[Chem. Pharm. Bull. 30(5)1594—1601(1982)]

Reactivity of Isocoumarins. V.[1] Reaction of 1-Ethoxyisochroman with Active Methylene Compounds

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(Received September 21, 1981)

Active methylene compounds, diethyl malonate, α-tetralone, dimedone, acetylacetone, malononitrile, and diketene, were reacted with 1-ethoxyisochroman (**1**) to give the corresponding 1-substituted isochroman derivatives, **4**, **5**, **6**, **7**, **8**, **9**, **10**, and **11**, respectively.

When **4** was treated with sodium ethoxide or potassium *tert*-butoxide, ethyl 1,4-dihydro-2-naphthoate (**14a**), ethyl 1,2-dihydro-2-naphthoate (**14b**), and ethyl 2-naphthoate (**13**) were obtained. On the other hand, the reaction of 2-(1-isochromanyl)cyclohexanone (**3**) with potassium *tert*-butoxide afforded 9-formyl-1,2,3,4-tetrahydroanthracene (**20**) and 1,2,3,4,9,10-hexahydroanthracene (**21**).

The conversion mechanisms of 1-substituted isochromans (**2**, **3**, **4**, and **7**) into naphthalenes (**13**, **14a**, **b**, and **18**) and 1,2,3,4-tetrahydroanthracenes (**20** and **21**) are proposed.

Keywords——1-ethoxyisochroman; ethyl 1,4-dihydro-2-naphthoate; ethyl 2-naphthoate; 9-formyl-1,2,3,4-tetrahydroanthracene; 1,2,3,4,9,10-hexahydroanthracene; ring conversion; reaction mechanism

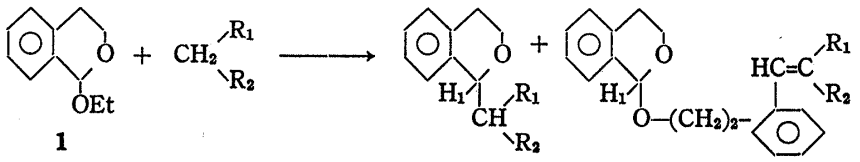
In our previous work on the reaction of 1-ethoxyisochroman (**1**) with nucleophilic reagents,[2] it was found that active methylene compounds such as ethyl acetoacetate and cyclohexanone were sufficiently reactive with **1** as to give corresponding 1-isochroman derivatives, ethyl 2-(1-isochromanyl)acetoacetate (**2**) and 2-(1-isochromanyl)cyclohexanone (**3**), simply on heating the mixture.

We are interested in the reactivity of **1** with a variety of active methylene compounds, and in the present work we examined the ring conversion of the resulting 1-substituted compounds into naphthalenes or anthracenes.

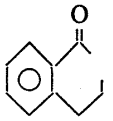
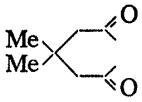
First, the reactions of **1** with active methylene compounds, diethyl malonate, acetylacetone, α-tetralone, dimedone, malononitrile, and diketene, were examined and the results are listed in Table I.

The reaction of **1** with diethyl malonate did not proceed upon simply heating the mixture at 140—150°C for five hours, but it took place upon addition of boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) to the same reaction mixture to give diethyl 1-isochromanylmalonate (**4**) in 21% yield. Similarly, the reaction of **1** with α-tetralone gave 2-(1-isochromanyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (**5**) in 59% yield. In the case of the reaction of **1** with dimedone, heating of the mixture at 120°C without any catalyst gave 2-(1-isochromanyl)-5-dimethyl-1,3-dioxocyclohexane (**6**) in 80% yield. On the other hand, the reaction of **1** with acetylacetone gave 3-(1-isochromanyl)-2,4-dioxopentane (**7**) and 3-{2-[β-(1-isochromanyloxy)ethyl]benzylidene}acetylacetone (**8**) in 59 and 9% yields, respectively. Similarly, the reaction of **1** with malononitrile gave 2-(1-isochromanyl)malononitrile (**9**) and 2-{2-[*p*-(1-isochromanyloxy)ethyl]benzylidene}malononitrile (**10**) in 6 and 30% yields, respectively. Acetonitrile and phenylacetonitrile did not react with **1** under any conditions tested in the presence or absence of catalyst. In the case of reaction of **1** with diketene, ethyl 4-(1-isochromanyl)-3-oxobutanate (**11**) was obtained in 71% yield on stirring **1** with diketene and titanium tetrachloride at −70°C, while **2** was obtained in 3% yield on heating a mixture of **1** and diketene at 130°C without the catalyst.

