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Reactivity of Isocoumarins. II.[1] Reaction of 1-Ethoxyisochroman with Nucleophilic Reagents

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The $C_{(1)}$-position of 1-ethoxyisochroman (3) is very susceptible to attack by various nucleophilic reagents. Reaction of **3** with various alcohols, such as benzyl alcohols, N,N-dimethylaminoethanol and ethyl lactate, gave corresponding 1-alkoxyisochromans (**5**, **7**, **8**, and **9**). Reaction of **3** with phenols, such as phenol and methyl *p*-hydroxybenzoate, gave 1-(hydroxyphenyl)isochromans (**11**, **12**, **13**, and **16**). Some monoalkoxybenzenes were unreactive with **3** but 1,3-dimethoxybenzene gave corresponding 1-(dimethoxyphenyl)isochromans (**14** and **15**). Reaction of **3** with an emanine such as 1-morpholino-1-cyclohexene gave 2-(1-isochromanyl)-1-(4-morpholino)cyclohexene, which was hydrolyzed to give 2-(1-isochromanyl)cyclohexanone (**17**). Reaction of **3** with ketones, *i.e.*, cyclohexanone and ethyl acetoacetate, gave **17** and ethyl α-(1-isochromanyl)acetoacetate (**18**), respectively.

Keywords——reactivity; isocoumarins; 1-ethoxyisochroman; nucleophilic reagents; 1-alkoxyisochromans; 1-arylisochromans; 1-alkylisochromans; enamine

In a previous paper, it was reported that the $C_{(1)}$-hydroxyl group of 1,8-dihydroxy-3-(3-hydroxy-4-methoxyphenyl)isochroman (**1**) was easily replaced by an ethoxyl group in the course of recrystallization of **1** from ethanol, and that the ethoxyl group of the resulting 1-ethoxy-8-hydroxy-3-(3-hydroxy-4-methoxyphenyl)isochroman (**2**) was changed into a benzyloxy group when **2** was heated with benzyl alcohol.[1]

Rieche and Schmitz described some reaction of 1-ethoxyisochroman (**3**): Autoxidation of **3** in air gave bis(1-isochromanyl)ether,[3] while oxidation of **3** with hydrogen peroxide gave 3,4-dihydroisocoumarin (**4**).[4] Reaction of **3** with 2,4-dinitrophenylhydrazine, acetic anhydride, acetyl chloride, and sodium bisulfite gave 2-(2-hydroxyethyl)benzaldehyde-2,4-dinitrophenylhydrazone, 1-acetylisochroman, 1-chloroisochroman, and sodium 1-isochromanyl sulfate, respectively.[3]

This paper deals with the reactions of **3** with alcohols, phenols, aromatic ethers, enamines, and compounds having an active methylene group.

Heating of **3** with benzyl alcohol afforded 1-benzyloxyisochroman (**5**) in 70% yield. The resulting **5** tended to change gradually into **4** and benzaldehyde on standing in air over a period of several days. The GC–MS spectrum of the mixture obtained by heating **5** at 200—220° in air showed the presence of **4** (in 8% yield) and isochroman (**6**) (in 6% yield), together with small amounts of benzaldehyde and benzyl alcohol. Under the same conditions, (±)-1-(α-methylbenzyloxy)isochroman (**7**) prepared by heating **3** with (±)-α-methylbenzyl alcohol gave **4** as a main product, accompanied by small amounts of **6**, acetophenone, (±)-α-methylbenzyl alcohol, and styrene.

In order to clarify the effect of oxygen on the yield of **4** or **6** upon heating **5** or **7**, a stream of oxygen or nitrogen was blown through the flask during heating. A marked increase in the

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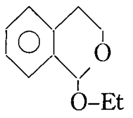
[1] Part I: M. Yamato, T. Ishikawa, T. Nagamatsu, S. Yoshikawa, and T. Koyama, *Chem. Pharm. Bull.*, **28**, 723 (1980).
[2] Location: *Tsushima-naka 1-1-1, Okayama 700, Japan.*
[3] A. Rieche and E. Schmitz, *Chem. Ber.*, **89**, 1254 (1956).
[4] A. Rieche and E. Schmitz, *Chem. Ber.*, **90**, 1094 (1957).



