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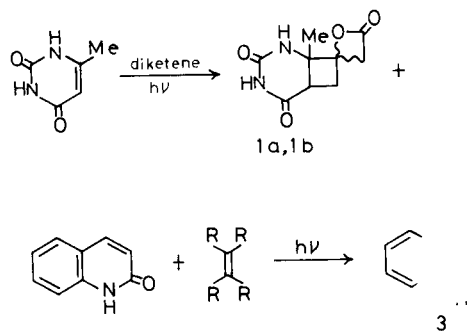
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Photoreaction of diketene with 4-methyl-2(1*H*)-quinolone and 1,4-dimethyl-2(1*H*)-quinolone gave 2*R**,2*aR**,8*bR**- and 2*R**,2*aS**,8*bS**-8*b*-methyl-3-oxo-1,2,2*a*,3,4,8*b*-hexahydrocyclobuta[*c*]quinoline-2-spiro-2'-(oxetan)-4'-one (**6a** and **6b**), and their 4-methyl derivatives **7a** and **7b**, respectively. Thermolysis of compounds **6** and **7** afforded 2*aR**,8*bS**-8*b*-methyl-2-methylene-3-oxo-1,2,2*a*,3,4,8*b*-hexahydrocyclobuta[*c*]quinoline (**8**) and its 4-methyl derivatives **9**, respectively. Similarly, photolysis of diketene and 4-acetoxy-2(1*H*)-quinolone gave 1*R**,2*aS**,8*bS**- and 1*R**,2*aR**,8*bR**-8*b*-acetoxy-3-oxo-1,2,2*a*,3,4,8*b*-hexahydrocyclobuta[*c*]quinoline (**11a** and **11b**). Alcoholysis of compounds **11a** and **11b** with hydrogen chloride in methanol gave 1-hydroxy-1-(methoxycarbonyl)methylcyclobuta[*c*]quinoline derivative **12** and **13** which were transformed to 4-acetyl-3-methyl-2(1*H*)-quinolone (**15**) by further alcoholysis. Photoreaction of diketene with 2(1*H*)-quinolone derivatives gave the corresponding cyclobuta[*c*]quinoline spirooxetanone derivatives **18** and **23**, which, by thermolysis, were transformed to 2-methylenecyclobuta[*c*]quinoline **23** and **25**, respectively.

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In a preceding paper of this series, we have reported the photoreaction of diketene with olefinic compounds to give [2 + 2] cycloaddition products (2-4). Similar [2 + 2] cycloadducts were obtained by the photolysis of diketene and heterocyclic compounds such as uracils (5,6). For instance, the *exo*-methylene of diketene added to the C₅-C₆ double bond of 6-methyluracil under irradiation to give spiro diazabicyclo[4.2.0]octane derivatives, **1** and **2** (5). On the other hand, the photoreaction of 2(1*H*)-quinolone with olefins was reported to give a [2 + 2] cycloadduct **3** (7-9). The object of the present paper is to describe the reaction of diketene with 2(1*H*)-quinolone derivatives when irradiated.

Scheme 1



Photoreaction of Diketene with 4-Methyl-2(1*H*)-quinolone (**4**) and 1,4-Dimethyl-2(1*H*)-quinolone (**5**).

Irradiation of a solution of diketene and 4-methyl-2(1*H*)-quinolone (**4**) in ethanol afforded a crystalline substance which was purified by silica gel column chromatography to give 2*R**,2*aR**,8*bR**-8*b*-methyl-3-oxo-1,2,2*a*,3,4,8*b*-hexahydrocyclobuta[*c*]quinoline-2-spiro-2'-(oxetan)-4'-one (**6a**), and its 2*R**,2*aS**,8*bS**-isomer **6b** in 53% and 27%

yields, respectively. Structural assignments were made as follows; elemental analyses indicated both products to be 1:1 adducts of diketene and **4**. Infrared (ir) spectra indicated the presence of the β -lactone carbonyl (**6a**, 1830 cm⁻¹; **6b**, 1825 cm⁻¹). Proton nuclear magnetic resonance (pmr) spectra showed the absorptions of methyl, two methylene, methine, and aromatic groups. These data are consistent with the spiro bicyclic structure **6**. As reported previously (5,6), the *cis* configuration of the C_{2a}-C_{8a} juncture is presumed to be more stable thermodynamically than the *trans*. Furthermore, the *cis* configuration was ascertained in view of the pmr study by Cantrell *et al.* (10). Namely, the shift position of the angular methyl protons of the *cis* bicyclo[4.2.0]octanone is downfield (1.20 ppm <) compared with that of the *trans* isomer (1.00 ppm >). The chemical shifts of C_{8a}-methyl protons of these products appeared at 1.68 ppm (**6a**) and 1.46 ppm (**6b**). These results are consistent with the *cis* structure.