Table I. Reaction of 1 with Active Methylene Compounds



1 4—7, 9 8, 10

Compd. No.	R_1	R_2	Temp. (°C) [Time (h)] Catalyst	Yield (%)	mp (°C) or bp (°C/mmHg)	^{1}H-NMR ($CDCl_3$) H_1 (δ)	IR ν_{max}^{Nujol} cm^{-1}	Formula	Analysis (%) Calcd (Found) C	H	N
4	CO_2Et	CO_2Et	110(8) $BF_3 \cdot Et_2O$	21	137—140/ 0.2	5.46 (d, J= 6.5 Hz)	1725 (C=O)	$C_{16}H_{20}O_5$	65.74 (65.95	6.90 6.86)	
5			40(4) $BF_3 \cdot Et_2O$	59	123—124	5.85 (d, J= 3 Hz)	1665 (C=O)	$C_{19}H_{18}O_2$	81.98 (81.85	6.52 6.49)	
6			120(2)	80	120—121	6.12 (s)	1630 (C=O)	$C_{17}H_{20}O_3$	74.97 (74.83	7.40 7.35)	
7	COMe	COMe	120(2)	59	90—91	5.64 (s)	1550 (C=O)	$C_{14}H_{16}O_3$	72.39 (72.19	6.94 7.13)	
8	COMe	COMe	120(2)	9	150—155/ 0.005	5.52 (s)	1710 (C=O)	$C_{23}H_{24}O_4$	75.80 (75.61	6.64 6.62)	
9	CN	CN	150(3)	6	140—145/1	5.29 (d, J= 4 Hz)	2225 (CN)	$C_{12}H_{10}N_2O$	72.71 (72.67	5.09 5.00	14.13 14.25)
10	CN	CN	150(3)	30	74—75	5.58 (s)	2225 (CN)	$C_{21}H_{18}N_2O_2$	76.34 (76.12	5.49 5.33	8.48 8.34)

An attempt to prepare diethyl 2-ethyl-2-(1-isochromanyl)malonate (**12**)[3] by heating a mixture of **4** and ethyl iodide in the presence of sodium ethoxide or potassium *tert*-butoxide under a nitrogen atmosphere was unsuccessful and the compounds **14a** and **14b**, which were distilled at the same boiling point (bp 150°C/3 mmHg), and ethyl 2-naphthoate (**13**)[4] were obtained in 58 and 3% yields, respectively. The gas chromatographic-mass (GC–MS) spectral data of the mixture of compounds **14a** and **14b** showed that the two peaks due to **14a** and **14b** have the same formula, $C_{13}H_{14}O_2$ (m/e: 202). The compounds **14a** and **14b** were isolated by column chromatography, and their structures were established to be ethyl 1,4-dihydro-2-naphthoate[5] and ethyl 1,2-dihydro-2-naphthoate[6] by proton magnetic resonance (^{1}H-NMR) spectroscopy, respectively. In the ^{1}H-NMR spectrum of **14a**, a pair of triplet-quartet patterns (J=8 Hz) at δ: 1.32 and 4.32 due to ethoxylcarbonyl protons and a singlet with a shoulder at δ: 3.59 due to the protons of the C_1 and C_4 positions of ethyl 1,4-dihydro-2-naphthoate were observed. In the ^{1}H-NMR spectrum of **14b**, a pair of triplet-quartet patterns (J=7 Hz) at δ: 1.25 and 4.25 due to ethoxycarbonyl protons and a multiplet at δ: 2.94—3.24 due to the protons of the C_1 and C_4 positions of ethyl 1,2-dihydro-2-naphthoate were observed. The structures of **14a** and **14b** were suported by the following observations: the saponification of **14a** with methanolic potassium hydroxide gave 1,4-dihydro-2-naphthoic acid (**15**),[7] and dehydrogenation on palladium–carbon of the mixture of **14a** and **14b** followed by saponification gave only 2-naphthoic acid (**16**).[8] The compounds **14a** and **14b** were also obtained by heating **4** with potassium *tert*-butoxide in dry *tert*-butyl alcohol without ethyl iodide. When **4** was heated with sodium ethoxide in a stream of dry air, an increased yield (33%) of **13** and decreased yield (29%) of the mixture of **14a** and **14b** were obtained.

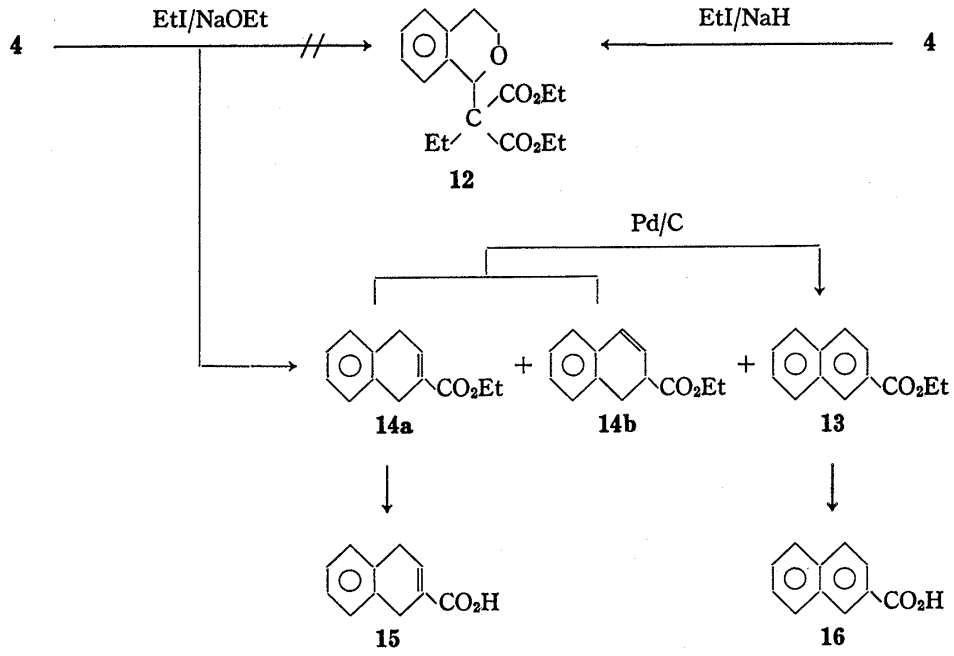


Chart 1

Hauser and Pogany reported the reaction of isocoumarin and lithio ethyl acetate to give ethyl 1-hydroxy-2-naphthoate,[9] but the conversion of 1-substituted isochroman to naphthalene derivatives has not previously been reported.