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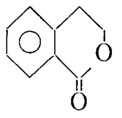

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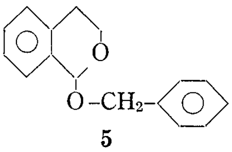

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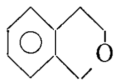

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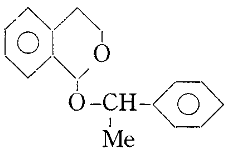

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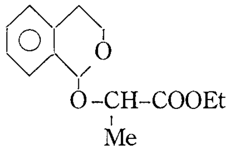
yield of **4** and a decrease in the yield of **6** were observed on heating **5** in oxygen; the yield of **4** rose to 47%. In contrast, in a stream of nitrogen, most of **5** was recovered unchanged. A benzene solution of **5** gave a positive test with *p*-aminodimethylaniline reagent after being refluxed in a stream of oxygen. This suggested the formation of a peroxide as an intermediate in this reaction.

Reaction of **3** with (±)-ethyl lactate and N,N-dimethylaminoethanol gave (±)-1-(α-ethoxycarbonylethoxy)isochroman (**8**) (in 63% yield) and 1-(N,N-dimethylaminoethoxy)-isochroman (**9**) (in 50% yield), respectively. Heating of **3** with phenylmethanethiol gave 1-benzylthioisochroman (**10**) in 59% yield.



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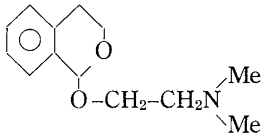

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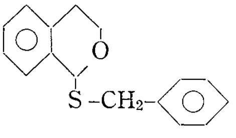


10

In the reaction of **3** with phenol, 1-(2-hydroxyphenyl)isochroman (**11**), 1-(4-hydroxyphenyl)isochroman (**12**), and 2,4-bis(1-isochromanyl)phenol (**13**) were obtained in 21%, 22%, and 9% yields, respectively.

In the heating of **3** with aromatic ethers, monoalkoxybenzene derivatives such as anisole, phenetole, isopropoxybenzene, and benzyloxybenzene were all unreactive, but 1,3-dimethoxy-

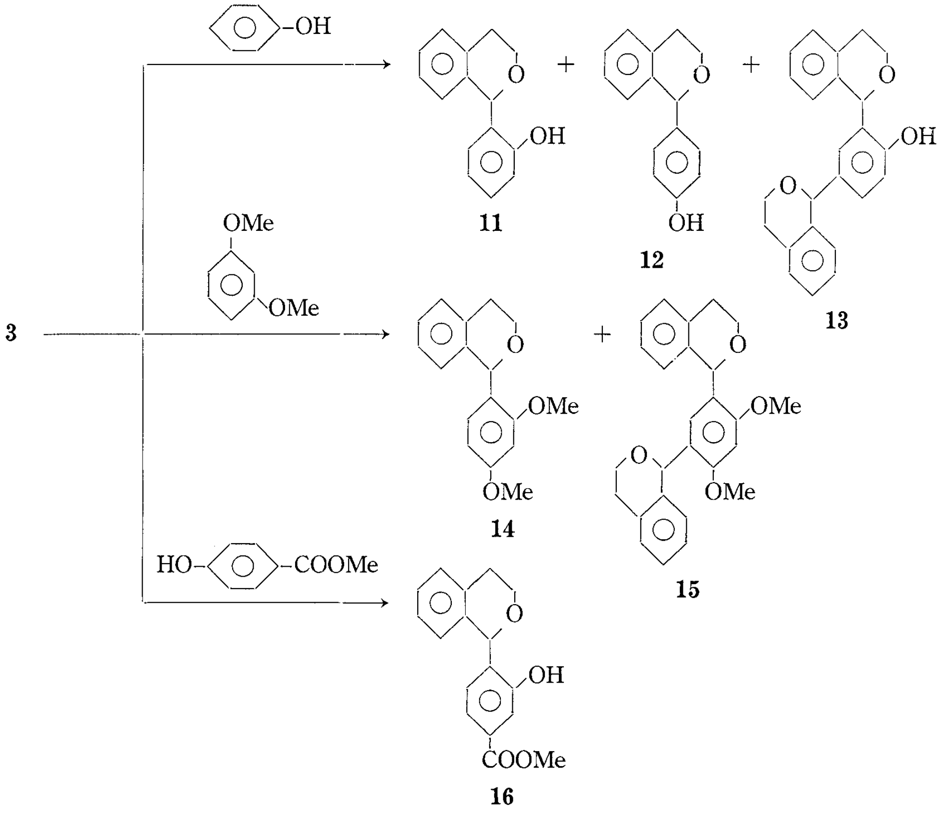
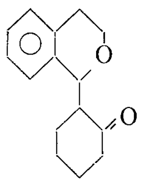


