solid, which was solidified on trituration with petroleum ether and recrystallization from petroleum ether gave pure (IX) (287 mg, 37.9%) as needles, mp 123—124.5°. *Anal.* Calcd. for $C_{27}H_{45}OCl$: C, 77.01; H, 10.77. Found: C, 77.13; H, 10.85. $[\alpha]_D^{18}$ −43.9° (c=1.00, $CHCl_3$); IR ν_{max}^{KBr} (cm^{-1}): 3300 (OH); NMR δ: 0.71 (s, 3H, 18–Me), 1.60 (s, 1H, OH), 3.60 (m, 1H, 3–H), 3.58 and 3.83 (dd, 2H, J=10 Hz, 19–CH_2Cl), and 5.64 ppm (m, 1H, vinylic).

Reaction of V with LiBr——A solution of V (104 mg) and anhydrous LiBr (47 mg) in isopropanol (20 ml) was gently refluxed. After 5.5 hr, TLC showed the presence of two products with the absence of unchanged starting material. The solution was concentrated to about 5 ml *in vacuo* and poured into ice–H_2O. The resulting mixture was extracted with ether. The ether was washed with H_2O and dried over Na_2SO_4. The residue obtained after evaporation of the ether was proved to be a mixture of III and VIII by the NMR spectroscopy. The ratio of III and VIII was estimated to be 1: 2 on the basis of integration of their C_{18}–methyl signals in the NMR spectrum.

Rearrangement of VIII to 6β-Bromomethyl-19-norcholest-5(10)-en-3β-ol (III)——(i) A solution of VIII (274 mg) in glacial AcOH (28 ml) was heated at 80—90° for 5 hr. TLC then showed complete disappearance of the starting material. The resulting solution was cooled to room temperature and shaken with a mixture of ether and H_2O. The separated aqueous layer was extracted with ether. The combined ether was washed with H_2O, 5% $NaHCO_3$, and H_2O. The ether solution was dried over Na_2SO_4 and evaporated to dryness *in vacuo*. The residual oil was chromatographed on silica gel eluting with $CHCl_3$ to give III (211 mg, 77%) as glass. *Anal.* Calcd. for $C_{27}H_{45}OBr$: C, 69.66; H, 9.74. Found: C, 69.64; H, 9.68. $[\alpha]_D^{18}$ +38.5° (c=1.00, $CHCl_3$); IR ν_{max}^{KBr} (cm^{-1}): 3360 (OH); NMR δ: 0.68 (s, 3H, 18–Me), 1.58 (s, 1H, OH), 3.30 (t, 1H, J=10 Hz, 6–CH_2Br) and 3.61 (dd, 1H, J=10, 2 Hz, 6–CH_2Br), and 4.0 ppm (m, 1H, 3–H).

(ii) A solution of VIII (100 mg) in acetonitrile (15 ml) was refluxed for 22.5 hr. After removal of the solvent *in vacuo*, the residual oil was chromatographed on silica gel eluting with $CHCl_3$ to give III (72 mg, 72%) as glass.

Rearrangement of IX to 6β-Chloromethyl-19-norcholest-5(10)-en-3β-ol (IV)——A solution of IX (183 mg) in glacial AcOH (20 ml) was heated at 80—90° for 13.5 hr. After the reaction mixture was treated as in the case of rearrangement of VIII, the obtained residual oil was chromatographed on silica gel. The first effluent with $CHCl_3$ gave a mixture of the acetyl compounds of both IX and IV (81 mg), as shown by NMR analysis. The second effluent with $CHCl_3$ gave IV (39 mg, 21.3%) as glass. *Anal.* Calcd. for $C_{27}H_{45}OCl$: C, 77.01; H, 10.77. Found: C, 76.86; H, 10.76. $[\alpha]_D^{20}$ +22.2° (c=0.60, $CHCl_3$); IR ν_{max}^{KBr} (cm^{-1}): 3380 (OH); NMR δ: 0.67 (s, 3H, 18–Me), 1.54 (s, 1H, OH), 3.40 (t, 1H, J=10 Hz, 6–CH_2Cl) and 3.68 (dd, 1H, J=10, 2 Hz, 6–CH_2Cl), and 4.0 ppm (m, 1H, 3–H). The third effluent with $CHCl_3$ gave the starting material (69 mg).

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Photodimerization of Ethyl 2-Ethoxy-1,2-dihydroquinoline-1-carboxylate

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Irradiation of ethyl 2-ethoxy-1,2-dihydroquinoline-1-carboxylate (**1**) in ether and ethanol resulted in the formation of a *trans* head-to-head dimer **2** and an ethanol adduct **5** in 66 and 45% yields, respectively.