In order to elucidate the scope of the reaction, compound **2** was treated under the conditions used to convert **4** to **14a, b**. The resulting product was not 2-acetylnaphthalene but a mixture of **14a** and **14b** (33% yield), ethyl 2-(1-isochromanyl)acetate (**17**) (21% yield), and a small amount of **13**. On the other hand, compound **7** was resistant to this reaction; prolonged reaction (8 h) gave 2-acetylnaphthalene (**18**)[10] and 1-isochromanylacetylacetone (**19**) in 2 and 59% yields, respectively. The structure of **18** was confirmed by preparation of its 2,4-dinitrophenylhydrazone, which was identical with an authentic sample.[11] The compounds **12** and **17** were unreactive with sodium ethoxide under any conditions tested.

The mechanism of the conversion from isochroman derivatives (**2**, **4**, and **7**) into the naphthalene derivatives (**13**, **14a**, **14b**, and **18**) was considered to be as shown in Chart 2. Compound **4** is presumably converted into the intermediate, sodium complex of the dienolate form of 2-ethoxycarbonyl-3,4-dihydronaphthalene, *via* path (b), and this is isomerized into **14a** and **14b** by acidification after the reaction; **13** is presumably formed from the same intermediate by air oxidation during the reaction. On the other hand, **2** is presumably converted into **13** *via* path (a) because the original ethoxycarbonyl group of **2** remains in the molecule of the product **13**. Similarly, **7** might be converted into **18** *via* path (a). Compound **3**, which is an isochroman derivative having a cyclic carbonyl group at the C_1 position, was treated under the same conditions as **4** give **14a, b**. The resulting products were 9-formyl-1,2,-3,4-tetrahydroanthracene (**20**)[12] and 1,2,3,4,9,10-hexahydroanthracene (**21**).[13] The structures of **20** and **21** were estabilished on the basis of infrared (IR), mass, ^{1}H-NMR and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectral data given in the experimental section. Furthermore, the structure of **20** was confirmed by preparation of its oxime derivative (**22**).[12] Compound 21 tended to change gradually into 1,2,3,4-tetrahydroanthracene (**23**)[14] on standing in air over a period of several days. Furthermore, **21** was dehydrogenated on palladium-carbon to give **23**. When **3** was treated with pottasium *tert*-butoxide in a stream of dry air, **20** and **21** were obtained in 8 and 19% yields, respectively. But the presence of **23** was not detected in the reaction mixture.

