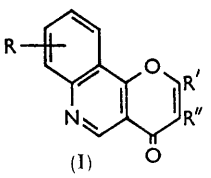
545. *Pyranoquinolines. Part II.*[1]

By K. Elliott and E. Tittensor.

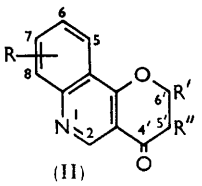
Further examples are described of the synthesis of pyranoquinolines by the application of the Kostanecki–Robinson reaction to derivatives of 3-acetyl-4-hydroxyquinoline. Dihydropyranoquinolines have been prepared by condensing derivatives of 3-acetyl-4-hydroxyquinolines with benzaldehyde.

We have found that in certain cases Snyder and Jones's [2] method for the synthesis of ethyl α-acetyl-β-anilinoacrylates gives only α-acetyl-β-*N*-arylacrylamides, not previously recorded. The acrylates unobtainable by Snyder and Jones's method were, however, prepared by Claisen's method.[3]

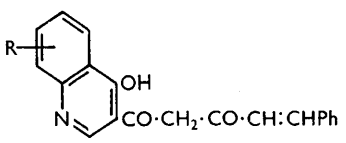
The 3-acetyl-4-hydroxyquinolines obtained by thermal cyclisation of the anilinoacrylates in diphenyl ether [2] were heated with various acid anhydrides in the presence of triethylamine. From 3-acetyl-4-hydroxyquinoline and its 6-methoxy- and 6-methyl derivative with benzoic anhydride the sole product, in each case, was the 4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (I; R = H, OMe, or Me, R′ = Ph, R″ = H), whereas with furoic anhydride the sole product was in each case a 5′-furoyl-6′-furyl-4′-oxo-pyrano-(3′,2′-3,4)quinoline (I; R = H or OMe, or Me, R′ = C_4H_3O, R″ = C_4H_3O·CO). When cinnamic anhydride was used the 6-methoxy-derivative yielded a 5′-cinnamoyl-6′-styrylpyrano(3′,2′-3,4)quinoline (I; R = OMe, R′ = Ph·CH=CH, R″ = Ph·CH=CH·CO), whereas the parent acetylhydroxyquinoline gave the uncyclised product (III; R = H). No product was isolated from the reaction of the 6-methyl derivative with cinnamic anhydride.



(I)



(II)



(III)

No products could be isolated after reaction of 3-acetyl-4-hydroxy-6-, -7-, or -8-nitroquinoline and 3-acetyl-7-chloro-4-hydroxyquinoline with acetic anhydride, but the 5′-acetyl derivatives of the methylpyranoquinolines (I; R = H, Br, OMe, or Me, R′ = Me, R″ = Me·CO) were obtained from 3-acetyl-4-hydroxyquinoline, 3-acetyl-6-bromo-4-hydroxyquinoline, and 3-acetyl-4-hydroxy-6-methoxy- and -6-methyl-quinoline.

The phenyl-, furyl-, and styryl-pyranoquinolines gave the characteristic colours with concentrated sulphuric acid, described in Part I,[1] whereas the methylpyranoquinolines gave only brown colours.

The ultraviolet absorption spectra of the phenyl- and furyl-pyranoquinolines described above and in Part I are indicated in Table I. The spectra show a similarity to those of the corresponding naphtho(1′,2′-2,3)pyrans, which are included for comparison. 5-Furoyl-6-furyl-4-oxonaphtho(1′,2′-2,3)pyran, not previously recorded, was prepared by the interaction of 2-acetyl-1-naphthol with furoic anhydride, in the presence of triethylamine.