The C₃'-methylene protons of compound **6a** were represented by the AB quartet at higher field (3.10 and 3.38 ppm) than those of compound **6b** (3.45 and 3.97 ppm). This observation suggests that the C₃'-methylene of compound **6a** exists on the opposite side to the C₃-carbonyl, while that of compound **6b** on the same side. Therefore, we concluded that the C₂-C_{2a} configuration of compound **6a** is *cis*, and that of compound **6b** is *trans*.

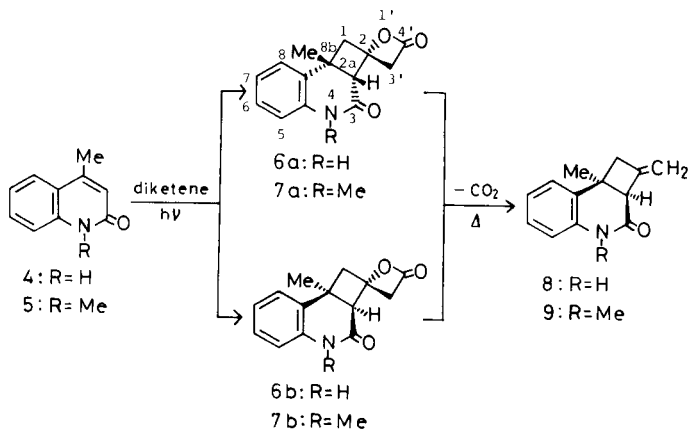
Similarly, photolysis of diketene and 1,4-dimethyl-2(1*H*)-quinolone (**5**) gave 2*R**,2*aR**,8*bR**-4,8*b*-dimethyl-3-oxo-1,2,2*a*,3,4,8*b*-hexahydrocyclobuta[*c*]quinoline-2-spiro-2'-(oxetan)-4'-one (**7a**) and its 2*R**,2*aS**,8*bS**-isomer **7b** in 47% and 23% yields, respectively. As described in the experimental section, elemental analyses and spectroscopic data are consistent with the spiro bicyclic structures.

Heating of compound **6a** at a decomposition point resulted in the elimination of carbon dioxide to give

$2aR^*$, $8bS^*$ -8b-methyl-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (**8**) in 46% yield. Compound **8** was also obtained from compound **6b** under the same reaction condition.

Similarly, thermolysis of compounds **7a** and **7b** gave the same product, $2aR^*$, $8bS^*$ -4,8b-dimethyl-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (**9**). Structural assignments of **8** and **9** were made on the basis of elemental analyses and spectroscopic data.

Scheme 2



Photoreaction of Diketene with 4-Acetoxy-2(1H)quinolone (**10**).

When a solution of diketene and 4-acetoxy-2(1H)quinolone (**10**) in acetone was irradiated, a crystalline substance was obtained. Purification by silica gel column chromatography afforded $1R^*$, $2aS^*$, $8bS^*$ -8b-acetoxy-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-1-spiro-2'-(oxetan)-4'-one (**11a**) and its $1R^*$, $2aR^*$, $8bR^*$ -isomer **11b** in 19% and 40% yields, respectively. Structural assignments were made as follows; elemental analyses indicated their empirical formulae to be 1:1 adducts of diketene and **10**. The ir spectra showed the presence of β -lactone carbonyl (**11a**, 1825 cm^{-1} ; **11b**, 1845 cm^{-1}) and acetoxy carbonyl (**11a**, 1750 cm^{-1} ; **11b**, 1730 cm^{-1}). The pmr spectra showed the absorption of methyl, two methylene, methine, and aromatic groups. These data are consistent with the spiro

bicyclic structure **11**. The peak due to the C_3' -methylene protons of **11a** appeared at higher field (3.42 ppm and 3.96 ppm) than that of **11b** (3.81 ppm and 4.41 ppm) by the deshielding effect of acetoxy group. Therefore, the configuration of the C_1 - C_{8b} linkage of compounds **11a** and **11b** were assigned as *cis* and *trans*, respectively.