Chart 1

benzene was reactive, and gave 1-(2,4-dimethoxyphenyl)isochroman (**14**) in 37% yield together with a small amount of 4,6-bis(1-isochromanyl)-1,3-dimethoxybenzene (**15**).

Although methyl salicylate and *o*-hydroxyacetophenone were unreactive with **3**, the reaction of **3** with methyl *p*-hydroxybenzoate gave 1-(2-hydroxy-4-methoxycarbonylphenyl)-isochroman (**16**) in 41% yield under the same conditions.



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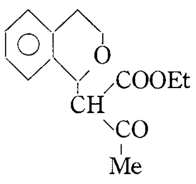

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Heating of **3** with 1-morpholino-1-cyclohexene followed by hydrolysis of the resulting product gave 2-(1-isochromanyl)cyclohexanone (**17**) in 51% yield. The product **17** was also obtained by heating **3** with cyclohexanone. Similarly, reaction of **3** with ethyl acetoacetate gave (±)-ethyl α-(1-isochromanyl)acetoacetate (**18**) in 25% yield.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. PMR spectra were obtained on a Hitachi R-22 spectrometer at 90 MHz, and CMR spectra were obtained on a Hitachi R-22 FTS spectrometer at 22.6 MHz, employing tetramethylsilane as an internal standard. Mass and GC–MS spectra were measured with a Shimadzu LKB-9000 spectrometer. IR spectra were recorded on a Nihon Bunko A-102 spectrometer. GC was run on a Shimadzu GC-6 AM gas chromatograph using a glass column (1.5 m×3 mm or 2 m×3 mm) packed with 3% OV-1 or OV-17. Optical rotations were measured on a Nihon Bunko DIP-4 digital polarimeter.

1-Benzyloxyisochroman (5)——A mixture of **3** (5 g) and benzyl alcohol (3 g) was heated with stirring at 140—150° for 4 hr. The resulting product was purified by distillation *in vacuo* to give 4.7 g (70%) of **5**, bp 170—175° (5 mmHg). *Anal.* Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.88; H, 6.76. PMR (CCl_4) δ: 2.25—3.07 (2H, m, $C_{(4)}H_2$), 3.25—4.38 (2H, m, $C_{(3)}H_2$), 4.56 (1H, d, J=13 Hz, O-C$\underline{H}$-C_6H_5), 4.77 (1H, d, J=13 Hz, O-C$\underline{H}$-C_6H_5), 5.40 (1H, s, $C_{(1)}H$), 6.65—7.58 (9H, m, aromatic protons). MS *m/e*: 240 (M^+), 149 ($M^+-CH_2C_6H_5$), 133 ($M^+-O-CH_2-C_6H_5$).

