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Extensive studies of the Knoevenagel condensation of aromatic aldehydes and active methylene compounds have been reported (2). In 1894, Knoevenagel reported (3) the reaction of benzaldehyde with ethyl benzoylpyruvate in the presence of piperidine to give ehtyl benzyl-(bisbenzoyl)pyruvate, m.p. 162°, but no yield of the product was reported. This paper deals with the interesting results of the reactions of ethyl acetylpyruvate (**2**) (4) and ethyl benzoylpyruvate (**3**) (5) with some aromatic aldehydes (**1a-f**).

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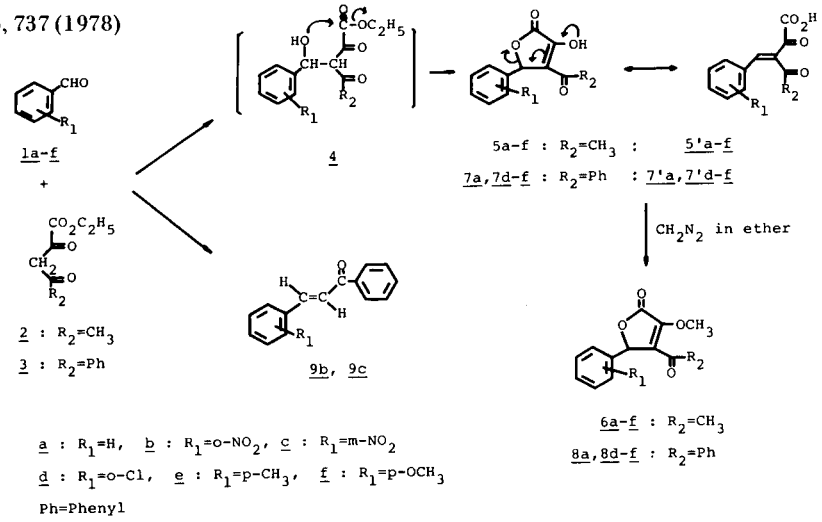


Scheme I

Benzaldehyde (**1a**) reacted with an equivalent amount of **2** in the presence of a catalytic amount of piperidine to give a crystalline product (**5a**, m.p. 169-170°) in 69% yield, which is soluble in sodium bicarbonate with the evolution of carbon dioxide, indicating the presence of a carboxyl group. The ir spectrum of **5a** showed absorption bands in the regions of 1770 and 1660 cm^{-1}, while its pmr spectrum showed no ester ethyl protons. These data provided the evidence that the structure of **5a** is the Knoevenagel condensation product with hydrolysis of the ester group, 3-benzylidene-2,4-dioxopentanoic acid (**5'a**). It should be noted, however, that the uv spectrum [λ max nm (log ε)] of **5'a** showed absorption maxima at 267 (3.97) and 323 (3.67) in 95% ethanol, which dramatically changed to an absorption maximum at 323 (4.22) upon the addition of sodium bicarbonate solution. Moreover, **5'a** showed an absorption maximum at 318 (4.20) in water, which is similar to that exhibited in 95% ethanol-sodium bicarbonate solution, and 256 (3.95) in chloroform as shown in Figure 1. In addition, the ferric chloride test of **5'a** showed a red-violet color, indicating the presence of an enol group. We therefore concluded that the structure of the condensation product of **1a** and **2** is 3-acetyl-2,4-dihydroxy-4-phenylcrotonic acid lactone (**5a**), which was obtained by the cyclization of the intermediate hydroxy derivative (**4**) with the loss of ethanol. The lactone (**5a**) would preferrentially take the open-form (**5'a**) in polar solvents such as water or ethanol-sodium bicarbonate solution and exist partially in the open-form in