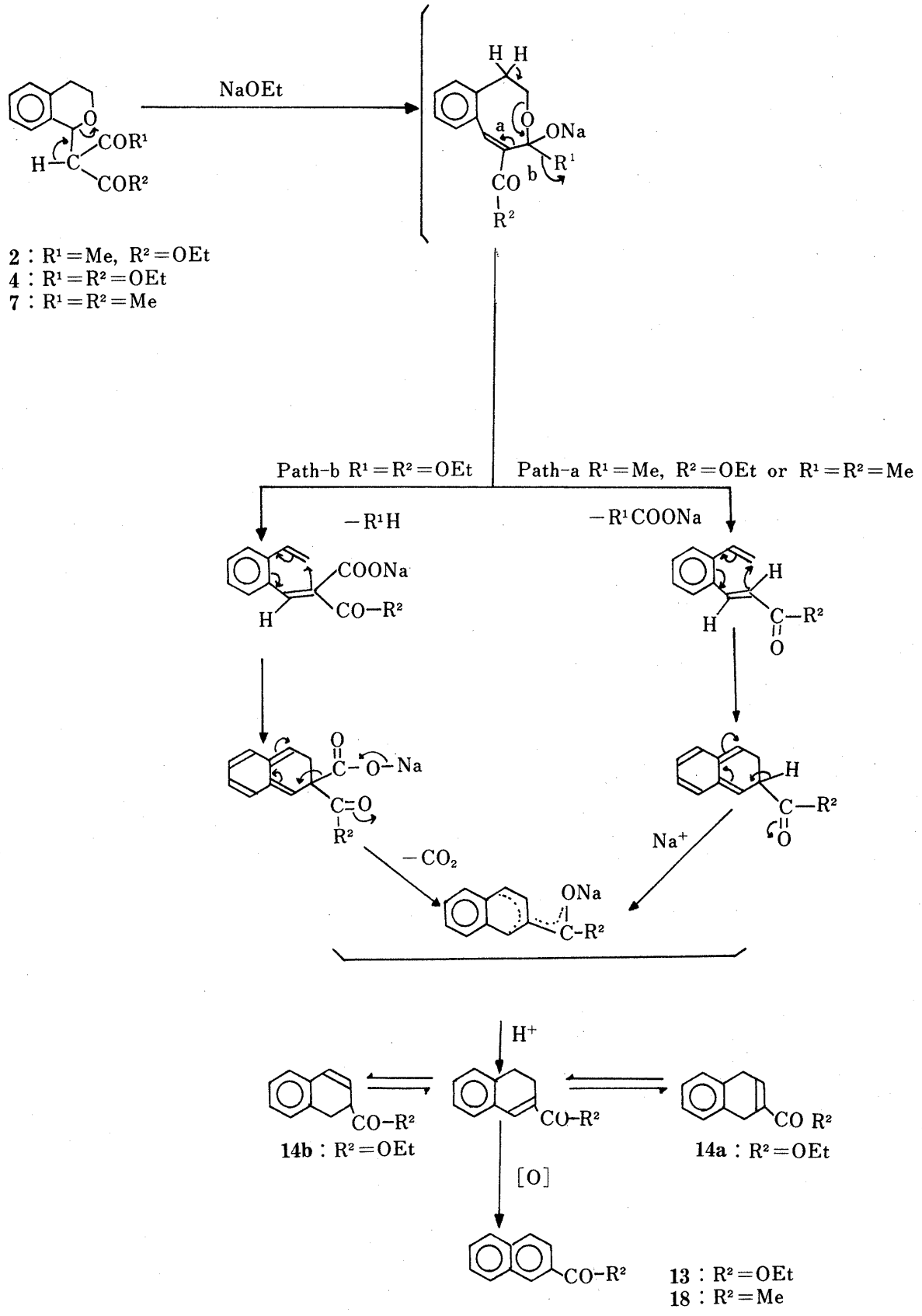
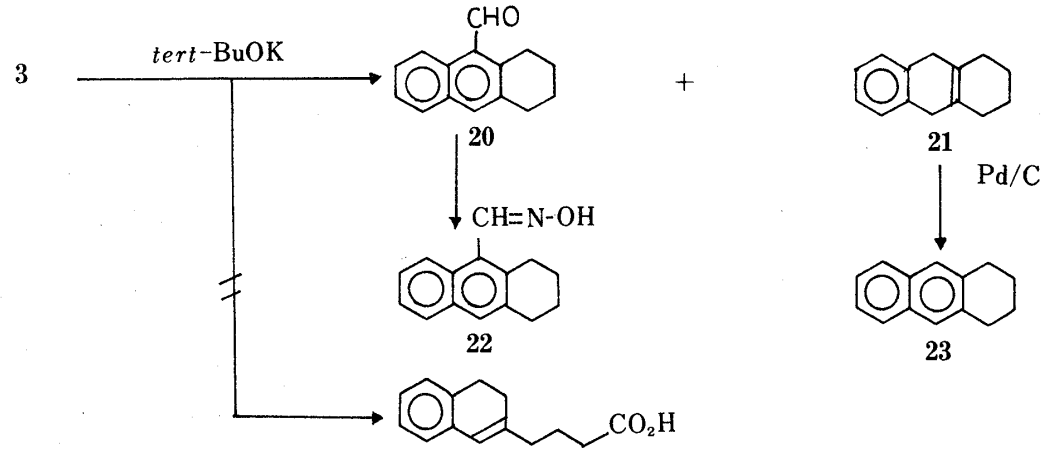


Chart 2



Mechanism :

