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7-Formyl-8-quinolinols

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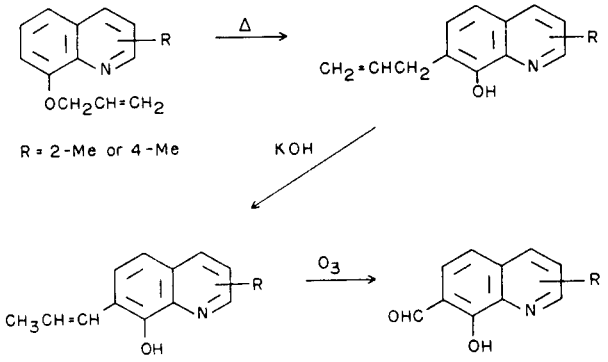
In order to prepare some photochromic chelating agents (1) a number of 7-formyl-8-quinolinols were needed. Only the parent compound of this series and its 5-methyl derivative have been reported (2).

8-Hydroxyquinaldine and 8-hydroxylepidine (3) were converted to their allyl ethers which were rearranged by heat to the 7-allyl derivatives; isomerization with alkali to the 7-propenyl derivatives and ozonization at low temperatures completed the syntheses:



Bromination and iodination of 7-formyl-8-hydroxyquinaldine readily gave the 5-bromo and 5-iodo derivatives, but chlorination displaced the carbonyl group to yield only 5,7-dichloro-8-hydroxyquinaldine.

5-Nitro-7-formyl-8-quinolinol was obtained through the Sommelet reaction of a Mannich base of 5-nitro-8-quinolinol. An attempt to prepare the 7-formyl derivative of 2,5-dimethyl-8-quinolinol proceeded no further than its 7-hydroxymethyl derivative. All compounds obtained in this work are listed in Table I and their spectra in neutral, acid and basic media in Table II.

Spectra of the 7-allyl compounds are quite similar to those of 7-methyl-8-quinolinols (4), although both groups are unexpectedly dissimilar to 8-quinolinols with simple substituents in other positions than adjacent to the hydroxyl. The 7-propenyl spectra are different from the allyl compounds as expected from the additional conjugation.

As chelating agents for metals the 7-formyl-8-quinolinols offer an interesting competition between an oxygen and a nitrogen coordinating center, with structural relationships to both salicylaldehyde and 8-quinolinol.

TABLE I

Substituted 8-Quinolinols

Substituents	M.p., °C	Yield, %	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found	% Nitrogen Calcd.	% Nitrogen Found
2-Me-8-allyloxy	166(5) (a)	81	78.36	78.19	6.58	6.71	7.02	7.12
2-Me-7-allyl	160(6) (a)	72						
2-Me-7-propenyl	86	58	78.36	78.59	6.58	6.73	7.02	6.91
2-Me-7-formyl	122	34	70.57	70.56	4.84	4.97	7.48	7.20
2-Me-7-CHO-5-Br (b)	172	70	49.61	49.44	3.02	2.94	5.26	5.07
2-Me-7-CHO-5-I	189	61	42.20	42.04	2.57	2.68	4.47	4.43
7-Formyl-5-nitro	255d.	50	55.04	54.82	2.77	2.81	12.83	12.70
4-Me-8-allyloxy	160(2.4) (a)	87						
4-Me-7-allyl	64	80						
4-Me-7-propenyl	116	51						
4-Me-7-formyl	161	30	70.57	70.31	4.84	4.65	7.48	7.44
2,5-Me_2-7-hydroxymethyl	103	54	70.95	70.70	6.45	6.34	6.89	6.78

(a) Boiling point (mm. pressure). (b) Also analyzed for Br: Calcd., 30.03. Found, 30.21.