Treatment of compounds **11a** and **11b** in absolute methanol saturated with dry hydrogen chloride afforded 1-hydroxy-1-(methoxycarbonyl)methyl-3-oxo-1,2,3,4-tetrahydrocyclobuta[c]quinoline (**12**) and $1R^*$, $2aR^*$, $8bR^*$ -1-hydroxy-1-(methoxycarbonyl)methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (**13**) in 46% and 83% yields, respectively.

Compounds **12** and **13** were treated with sodium methoxide in methanol to give the same product, 4-acetyl-3-methyl-2(1H)-quinolone (**15**).

Concerning the formation of compound **15**, a likely reaction pathway is considered as follows; ring fission of C_1 - C_2 bond of compounds **12** and **13** gives 4-(2-methoxycarbonylacetyl)-3-methyl-2(1H)-quinolone (**14**), which is hydrolyzed accompanied by decarboxylation to give compound **15**.

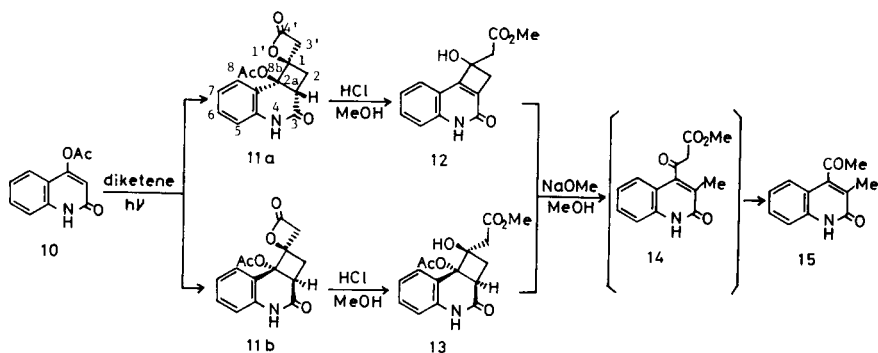
Photoreaction of 1-Methyl-2(1H)-quinolone (**16**) and 2(1H)-Quinolone (**17**).

Irradiation of diketene and **16** in acetone yielded $2R^*$, $2aR^*$, $8bR^*$ -8b-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-2-spiro-2'-(oxetan)-4'-one (**18a**), its $2R^*$, $2aS^*$, $8bS^*$ -isomer **18b**, and a dimer **19** (**11**) of **16**, in 40%, 16% and 12% yields, respectively.

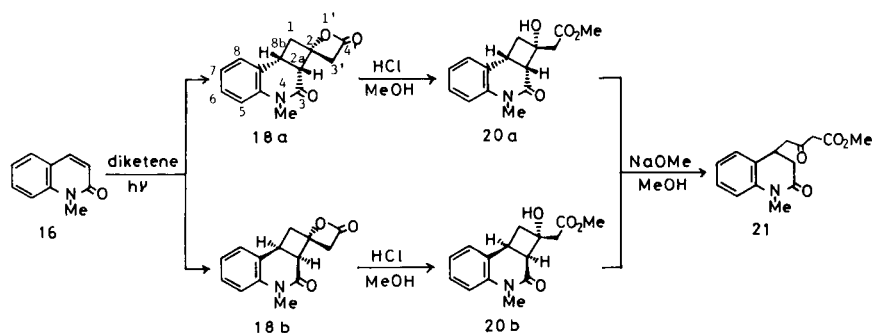
Treatment of compounds **18a** and **18b** with hydrogen chloride in methanol gave $2R^*$, $2aR^*$, $8bR^*$ -2-hydroxy-4-methyl-2-(methoxycarbonyl)methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (**20a**) and its $2R^*$, $2aS^*$, $8bS^*$ -isomer **20b** in 80% and 76% yields, respectively. Elemental analyses and spectroscopic data were consistent with those structures **20a** and **20b**.

Compounds **20a** and **20b** were heated under reflux in methanol in the presence of sodium methoxide to afford the same product, 4-(3-methoxycarbonyl-2-oxopropyl)-1-methyl-2-oxo-1,2,3,4-tetrahydroquinoline (**21**) in 70% yield.

