To three separate stirred solutions of 0.1 g of **2** in 4 ml of acetic acid were added 2.9, 5.8, and 14.5 mg, respectively, of anhydrous sodium acetate. The reaction mixtures were refluxed for 6 hr, poured into 20 ml of ice–water, and extracted with pentane. Samples were analyzed by glpc. One equivalent of sodium acetate gave a **3**:**5** plus **6** ratio of 81:19; 2 equiv gave 90:10, and 5 equiv gave 92:8.

Reaction of 1 with Dicyclohexylcarbodiimide.—To 0.61 g of dicyclohexylcarbodiimide was added 0.42 g of **1**. Stirring was begun and a trace of freshly prepared CuCl was added to the flask. The flask was heated to 150° for 20 min, at which time the material in the flask had solidified. The volatile components were removed by distillation at 150° (10 mm) to give 0.28 g (76%) of **3**.

Reaction of 2 with NaH–DMSO.—In a flask was placed 0.3 g of sodium hydride–mineral oil dispersion. After the solution was washed three times with pentane, 10 ml of dimethyl sulfoxide was added by syringe and the mixture was heated under nitrogen at 70–80° for 45 min. After cooling, 1 g of **2** in 10 ml of dimethyl sulfoxide was added and the mixture was allowed to stir at room temperature for 6 hr. The product was extracted with pentane and concentrated to give 0.34 g (78%) of **3**.

Reaction of 2 with KO-*t*-Bu.—To 1 g of **2** in 50 ml of anhydrous ether under a nitrogen atmosphere was added 1 g of KO-*t*-Bu. The reaction was stirred for 6 hr at room temperature, at which time the solid material was removed by filtration and washed with ether. The ether extracts were washed with water and concentrated to yield 0.42 g (90%) of **3**.

Reaction of 2 with K_2CO_3–DMF.—To 1 g of **2** in 30 ml of DMF was added 1.0 g of anhydrous K_2CO_3. The mixture was heated to 85° for 4 hr. Water was added and the mixture was extracted with pentane. The extracts were washed with distilled water, dried, and concentrated to give 0.24 g (50%) of **3**.

Acetolysis of 8.—Reaction as described above for **2** gave 0.37 g (87%) of an oil containing two products in the ratio 94:6. The major product was **6**; the minor one was **10**.[9]

Reaction of 7 with Dicyclohexylcarbodiimide.—To 0.61 g of dicyclohexylcarbodiimide was added 0.42 g of **7**. Stirring was begun and a trace of freshly prepared CuCl was added to the flask. The flask was heated to 150° for 5 hr, at which time it was observed that no precipitate had formed. The reaction was then heated to 200° for 8 hr and cooled to 150°, and the volatile components were removed by distillation. Only small amounts of starting material were recovered.

Reaction of 8 with K_2CO_3–DMF.—Reaction as described for **2** gave only starting material.

Reaction of 8 with NaH–DMSO.—Reaction as described for **2** gave 0.3 g (71%) of an oil identified as **9**:[10] ir 5.85 μ; nmr δ 2.5–3.2 (m, 2) and 1.2–2.5 (m, 10); 2,4-DNP, mp 178–179.5° (lit.[11] mp 179.5–180°).

Reaction of 8 with KO-*t*-Bu.—Reaction as described for **2** gave 0.39 g (90%) of **9**.

Reaction of 11 with K_2CO_3–DMF.—To 2 g of **11**[12] dissolved in 60 ml of DMF was added 4 g of anhydrous K_2CO_3. The mixture was heated to 140° for 72 hr with stirring. The solid materials were removed by filtration and the DMF was removed by distillation at reduced pressure. The solid residue was removed by filtration and washed with ether. The filtrate was concentrated to give 1.8 g (89%) of **12**: ir 3.0, 3.45, 6.0, 8.75, 10.35, and 12.6 μ; nmr δ 4.1 (s, 1), 3.4 (s, 1), 2.15–1.15 (m, 8), 0.8 (m, 1), and 0.4 (m, 1).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.82; H, 8.75.

Reaction of 11 with KO-*t*-Bu.—A slurry of 1 g of **11**, 2 g of KO-*t*-Bu, and 30 ml of anhydrous ether was stirred under nitrogen at room temperature for 12 hr, poured into saturated NH_4Cl solution, and extracted with ether. The ether extract was washed with water, dried, and concentrated to give 0.9 g (90%) of **12**.

Registry No.—**2**, 34958-36-6; **8**, 34958-37-7; **11**, 34958-38-8; **12**, 34958-39-9.

(9) C. Ganter and J. F. Moser, *Helv. Chim. Acta*, **52** (3), 735 (1969).
(10) A. C. Cope and R. W. Gleason, *J. Amer. Chem. Soc.*, **84**, 1933 (1962).
(11) H. O. House and T. O. Cronin, *J. Org. Chem.*, **30**, 1069 (1965).
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Acknowledgment.—We thank the National Science Foundation for financial support and the Badische Anilin- und Soda-Fabrik Akt.-Ges. for generously providing samples of **1** and **7**.