Condensing 3-acetyl-4-hydroxyquinoline with benzaldehyde in refluxing methanolic sodium hydroxide, cold ethanolic sodium hydroxide [4] or in the presence of piperidine [5] gave only the dihydropyrano(3′,2′-3,4)quinoline (II; R = R″ = H, R′ = Ph). 3-Acetyl-6-bromo-4-hydroxyquinoline condensed with benzaldehyde in refluxing methanolic sodium hydroxide to give a mixture of the dihydropyranoquinoline (II; R = Br, R′ = Ph, R″ = H) and 6-bromo-4-hydroxy-3-quinolyl styryl ketone. When the condensation was carried

[1] Part I, Elliott and Tittensor, *J.*, 1959, 484.
[2] Snyder and Jones, *J. Amer. Chem. Soc.*, 1946, **68**, 1253.
[3] Claisen, *Annalen*, 1897, **297**, 1.
[4] Geissman and Clinton, *J. Amer. Chem. Soc.*, 1946, **68**, 697.
[5] Algar and Hanlon, *Proc. Royal Irish Acad.*, 1929, **38**, *B*, 175.

out in cold ethanolic sodium hydroxide or with piperidine as catalyst the latter compound was the sole product.

TABLE 1. *Ultraviolet spectra* (λ *in* mμ) *for the pyranoquinolines* (I).

R	R′	R″	$\lambda_{max.}$		log ε		$\lambda_{min.}$	log ε
H	Ph	H	222	270	4·56	4·41	240	3·95
7-Cl	Ph	H	230	270	4·38	4·58	240	4·19
6-Br	Ph	H	224	268	4·65	4·56	244	4·26
6-NO_2	Ph	H	224	254	4·35	4·75	—	—
7-NO_2	Ph	H	—	264	—	4·59	230	4·17
8-NO_2	Ph	H	—	268	—	4·42	248	4·17
6-Me	Ph	H	226	272	4·56	4·42	244	3·96
6-OMe	Ph	H	232	266	4·85	4·79	248	4·61
4-Oxo-6-phenylnaphtho(1′,2′-2,3)pyran			252	280	4·67	4·53	263	4·39
6-NO_2	Ph	–COPh	236	262	4·47	3·96	228	4·40
7-NO_2	Ph	–COPh	—	272	—	4·72	—	—
8-NO_2	Ph	–COPh	—	268	—	4·63	236	4·42
5-Benzoyl-4-oxo-6-phenylnaphtho(1′,2′-2,3)pyran			—	268	—	5·16	242	4·19
H	C_4H_3O	C_4H_3O·CO	224	278	4·73	4·61	246	4·26
7-Cl	C_4H_3O	C_4H_3O·CO	230	282	4·57	4·59	250	4·18
6-Br	C_4H_3O	C_4H_3O·CO	232	276	4·31	4·27	250	4·04
6-NO_2	C_4H_3O	C_4H_3O·CO	—	258	—	4·62	—	—
7-NO_2	C_4H_3O	C_4H_3O·CO	—	282	—	4·6	242	4·35
8-NO_2	C_4H_3O	C_4H_3O·CO	222	280	4·54	4·49	244	4·24
6-Me	C_4H_3O	C_4H_3O·CO	228	280	4·63	4·49	248	4·18
6-OMe	C_4H_3O	C_4H_3O·CO	232	276	4·66	4·54	250	4·32
5-Furoyl-6-furyl-4-oxonaphtho-(1′,2′-2,3)pyran			226	284	4·62	4·59	250	4·22

The dihydropyranoquinoline (II; R = Br, R′ = Ph, R″ = H) was recovered unchanged after attempted ozonolysis in chloroform, and no identifiable products were isolated on ozonolysis of the isomeric styryl ketone.

Bromination of 5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (II; R = R″ = H, R′ = Ph) gave the 5′-bromo-derivative which was dehydrobrominated in pyridine to the pyrano(3′,2′-3,4)quinoline (I; R = R″ = H, R′ = Ph). Bromination of either 6-bromo-5′,6′-dihydro-4′-oxo-6-phenylpyrano(3′,2′-3,4)quinoline or the 6-bromo-4-hydroxy-3-quinolyl styryl ketone gave the 5′,6-dibromophenylpyrano(3′,2′-3,4)quinoline (II; R = R″ = Br, R′ = Ph), which was dehydrobrominated to 6-bromo-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (I; R = Br, R′ = Ph, R″ = H).

5′,6′-Dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline and its 6-bromo-derivative were dehydrogenated by *N*-bromosuccinimide [6] or selenium dioxide [7] to 4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (I; R = R″ = H, R′ = Ph) and the 6-bromo-compound (I; R = Br, R′ = Ph, R″ = H) respectively. Treatment of 6-bromo-4-hydroxy-3-quinolyl styryl ketone with selenium dioxide caused simultaneous cyclisation and dehydrogenation, yielding 6-bromo-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (I; R = Br, R′ = Ph, R″ = H).