Scheme 3



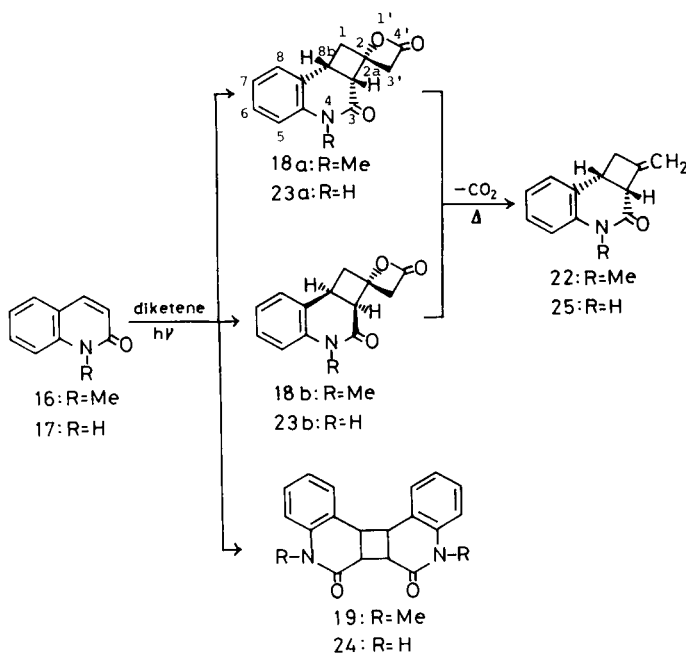
Scheme 4



Thermolysis of compounds **18a** and **18b** gave the same product, **2aR*,8bR*-4-methyl-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (22)**.

Photolysis of diketene and **2(1H)-quinolone (17)** yielded the mixture of compounds **23a** and **23b**. The mixture of **23a** and **23b** was heated at 200-205° to give **2aR*,8bR*-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (25)** in 85% yield.

Scheme 5



EXPERIMENTAL

Melting points are uncorrected. The ir spectra were taken on a JASCO IR-S spectrometer. The pmr spectra were recorded on a JEOL PS 100 spectrometer (for **6a**, **6b**, **7a**, **7b**, **11a**, **11b**, and **21**) with tetramethylsilane as an internal standard, and on a JEOL JNM-PMX 60 spectrometer with tetramethylsilane or 3-(trimethylsilyl)propanesulfonic acid sodium salt as an internal standard.

Reaction of Diketene with 4-Methyl-2(1H)-quinolone (4).

A solution of compound **4** (1.59 g, 0.01 mole) and diketene (8.4 g, 0.1 mole) in ethanol (150 ml) and acetone (20 ml) was photolyzed with ice-

cooling for 4 hours. Removal of the solvent and excess diketene gave a semicrystalline residue, which was subjected to silica gel (50 g) column chromatography using chloroform as an eluant. The chloroform elution gave a crystalline product, which was recrystallized from methanol to give 1.3 g (53%) of **2R*,2aR*,8bR*-8b-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-2-spiro-2'-(oxetan)-4'-one (6a)** as leaves, mp 185-186° dec; ir (potassium bromide): 3200 1830, 1660 cm⁻¹; pmr (pyridine-d₅): δ 1.68 (s, CH₃, 3H), 2.84-3.44 (m, C₁-H and C_{2a}-H, 3H), 3.10, 3.38 (ABq, C₃-H, 2H, J = 16 Hz), 7.04-7.40 (m, aromatic, 4H).

Anal. Calcd. for C₁₄H₁₃NO₃: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.95; H, 5.29; N, 5.78.

Elution was continued with the same solvent to give 0.65 g (27%) of the **2R*,2aS*,8bS*-isomer 6b** as prisms, mp 208-209°; ir (potassium bromide): 3210, 1825, 1665 cm⁻¹; pmr (pyridine-d₅): δ 1.46 (s, CH₃, 3H), 2.70-2.92 (m, C₁-H and C_{2a}-H, 3H), 3.45, 3.97 (ABq, C₃-H, 2H, J = 16 Hz), 7.02-7.42 (m, aromatic, 4H).

Anal. Calcd. for C₁₄H₁₃NO₃: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.04; H, 5.39; N, 5.79.

Reaction of Diketene with 1,4-Dimethyl-2(1H)-quinolone (5).