2,3-Annelations on Quinoline and Pyridine 1-Oxides

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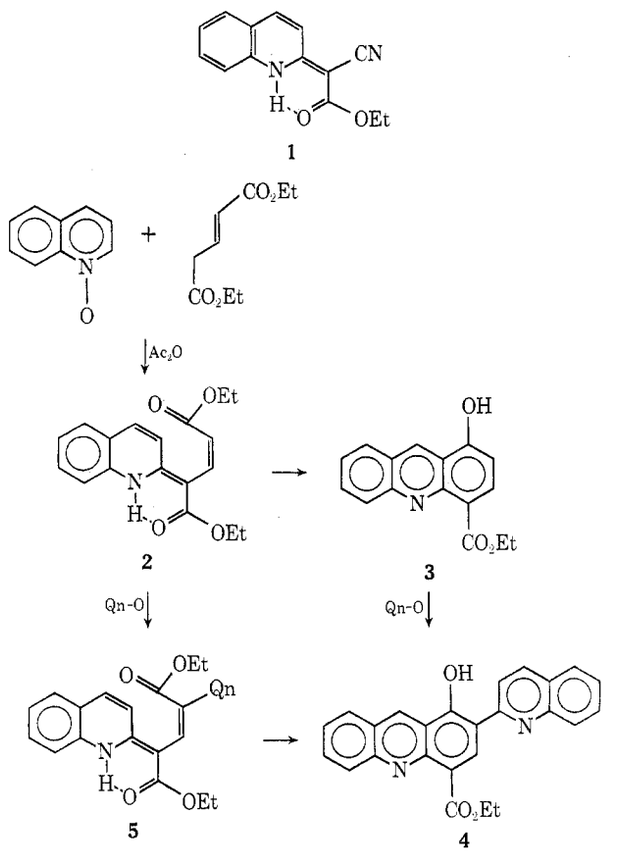
Received March 14, 1972

Ethyl α-(2-quinolyl)cyanoacetate, the product of the reaction of quinoline 1-oxide with ethyl cyanoacetate in the presence of acetic anhydride,[1] exists exclusively in the tautomeric form **1**.[2] This finding prompted us



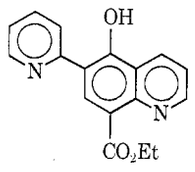
to study the possibilities of achieving 2,3-annelations on the quinoline nucleus *via* intermediates having the salient structural features of **1**. We chose to investigate the reaction of diethyl glutaconate with quinoline 1-oxide, with the idea that if intermediate **2** were formed,[3] its geometry should be such as to permit nucleophilic attack by C-3 on the terminal ester function to yield the acridinol **3**.

The product of the reaction proved to be 4-ethoxycarbonyl-2-(2′-quinolyl)-1-acridinol (**4**) rather than **3**.

(1) M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.*, **11**, 415 (1963).
(2) J. E. Douglass and J. M. Wesolosky, *J. Org. Chem.*, **36**, 1165 (1971).
(3) The cis geometry shown about the terminal carbon–carbon double bond in **2** is not unreasonable in view of the expected rotational lability of this grouping.

The unexpected introduction of a quinolyl group onto the acridine nucleus could have occurred in one of two ways: a second mole of quinoline 1-oxide reacts (i) with **2** to give intermediate **5** which ring closes to **4** or (ii) with **3** to yield **4**. The latter path appears unlikely in view of our failure to detect any reaction of quinoline 1-oxide with several representative phenols. Efforts to isolate either intermediate **2** or **5** have been fruitless.

Pyridine 1-oxide reacts in an analogous manner to afford 8-ethoxycarbonyl-6-(2′-pyridyl)-5-quinolinol (**6**),



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although it could only be isolated from the reaction mixture as its fluoroborate salt and in very low yield.

Experimental Section[4]

4-Ethoxycarbonyl-2-(2′-quinolyl)-1-acridinol (**4**).—A mixture of 20 mmol of anhydrous quinoline 1-oxide, 20 mmol of diethyl glutaconate (Aldrich Chemical Co.), and 40 mmol of acetic anhydride was stirred at room temperature under nitrogen for 24 hr. The solid which formed was filtered off and recrystallized from chloroform–acetone to yield 2.37 g of very fine, orange needles, mp 204–205°. High-resolution mass spectrometry indicated the composition of the molecular ion (*m/e* 394) to be $C_{25}H_{18}N_2O_3$; ir (KBr) 3550 (OH) and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.43 (t, 3, CH_3), 4.38 (q, 2, OCH_2), 7.56–7.92 (m, 7), 8.13 (s, 1, 3-H), 8.17 (d, 1, J = 8 Hz, 3′-H), 8.55 (d, 1, J = 8 Hz, 4′-H), 8.86 (d, 1, J = 10 Hz, 5-H), 9.26 (s, 1, 9-H),[5] and 10.46 ppm (s, 1, OH); mass spectrum (60 eV) *m/e* 394 (100, M^+), 365 [96, $M^+ - (H + C_2H_4)$], and 128 (35, $C_9H_6N^+$); uv max ($CHCl_3$) 246 nm (log ϵ 4.52), 288 (4.23), and 438 (4.39).[6]

Anal. Calcd for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N, 7.10. Found: C, 76.15; H, 4.55; N, 7.04.