Pyrolysis of 5——Procedure a) Five grams of **5** was heated in air with stirring at 200—220° for 4 hr. The resulting mixture was chromatographed on a silica gel column, eluting with CH_2Cl_2–benzene, to give 0.23 g (6%) of **6**, bp 87—88° (10 mmHg), 0.33 g (8%) of **4**, bp 157—160° (11 mmHg), a small amount of benzaldehyde, and benzyl alcohol. The PMR, GC, and GC–MS spectra of samples were identical with those of authentic samples of **6**, **4**, benzaldehyde, and benzyl alcohol, respectively.

Procedure b) Two grams of **5** was heated at 200—220° in a stream of oxygen for 4 hr with stirring. The resulting mixture was chromatographed on a silica gel column, eluting with CH_2Cl_2–benzene, to give 0.58 g (47%) of **4**, bp 157—160° (11 mmHg), which was identified by comparing its PMR and MS spectra with those of authentic **4**.

(±)-1-(α-Methylbenzyloxy)isochroman (7)——A mixture of **3** (3 g) and (±)-α-methylbenzyl alcohol (2.5 g) was heated with stirring at 140—150° for 3 hr. The resulting product was purified by distillation *in vacuo* to give 3.6 g (84%) of **7**, bp 175—180° (5 mmHg). *Anal.* Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.31; H, 6.95. PMR ($CDCl_3$) δ: 1.45 (3H, d, J=6 Hz, CH_3), 2.42—3.30 (2H, m, $C_{(4)}H_2$), 3.40—4.52 (2H, m, $C_{(3)}H_2$), 4.90 (1H, q, J=6 Hz, CH), 5.20 (1H, s, $C_{(1)}H$), 6.60—7.50 (9H, m, aromatic protons). MS *m/e*: 254 (M^+), 133 ($M^+-O-CH(CH_3)-C_6H_5$).

Pyrolysis of 7——Three grams of **7** was heated at 200—220° with stirring for 4 hr in air. The resulting products were analyzed by GC without purification. The GC spectrum gave five peaks, a major one and four minor ones. The GC–MS spectrum of these peaks showed that the major peak was due to **4** and the four minor peaks to **6**, acetophenone, (±)-α-methylbenzyl alcohol, and styrene, respectively.

(±)-1-(α-Ethoxycarbonylethoxy)isochroman (8)——A mixture of **3** (5 g) and (±)-ethyl lactate (7 g) was heated with stirring at 140—150° for 2 hr. The resulting product was purified by distillation *in vacuo* to give 4.45 g (63%) of **8**, bp 140—141° (2 mmHg). *Anal.* Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.32; H, 7.38. PMR ($CDCl_3$) δ: 1.28 (3H, t, J=6 Hz, O-CH_2-C$\underline{H}_3$), 1.43 (3H, d, J=6 Hz, CH_3), 2.30—3.25 (2H, m, $C_{(4)}H_2$), 3.65—4.60 (5H, m, $C_{(3)}H_2$, CH, and O-C$\underline{H}_2$-CH_3), 5.65 (1H, s, $C_{(1)}H$), 7.04—7.30 (3H, m, aromatic protons), 7.51 (1H, d.d, J=5 and 3 Hz, $C_{(8)}H$). MS *m/e*: 250 (M^+), 149 ($M^+-\underset{CH_3}{\underset{|}{CH}}-COOC_2H_5$), 133 ($M^+-O\underset{CH_3}{\underset{|}{CH}}-COOC_2H_5$). IR ν_{max}^{neat} cm^{-1}: 1730 (C=O).