A solution of compound **5** (3.46 g, 0.02 mole) and diketene (16.8 g, 0.2 mole) in acetonitrile (200 ml) was irradiated for 6 hours. The reaction mixture was concentrated under reduced pressure. The resulting residue was chromatographed on a silica gel (50 g) column using benzene as an eluant. The benzene elution gave 2.4 g (47%) of **2R*,2aR*,8bR*-4,8b-dimethyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-2-spiro-2'-(oxetan)-4'-one (7a)** as prisms (from benzene), mp 122-124°; ir (chloroform): 1835, 1655 cm⁻¹; pmr (deuteriochloroform): 1.72 (s, C-CH₃, 3H), 2.66-3.48 (m, C₁-H and C_{2a}-H, 3H), 2.95, 3.18 (ABq, C₃-H, 2H, J = 16 Hz), 3.40 (s, N-CH₃, 3H), 7.00-7.48 (m, aromatic, 4H).

Anal. Calcd. for C₁₅H₁₅NO₃: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.79; H, 5.88; N, 5.19.

Elution was continued with chloroform to give 1.2 g (23%) of the **2R*,2aS*,8bS*-isomer 7b** as needles (from benzene), mp 165-166° dec; ir (chloroform): 1845, 1655 cm⁻¹; pmr (deuteriochloroform): δ 1.52 (s, C-CH₃, 3H), 2.66-2.84 (m, C₁-H and C_{2a}-H, 3H), 3.40 (s, N-CH₃, 3H), 3.38, 3.79 (ABq, C₃-H, 2H, J = 16 Hz), 7.02-7.44 (m, aromatic, 4H).

Anal. Calcd. for C₁₅H₁₅NO₃: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.26; H, 5.79; N, 5.23.

2aR*,8bS*-8b-Methyl-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (8).

Method A.

Compound **6a** (100 mg, 0.4 mmole) was heated at 205-210° for 10 minutes. The residual crystalline mass was recrystallized from benzene to give 38 mg (46%) of the product **8** as needles, mp 208-209°; ir (nujol): 1660 cm⁻¹; pmr (trifluoroacetic acid): δ 1.60 (s, CH₃, 3H), 3.23 (s-broad, C₁-H and C_{2a}-H, 3H), 4.78-4.98 (m, *exo*-methylene, 1H), 4.99-5.19 (m, *exo*-methylene, 1H), 6.80-7.50 (m, aromatic, 4H), 9.93-10.33 (broad, NH, 1H).

Anal. Calcd. for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.48; H, 6.49; N, 7.01.

Method B.

Similarly, heating of compound **6b** (100 mg, 0.4 mmole) gave 42 mg (51%) of the product **8**.

2aR*,8bS*-4,8b-Dimethyl-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (9).

Method A.

Compound **7a** (450 mg, 1.8 mmoles) was heated at 140-155° for 1.5 hours to give a crystalline product, which was recrystallized from petroleum ether to give 81 mg (27%) of the product **9** as needles, mp 48.5-50°; ir (chloroform): 1645 cm^{-1} ; pmr (deuteriochloroform): δ 1.45 (s, C-CH₃, 3H), 3.20 (s-broad, C₁-H and C_{2a}-H, 3H), 3.31 (s, N-CH₃, 3H), 4.73-4.85 (m, *exo*-methylene, 1H), 4.97-5.13 (m, *exo*-methylene, 1H), 6.80-7.36 (m, aromatic, 4H).

Anal. Calcd. for $C_{14}H_{13}NO$: C, 78.84; H, 7.09; N, 6.59. Found: C, 78.61; H, 6.96; N, 6.38.

Method B.

Similarly, heating of compound **7b** (300 mg, 1.2 mmoles) at 165-180° for 0.5 hour yielded 72 mg (29%) of the product **9**.

Reaction of Diketene with 4-Acetoxy-2(1*H*)-quinolone (10).

Photolysis of diketene (8.4 g, 0.1 mole) and compound **10** (2.03 g, 0.01 mole) in acetone (200 ml) for 9 hours gave a crystalline mass which was subjected to column chromatography on silica gel using chloroform as an eluant. The chloroform elution gave 0.55 g (19%) of **1R*,2aS*,8bS*-8b-acetoxy-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-1-spiro-2'-(oxetan)-4'-one (11a)** as prisms, mp 201-202° dec; ir (nujol): 1825, 1750, 1700 cm^{-1} ; pmr (pyridine-*d*₅): δ 1.88 (s, CH₃CO, 3H), 2.51, 2.91 (ABq, d, C₂-H, 2H, J = 14 Hz, J = 10 Hz), 3.42, 3.96 (ABq, C₃-H, 2H, J = 16 Hz), 4.1 (t, C_{2a}-H, 1H, J = 10 Hz), 7.16-7.76 (m, aromatic 4H).