The action of pentyl nitrite [8] on 5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline and the 6-bromodihydropyranoquinoline (II; R = Br, R′ = Ph, R″ = H) gave in both cases the 5′-hydroxyimino-compound (II; R = H or Br, R′ = Ph, R″ = :N·OH) which was hydrolysed in 50% sulphuric acid to the corresponding 5′-hydroxy-compound. Treatment of 5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (II; R = R″ = H, R′ = Ph) with alkaline hydrogen peroxide [9] gave directly 5′-hydroxy-4′-oxo-6′-phenylpyrano-(3′,2′-3,4)quinoline (I; R = H, R′ = Ph, R″ = OH). Under similar conditions 6-bromo-5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline and 6-bromo-4-hydroxy-3-quinolyl

[6] Lorette, Gage, and Wender, *J. Org. Chem.*, 1951, **16**, 930.
[7] Mahal, Rai, and Venkataraman, *J.*, 1935, 866.
[8] Kostanecki and Lampe, *Ber.*, 1904, **37**, 773.
[9] Oyamada, *J. Chem. Soc. Japan*, 1934, **55**, 1256.

styryl ketone gave 6-bromo-5′-hydroxy-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (I; R = Br, R′ = Ph, R″ = OH).

Experimental

Ethyl α-Acetyl-β-anilinoacrylates and α-Acetyl-β-anilino-N-phenylacrylamides.—The anilinoacrylates prepared by Snyder and Jones's method [2] (cf. Part I [1]) are recorded in Table 2, nos. 1—3. The corresponding acrylamides, obtained simultaneously, are shown in Table 3, nos. 1—3. Only the acrylamides were isolated in experiments 4—11 of Table 3. Ethyl α-acetyl-β-anilino-, -*p*-anisidino-, and -*p*-toluidino-acrylate (Table 2, nos. 12—14) were prepared by Claisen's method.[3]

Table 2. *Ethyl α-acetyl-β-anilinoacrylates*, $R{\cdot}C_6H_4{\cdot}NH{\cdot}CH{:}CAc{\cdot}CO_2Et$.

				Required (%)				Found (%)		
No.	R	Solvent	M. p.	C	H	N	Formula	C	H	N
1	*p*-Cl	A	87—89°	58·3	5·2	5·2	$C_{13}H_{14}ClNO_3$	58·2	5·0	5·3
2	*o*-Br	B	92—94	50·0	4·5	4·5	$C_{13}H_{14}BrNO_3$	50·0	4·4	4·8
3	*m*-Br	B	94—96	50·0	4·5	4·5	$C_{13}H_{14}BrNO_3$	50·0	4·6	4·8
Prepared by Claisen's method:										
12	H	D	41—43	—	—	—		—	—	—
13	*p*-Me	D	50—51	68·0	6·8	5·7	$C_{14}H_{17}NO_3$	68·0	7·0	5·9
14	*p*-OMe	A	87—88	—	—	—		—	—	—

A, MeOH. B, EtOH. C, Toluene. D, Light petroleum (b. p. 60—80°).

Table 3. *α-Acetyl-β-anilino-N-arylacrylamides*, $R{\cdot}C_6H_4{\cdot}NH{\cdot}CH{:}CAc{\cdot}CO{\cdot}NH{\cdot}C_6H_4R$.