Various types of photochemical reactions of 1-acyl-1,2-dihydroquinolines have been reported. These include (i) rearomatization to quinolines,[2,3] (ii) (2+2)π dimerization,[2] (iii)

1) Location: *133-1, Yamada-kami, Suita, Osaka, 565, Japan.*
2) P.T. Izzo and A.S. Kende, *Tetrahedron Letters*, **1966**, 5731.
3) Irradiation of ethyl 2-phenyl-1,2-dihydroquinoline-1-carboxylate in ether gave a mixture of at least four products, from which 2-phenylquinoline was isolated in 20% yield (unpublished result).

isomerization of 1-cyano-2-hydroxy-1,2-dihydroquinoline to N-cyano-*o*-aminocinnamaldehyde,[4] (iv) isomerization to allenic compounds,[5] (v) isomerization to 2,3-homoindoles,[6,7] (vi) isomerization to benzoazetines,[7] and (vii) addition of alcoholic solvents.[5] These reaction courses highly depend upon the nature and position of the substituent on the quinoline ring (in particular at the 1 and 4 positions), and the solvent used. We now examined the photochemical behavior of ethyl 2-ethoxy-1,2-dihydroquinoline-1-carboxylate (**1**) in order to see the effect of an ethoxyl group at the 2-position.

Irradiation of a solution of **1** in ether at room temperature with a 300W high-pressure mercury lamp in a Pyrex vessel led to the formation of a single photoproduct **2** in 66% yield. The *trans* head-to-head dimeric structure of the photoproduct was apparent from its spectral data and chemical transformation. Its elemental analysis and molecular weight determination confirmed the dimeric structure. The nuclear magnetic resonance (NMR) spectrum indicates a singlet (Ha) at τ 4.13, and two doublets due to cyclobutane ring protons at τ 6.85 and 7.15 with a coupling constant of 8 Hz. Reduction of **2** with lithium aluminum hydride gave compound **3** in 90% yield, whose structure and stereochemistry have been firmly established.[8]

This result is in sharp contrast to the behavior of ethyl 2-cyano-1,2-dihydroquinoline-1-carboxylate (**6**), which undergoes ready 1,2-bond cleavage followed by 1,5-hydrogen shift to give an allenic compound (**7**).[4] It is suggested that the process leading to allenes is greatly affected by the nature of the substituent at the 2-position. Similar $(2+2)\pi$ photodimerizations have been reported with 1-benzoyl-2-cyano-1,2-dihydroquinoline (the structure and stereochemistry of the dimer were not determined),[2] quinolin-2-ones,[8] and coumarines.[9]

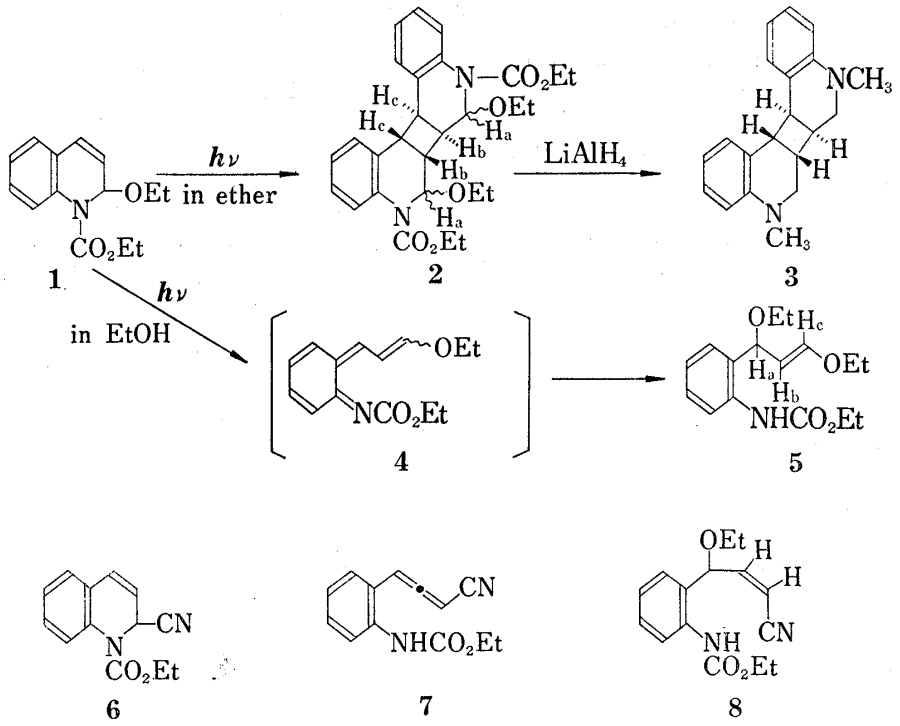

Chart 1

4) J. Kolc and R.S. Becker, *J. Chem. Soc.* (*B*), **1972**, 17.
5) M. Ikeda, S. Matsugashita, H. Ishibashi, and Y. Tamura, *J. C. S. Chem. Commun.*, **1973**, 922.
6) M. Ikeda, S. Matsugashita, F. Tabusa, H. Ishibashi, and Y. Tamura, *J. C. S. Chem. Commun.*, **1974**, 433.
7) M. Ikeda, S. Matsugashita, F. Tabusa, H. Ishibashi, and Y. Tamura, *J. C. S. Chem. Commun.*, **1975**, 575.
8) O. Buchardt, *Acta Chem. Scand.*, **18**, 1389 (1964).
9) *a*) G.S. Hammond, C.A. Stout, and A.A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964); *b*) H. Morrison, H. Curtius, and T. McDowell, *ibid.*, **88**, 5415 (1966); *c*) C.H. Krauch, S. Farid, and G.O. Schenck, *Chem. Ber.*, 99, 624 (1966).

