4, m, 6-H_2), 2.11-2.17 (1H x 1/4, m, 6a-H), 2.70-2.75, 2.83-2.88, 2.92-2.96, and 3.05-3.09 (each 1H x 1/4, each m, 5-H_2 and 7-H_2), 7.11-7.44 (9H x 1/4, m, ArH). The second fraction gave 0.38 g (7%) of 5,6-dihydro-12-benz[a]anthracenecarbaldehyde (13g), mp 128-130°C (from cyclohexane). IR (Nujol): 1675 cm^{-1} (CO). *Anal.*Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.38; H, 5.32. NMR ($CDCl_3$) δ: 2.96 (4H, s, 5-H_2 and 6-H_2), 7.14-8.09 (8H, m, ArH), 9.04-9.40 (1H, m, ArH), 10.32 (1H, s, CHO). MS *m/e*: 258 (M^+). The third fraction gave 1.43 g (24%) of *erythro*-3'-hydroxy-2,2'-spirobi(1,2,3,4-tetrahydronaphthalen)-1-one (*erythro*-3g), mp 140-141°C (from benzene). *Anal.*Calcd for $C_{19}H_{18}O_2$:C, 81.98; H, 6.52. Found: C, 81.66; H, 6.48. IR (Nujol): 3600 cm^{-1}(OH), 1680 cm^{-1}(CO). NMR ($CDCl_3$) δ: 1.77-2.15 (2H,

m, 3-H_2), 2.47-3.37 (6H, m, 4-H_2, 1'-H_2 and 4'-H_2), 4.25-4.51 (1H, m, 3'-H), 4.66 (1H, s, OH), 6.88-7.20 (7H, m, ArH), 8.15 (1H, dd, J=8 and 2 Hz, 8-H). MS *m/e*: 278 (M^+). The fourth fraction gave 0.77 g (13%) of *threo*-3'-hydroxy-2,2'-spirobi(1,2,3,4-tetrahydronaphthalen)-1-one (*threo*-3g), mp 130-132°C (from petr. ether-AcOEt). *Anal.* Calcd for $C_{19}H_{18}O_2$: C, 81.98, H, 6.52. Found: C, 81.95; H, 6.61. IR (Nujol): 3460 cm^{-1} (OH), 1660 cm^{-1} (CO). NMR ($CDCl_3$) δ: 1.60-2.18 (2H, m, 3-H_2), 2.18-3.25 (6H, m, 4-H_2, 1'-H_2, and 4'-H_2), 2.72 (1H, br, OH), 4.58-5.04 (1H, m, 3'-H), 6.90-7.90 (7H, m, ArH), 8.12 (1H, dd, J=8 and 2 Hz, 8-H). MS *m/e*: 278 (M^+).

Reaction of 2h with *tert*-BuOK

A mixture of 2h (4 g, 16 mmol), *tert*-BuOK (2.1 g, 19 mmol), and dry benzene (100 ml) was stirred at 50°C for 30 min in a N_2 atmosphere and treated in the same manner as described for 2c. The residue from the extract was chromatographed on silica gel with petr. ether-AcOEt (12:1) to give 1.18 g (36%) of 1,2,3,4,4a,10-hexahydroanthracene (10h), mp 44-45°C (from MeOH). *Anal.* Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.02; H, 9.82. NMR ($CDCl_3$) δ: 1.12 (3H, s, Me), 1.29 (3H, s, Me), 1.41-3.10 (9H, m, 2-H_2, 3-H_2, 4-H_2, 4a-H, and 10-H_2), 6.39 (1H, s, 9-H), 7.15 (4H, s, ArH). MS *m/e*: 212 (M^+). The second fraction gave 0.163 g (4%) of 1,1-dimethyl-9a-hydroxy-1,2,3,4,4a,10-hexahydro-9-anthracenecarbaldehyde (12h), mp 136-137°C (from Et_2O). *Anal.* Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.13; H, 8.76. IR (Nujol): 3500 cm^{-1} (OH), 1690 cm^{-1} (CO). NMR ($CDCl_3$) δ: 1.10 (6H, s, Me x 2), 1.30-1.75 (7H, m, 2-H_2 3-H_2, 4-H_2, and 4a-H), 2.00 (1H, br, OH), 2.50-3.00 (2H, m, 5-H_2), 3.91 (1H, d, J=4 Hz, 10-H), 6.90-7.40 (4H, m, ArH), 9.71 (1H, d, J=4 Hz, CHO). MS *m/e*: 258 (M^+). The third fraction gave 0.52 g (13%) of *erythro*-3,3-dimethyl-3'-hydroxyspiro[cyclohexane-1,2'-(1',2',3',4'-tetrahydronaphthalen)]-2-one (*erythro*-3h), as a viscous oil. *Anal.* Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.53; H, 9.22. IR (Neat): 3500 cm^{-1} (OH), 1675 cm^{-1} (CO). NMR (CCl_4) δ: 1.09 (3H, s, Me), 1.19 (3H, s, Me), 1.45-2.00 (6H, m, 4-H_2, 5-H_2, and 6-H_2), 2.58-3.38 (4H, m, 1'-H_2), 3.81-4.06 (1H, m, 3'-H), 4.30 (1H, br, OH), 7.08 (4H, s, ArH). MS *m/e*: 258 (M^+). The fourth fraction gave 0.277 g (7%) of *threo*-3,3-dimethyl-3'-hydroxyspiro[cyclohexane-1,2'-(1',2',3',4'-tetrahydronaphthalen)]-2-one (*threo*-3h), as a viscous oil. *Anal.* Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.10; H, 8.82. IR (Neat): 3500 cm^{-1} (OH), 1690 cm^{-1} (CO). NMR (CCl_4) δ: 1.10 (3H, s, Me), 1.20 (3H, s, Me), 1.45-2.05 (6H, m, 4-H_2, 5-H_2, and 6-H_2), 2.28 (1H, br, OH),

2.57-3.09 (4H, m, 1'-H_2 and 4'-H_2), 4.32-4.72 (1H, m, 3'-H), 7.04 (4H, s, ArH).
MS *m/e*: 258 (M^+).

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8. The mechanism for the ring transformation of 2a,b was previously reported (Ref. 1); but on the basis of the previous results for 2c-h, the machanism was corrected as shown in Chart 3.
9. Compound 10c and 2-phenylnaphthalene were identified by gas chromatographic comparison with an authentic sample prepared according to the method of Farbenind: See Ref. 3.
10. The structures and ratio of 6d, 7d, and 8d were determined by GC-MS and NMR spectral data, and from the result that dehydrogenation on palladium-carbon of a mixture of 6d, 7d, and 8d afforded 7d.
11. The structures and ratio of 9e, 10e, 11e, 13e, and 14e were determined by GC-MS and NMR spectral data.
12. The structures and ratio of 9g and 10g were determined from data obtained by 400 MHz decoupling experiments, and from GC-MS spectral data.

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