Anal. Calcd. for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.56; N, 4.88. Found: C, 62.44; H, 4.47; N, 4.80.

Subsequent elution with chloroform gave 1.14 g (40%) of the **1R*,2aR*,8bR*-isomer 11b** as prisms, mp 228-229° dec; ir (nujol): 1845, 1730, 1685 cm^{-1} ; pmr (pyridine-*d*₅): δ 1.92 (s, CH₃CO, 3H), 2.54, 2.88 (ABq, d, C₂-H, 2H, J = 12 Hz, J = 10 Hz), 3.56 (t, C_{2a}-H, 1H, J = 10 Hz), 3.81, 4.41 (ABq, C₃-H, 2H, J = 18 Hz), 7.08-7.64 (m, aromatic, 4H).

Anal. Calcd. for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.56; N, 4.88. Found: C, 62.93; H, 4.61; N, 4.71.

1-Hydroxy-1-(methoxycarbonyl)methyl-3-oxo-1,2,3,4-tetrahydrocyclobuta[c]quinoline (12).

Compound **11a** (287 mg, 1 mmole) was stirred in absolute methanol (5 ml) saturated with dry hydrogen chloride for 1 hour. The reaction mixture was concentrated under reduced pressure and purified by chromatography on a silica gel column. Elution with ethyl acetate gave 146 mg (46%) of the product **12** as needles (from ethyl acetate), mp 161-162° dec; ir (potassium bromide): 3275, 1725, 1650 cm^{-1} ; pmr (DMSO-*d*₆): δ 2.93, 3.35 (ABq, C₂-H, 2H, J = 14 Hz), 2.97 (s, CH₃CO, 2H), 6.26 (s, OH, 1H), 7.00-7.67 (m, aromatic, 4H), 11.50-11.60 (broad, NH 1H).

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.60; H, 5.03; N, 5.35.

1R*,2aR*,8bR*-1-Hydroxy-1-(methoxycarbonyl)methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (13).

Compound **11b** (574 mg, 2 mmoles) was stirred in absolute methanol (5 ml) saturated with dry hydrogen chloride for 1.5 hours. The precipitated crystalline mass was filtrated and purified by recrystallization from ethyl acetate to yield 500 mg (83%) of the product **13** as prisms, mp 208-210° dec; ir (potassium bromide): 3540, 1730, 1680 cm^{-1} ; pmr (trifluoroacetic acid): δ 2.08 (s, CH₃CO, 3H), 2.16, 2.70 (ABq, d, C₂-H, 2H, J = 12 Hz, J = 10 Hz), 3.00, 3.25 (ABq, CH₃CO, 2H, J = 17 Hz), 3.51 (t, C_{2a}-H, 1H, J = 10 Hz), 3.95 (s, OCH₃, 3H), 6.95-7.35 (m, aromatic, 4H), 9.77-10.03 (broad,

NH, 1H).

Anal. Calcd. for $C_{16}H_{17}NO_5$: C, 60.18; H, 5.37; N, 4.39. Found: C, 59.82; H, 5.42; N, 4.29.

4-Acetyl-3-methyl-2(1*H*)-quinolone (15).

Method A.

A solution of compound **12** (259 mg, 1 mmole) and sodium methoxide (54 mg, 1 mmole) in methanol (5 ml) was refluxed for 2 hours. The resulting crystalline residue was recrystallized from ethyl acetate to give 147 mg (73%) of product **15** as prisms, mp 193-194°; ir (potassium bromide): 3150, 1700, 1640 cm^{-1} ; pmr (trifluoroacetic acid): δ 2.35 (s, C₃-CH₃, 3H), 2.85 (s, COCH₃, 3H), 7.50-7.95 (m, aromatic, 4H).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.91; H, 5.53; N, 7.02.

Method B.

Similarly, compound **13** (957 mg, 3 mmoles) was treated with sodium methoxide (162 mg, 3 mmoles) in methanol (10 ml) to give the product **15** (451 mg, 79%).