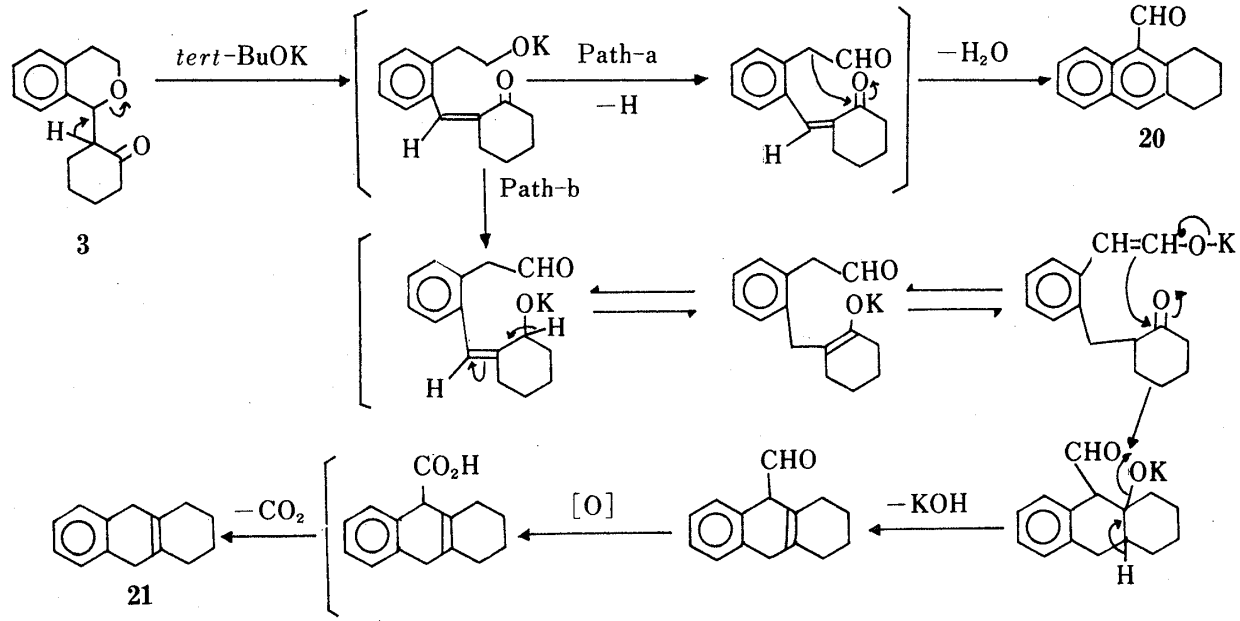


Chart 3

The mechanism of the conversion from **3** into **20** and **21** was assumed to be as shown in Chart 3. Compound **20** might be formed *via* path (a) by Claisen condensation of 2-(2-oxocyclohexylidenemethyl)phenylacetaldehyde which is formed by intermolecular Oppenauer oxidation of 2-(2-oxocyclohexylidenemethyl)-phenethyl alcohol in the presence of pottasium *tert*-butoxide. On the other hand, **21** might be formed *via* path (b) by Claisen condensation of 2-(2-oxocyclohexylmethyl)phenylacetaldehyde formed by intramolecular Oppenauer oxidation of 2-(2-oxocyclohexylidenemethyl)-phenethyl alcohol in the presence of pottasium *tert*-butoxide.

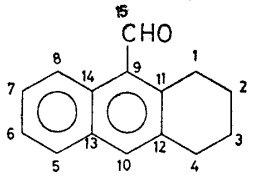


Fig. 1 **20**

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H-NMR spectra were obtained on a Hitachi R-24 spectrometer at 60 MHz, and ^{13}C-NMR spectra were obtained on a Hitachi R-22 FTS spectrometer at 22.6 MHz, with tetramethylsilane as an internal standard.

MS and GC-MS were measured with a Shimadzu LKB-9000 spectrometer. IR spectra were recorded on a Nihon Bunko A-102 spectrometer.

General Procedure for Syntheses of 1-Substituted Isochromans (4 and 5) by Reaction of 1 with Active Methylene Compounds in the Presence of a Catalyst——A Typical Example: 2-(1-Isochromanyl)-1-oxo-1,2,-3,4-tetrahydronaphthalene (5): A solution of 1 (12.8 g, 72 mmol), α-tetralone (7 g, 48 mmol), and $BF_3 \cdot Et_2O$ (2 ml) in dry benzene (30 ml) was heated at 40°C for 4 h, then cooled. The benzene layer was washed with 5% $KHCO_3$ and H_2O, dried over $MgSO_4$, and concentrated. The resulting precipitate was collected by suction and recrystallized from Et_2O–petr. ether to give 7.7 g (59%) of **5**, mp 123—124°C. ^{1}H-NMR ($CDCl_3$) δ: 1.72—3.12 (7H, m, C_2H, C_3H_2, C_4H_2, and $C_4'H_2$), 3.52—4.27 (2H, m, $C_3'H_2$), 5.85 (1H, d, J=3 Hz, $C_1'H$), 8.19 (1H, dd, J=7, 2 Hz, C_8H). MS *m/e*: 278 (M^+), 133 (C_9H_9O, base peak).

Data for **4** prepared as described above are listed in Table I. ^{1}H-NMR and mass spectral data are as follows.

Diethyl 1-Isochromanylmalonate (**4**): ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, t, J=7 Hz, $OCH_2\underline{CH_3}$), 1.20 (3H, t, J=7 Hz, $OCH_2\underline{CH_3}$), 3.50—4.34 (6H, m, $C_3'H_2$ and $2\times OC\underline{H_2}CH_3$), 3.94 (1H, d, J=6.5 Hz, CH), 5.45 (1H, d, J=6.5 Hz, $C_1'H$). MS *m/e*: 292 (M^+), 219 (M^+-CO_2Et), 133 (C_9H_9O, base peak).

General Procedure for Syntheses of 1-Substituted Isochromans (6—10) by Reaction of 1 with Active Methylene Compounds in the Absence of a Catalyst——A Typical Example: 3-(1-Isochromanyl)-2,4-dioxopentane (**7**) and 3-{2-[β-(1-isochromanyloxy)ethyl]benzylidene}acetylacetone (**8**): A mixture of **1** (5 g, 28 mmol) and acetylacetone (5.6 g, 56 mmol) was heated at 120°C for 2 h. The resulting mixture was chromatographed on a column of silica gel with petr. ether–AcOEt (4: 1). The first fraction gave 3.8 g (59%) of **7**, mp 90—91°C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (6H, s, $2\times CH_3$), 2.72—3.24 (2H, m, $C_4'H_2$), 3.43—4.49 (2H, m, $C_3'H_2$), 5.64 (1H, s, $C_1'H$), 17.45 (1H, s, enolic OH). MS *m/e*: 232 (M^+), 214 (M^+-H_2O), 189 (M^+-COCH_3), 133 (C_9H_9O, base peak). The second fraction gave 0.87 g (9%) of **8**, bp 150—155°C (0.005 mmHg). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, $COCH_3$), 2.21 (3H, s, $COCH_3$), 2.61—3.15 (2H, m, $C_2''H_2$), 3.09 (2H, t, J= 6 Hz, $OCH_2\underline{CH_2}$), 3.69—4.28 (4H, m, $C_3''H_2$ and $OC\underline{H_2}CH_2$), 5.52 (1H, s, $C_1''H$), 7.94 (1H, s, CH=C). MS *m/e*: 364 (M^+), 133 (C_9H_9O, base peak).

Data for the isochromans **6**—**10** prepared as described above are listed in Table I. ^{1}H-NMR and MS spectral data are as follows.