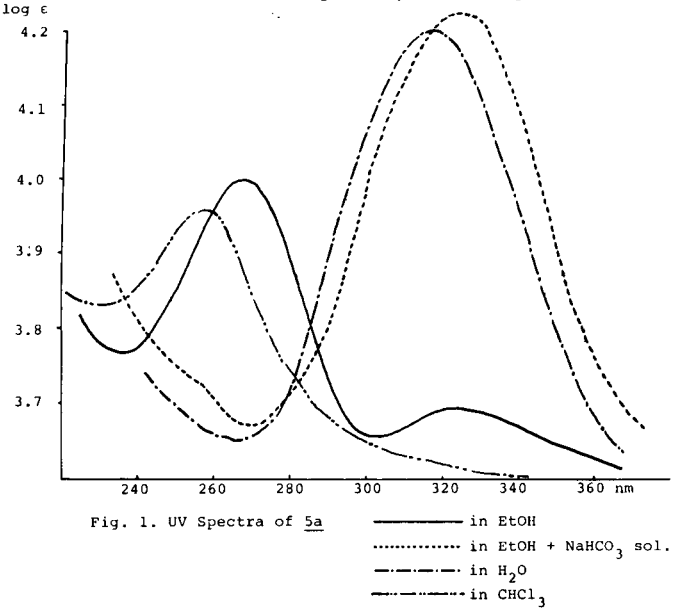


Fig. 1. UV Spectra of 5a

Table I

Physical Data for Compounds **5a-f**

Compound No.	Reaction Temp. (°C)	Reaction Time (hours)	Yield (%)	M.p. (°C) (Recryst. Solv.)	Formula	Analyses (%) Calcd. (Found) C	H	N
5a	50	72	69	169-170 (a)	$C_{12}H_{10}O_4$	66.05 (65.99)	4.26 (4.48)	
5b	30	24	68	183-185 (b)	$C_{12}H_9NO_6$	54.76 (55.00)	3.45 (3.55)	5.32 (5.43)
5c	30	24	65	170-172 (b)	$C_{12}H_9NO_6$	54.76 (54.98)	3.45 (3.48)	5.32 (5.26)
5d	40	24	66	189-190 (b)	$C_{12}H_9O_4Cl$	57.04 (57.32)	3.58 (3.74)	
5e	60	240	37	161-162 (b)	$C_{13}H_{12}O_4$	67.23 (67.49)	5.21 (5.31)	
5f	60	240	41	161-162 (a)	$C_{13}H_{12}O_5$	62.90 (63.08)	4.87 (4.71)	

(a) Methanol. (b) Ethanol.

Table II

Spectral Data for Compounds **5a-f**

Compound No.	Infrared Absorption in cm^{-1} (KBr)	Ultraviolet Absorption in nm (log ϵ)	Pmr δ -$COCH_3$	-CH
5a	1770, 1660	(a) 267 (3.97), 323 (3.67) (b) 323 (4.22) (c) 318 (4.20) (d) 256 (3.95)	2.36	6.10
5b	1795, 1660	(a) 266 (4.05), 318 (3.70) (b) 253 (3.78), 320 (4.16) (c) 257 (3.76), 316 (4.12) (d) 261 (4.17)	2.40	6.65
5c	1785, 1660	(a) 265 (4.26), 320 (3.73) (b) 260 (3.99), 320 (4.27) (c) 265 (3.96), 314 (4.17) (d) 257 (4.28)	2.40	6.32
5d	1800, 1650	(a) 268 (3.97), 320 (3.66) (b) 320 (4.12) (c) 318 (4.13) (d) 259 (3.99)	2.41	6.40
5e	1780, 1640	(a) 265 (3.92), 321 (3.79) (b) 321 (4.20) (c) 320 (4.20) (d) 259 (3.98)	2.37	6.11
5f	1770, 1660	(a) 267 (3.83), 322 (3.96) (b) 322 (4.17) (c) 318 (4.22) (d) 257 (4.08)	2.40	6.32

(a) In 95% ethanol. (b) In 95% ethanol + sodium bicarbonate solution. (c) In water. (d) In chloroform.

95% ethanol. The condensation of **1a** and **2** with piperidine in ethanol or with boron trioxide in benzene (**6**) did not give satisfactory results.

Similarly, the reactions of **1b-f** with **2** gave the corresponding lactones (**5b-f**). The reaction conditions, yields, and spectral and analytical data are listed on Tables I and II.