Reaction of Diketene with 1-Methyl-2(1*H*)-quinolone (16).

A solution of diketene (12.6 g, 0.15 mole) and compound **16** (2.39 g, 0.015 mole) in acetone (150 ml) was photolyzed with ice-cooling for 9 hours. Removal of the solvent and excess diketene gave a crystalline residue, which was chromatographed on a silica gel column. Elution with benzene-ethyl acetate (50:1) gave 1.5 g (40%) of **2R*,2aR*,8bR*-4-methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-2-spiro-2'-(oxetan)-4'-one (18a)** as prisms (from benzene), mp 138-139° dec; ir (chloroform): 1835, 1655 cm^{-1} ; pmr (deuteriochloroform): δ 2.74-3.36 (m, C₁-H and C_{2a}-H, 3H), 2.95, 3.13 (ABq, C₃-H, 2H, J = 16 Hz), 3.36 (s, CH₃, 3H), 4.08-4.18 (m, C_{8b}-H, 1H), 6.90-7.40 (m, aromatic, 4H).

Anal. Calcd. for $C_{14}H_{13}NO_5$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.98; H, 5.51; N, 5.56.

Elution was continued with benzene-ethyl acetate (10:1) to give 0.6 g (16%) of the **2R*,2aS*,8bS*-isomer (18b)** as prisms (from benzene), mp 168-169° dec; ir (chloroform): 1845, 1660 cm^{-1} ; pmr (deuteriochloroform): δ 2.88-3.34 (m, C₁-H, and C_{2a}-H, 3H), 3.36 (s, CH₃, 3H), 3.52 (s, C₃-H, 2H), 3.98-4.02 (m, C_{8b}-H, 1H), 6.96-7.38 (m, aromatic, 4H).

Anal. Calcd. for $C_{14}H_{13}NO_5$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.40; H, 5.59; N, 5.48.

Subsequent elution with benzene-ethyl acetate (5:1) gave 0.4 g (12%) of dimer **19** as prisms, mp 212-213° (lit (11) mp 211.5-212°).

2aR*,8bR*-4-Methyl-2-methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (22).

Method A.

Thermolysis of compound **18a** (365 mg, 1.5 mmoles) at 150-155° for 2 hours gave a semicrystalline product which was chromatographed on a silica gel column. Elution with chloroform gave 215 mg (72%) of product **22** as prisms (from hexane), mp 92-93°; ir (chloroform): 1640 cm^{-1} ; pmr (deuteriochloroform): δ 2.97-3.53 (m, C₁-H and C_{2a}-H, 3H), 3.40 (s, CH₃, 3H), 4.03-4.30 (m, C_{8b}-H, 1H), 4.66-4.80 (m, *exo*-methylene, 2H), 6.77-7.23 (m, aromatic, 4H).

Anal. Calcd. for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.33; H, 6.57; N, 7.03.

Method B.

Similarly, heating of compound **18b** (243 mg, 1 mmole) at 180-185° gave 155 mg (78%) of the product **22**.

2R*,2aR*,8bR*-2-Hydroxy-4-methyl-2-(methoxycarbonyl)methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (20a).

A solution of compound **18a** (486 mg, 2 mmoles) in absolute methanol (5 ml) saturated with dry hydrogen chloride was stirred at room temperature for 1 hour. The reaction mixture was concentrated *in vacuo*, and the resulting residue was dissolved in chloroform. The chloroform solution

was washed with water, dried over sodium sulfate, and concentrated. The crystalline residue was recrystallized from benzene to give 414 mg (80%) of product **20a** as prisms, mp 123-124°; ir (chloroform): 3520, 1710, 1655 cm^{-1} ; pmr (deuteriochloroform): δ 2.36 (s, COCH_2 , 2H), 3.33-3.53 (m, C_1 -H, and C_{2a} -H, 3H), 3.40 (s, N-CH_3 , 3H), 3.40 (s, OCH_3 , 3H), 3.70-4.00 (m, C_{8a} -H, 1H), 4.63-4.83 (broad, OH, 1H), 6.87-7.33 (m, aromatic, 4H).

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.55; H, 6.23; N, 5.06.

2R*,2aS*,8bS*-2-Hydroxy-4-methyl-2-(methoxycarbonyl)methyl-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (20b).