2-(1-Isochromanyl)-5-dimethyl-1,3-dioxocyclohexane (**6**): ^{1}H-NMR ($CDCl_3$) δ: 1.06 (3H, s, CH_3), 1.20 (3H, s, CH_3), 2.32 (4H, s, C_4H_2 and C_6H_2), 2.70—3.32 (2H, m, $C_4'H_2$), 3.76—4.52 (2H, m, $C_3'H_2$), 6.12 (1H, s, $C_1'H$), 9.42 (1H, s, OH). MS *m/e*: 272 (M^+), 254 (M^+-H_2O, base peak).

1-Isochromanylmalononitrile (**9**): ^{1}H-NMR ($CDCl_3$) δ: 2.71—3.26 (2H, m, $C_4'H_2$), 3.70—4.35 (2H, m, $C_3'H_2$), 4.29 (1H, d, J=4 Hz, CH), 5.29 (1H, d, J=4 Hz, $C_1'H$). MS *m/e*: 198 (M^+), 133 (C_9H_9O, base peak).

2-{2-[β-(1-Isochromanyloxy)ethyl]benzylidene}malononitrile (**10**): ^{1}H-NMR ($CDCl_3$) δ: 2.45—3.31 (2H, m, $C_4''H_2$), 3.09 (2H, t, J=6 Hz, $OCH_2\underline{CH_2}$), 3.68—4.23 (4H, m, $C_3''H_2$ and $OC\underline{H_2}CH_2$), 5.58 (1H, s, $C_1''H$), 8.41 (1H, s, CH=C). MS *m/e*: 330 (M^+), 133 (C_9H_9O, base peak).

Reaction of 1 with Diketene in the Presence of $TiCl_4$——A solution of **1** (5 g) in dry CH_2Cl_2 (40 ml) was added dropwise to a vigorously stirred solution of $TiCl_4$ (6.3 g) in dry CH_2Cl_2 (30 ml) at −70°C, and then a solution of diketene (5 g) in dry CH_2Cl_2 (10 ml) was added at once. The reaction mixture was stirred at −70°C for 1 h, and then abs. EtOH (20 ml) was added to the mixture. After being stirred at −20°C for 0.5 h, the reaction mixture was poured into an ice-cooled 10% K_2CO_3 solution. After removal of the insoluble yellow precipitate by filtration, the filtrate was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with sat. NaCl solution, and dried over $MgSO_4$. The solvent was evaporated off. The residue was chromatographed on a column of silica gel with petr. ether–AcOEt (8: 1) to give 5.25 g (71%) of ethyl 4-(1-isochromanyl)-3-oxobutanate (**11**), bp 125—130°C (0.006 mmHg). *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.75; H, 6.86. ^{1}H-NMR ($CDCl_3$) δ: 1.28 (3H, t, J=7 Hz, $OCH_2\underline{CH_3}$), 2.42—3.04 (2H, m, $C_4'H_2$), 3.00 (2H, d, J=6 Hz, CH_2), 3.55 (2H, s, $COCH_2CO$), 3.74—4.28 (2H, m, $C_3'H_2$), 4.21 (2H, q, J=7 Hz, $OC\underline{H_2}CH_3$), 5.26 (1H, t, J=6 Hz, $C_1'H$). MS *m/e*: 262 (M^+), 133 (C_9H_9O, base peak). IR ν_{max}^{neat} cm^{-1}: 1740, 1710 (C=O).

Reaction of 1 with Diketene without Catalyst——A solution of **1** (5 g) and diketene (5 g) in dry xylene (10 ml) was heated at 130°C for 5 h. Unreacted diketene was distilled off *in vacuo*, and the residue was chromatographed on a column of silica gel with petr. ether–AcOEt (6: 1). The first eluate gave 3.55 g (71%) of **1** and the second eluate gave 0.2 g (3%) of **2**, which was identical with an authentic sample (comparison of ^{1}H-NMR and IR spectra).

Diethyl 2-Ethyl-2-(1-isochromanyl)malonate (12)——NaH (50% oil, 0.4 g) was added to a solution of **4** (2 g) in dry dimethylformamide (DMF) (10 ml) with stirring and cooling, then a solution of EtI (4 g) in dry benzene (10 ml) was added dropwise to the mixture at room temperature. The mixture was heated at 50°C for 1 h, poured into ice water, and extracted with Et_2O. The Et_2O layer was washed with sat. NaCl solution, dried over $MgSO_4$, and concentrated. The residue was distilled to give 2 g (91%) of **12**, bp 130—140°C (0.01 mmHg). *Anal.* Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.53; H, 7.85. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, t, J=7 Hz, $CH_2\underline{CH_3}$), 1.02 (3H, t, J=7 Hz, $OCH_2\underline{CH_3}$), 1.22 (3H, t, J=7 Hz, $OCH_2\underline{CH_3}$), 2.12 (2H, q, J=7 Hz, $C\underline{H_2}CH_3$), 2.57—3.02 (2H, m, $C_4'H_2$), 3.43—4.44 (6H, m, $C_3'H_2$ and $2\times OC\underline{H_2}CH_3$), 5.54 (1H, s, $C_1'H$). MS *m/e*: 320 (M^+), 133 (C_9H_9O, base peak). IR ν_{max}^{neat} cm^{-1}: 1730 (C=O).