When the amounts of quinoline 1-oxide and acetic anhydride were doubled, the yield of **4** was increased to 4.52 g (57%).

8-Ethoxycarbonyl-6-(2′-pyridyl)-5-quinolinol (**6**).—Diethyl glutaconate (9.3 g, 0.050 mol) was added over a period of 30 min to a stirred, ice-cold solution of 9.5 g (0.10 mol) of anhydrous pyridine 1-oxide in 22.4 g (0.22 mol) of acetic anhydride under nitrogen. After the addition was complete, the mixture was allowed to warm to room temperature and stand overnight. Water (100 ml) was added and the water–acetic acid azeotrope was removed on a rotary evaporator until no acetic acid could be detected in the distillate. The reddish-black, viscous residue was triturated with water to remove any unreacted pyridine 1-oxide, taken up in 50 ml of ether, and then treated with 5% fluoroboric acid (to pH 3). The precipitate which formed was filtered off, washed successively with cold water and ether, and recrystallized twice from 80% aqueous ethanol to afford 0.72 g (4%) of yellowish-orange needles: mp 235–240° dec; ir (KBr) 3510 (OH), 1720 (C=O), and 1070 cm^{-1} (BF_4^-); nmr (DMSO-d_6) δ 1.44 (t, 3, CH_3), 4.38 (q, 2, OCH_2), 7.6–9.5 (m, 9), and 10.7 ppm (broad s, 1, OH).

Anal. Calcd for $C_{17}H_{15}BF_4N_2O_3$: C, 53.43; H, 3.96; N, 7.33. Found: C, 53.12; H, 3.59; N, 7.41.

Registry No.—**4**, 34918-49-5; **6**, 34903-57-6.

Acknowledgment.—Support for part of this work by a grant from the Marshall University Foundation is gratefully acknowledged.

(4) Melting points were determined on a calibrated Mel-Temp apparatus. Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer, nmr spectra on a Varian A-60A spectrometer, and uv spectra on a Beckman DK spectrophotometer. The mass spectrum was kindly provided by the Union Carbide Technical Center, South Charleston, West Virginia.

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γ-Butyrolactones from the Irradiation of Unsaturated Esters in Alcohols

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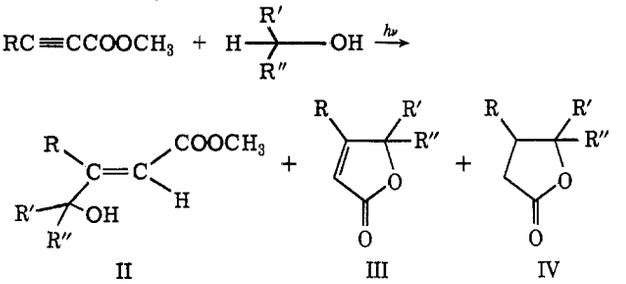
Received November 29, 1971

In view of its intrinsic importance in natural product chemistry, γ-lactone synthesis has been a subject of several investigations. A photochemical method first explored by Schenck and coworkers[1] led to the synthesis of some γ-lactones which are not otherwise easily accessible.[2,3] It involves irradiation of an α,β-unsaturated acid in alcohol in the presence of a sensitizer. However, in many instances, particularly when primary alcohols are employed, this method gives poor yields of the lactones. More recently, direct irradiation of α,β-acetylenic esters I (R = CH_3, $COOCH_3$, or H) in alcohols has also been shown to yield γ-butyrolactones IV as secondary photolysis products, the primary products being the hydroxy esters II and the unsaturated lactones III.[4,5] The facility with which the adducts II and III are formed prompted us to investigate the possible synthesis of γ-butyrolactones by direct irradiation of olefinic esters.



Photochemical studies with olefinic esters have mainly been concerned with double bond migration *via* γ-hydrogen abstraction[6] and cycloaddition to olefins.[7] The purpose of this communication is to present some synthetic and mechanistic aspects of unsensitized addition of alcohols to olefinic esters.

Irradiation of dilute alcoholic solutions of the ester leads to disappearance of the latter and a concomitant formation of the corresponding lactone. The yields of the lactones were determined by vacuum distillation of the concentrated reaction mixtures (Table I).

The formation of γ-butyrolactones suggests that addition of the alcohol takes place across the double bond of the ester to give an open-chain γ-hydroxy ester which would readily cyclize to form the observed lactone.

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