The reactions of **5a-f** with diazomethane in ether gave the corresponding methyl ethers (**6a-f**) in good yield, the structures of which were assigned easily by uv spectral data. The spectral and microanalytical data of these compounds are listed on Table III

Next, the reactions of **3** and **1a-f** were examined. Reactions of **1a**, **1d-f** with **3** at 50° for 72 hours gave 3-benzoyl-2,4-dihydroxy-4-phenylcrotonic acid lactones (**7a**, **7d-f**) (Table IV), the structures of which were determined by ir, pmr and especially uv spectral data (Table V). These data are similar to that obtained for **5a-f**. These compounds were reacted to give the corresponding methyl ethers (**8a**, **8c-f**) in good yields by the action of diazomethane (Table VI).

On the other hand, nitrobenzaldehydes (**1b,c**) reacted with **3** at 40° to give 2- or 3-nitrobenzalacetophenones (chalcones) (**9b,c**), the structures of which were determin-

Table III

Physical and Spectral Data for Compounds **6a-f**

Compound No.	M.p. (°C) (Recryst. Solv.)	Formula	Analyses (%) Calcd. (Found) C	H	N	Pmr Data (δ) -$COCH_3$	-$COOCH_3$	-CH	Uv Data in Ethanol nm (log ε)
6a	78-79 (a)	$C_{13}H_{12}O_4$	67.23 (67.00)	5.21 (5.50)		2.35	4.30	6.15	267 (4.20)
6b	99-100 (b)	$C_{13}H_{11}NO_6$	56.32 (56.20)	4.00 (4.17)	5.05 (5.03)	2.40	4.40	6.90	266 (4.20)
6c	149-150 (b)	$C_{13}H_{11}NO_6$	56.32 (56.45)	4.00 (4.22)	5.05 (5.02)	2.45	4.45	6.10	267 (4.08)
6d	90-91 (c)	$C_{13}H_{11}O_4Cl$	58.54 (58.27)	4.15 (4.25)		2.40	4.32	6.45	269 (4.05)
6e	60-61 (a)	$C_{14}H_{14}O_4$	68.28 (68.37)	5.73 (5.87)		2.35	4.30	6.15	264 (4.04)
6f	82-83 (a)	$C_{14}H_{14}O_5$	64.11 (64.37)	5.38 (5.28)		2.35	4.30	6.15	266 (4.06)

(a) Ligroin. (b) Methanol. (c) Petroleum ether.

Table IV

Physical Data for Compounds **7a**, **7d-f**

Compound No.	Yield (%)	M.p. (°C) (Recryst. Solv.)	Formula	Analyses (%) Calcd. (Found) C	H
7a	50	219-220 (a)	$C_{17}H_{12}O_4$	72.85 (72.74)	4.32 (4.11)
7d	52	237-239 (a)	$C_{17}H_{11}O_4Cl$	64.87 (65.00)	3.52 (3.37)
7e	25	227-228 (a)	$C_{18}H_{14}O_4$	73.46 (73.68)	4.80 (4.66)
7f	30	182-183 (b)	$C_{18}H_{14}O_5$	69.67 (69.76)	4.55 (4.77)

(a) Methanol. (b) Ethanol.

Table V

Spectral Data for Compounds **7a**, **7c-f**

Compound No.	Infrared Absorption in cm^{-1} (KBr)	Ultraviolet Absorption in nm (log ε)				Pmr δ -CH
7a	1765, 1640	(a) 259 (3.97), (c) 254 (3.96),	350 (3.78) 377 (3.95)	(b) 251 (3.96), (d) 273 (4.04)	350 (4.07)	6.40
7c	1775, 1640	(a) 257 (4.24), (c) 262 (4.10),	347 (3.97) 342 (4.05)	(b) 256 (4.23), (d) 268 (4.29)	347 (4.16)	6.55
7d	1765, 1645	(a) 256 (3.88), (c) 253 (3.67),	348 (3.94) 343 (3.73)	(b) 250 (3.92), (d) 276 (4.04)	348 (4.06)	6.68
7e	1770, 1645	(a) 258 (4.06), (c) 257 (4.03),	350 (3.88) 330 (4.10)	(b) 251 (4.06), (d) 267 (4.11)	350 (4.14)	6.35
7f	1765, 1640	(a) 254 (3.99), (c) 248 (4.04),	399 (3.99) 341 (4.17)	(b) 248 (4.02), (d) 268 (4.11)	342 (4.09)	6.32

(a) In 95% ethanol. (b) In 95% ethanol + sodium bicarbonate solution. (c) In water. (d) In chloroform.