Reaction of 4 with NaOEt——Procedure a) A solution of **4** (19 g) in abs. EtOH (100 ml) was added to a solution of NaOEt (1.5 g of Na in 100 ml of abs. EtOH) in a stream of nitrogen with stirring. After refluxing for 3 h, the mixture was poured into ice water and extracted with Et_2O. The Et_2O layer was washed with sat. NaCl solution, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with petr. ether–AcOEt (16: 1). The first fraction gave 1 g (8%) of ethyl 1,2-dihydro-2-naphthoate (**14b**), colorless oil, bp 140—150°C (3 mmHg). *Anal.* Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: 77.30; H, 6.85. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, J=7 Hz, $OCH_2\underline{CH_3}$), 2.94—3.24 (3H, m, C_1H_2 and C_2H), 4.25 (2H, q, J=7 Hz, $OC\underline{H_2}CH_3$), 6.17 (1H, q, AB type, J=10, 2 Hz, C_3H), 6.64 (1H, q, AB type, J=10, 2 Hz, C_4H). MS *m/e*: 202 (M^+), 129 (M^+-CO_2Et, base peak). IR ν_{max}^{neat} cm^{-1}: 1710 (C=O). The second fraction gave 6.6 g (50%) of ethyl 1,4-dihydro-2-naphthoate (**14a**), colorless oil, bp 150°C (3 mmHg). *Anal.* Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.04; H, 6.79. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, t, J=8 Hz, $OCH_2\underline{CH_3}$), 3.59 (4H, s, with shoulder, C_1H_2 and C_4H_2), 4.32 (2H, q, J=8 Hz, $OC\underline{H_2}CH_3$). MS *m/e*: 202 (M^+), 129 (M^+-CO_2Et, base peak). IR ν_{max}^{neat} cm^{-1}: 1710 (C=O). The final fraction gave 0.39 g (3%) of ethyl 2-naphthoate (**13**), colorless oil, bp 155°C (5 mmHg). *Anal.* Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.85; H, 6.01. ^{1}H-NMR ($CDCl_3$) δ: 1.45 (3H, t, J=8 Hz, $OCH_2\underline{CH_3}$), 4.45 (2H, q, J=8 Hz, $OC\underline{H_2}CH_3$), 8.62 (1H, s, C_1H). MS *m/e*: 200 (M^+, base peak), 155 (M^+-OEt). IR ν_{max}^{neat} cm^{-1}: 1710 (C=O).

Procedure b) A solution of **4** (3.37 g) in abs. EtOH (10 ml) was added to a solution of NaOEt (0.29 g of Na in 10 ml of abs. EtOH) in a stream of dry air with stirring. After refluxing for 3 h, the resulting mixture was purified by the method described for procedure (a) to give 0.76 g (33%) of **13**, 0.41 g (21%) of **14a**, and 0.19 g (8%) of **14b**, respectively. The ^{1}H-NMR and GC-MS spectra of **13**, **14a**, or **14b** were identical with those of corresponding samples obtained by procedure (a).

The hydrolysis of **14a** with 10% KOH–MeOH gave 1,4-dihydro-2-naphthoic acid (**15**), mp 159—160°C (162°C).[7] Similarly, the hydrolysis of **13** gave 2-naphthoic acid (**16**), mp 182—184°C (184—185°C).[8] Compounds **15** and **16** were identical with the corresponding authentic samples (comparison of IR and ^{1}H-NMR spectra).

Dehydrogenation of 14a, b to Give Ethyl 2-Naphthoate (**13**)——A solution of a mixture of **14a** and **14b** (2 g) in *p*-cymene (30 ml) was refluxed with 5% Pd–carbon (1.5 g) for 5 h, then cooled. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was distilled to give 1.2 g (60%) of **13**, bp 155°C (5 mmHg), which was identical with an authentic sample as judged by comparison of ^{1}H-NMR spectra. The hydrolysis of **13** gave **16**, which was identical with an authentic sample (IR comparison).

Reaction of 2 with NaOEt——A solution of **2** (2.4 g) in abs. EtOH (20 ml) was added to a solution of NaOEt (0.31 g of Na in 20 ml of abs. EtOH) in a stream of nitrogen with stirring. After refluxing for 4 h, the mixture was poured into ice water and extracted with Et_2O. The Et_2O layer was washed with sat. NaCl solution, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with petr. ether–AcOEt (16: 1). The first fraction gave 0.06 g (3%) of **14b**, bp 150°C (5 mmHg) and the second fraction gave 0.55 g (30%) of **14a**, bp 150°C (5 mmHg). The third fraction gave 0.02 g (1%) of **13**. The ^{1}H-NMR spectra and GC-MS of **13**, **14a**, and **14b** were identical with those of corresponding authentic samples. The final fraction gave 0.42 g (21%) of ethyl 1-isochromanylacetate (**17**), bp 110—115°C (0.1 mmHg). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.60; H, 7.51. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, t, J=8 Hz, $OCH_2\underline{CH_3}$), 2.30—2.99 (2H, m, $C_4'H_2$), 2.81 (2H, d, J=5 Hz, CH_2), 3.61—4.25 (2H, m, $C_3'H_2$), 4.19 (2H, q, J=8 Hz, $OC\underline{H_2}CH_3$), 5.24 (1H, t, J=5 Hz, $C_1'H$). MS *m/e*: 220 (M^+), 133 (C_9H_9O, base peak). IR ν_{max}^{neat} cm^{-1}: 1735 (C=O).