				Required (%)				Found (%)		
No.	R	Solvent	M. p.	C	H	N	Formula	C	H	N
1	*p*-Cl	C	202—204°	58·5	4·0	8·0	$C_{17}H_{14}Cl_2N_2O_2$	58·8	4·3	8·2
2	*o*-Br	C	163—165	46·5	3·2	6·4	$C_{17}H_{14}Br_2N_2O_2$	46·9	3·2	6·3
3	*m*-Br	C	155—156	46·5	3·2	6·4	,,	46·9	3·1	6·5
4	H	A	156—157	72·7	5·7	10·0	$C_{17}H_{16}N_2O_2$	72·7	5·6	11·2, 11·0
5	*o*-Cl	A	136—138	58·5	4·0	8·0	$C_{17}H_{14}Cl_2N_2O_2$	58·5	4·0	8·4
6	*o*-Me	B	170—171	74·0	6·5	9·1	$C_{19}H_{20}N_2O_2$	73·7	6·2	9·0
7	*m*-Me	B	132—134	,,	,,	,,	,,	74·0	6·6	9·4
8	*p*-Me	B	174—175	,,	,,	,,	,,	74·1	6·6	9·4
9	*o*-OMe	B	139—141	67·1	5·9	8·2	$C_{19}H_{20}N_2O_4$	66·9	5·9	8·1
10	*m*-OMe	B	137—139	,,	,,	,,	,,	67·3	5·8	8·2
11	*p*-OMe	A	130—132	,,	,,	,,	,,	67·3	5·8	7·9

A—D, as in Table 2.

3-Acetyl-4-hydroxyquinolines.—3-Acetyl-4-hydroxyquinoline and 3-acetyl-4-hydroxy-6-methyl- and -6-methoxy-quinoline were prepared as described in Part I.

4′-Oxo-6′-phenylpyrano(3′,2′-3,4)quinoline.—3-Acetyl-4-hydroxyquinoline (1·8 g.) was refluxed with benzoic anhydride (11·3 g.) and triethylamine (8·3 c.c.) at 170—180° for 2 hr., the cooled mixture extracted with ether (50 c.c.), and the insoluble material (0·9 g.) crystallised from ethanol, to give *4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline*, needles, m. p. 231—232° (Found: C, 78·6; H, 4·0; N, 5·4. $C_{18}H_{11}NO_2$ requires C, 79·1; H, 4·0; N, 5·1%).

Similarly 3-acetyl-4-hydroxy-6-methyl- and -6-methoxy-quinoline at 170—180° (2 and 3 hr., respectively) gave the following ether-insoluble 4′-oxo-6′-phenylpyranoquinolines; *6-methyl-*, needles (from ethanol), m. p. 216—218° (Found: C, 79·3; H, 4·5; N, 4·9. $C_{19}H_{13}NO_2$ requires C, 79·5; H, 4·5; N, 4·9%), *6-methoxy-*, needles (from ethanol), m. p. 202—204° (Found: C, 75·7; H, 4·4; N, 4·4. $C_{19}H_{13}NO_3$ requires C, 75·3; H, 4·3; N, 4·6%).

3-Cinnamoylacetyl-4-hydroxyquinoline.—3-Acetyl-4-hydroxyquinoline (1·8 g.), cinnamic anhydride (13·9 g.), and triethylamine (8·5 c.c.) were refluxed at 190—200° for 3 hr. The tarry mixture was extracted with ether, and the insoluble material crystallised from propanol, to give *3-cinnamoylacetyl-4-hydroxyquinoline*, prisms, m. p. 210—214° (decomp.) (Found: C, 76·9; H, 4·6; N, 4·7. $C_{20}H_{15}NO_3$ requires C, 76·0; H, 4·7; N, 4·4%).

5′-Cinnamoyl-6-methoxy-4′-oxo-6′-styrylpyrano(3′,2′-3,4)quinoline.—3-Acetyl-4-hydroxy-6-methoxyquinoline (2·2 g.) was refluxed with cinnamic anhydride (13·9 g.) and triethylamine (8·3 c.c.) at 190—200° for 3·5 hr., the cooled mixture extracted with methanol, and the insoluble

material (0·3 g.) crystallised from 2-ethoxyethanol to give *5′-cinnamoyl-6-methoxy-4′-oxo-6′-styrylpyrano(3′,2′-3,4)quinoline* as yellow needles, m. p. 250—252° (Found: C, 79·0; H, 4·6; N, 2·8. $C_{30}H_{21}NO_4$ requires C, 78·6; H, 4·6; N, 3·0%).