Reaction of 3 with Phenol——A mixture of **3** (15 g) and phenol (7.95 g) was heated at 150—160° for 3 hr. The reaction mixture was chromatographed on a column of silica gel, eluting with CH_2Cl_2. The first fraction gave 3.97 g (21%) of 1-(2-hydroxyphenyl)isochroman (**11**), which was recrystallized from MeOH, mp 150—151°. *Anal.* Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.32; H, 6.20. PMR ($CDCl_3$) δ: 2.57—3.11 (2H, m, $C_{(4)}H_2$), 3.64—4.37 (2H, m, $C_{(3)}H_2$), 6.00 (1H, s, $C_{(1)}H$), 6.72—7.08 (8H, m, aromatic protons), 7.90 (1H, s, OH). CMR ($CDCl_3$) δ: 78.77 ($C_{(1)}$), 64.18 ($C_{(3)}$), 28.47 ($C_{(4)}$), 126.21, 127.43 ($C_{(5)}$, $C_{(8)}$), 128.93, 128.43 ($C_{(6)}$, $C_{(7)}$), 132.94, 135.33 ($C_{(9)}$, $C_{(10)}$), 126.20 ($C_{(1')}$), 155.68 ($C_{(2')}$), 117.26 ($C_{(3')}$), 129.55 ($C_{(4')}$), 129.71 ($C_{(5')}$), 119.62 ($C_{(6')}$). MS *m/e*: 226 (M^+), 208 (M^+-H_2O), 181 (M^+-COOH). The second fraction gave 2,4-bis(1-isochromanyl)phenol (**13**), (2.85 g, 9%), which was recrystallized from pet. ether, mp 52—53.5°. *Anal.* Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.36; H, 6.30. PMR ($CDCl_3$) δ: 2.71—3.34 (4H, m, $2\times C_{(4)}H_2$), 3.62—4.38 (4H, m, $2\times C_{(3)}H_2$), 5.57 (1H, s, $C_{(1)}H$), 5.71 (1H, s, $C_{(1)}H$), 6.66—7.36 (12H, m, aromatic protons and OH). MS *m/e*: 358 (M^+). The final fraction gave 4.26 g (22%) of 1-(4-hydroxyphenyl)-isochroman (**12**), which was recrystallized from benzene, mp 113—114.5°. *Anal.* Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.39; H, 6.33. PMR ($CDCl_3$) δ: 2.60—3.11 (2H, m, $C_{(4)}H_2$), 3.52—4.32 (2H, m, $C_{(3)}H_2$), 5.20 (1H, broad s, OH), 5.71 (1H, s, $C_{(1)}H$), 6.74 (2H, d.d, $J=8$ and 2 Hz, $C_{(3')}H$ and $C_{(5')}H$), 7.04—7.27 (6H, m, aromatic protons). CMR ($CDCl_3$) δ: 79.27 ($C_{(1)}$), 63.56 ($C_{(3)}$), 28.83 ($C_{(4)}$), 124.49, 126.60 ($C_{(5)}$, $C_{(8)}$), 126.71, 126.96 ($C_{(6)}$, $C_{(7)}$), 133.83, 137.22 ($C_{(9)}$, $C_{(10)}$), 128.66 ($C_{(1')}$), 130.41 ($C_{(2')}$), 115.37 ($C_{(3')}$), 155.91 ($C_{(4')}$), 115.37 ($C_{(5')}$), 130.41 ($C_{(6')}$).

Reaction of 3 with 1,3-Dimethoxybenzene——A mixture of **3** (5 g) and 1,3-dimethoxybenzene (6.2 g) was heated at 170—180° for 3 hr. After cooling the mixture, the resulting precipitate was collected by suction and recrystallized from cyclohexane to give 0.58 g (5%) of 4,6-bis(1-isochromanyl)-1,3-dimethoxybenzene (**15**), mp 198—200°. *Anal.* Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.64; H, 6.48. PMR ($CDCl_3$) δ: 2.54—2.97 (4H, m, $2\times C_{(4)}H_2$), 3.81 (6H, s, $2\times OCH_3$), 3.93—4.18 (4H, m, $2\times C_{(3)}H_2$), 6.40 (2H, s, $2\times C_{(1)}H$), 6.52—7.23 (10H, m, aromatic protons). MS *m/e*: 402 (M^+), 269 ($M^+-C_9H_9O$), 133 (C_9H_9O). The mother liquid was chromatographed on a column of alumina, eluting with pet. ether–Et_2O (4: 1) to give 2.8 g (37%) of 1-(2,4-dimethoxyphenyl)isochroman (**14**), a viscous oil, bp 150—160° (0.07 mmHg). *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.58; H, 6.99. PMR ($CDCl_3$) δ: 2.64—3.05 (2H, m, $C_{(4)}H_2$), 3.77 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 3.87—4.22 (2H, m, $C_{(3)}H_2$), 6.18 (1H, s, $C_{(1)}H$), 6.37 (1H, d.d, $J=9$ and 2 Hz, $C_{(5')}H$), 6.51 (1H, d, $J=2$ Hz, $C_{(3')}H$), 6.96 (1H, d, $J=9$ Hz, $C_{(6')}H$), 6.73—7.11 (4H, m, aromatic protons). MS *m/e*: 270 (M^+), 255 (M^+-CH_3), 239 (M^+-OCH_3).