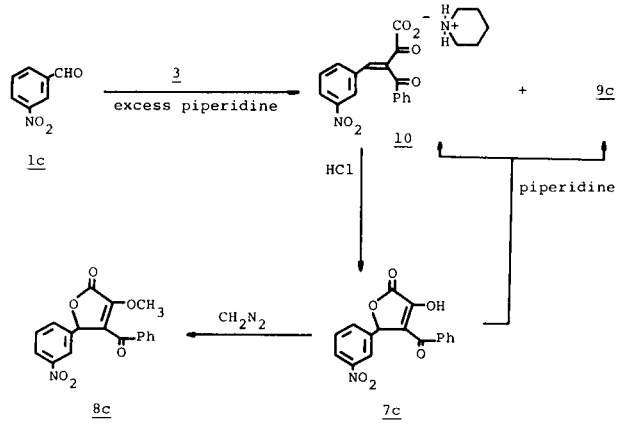
Table VI

Physical and Spectral Data for Compounds **8a**, **8c-f**

Compound No.	M.p. (°C) (Recryst. Solv.)	Formula	Analyses (%) Calcd. (Found) C	H	N	Pmr Data (δ) -COOCH$_3$	-CH	Uv Data in Ethanol nm (log ε)
8a	117-118 (a)	$C_{18}H_{14}O_4$	73.46 (73.61)	4.80 (4.69)		3.90	6.40	262 (4.04)
8c	86-87 (b)	$C_{18}H_{13}NO_6$	63.72 (63.66)	3.86 (3.77)	4.13 (4.07)	4.05	6.40	260 (4.29)
8d	114-115 (c)	$C_{18}H_{13}O_4Cl$	65.76 (65.74)	3.98 (4.11)		3.95	6.75	263 (3.98)
8e	122-124 (b)	$C_{19}H_{16}O_4$	74.01 (74.17)	5.23 (5.19)		3.90	6.35	260 (4.10)
8f	120-121 (c)	$C_{19}H_{16}O_5$	70.36 (70.42)	4.98 (5.01)		3.95	6.25	262 (4.13)

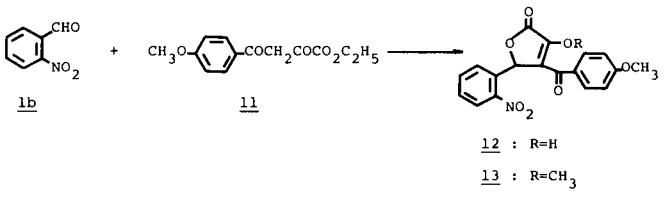
(a) Ligroin. (b) Ethanol. (c) Methanol.

ed by alternative synthesis according to Sorge (7). It could be considered that these chalcones were formed *via* 3-benzoyl-2,4-dihydroxy-4-nitrophenylcrotonic acid lactones as intermediates, followed by decarbonylation and decarboxylation. Alternatively, treatment of **1c** with **3** in the presence of a large excess of piperidine gave a mixture of **9c** in 28% yield and 3-(*m*-nitrobenzylidene)benzoylpyruvic acid piperidinium salt (**10**), m.p. 165-166°, in 26% yield. The structural assignment of **10** was supported by its ir spectrum, which gave a characteristic absorption band at 3000-2600 cm^{-1} due to a quarternary ammonium salt, and its uv spectrum, which is discussed below. Compound **10** was subsequently converted to the lactone (**7c**) (Table V) in quantitative yield by treatment with hydrochloric acid. The uv spectrum of **7c** showed an absorption maxima at 262 (4.10) and 342 (4.05) in water, but showed an absorption maximum at 268 (4.29) in chloroform. The spectrum of **10**, however, showed the same absorption pattern in water and in chloroform. This result clearly indicated that compound **10** has the open-form structure. Treatment of **7c** with excess piperidine afforded a mixture of **9c** and the salt (**10**), which was readily changed to **9c** upon heating past its melting point.