5′-Furoyl-6′-furyl-4′-oxopyrano(3′,2′-3,4)quinoline.—3-Acetyl-4-hydroxyquinoline (1·8 g.) was refluxed with furoic anhydride (10·3 g.) and triethylamine (8·3 c.c.) at 170—180°, for 2 hr., the black oil diluted with acetone, and the precipitated solid (1·6 g.) crystallised from nitrobenzene, to give *5′-furoyl-6′-furyl-4′-oxopyrano(3′,2′-3,4)quinoline* as needles, m. p. 278—279° (Found: C, 70·4; H, 3·1; N, 4·3. $C_{21}H_{11}NO_5$ requires C, 70·6; H, 3·1; N, 3·9%).

Similarly 3-acetyl-4-hydroxy-6-methyl- and -6-methoxy-quinoline, reacting at 170—180° for 2 hr., gave the 6-*methyl*-, needles (from acetic acid), m. p. >300° (Found: C, 71·3; H, 3·5; N, 3·9. $C_{22}H_{13}NO_5$ requires C, 71·0; H, 3·5; N, 3·8%), and the 6-*methoxy*-derivative, needles (from 2-ethoxyethanol), m. p. >300° (Found: C, 67·6; H, 3·5; N, 3·4. $C_{22}H_{13}NO_6$ requires C, 68·2; H, 3·4; N, 3·6%).

5′-Acetyl-6′-methyl-4′-oxopyrano(3′,2′-3,4)quinoline.—3-Acetyl-4-hydroxyquinoline (1·8 g.), acetic anhydride (9·4 c.c.), and triethylamine (8·3 c.c.) were refluxed at 180—190° for 6 hr. The cooled mixture was diluted with ether, and the light brown solid collected and treated with 2N-sodium hydroxide. The insoluble material crystallised from propanol, giving *5′-acetyl-6′-methyl-4′-oxopyrano(3′,2′-3,4)quinoline* (0·7 g.) as prisms, m. p. 270—275° (decomp.) (Found: C, 71·8; H, 4·4; N, 5·3. $C_{15}H_{11}NO_3$ requires C, 71·2; H, 4·4; N, 5·5%).

Similarly 3-acetyl-6-bromo-4-hydroxyquinoline and 3-acetyl-4-hydroxy-6-methyl- and -6-methoxy-quinoline gave the 6-*bromo*- (prepared at 160—170°; 3 hr.), prisms (from aqueous ethanol), m. p. 275—277° (Found: C, 54·0; H, 3·1; N, 4·8. $C_{15}H_{10}BrNO_3$ requires C, 54·2; H, 3·0; N, 4·2%), 6-*methyl*- (prepared at 210—220°; 7·5 hr.), prisms (from propanol), m. p. >300° (Found: C, 72·3; H, 5·1; N, 4·6. $C_{16}H_{13}NO_3$ requires C, 71·9; H, 4·9; N, 5·2%), and 6-*methoxy-analogue* (prepared at 210—220°; 6 hr.), prisms (from cyclohexanol), m. p. >300° (Found: C, 67·4; H, 4·8; N, 4·7. $C_{16}H_{13}NO_4$ requires C, 67·8; H, 4·6; N, 5·0%).

Condensation of 3-Acetyl-4-hydroxyquinoline with Benzaldehyde.—(a) *In hot methanolic sodium hydroxide.* 3-Acetyl-4-hydroxyquinoline (1·0 g.), methanol (10·0 c.c.), 10% aqueous sodium hydroxide (20 c.c.), and benzaldehyde (2·5 c.c.) were refluxed for 0·5 hr. After acidification of the cooled solution the precipitate was collected and crystallised from propanol, to give *5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline* as prisms, m. p. 269—271° (Found: C, 78·6; H, 5·0; N, 5·2. $C_{18}H_{13}NO_2$ requires C, 78·5; H, 4·8; N, 5·1%).

(b) *In cold alcoholic sodium hydroxide.* A suspension of 3-acetyl-4-hydroxyquinoline (1·0 g.) in 60% sodium hydroxide (14 c.c.) was treated with ethanol (50 c.c.) and benzaldehyde (0·59 c.c.). The mixture was kept at 0—5° for 48 hr. and then acidified. The precipitate was crystallised from propanol, giving 5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline, m. p. and mixed m. p. 269—271°.