1-(2-Hydroxy-4-methoxycarbonylphenyl)isochroman (16)——A mixture of **3** (5 g) and methyl *p*-hydroxybenzoate (4.3 g) was heated with stirring at 150—160° for 3 hr. The resulting product was purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 3.22 g (41%) of **16** (mp 142—143.5°). *Anal.* Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.88; H, 5.85. PMR (CD_3COCD_3) δ: 2.55—3.15 (2H, m, $C_{(4)}H_2$), 3.79 (3H, s, OCH_3), 3.75—4.45 (2H, m, $C_{(3)}H_2$), 6.18 (1H, s, $C_{(1)}H$), 6.75—7.19 (5H, m, aromatic protons), 7.87 (1H, d, $J=2$ Hz, $C_{(6')}H$), 7.93 (1H, d.d, $J=5$ and 2 Hz, $C_{(4')}H$), 9.08 (1H, broad s, OH). MS *m/e*: 284 (M^+), 266 (M^+-H_2O), 253 (M^+-OCH_3), 239 (M^+-COOH). IR ν_{max}^{Nujol} cm^{-1}: 3250 (OH), 1700 (C=O).

1-Benzylthioisochroman (10)——A mixture of **3** (10 g) and phenylmethanethiol (6.97 g) was heated with stirring at 100° for 1.5 hr. The resulting product was purified by column chromatography on silica gel, eluting with benzene to give 8.5 g (59%) of **10** as an oil, bp 156—159° (0.06 mmHg). *Anal.* Calcd for $C_{16}H_{16}OS$: C, 74.98; H, 6.29. Found: C, 74.90; H, 6.23. PMR ($CDCl_3$) δ: 2.35—3.25 (2H, m, $C_{(4)}H_2$), 3.70—4.65 (2H, m, $C_{(3)}H_2$), 3.79 (1H, s, $S-C\underline{H}-C_6H_5$), 3.89 (1H, s, $S-C\underline{H}-C_6H_5$), 5.99 (1H, s, $C_{(1)}H$), 7.05 (5H, broad s, aromatic protons), 7.16—7.35 (4H, m, aromatic protons). MS *m/e*: 256 (M^+), 133 ($M^+-S-CH_2-C_6H_5$).

1-(N,N-Dimethylaminoethoxy)isochroman (9)——A mixture of **3** (3 g), N,N-dimethylaminoethanol (1.7 g), and dry pyridine (1.5 g) was heated with stirring at 155° for 24 hr. The resulting product was purified by distillation *in vacuo* to give 1.85 g (50%) of **9**, bp 126—131° (4 mmHg). *Anal.* Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.32; H, 8.66; N, 6.24. PMR ($CDCl_3$) δ: 2.21 (6H, s, $-N(CH_3)_2$), 2.40—2.99 (4H, m, $C_{(4)}H_2$ and CH_2-N), 3.38—4.27 (4H, m, $C_{(3)}H_2$ and $O-CH_2$), 5.45 (1H, s, $C_{(1)}H$), 6.86—7.42 (4H, m, aromatic protons). MS *m/e*: 221 (M^+), 133 ($M^+-O-CH_2CH_2N(CH_3)_2$).