The dimerization was completely suppressed by the use of alcoholic solvent. Thus, irradiation of **1** in ethanol afforded an oily product **5** in 45% yield, whose structure was assigned on the basis of its high resolution mass spectrometry and spectral comparison with those of the related compound **8**.[4] The *trans*-stereochemistry of the double bond was tentatively assigned by comparison of the coupling constant of 12 Hz with the value reported for *trans*-ethyl vinyl ether.[10] This reaction is presumed to proceed *via* benzoazahexatriene intermediate **4**.[5]

Experimental

All melting points are uncorrected. The NMR spectra were recorded with a Hitachi R-20A (60 MHz) spectrometer with tetramethylsilane as internal reference, infrared (IR) spectra with a Hitachi EPI-G2 spectrophotometer, ultraviolet (UV) spectra with a Hitachi 124 spectrophotometer and a high resolution mass spectrum with a JEOL-JMS-OlSG instrument (75 eV). A molecular weight was determined with a Hitachi 115 Molecular Weight apparatus. Irradiations were carried out using an Eikosha 300W high-pressure mercury lamp in a Pyrex vessel.

Irradiation of 1 in Ether——A solution of **1** (7.5 g) in ether (1 liter) was irradiated until the starting material disappeared (15 hr) (checked by UV spectra). Evaporation of ether afforded crude crystalline material which was recrystallized from petroleum benzin to give colorless needles of **2** (4.95 g) (66%), mp 186—187°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690 (C=O). UV λ_{max}^{EtOH} nm: 207 (log ε 4.62), 233 (4.40). NMR ($CDCl_3$) τ: 2.49—3.18 (8H, m, arom. protons), 4.13 (2H, s, Ha×2), 5.68 (4H, q, $CO_2\underline{CH_2}CH_3\times2$), 6.53 (4H, q, $O\underline{CH_2}CH_3\times2$), 6.85 (2H, d, Hc or Hb×2, J=8 Hz), 7.15 (2H, d, Hb or Hc×2, J=8 Hz), 8.64 (6H, t, $CO_2CH_2\underline{CH_3}\times2$), and 9.00 (6H, t, $OCH_2\underline{CH_3}\times2$). *Anal.* Calcd. for $C_{28}H_{34}O_6N_2$: C, 67.99; H, 6.93; N, 5.66; mol. wt., 494. Found: C, 67.87; H, 7.03; N, 5.47; mol. wt., 480.

Lithium Aluminum Hydride Reduction of 2——A suspension of **2** (100 mg) and lithium aluminum hydride (100 mg) in anhydrous ether (15 ml) was refluxed for 6 hr. Usual work up gave a solid, which was recrystallized from petroleum benzin to yield white crystals of **3** (60.8 mg) (90%), mp 188—189° (lit.[8] 184—185°). The NMR spectral data was identical with the reported values.[8]

The mono-methiodide: mp 189—190° (from EtOH–H_2O) (lit.[8] 185—186°).

Irradiation of 1 in Ethanol——A solution of **1** (150 mg) in EtOH (20 ml) was irradiated until the starting material disappeared (11 hr) (checked by thin-layer chromatography (TLC)). After evaporation of the solvent, the crude material was purified by preparative TLC on alumina using benzene–petroleum ether (1: 1) as solvent to give an oily product. Mass Spectrum *m/e*: 293 (M^+, Calcd. for $C_{16}H_{23}O_4N$: 293.1627. Found, 293.1648). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (NH) and 1720 (C=O). NMR ($CDCl_3$) τ: 2.05—3.20 (4H, m, arom. protons), 3.50 (1H, d, Hc, Jbc=12 Hz), 4.12 (1H, q, Hb, Jab=8 Hz, Jbc=12 Hz), 5.22 (1H, d, Ha, Jab=8 Hz), 5.90 (2H, q, $NHCO_2\underline{CH_2}CH_3$), 6.52 and 6.60 (2H×2, q×2, $O\underline{CH_2}CH_3\times2$), and 8.75 (9H, q, $CH_2\underline{CH_3}\times3$).

10) P. Laszlo and P.R. Schleyer, *Bull. Soc. Chim. France*, 1964, 87.