In the manner described for **20a**, treatment of compound **18b** (486 mg, 2 mmoles) in absolute methanol (5 ml) with dry hydrogen chloride gave 393 mg (76%) of the product **20b** as needles, mp 129-130°; ir (chloroform): 3480, 1720, 1640 cm^{-1} ; pmr (deuteriochloroform): δ 2.30-3.30 (m, C_1 -H, C_{2a} -H, and OH, 4H), 2.80 (s, COCH_2 , 2H), 3.33 (s, N-CH_3 , 3H), 3.63-3.84 (m, C_{8a} -H, 1H), 3.74 (s, OCH_3 , 3H), 6.90-7.33 (m, aromatic, 4H).

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.12; H, 6.28; N, 5.21.

4-(3-Methoxycarbonyl-2-oxopropyl)-1-methyl-2-oxo-1,2,3,4-tetrahydroquinoline (21).

A solution of compounds **20a** and **20b** (2.59 g, 0.01 mole) in sodium methoxide (0.54 g, 0.01 mole)-methanol (20 ml) was refluxed for 5 hours. The reaction mixture was concentrated *in vacuo*. The resulting residue was dissolved in water and extracted with chloroform. The chloroform layer was dried over sodium sulfate and concentrated. The oily residue was chromatographed on a silica gel column. Elution with hexane-ethyl acetate (10:1) gave the oil, which was purified by distillation to give 1.82 g (70%) of the product **21**, bp 195-199° (0.001 mm Hg); ir (chloroform): 1740, 1715, 1650 cm^{-1} ; pmr (deuteriochloroform): δ 2.54-3.24 (m, COCH_2 , C_3 -H, and C_4 -H, 5H), 3.32 (s, N-CH_3 , 3H), 3.60 (s, COCH_2CO , 2H), 3.72 (s, OCH_3 , 3H), 6.88-7.24 (m, aromatic, 4H).

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.73; H, 6.48; N, 4.92.

Reaction of Diketene with 2(1*H*)-Quinolone (**17**).

A solution of diketene (16.8 g, 0.2 mole) and compound **17** (2.9 g, 0.02 mole) in ethanol (400 ml) was irradiated in the presence of acetone (40 ml) as a sensitizer under ice-cooling for 9 hours. The precipitate was filtrated and purified by recrystallization from acetic acid to give 1.35 g (23%) of dimer **24** of compound **17** as needles, mp 295-297° (lit (12) mp 300°). The filtrate was concentrated *in vacuo*. The resulting residue was chromatographed on a silica gel column. Elution with ethyl acetate gave 2.81 g (58%) of a stereoisomeric mixture of **2aR*,8bR*-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline-2-spiro-2'-(oxetan)-4'-one (23a and 23b)**, mp 171-174° dec; ir (potassium bromide): **21a**: 3200, 1835, 1650 cm^{-1} ; **21b**: 3200, 1830, 1650 cm^{-1} ; pmr (trifluoroacetic acid): δ **21a**:

2.93-3.97 (m, C_1 -H and C_{2a} -H, 3H), 3.15, 3.40 (ABq, C_3 -H, 2H, $J = 10$ Hz), 4.36-4.56 (m, C_{8a} -H, 1H), 6.97-7.56 (m, aromatic, 4H); **21b**: 3.07-3.87 (m, C_1 -H and C_{2a} -H, 3H), 3.70 (s, C_3 -H, 2H), 4.26-4.46 (m, C_{8a} -H, 1H), 6.90-7.40 (m, aromatic, 4H).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{NO}_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.17; H, 4.84; N, 6.17.

2aR*,8bR*-2-Methylene-3-oxo-1,2,2a,3,4,8b-hexahydrocyclobuta[c]quinoline (25).

The mixture of compounds **23a** and **23b** was heated at 200-205° for 10 minutes. The residual solid was purified by recrystallization from ethyl acetate to give 469 mg (85%) of the product **25** as prisms, mp 175-177°; ir (potassium bromide): 3200, 1660 cm^{-1} ; pmr (deuteriochloroform): δ 3.16-3.55 (m, C_{2a} -H, 1H), 3.18, 3.38 (ABq, C_1 -H, $J = 11$ Hz, 2H), 4.17-4.40 (m, C_{8a} -H, 1H), 4.74-4.84 (m, *exo*-methylene, 2H), 6.74-7.26 (m, aromatic, 4H), 9.53-9.84 (broad, NH, 1H).

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.48; H, 6.14; N, 7.41.

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