2-(1-Isochromanyl)cyclohexanone (17)——Method A) A mixture of **3** (4.3 g) and 1-morpholino-1-cyclohexene (4 g) was heated with stirring at 150—160° for 2 hr. The resulting reactant was chromatographed on a column of alumina, eluting with CH_2Cl_2 to give 4.3 g (60%) of 2-(1-isochromanyl)-1-(4-morpholino)-cyclohexene, bp 180° (0.09 mmHg). *Anal.* Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.13; H, 8.45; N, 4.64. PMR ($CDCl_3$) δ: 1.42—2.50 (8H, m, $C_{(3')}H_2$, $C_{(4')}H_2$, $C_{(5')}H_2$, and $C_{(6')}H_2$), 2.70—3.05 (6H, m, $C_{(4)}H_2$ and $N\left\langle\begin{matrix}CH_2-\\CH_2-\end{matrix}\right.$), 3.61—4.10 (6H, m, $C_{(3)}H_2$ and $O\left\langle\begin{matrix}CH_2-\\CH_2-\end{matrix}\right.$), 5.42 (1H, s, $C_{(1)}H$), 7.01—7.38 (4H, m, aromatic protons). MS *m/e*: 299 (M^+), 133 (C_9H_9O). A solution of 2-(1-isochromanyl)-1-(4-morpholino)cyclohexene (1.94 g) in 10 ml of $CHCl_3$ was mixed with 5 ml of conc. HCl and 5 ml H_2O. The solution was refluxed on a water-bath for 1.5 hr. The $CHCl_3$ layer was washed with sat. NaCl solution, dried over $MgSO_4$, and the solvent was evaporated off. The residue was chromatographed on a column of silica gel, eluting with CH_2Cl_2 to give 0.76 g (51%) of **17**, bp 110° (0.08 mmHg). *Anal.* Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.12; H, 7.84. PMR ($CDCl_3$) δ: 1.30—2.11 (6H, m, $C_{(3')}H_2$, $C_{(4')}H_2$, and $C_{(5')}H_2$), 2.28—3.05 (5H, m, $C_{(4)}H_2$, $C_{(2')}H$, and $C_{(6')}H_2$), 3.53—4.34 (2H, m, $C_{(3)}H_2$), 5.46 (1H, d, $J=2$ Hz, $C_{(1)}H$), 7.12

(4H, s with shoulder, aromatic protons). MS *m/e*: 230 (M^+), 201 ($M^+ - CO\text{–}H$), 185 ($M^+ - COOH$). IR ν_{max}^{neat} cm^{-1}: 1700 (C=O).

Method B) A mixture of **3** (3 g) and cyclohexanone (3.4 g) was heated with stirring at 140—150° for 2 hr. After the reaction, unreacted cyclohexanone was removed by distillation *in vacuo*, and the residue was chromatographed on a silica gel column, eluting with CH_2Cl_2 to give 1.29 g (33%) of **17**, which was identified by comparing its PMR, MS, and IR spectra with those of **17** prepared by method A.

(±)-Ethyl α-(1-Isochromanyl)acetoacetate (**18**)——A mixture of **3** (3 g) and ethyl acetoacetate (2.5 g) was heated with stirring at 140—150° for 2 hr. The resulting reaction mixture was purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 1.1 g (25%) of **18**, bp 120—130° (0.1 mmHg). *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.49; H, 7.06. PMR ($CDCl_3$) δ: 1.22 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 2.23 (3H, s, $COCH_3$), 2.70—3.22 (2H, m, $C_{(4)}H_2$), 3.73—4.39 (4H, m, $C_{(3)}H_2$ and $C\underline{H}_2CH_3$), 3.96 (1H, d, $J=7$ Hz, COCH), 5.53 (1H, d, $J=7$ Hz, $C_{(1)}H$), 7.11 (4H, s with shoulder, aromatic protons). MS *m/e*: 262 (M^+), 219 ($M^+ - COCH_3$), 217 ($M^+ - OCH_2CH_3$), 189 ($M^+ - COOC_2H_5$). IR ν_{max}^{neat} cm^{-1}: 1700 (C=O).