(c) *In the presence of piperidine.* A solution of 3-acetyl-4-hydroxyquinoline (1·0 g.), benzaldehyde (0·59 c.c.), and piperidine (2·9 c.c.) in ethanol (25 c.c.) was refluxed for 3·75 hr. A bright yellow precipitate was slowly deposited. The solid crystallised from propanol, giving the same dihydropyranoquinoline as described in (a) above (m. p. and mixed m. p. 269—271°).

Condensation of benzaldehyde with 3-acetyl-6-bromo-4-hydroxyquinoline under the conditions described in (a) gave as the main product 6-*bromo-5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline* as prisms (from propanol), m. p. 290—292° (Found: C, 60·8; H, 3·5; N, 4·1. $C_{18}H_{12}BrNO_2$ requires C, 61·0; H, 3·4; N, 4·0%) (isolated as a sodium salt).

Dilution and acidification of the methanolic filtrate gave a brown precipitate which crystallised from 2-ethoxyethanol, giving 6-*bromo-4-hydroxy-3-quinolyl styryl ketone* as prisms, m. p. 270—271° (Found: C, 60·8; H, 3·5; N, 4·2. $C_{18}H_{12}BrNO_2$ requires C, 61·0; H, 3·4; N, 4·0%).

5′,6-Dibromo-5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline.—(*a*) A suspension of 6-bromo-5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline (2·3 g.) in chloroform (50 c.c.) was treated with bromine (1·04 g.) in chloroform (25 c.c.), and then the pale yellow solution was evaporated. The residual gum crystallised from methanol, giving *5′,6-dibromo-5′,6′-dihydro-4′-oxo-6′-phenylpyrano(3′,2′-3,4)quinoline* (2·8 g.) as prisms, m. p. 260° (decomp.) (Found: Br, 37·0. $C_{18}H_{11}Br_2NO_2$ requires Br, 36·8%).

(*b*) A solution of bromine (0·18 c.c.) in chloroform (15 c.c.) was added to a suspension of 6-bromo-4-hydroxy-3-quinolyl styryl ketone (0·5 g.) in chloroform (15 c.c.). Evaporation gave a glass which crystallised from ethanol, giving the preceding compound, m. p. 258—260° (decomp.) (Found: Br, 36·6%).

5'-Bromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)*quinoline*.—Bromination of 5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline as above gave the *5'-bromo-derivative* as prisms, m. p. >300° (Found: Br, 23·2. $C_{18}H_{12}BrNO_2$ requires Br, 22·6%).

6-Bromo-4'-oxo-6'-phenylpyrano(3',2'-3,4)*quinoline*.—(a) *Dehydrobromination with pyridine*. A solution of 5',6-dibromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline (0·2 g.) in pyridine (1·5 c.c.) was heated at 95° for 15 min. On cooling, 6-bromo-4'-oxo-6'-phenylpyrano-(3',2'-3,4)quinoline was deposited as needles, m. p. and mixed m. p. 228—230°

(b) N-*Bromosuccinimide*. 6-Bromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline (0·5 g.), *N*-bromosuccinimide (0·3 g.), benzoyl peroxide (0·02 g.), and acetic acid (25 c.c.) were refluxed for 1·5 hr. The cooled solution was diluted with water (100 c.c.) and kept for 3 days. The precipitate was collected and extracted with chloroform. Evaporation then gave 6-bromo-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline, m. p. and mixed m. p. 229—231°.

(c) *Selenium dioxide*. Selenium dioxide (0·55 g.), 6-bromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline (0·5 g.), and dioxan (10 c.c.) were refluxed for 1·75 hr. The hot mixture was filtered and the dioxan evaporated. Trituration of the residual gum with ethanol gave the preceding compound (0·2 g.), m. p. and mixed m. p. 229—231°.

(d) Treatment of 6-bromo-4-hydroxyquinolyl styryl ketone (0·5 g.) with selenium dioxide (0·5 g.) as in (c) gave the same 6-bromo-compound, m. p. and mixed m. p. 228—230°.

4'-Oxo-6'-phenylpyrano(3',2'-3,4)*quinoline*.—Treatment of 5'-bromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2',3,4)quinoline as in (a) above gave 4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline, m. p. and mixed m. p. 230—232°.