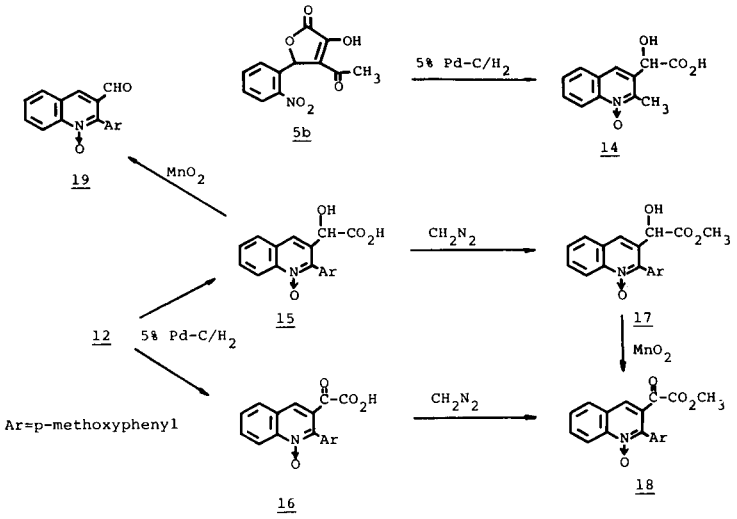
Scheme II

Attempted formation, however, of the piperidinium salt of the *ortho*-nitro derivative failed, and gave only **9b**. We assumed that the readiness of this decarbonylation and decarboxylation is facilitated by the *ortho*-substituted electron-withdrawing nitro group. With this in mind, **1b** was condensed with ethyl *p*-methoxybenzoylpyruvate (**11**) (5) in the presence of excess piperidine giving a 31% yield of 2,4-dihydroxy-3-(*p*-methoxybenzoyl)-4-(*o*-nitrophenyl)-crotonic acid lactone (**12**), the structure of which was determined by the spectral and microanalytical data, and by the ferric chloride test (red-violet). The reaction of **12** with diazomethane gave the corresponding methyl ether (**13**).



Scheme III

Recently we have reported (8) the reductive cyclization of **5b** in the presence of 5% palladium-carbon to give α-hydroxy-2-methyl-3-quinolineacetic acid 1-oxide (**14**) in 88% yield. Here we tried the catalytic hydrogenation of **12** in a large quantity of methanol with 5% palladium-carbon, which gave α-hydroxy-2-(*p*-methoxyphenyl)-3-quinolineacetic acid 1-oxide (**15**), m.p. 252-253°, in 72%



Scheme IV

yield. Similarly, hydrogenation of **12** in a small quantity of methanol resulted in a simultaneous cyclization to 2-(*p*-methoxyphenyl)-3-quinolineglyoxylic acid 1-oxide (**16**), m.p. 234-235°, in 66% yield. To confirm the structures of **15** and **16**, the following reactions were carried out. These compounds were reacted to give the methyl esters **17** and **18**, respectively, by the action of diazomethane. The hydroxy ester (**17**) was further smoothly oxidized by manganese dioxide to **18**. Finally, the hydroxy acid (**15**) was oxidized by manganese dioxide in dimethyl sulfoxide to 2-(*p*-methoxyphenyl)-3-quinolinecarboxaldehyde 1-oxide (**19**).

EXPERIMENTAL

All melting points are uncorrected. Infrared (ir) and ultraviolet (uv) spectra were taken on a JASCO IRA-1 and a Schimadzu UV-200 spectrophotometer respectively. Proton magnetic resonance (pmr) spectra were run in deuteriodimethylsulfoxide, with TMS as the internal standard, with a Hitachi spectrometer.