Reaction of 7 with NaOEt——A solution of **7** (1.7 g) in abs. EtOH (20 ml) was added to a solution of NaOEt (0.17 g of Na in 20 ml of abs. EtOH) in a stream of nitrogen with stirring. After refluxing for 8 h, the mixture was poured into ice water and extracted with Et_2O. The Et_2O layer was washed with sat. NaCl solution, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with petr. ether–AcOEt (16: 1). The first eluate gave 0.03 g (2%) of 2-acetylnaphthalene (**18**) as a colorless oil, bp 135—140°C (3 mmHg). *Anal.* Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.66; H, 5.90. ^{1}H-NMR ($CDCl_3$) δ: 2.72 (3H, s, $COCH_3$), 8.58 (1H, s, C_1H). MS *m/e*: 170 (M^+, base peak), 127 (M^+-COCH_3). IR ν_{max}^{neat} cm^{-1}: 1680 (C=O). 2,4-Dinitrophenylhydrazone, mp 263—264°C (262°C).[11] *Anal.* Calcd for $C_{18}H_{14}N_4O_4$: C, 61.71; H, 4.03; N, 16.00. Found: C, 61.04; H, 3.89; N, 15.80. MS *m/e*: 350 (M^+, base peak). The second fraction gave 0.82 g (59%) of 1-isochromanylacetone (**19**) as a colorless oil, bp 105—110°C (0.02 mmHg). *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.73; H, 7.40. ^{1}H-NMR ($CDCl_3$) δ: 2.21 (3H, s, $COCH_3$), 2.68—3.11 (2H, m, $C_4'H_2$), 2.87 (2H, d, J=6 Hz, CH_2CO), 3.52—4.29 (2H, m, $C_3'H_2$), 5.23 (1H, t, J=6 Hz, $C_1'H$). MS *m/e*: 190 (M^+), 133 (C_9H_9O, base peak). IR ν_{max}^{neat} cm^{-1}: 1710 (C=O).

Reaction of 3 with *tert*-BuOK——Procedure a) A solution of **3** (2.91 g) in dry *tert*-BuOH (10 ml) was added to a solution of *tert*-BuOK (0.49 g of K in 10 ml of dry *tert*-BuOH) under a stream of nitrogen with stirring. After refluxing for 1.5 h, the resulting mixture was poured into ice water and extracted with Et_2O. The Et_2O layer was washed with sat. NaCl solution, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with petr. ether–AcOEt (16: 1). The first fraction gave 0.12 g (5%) of 1,2,3,4,9,10-hexahydroanthracene (**21**), which was recrystallized from MeOH under a nitrogen

atmosphere, mp 76—78°C (78°C).[13] ^{1}H-NMR ($CDCl_3$) δ: 1.54—2.21 (8H, m, C_1H_2, C_2H_2, C_3H_2, and C_4H_2), 3.20 (4H, s, with shoulder, C_9H_2 and $C_{10}H_2$), 7.09 (4H, s, with shoulder, Ar–H). MS *m/e*: 184 (M^+). The second fraction gave 0.69 g (26%) of 9-formyl-1,2,3,4-tetrahydroanthracene (**20**), bp 160°C (0.03 mmHg), mp 55—56°C (petr. ether). ^{1}H-NMR ($CDCl_3$) δ: 1.70—1.90 (4H, m, C_2H_2 and C_3H_2), 2.72—3.27 (4H, m, C_1H_2 and C_4H_2), 8.81 (1H, dd, J=8, 3 Hz, C_8H), 10.99 (1H, s, CHO). MS *m/e*: 210 (M^+, base peak), 181 (M^+−CHO). IR ν_{max}^{neat} cm^{-1}: 1680 (C=O). ^{13}C-NMR ($CDCl_3$) δ: 22.29, 23.07 (C_2 or C_3), 26.68 (C_4), 30.38 (C_1), 124.74, 126.43, 128.38, 128.38, 134.43 (C_5, C_6, C_7, C_8, or C_{10}), 128.64, 131.02, 132.70, 136.47, 142.94 (C_9, C_{11}, C_{12}, C_{13}, or C_{14}), 194.83 (C_{15}). The oxime of **20** was prepared according to the literature,[12] mp 158—159°C (dil. MeOH) (158.5—160°C).[12] *Anal.* Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.08; H, 6.56; N, 5.98. MS *m/e*: 225 (M^+), 208 (M^+−OH, base peak).

Dehydrogenation of 21 to give 1,2,3,4-Tetrahydroanthracene (23)——A solution of **21** (0.23 g) in *p*-cymene (20 ml) was refluxed with 5% Pd–carbon (0.5 g) for 5 h, then cooled. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was recrystallized from MeOH to give 0.13 g (59%) of **23**, mp 100—101°C (98—100°C).[14] *Anal.* Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.85. ^{1}H-NMR ($CDCl_3$). δ: 1.72—1.94 (4H, m, C_2H_2 and C_3H_2), 2.83—3.08 (4H, m, C_1H_2 and C_4H_2). MS *m/e*: 182 (M^+, base peak), 154 (M^+−CH_2=CH_2).

Procedure b): A solution of **3** (2.81 g) in dry *tert*-BuOH (10 ml) was added into a solution of *tert*-BuOK (0.48 g of K in 10 ml of dry *tert*-BuOH) in a stream of dry air with stirring. After refluxing for 1.5 h, the resulting mixture was purified by the method described for procedure (a) to give 0.2 g (8%) of **20** and 0.42 g (19%) of **21**. The ^{1}H-NMR and GC-MS spectra of **20** or **21** were identical with those of the corresponding samples obtained by procedure (a).

References and Notes

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