4'-Oxo-6'-phenylpyrano(3',2'-3,4)quinoline, m. p. and mixed m. p. 230—232°, was also obtained when 5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline was treated with *N*-bromosuccinimide or selenium dioxide as described above.

5'-Hydroxy-4'-oxo-6'-phenylpyrano(3',2'-3,4)*quinoline and its 6-Bromo-derivative*.—(a) *Hydrogen peroxide*. A suspension of 5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline (0·55 g.) in a mixture of N-sodium hydroxide (2 c.c.) and ethanol (20 c.c.) was treated with 30% hydrogen peroxide (1 c.c.). The solution was kept at room temperature for 24 hr., then acidified. The precipitate crystallised from aqueous dioxan, giving *5'-hydroxy-4'-oxo-6'-phenylpyrano*-(3',2'-3,4)*quinoline* as prisms, m. p. 290—292° (Found: C, 74·4; H, 4·1; N, 5·5. $C_{18}H_{11}NO_3$ requires C, 74·8; H, 3·8; N, 4·9%).

Similarly 6-bromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline and 6-bromo-4-hydroxy-3-quinolyl styryl ketone gave *6-bromo-5'-hydroxy-4'-oxo-6'-phenylpyrano*(3',2'-3,4)-*quinoline*, needles (from pyridine), m. p. 299—300° (Found: C, 58·4; H, 3·3; N, 3·8. $C_{18}H_{10}BrNO_3$ requires C, 58·7; H, 2·7; N, 3·8%).

(b) *Through the hydroxyimino-derivative*. Hydrochloric acid (10 c.c.) was added to a suspension of 5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline (1·0 g.) in a solution of pentyl nitrite (5 c.c.) in ethanol (25 c.c.). After 3 hr. at room temperature the mixture was basified with ammonia. The yellow precipitate was collected and crystallised from ethanol, giving *5',6'-dihydro-5'-hydroxyimino-4'-oxo-6'-phenylpyrano*(3',2'-3,4)*quinoline* as prisms, m. p. 190—191° (decomp.) (Found: C, 71·2; H, 4·1; N, 9·6. $C_{18}H_{12}N_2O_3$ requires C, 71·0; H, 4·0; N, 9·2%).

Hydrolysis of this product in refluxing 50% w/v sulphuric acid during 1·5 hr. gave 5'-hydroxy-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline, needles, m. p. and mixed m. p. 290—292°.

Similarly 6-bromo-5',6'-dihydro-4'-oxo-6'-phenylpyrano(3',2'-3,4)quinoline gave *6-bromo-5',6'-dihydro-5'-hydroxyimino-4'-oxo-6'-phenylpyrano*(3',2'-3,4)*quinoline*, prisms (from ethanol), m. p. 199—200° (decomp.) (Found: C, 56·1; H, 3·1; N, 7·1. $C_{18}H_{11}BrN_2O_3$ requires C, 56·4; H, 2·9; N, 7·3%).

Hydrolysis of the hydroxyimino-compound gave the 5'-hydroxy-compound, needles (from pyridine), m. p. and mixed m. p. 299—300° (Found: C, 58·4; H, 3·3; N, 3·8. Calc. for $C_{18}H_{10}BrNO_3$: C, 58·7; H, 2·7; N, 3·8%).

5-Furoyl-6-furyl-4-oxonaphtho(1',2'-2,3)*pyran*.—2-Acetyl-1-naphthol (3·7 g.), furoic anhydride (10·3 g.), and triethylamine (8·3 c.c.) were refluxed at 170—180° for 2 hr. The cooled black oil was treated with a mixture of ether and acetone (9 : 1; 10 c.c.). The precipitate was crystallised from ethanol, giving *5-furoyl-6-furyl-4-oxonaphtho*(1',2'-2,3)*pyran* as needles, m. p. 222—224° (Found: C, 73·4; H, 3·6. $C_{22}H_{12}O_5$ requires C, 74·1; H, 3·4%).

NOTTINGHAM AND DISTRICT TECHNICAL COLLEGE.
HUDDERSFIELD COLLEGE OF TECHNOLOGY.

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