3-Acetyl-2,4-dihydroxy-4-phenylcrotonic Acid Lactones (**5a-f**).

To a mixture of the appropriate benzaldehyde (**1a-f**) (0.02 mole) and ethyl acetylpyruvate (**2**) (0.02 mole) was added 5 drops of piperidine, and the solution was allowed to stand at 30-60° for 24-240 hours. The solid, precipitated with cold benzene, was collected by filtration and recrystallized (Tables I and II).

3-Acetyl-4-hydroxy-2-methoxy-4-phenylcrotonic Acid Lactones (**6a-f**).

To an ether solution containing excess diazomethane was added the appropriate acid (**5a-f**) with vigorous stirring under ice cooling. The precipitated solid was collected by filtration and recrystallized (Table III).

3-Benzoyl-2,4-dihydroxy-4-phenylcrotonic Acid Lactones (**7a**, **7d-f**).

To a mixture of the appropriate benzaldehyde (**1a**, **1d-f**) (0.02 mole) and ethyl benzoylpyruvate (**3**) (0.02 mole) was added 5 drops of piperidine, and the whole mixture was allowed to stand at 50° for 72 hours. The solid, precipited with cold benzene, was collected by filtration and recrystallized (Tables IV and V).

3-Benzoyl-4-hydroxy-2-methoxy-4-phenylcrotonic Acid Lactones (**8a**, **8c-f**).

To an ether solution containing excess diazomethane was added the appropriate acid (**7a**, **7c-f**) with vigorous stirring under ice cooling. The solid was collected by filtration and recrystallized (Table VI).

Reaction of **1b** with **3**.

A.

To a mixture of **1b** (3.02 g.) (0.02 mole) and **3** (4.40 g.) (0.02 mole) was added 5 drops of piperidine, and the mixture was allowed to stand at 40° for 2 days. The resulting viscous oil was dissolved in chloroform. The chloroform solution was washed with a saturated sodium bicarbonate solution, dried (sodium sulfate), and evaporated. The residual oil was passed through an alumina column eluted with benzene to give **9b** (1.11 g.) (22%), which was identical with an authentic sample by comparison of their ir spectra, and a mixed melting point determination. The sodium bicarbonate solution was acidified with hydrochloric acid, but no crystalline product was obtained.

B.

To a mixture of **1b** (1.51 g.) (0.01 mole) and **3** (2.20 g.) (0.01 mole) was added piperidine (4.75 g.) (0.06 mole), and the mixture was treated as described in A to give **9b** in 24% yield.

Reaction of **1c** with **3**.

A.

To a mixture of **1c** (1.51 g.) (0.01 mole) and **3** (2.20 g.) (0.01 mole) was added 5 drops of piperidine, and the mixture was allowed to stand at 40° for 2 days. By the same treatment as described in **1b**, **9c** (1.14 g.) (23%) was isolated. This compound was identical with an authentic sample by comparison of their ir spectra and a mixed melting point determination.

B.

To a mixture of **1c** (3.02 g.) (0.02 mole) and **3** (4.40 g.) (0.02 mole) was added piperidine (4.75 g.) (0.06 mole). A spontaneous

exothermic reaction took place, and the mixture solidified. The insoluble solid, deposited with benzene, was collected by filtration and recrystallized from methanol to give the piperidinium salt (**10**) (2.13 g.) (26%), m.p. 165-166°; ir ν max (potassium bromide) cm^{-1}: 3000-2600, 1760; pmr δ: 6.65 (1H, s, -CH); uv λ max nm (log ϵ): in ethanol, 256 (4.20), 347 (4.10); in water, 262 (4.12), 342 (4.11); in chloroform, 260 (4.18), 341 (4.04).

Anal. Calcd. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.50; H, 5.57; N, 6.55.

After concentration of the benzene filtrate, the residue was passed through an alumina column eluted with benzene to give **8c** (1.32 g.) (26%), which was identical with authentic sample in all respects.

3-Benzoyl-2,4-dihydroxy-4-(*m*-nitrophenyl)crotonic Acid Lactone (**7c**).