TABLE II

Ultraviolet Absorption Spectra of Substituted 8-Quinolinols

Substituents	Maxima, mμ (log ε) EtOH	0.1 *N* HCl	0.1 *N* NaOH
2-Me-7-propenyl	268 (4.65)	280 (4.48)	284 (4.59)
	272 (4.65)	364 (3.75)	361 (3.87)
	317 (3.78)		
4-Me-7-propenyl	266 (4.66)	278 (4.65)	281 (4.51)
	272 (4.67)	326s (3.52)	359 (3.91)
	317 (3.79)	367 (3.64)	
2-Me-7-allyl	249 (4.70)	257 (4.68)	262 (4.56)
	275s (3.48)	282s (3.58)	340 (3.50)
	311 (3.45)	314s (3.58)	360s (3.42)
		341s (3.34)	
		325 (3.69)	
4-Me-7-allyl	246 (4.73)	253 (4.35)	259 (4.16)
	276s (3.30)	285s (3.14)	337 (3.54)
	315 (3.46)	310s (3.38)	365 (3.53)
	329s (3.42)	320 (3.46)	
		351 (3.36)	
2-Me-7-formyl	231s (4.21)	231 (4.08)	292 (4.41)
	272 (4.43)	279 (4.54)	339 (3.56)
	293s (3.94)	305s (3.61)	409 (3.87)
	359 (3.45)	314 (3.62)	
		366 (3.32)	
2-Me-5-Br-7-formyl	255 (4.20)	232 (4.09)	263s (3.73)
	275 (4.45)	283 (4.55)	291 (4.08)
	293s (3.93)	320s (3.43)	350 (3.43)
	363 (3.52)	383 (3.43)	414 (3.74)
2-Me-5-I-7-formyl	255s (3.79)	216 (4.49)	234s (4.25)
	277 (4.09)	287 (4.49)	292 (4.33)
	294 (3.49)	325s (3.36)	352 (3.72)
	368 (3.51)	393 (3.41)	416 (3.79)
2,5-Me_2-7-CH_2OH	253 (4.67)	261 (4.66)	240s (3.90)
	318 (3.41)	317s (3.45)	265 (4.53)
	329s (3.40)	327 (3.51)	345 (3.55)
		361 (3.29)	371s (3.43)

EXPERIMENTAL

Allyl ethers and their Claisen rearrangements were obtained by the same procedures as for corresponding 8-quinolinol derivatives (5); Fiedler's method (2) was employed to prepare the 7-propenyl compounds in Table I.

Ozonizations were performed with a Welsbach Ozonator as follows: A stream of ozone was passed through a solution of 9.5 g. of 7-propenyl-8-hydroxyquinaldine (or 7-propenyl-8-hydroxylepidine) in 150 ml. of chloroform at -30° until the potassium iodide trap became dark red. The solution was then poured into 100 ml. of water and ice containing 5 g. of sodium bisulfite and stirred for an hour. The aldehyde was filtered, dried and recrystallized from ethanol-water mixtures. Additional product could be recovered by evaporation of the chloroform.

Bromination of 7-formyl-8-hydroxyquinaldine with the theoretical amount of bromine in glacial acetic acid at 18° gave the 5-bromo derivative as red platelets when crystallized slowly from ethanol, as yellow crystals when rapidly crystallized; the red platelets turn yellow at 160° and melt at the same point as the initially yellow ones. A 2,4-dinitrophenylhydrazone melted at 281° (decomposition).

Iodination in ethanol containing a small amount of sodium acetate of 7-formyl-8-hydroxyquinaldine yielded orange platelets of the 5-iodo derivative, recrystallized from 2-propanol; 2,4-dinitrophenylhydrazone melting at 251-252° (decomposition).

5-Nitro-7-formyl-8-quinolinol was obtained through the Sommelet reaction of 2.4 g. of 7-morpholinomethyl-5-nitro-8-quinolinol with 2.8 g. of hexamethylenetetramine in 40 ml. of 50% acetic acid. After refluxing for two hours the product was separated and heated for 15 minutes in 20 ml. *N* hydrochloric acid. Neutralization with sodium carbonate, filtration and recrystallization from 3:1 ethanol-benzyl alcohol gave the desired product; 2,4-dinitrophenylhydrazone melting at 297° (decomposition).

2,5-Dimethyl-7-hydroxymethyl-8-quinolinol was obtained from 2,5-dimethyl-8-quinolinol (17.3 g.) by adding 15 ml. of 36% formalin to a solution in 700 ml. of *N* sodium hydroxide solution and stirring for three days at 20°. Neutralization with acetic acid and filtration gave the product. The dry product was treated with 500 ml. ether and the insoluble residue discarded. Evaporation of the ether and recrystallization from benzene-ligroin mixtures gave a pure product.

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