A solution of **10** (410 mg.) (1 mmole) suspended in water (5 ml.) was acidified with concentrated hydrochloric acid, and the separated solid was collected by filtration. Recrystallization from methanol gave pale yellow needles (**7c**) (318 mg.) (98%), m.p. 204-205°. Spectral data is shown in Table V.

Anal. Calcd. for $C_{17}H_{11}NO_6$: C, 62.77; H, 3.41; N, 4.31. Found: C, 63.00; H, 3.32; N, 4.30.

Reaction of **7c** with Piperidine.

A mixture of **7c** (325 mg.) (1 mmole) and piperidine (3 ml.) was allowed to stand at 40° for 3 hours. The solid, precipated with hot benzene, was collected by filtration and recrystallized from methanol to give **10** (225 mg.) (55%), which was identical with an authentic sample in all respects. After concentration of the benzene filtrate, the residual oil was passed through an alumina column eluted with benzene to give a trace of **9c**.

Pyrolysis of **10**.

The piperidinium salt (**10**) (410 mg.) (1 mmole) was heated in a pre-heated oil bath at 170° until the evolution of gas ceased. The viscous brownish oil was dissolved in chloroform. The chloroform solution was washed with 5% hydrochloric acid, water, and dried (sodium sulfate). After evaporation of the solvent, the residual oil was passed through an alumina column eluted with benzene to give **9c** (172 mg.) (68%), which was identical with authentic sample in all respects.

2,4-Dihydroxy-3-(*p*-methylbenzoyl)-4-(*o*-nitrophenyl)crotonic Acid Lactone (**12**).

To a mixture of **1b** (3.02 g.) (0.02 mole) and **11** (5.0 g.) (0.02 mole) was added piperidine (5 ml.), and the mixture was allowed to stand at 50° for 2 days. Five percent sodium hydroxide solution (20 ml.) was added, and the mixture was stirred for 1 hour. After the insoluble oily layer was separated, the alkaline layer was washed with chloroform and neutralized with concentrated hydrochloric acid under ice cooling. The precipitated solid was collected by filtration and recrystallized from ethanol to give pale yellow needles (**12**) (2.10 g.) (31%), m.p. 182-183°; ir ν max (potassium bromide) cm^{-1}: 1785, 1640; uv λ max (ethanol) nm (log ϵ): 290 (4.00), 347 (3.96); pmr δ: 3.85 (3H, s, OCH_3), 6.85 (1H, s, -CH).

Anal. Calcd. for $C_{18}H_{13}NO_6$: C, 60.85; H, 3.68; N, 3.94. Found: C, 61.11; H, 3.75; N, 3.69.

4-Hydroxy-2-methoxy-3-(*p*-methoxybenzoyl)-4-(*o*-nitrophenyl)-crotonic Acid Lactone (**13**).

To an ether solution containing excess diazomethane was added **12** (355 mg.) (1 mmole), and the mixture was stirred vigorously at room temperature for 24 hours. The resulting solid was collected by filtration and recrystallized from methanol to give **13** (313 mg.) (85%), m.p. 150-151°; ir ν max (potassium bromide) cm^{-1}: 1795, 1650; uv λ max (ethanol) nm (log ϵ): 296 (4.18); pmr δ: 3.83 and 3.84 (each 3H, each s, 2 x $-OCH_3$), 6.87 (1H, s, -CH).

Anal. Calcd. for $C_{19}H_{15}NO_7$: C, 61.79; H, 4.09; N, 3.79. Found: C, 61.89; H, 4.00; N, 3.76.

Catalytic Hydrogenation of **12**.

A.

A mixture of **12** (1.13 g.) (0.003 mole) and 5% palladium-carbon (0.5 g.) in methanol (300 ml.) was hydrogenated at room temperature for 10 hours. The catalyst was removed by filtration and the filtrate was condensed *in vacuo* until the solid began to precipitate. The solution was chilled, and the solid was collected by filtration and dried to give **15** (0.77 g.) (72%), which was recrystallized from methanol to give an analytical sample, m.p. 252-253°; ir ν max (potassium bromide) cm^{-1}: 1720; pmr δ: 3.85 (3H, s, OCH_3), 4.90 (1H, s, -CH).

Anal. Calcd. for $C_{18}H_{15}NO_5$: C, 66.45; H, 4.65; N, 4.31. Found: C, 66.55; H, 4.73; N, 4.14.

B.

A mixture of **12** (1.13 g.) (0.003 mole), 5% palladium-carbon (0.5 g.) in methanol (50 ml.) was hydrogenated at room temperature for 10 hours. The resulting precipitate contaminated with catalyst was collected by filtration and dissolved in saturated sodium bicarbonate solution (20 ml.). After the catalyst was removed by filtration, the filtrate was acidified with concentrated hydrochloric acid and chilled. The precipitate was collected by filtration and dried to give **16** (0.74 g.) (66%), which was recrystallized from methanol to give an analytical sample, m.p. 234-235°; ir ν max (potassium bromide) cm^{-1}: 1705; pmr δ: 3.85 (3H, s, $-OCH_3$), 8.35 (1H, s, C_4-H).

Anal. Calcd. for $C_{18}H_{13}NO_2H_2O$: C, 63.34; H, 4.43; N, 4.10. Found: C, 63.52; H, 4.42; N, 3.90.

Methyl α-Hydroxy-2-(*p*-methoxyphenyl)-3-quinolineacetate 1-Oxide (**17**).

To an ether solution containing excess diazomethane was added **15** (325 mg.) (1 mmole) and the mixture was stirred vigorously at room temperature for 24 hours. The resulting solid was collected by filtration and recrystallized from methanol to give **17** (278 mg.) (82%), m.p. 159-160°; ir ν max (potassium bromide) cm^{-1}: 1760; pmr δ: 3.53 (3H, s, $-COOCH_3$), 3.83 (3H, s, $-OCH_3$), 5.40 (1H, d, J = 6 Hz, -CHOH), 6.40 (1H, d, J = 6 Hz, -CHO*H*).

Anal. Calcd. for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.50; H, 4.82; N, 3.95.

Methyl 2-(*p*-Methoxyphenyl)-3-quinolineglyoxylate 1-Oxide (**18**).

A.

To an ether solution containing excess diazomethane was added **16** (341 mg.) (1 mmole) and the mixture was stirred vigorously at room temperature for 24 hours. The resulting solid was collected by filtration and recrystallized from methanol to give **18** (290 mg.) (86%), m.p. 227-228°; ir ν max (potassium bromide) cm^{-1}: 1760; pmr δ: 3.40 (3H, s, $-COOCH_3$), 3.85 (3H, s, $-OCH_3$), 8.43 (1H, s, C_4-H).

Anal. Calcd. for $C_{19}H_{15}NO_5$: C, 67.65; H, 4.48; N, 4.15. Found: C, 67.47; H, 4.31; N, 4.15.

B.

To a solution of **16** (339 mg.) (1 mmole) in dry chloroform (20 ml.) was added manganese dioxide (0.5 g.). The mixture was warmed at 40° with stirring overnight. The manganese dioxide was removed by filtration, and the filtrate was evaporated to dryness. The solid was recrystallized from methanol to give **18** (286 mg.) (86%), which was identical with an authentic sample in all respects.

2-*p*-Methoxyphenyl-3-quinolinecarboxaldehyde 1-Oxide (**19**).

To a solution of **15** (325 mg.) (1 mmole) in dimethylsulfoxide (10 ml.) was added manganese dioxide (1.2 g.). After stirring overnight at room temperature, manganese dioxide was removed by filtration. The filtrate, diluted with water (200 ml.), was extracted with chloroform. The extract was washed with water several times, dried (sodium sulfate), and evaporated. The residue was recrystallized from methanol to give **19** (214 mg.) (77%), m.p. 247-248°; ir ν max (potassium bromide) cm^{-1}: 1700; pmr δ: 3.87 (3H, s, $-OCH_3$), 8.50 (1H, s, C_4-H), 9.73 (1H, s, -CHO).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.06; H, 4.64; N, 4.76.

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