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Chrysenoxazoles

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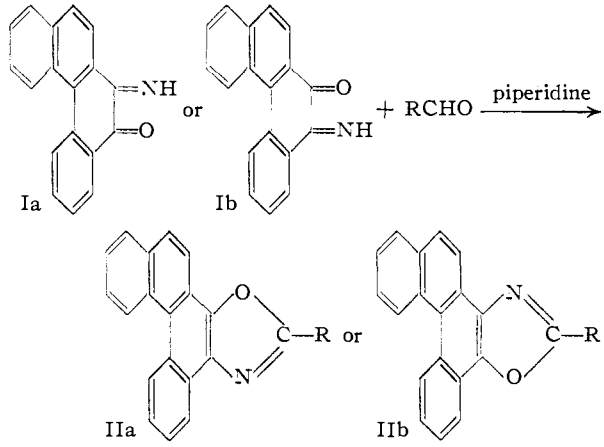
Various 2-arylchrysenoxazoles have been prepared by the interaction of aromatic aldehydes with chrysenequinonimine in the presence of piperidine as a catalyst. 2-Aryl and 2-alkylchrysenoxazoles were prepared by the interaction of chrysenequinone with amines. Chrysenequinonimine reacted with benzylamine to give 2-phenylchrysenoxazole. The parent compound, chrysenoxazole, was prepared by the action of diazomethane on chrysenequinonimine or chrysenequinonemonoxime. An attempt to prepare chrysenimidazole by the method used to make phenanthrimidazole failed and only chrysenoxazole was obtained.

Chrysenequinonimine (Ia or Ib),[1] which has been described in a German Patent,[2] was prepared in almost quantitative yield by the action of anhydrous alcoholic ammonia on chrysenequinone. We have prepared chrysenoxazoles (IIa or IIb) by the action of aromatic aldehydes on the imine with piperidine as a catalyst[3] according to the scheme

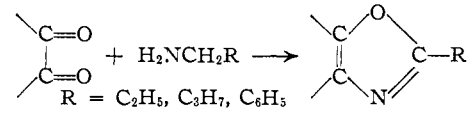


R = C_6H_5, p-$CH_3OC_6H_4$, o-ClC_6H_4, $CH_2O_2C_6H_3$, p-$NO_2C_6H_4$, o-HOC_6H_4, $C_6H_5CH{=}CH$, m-CH_3O-p-HOC_6H_3, p-$HOCC_6H_4$, 2-$HOC_{10}H_6$

In the absence of piperidine the imine was recovered unchanged. It should be noted that only one of the aldehyde groups in terephthalic aldehyde reacted with the quinonimine to form an oxazole. The reactions described support the suggestion of Stein and Day[3] that the quinonimine acts as an active hydrogen compound and adds to the aldehyde under the catalytic influence of piperidine.

2-Phenylchrysenoxazole was first prepared by Japp and Streatfeild,[4] by the action of ammonia and benzaldehyde on chrysenequinone in a sealed tube. We believe that the first step in this reaction is the formation of chrysenequinonimine which condenses with benzaldehyde to form the oxazole. This view is supported by the fact that ammonia reacts with the quinone to form the quinonimine. Schiedt[5] has prepared some of these oxazoles by the action of formamide and the corresponding aldehyde on the quinone; he does not describe any alkylchrysenoxazoles.

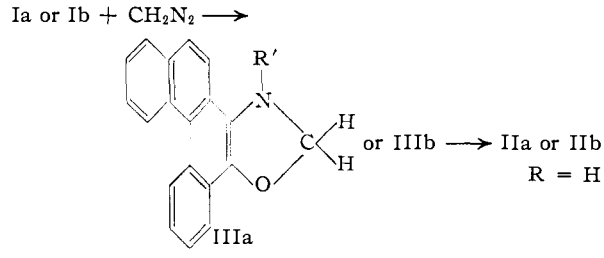
Aliphatic aldehydes did not react with chrysenequinonimine to give 2-alkylchrysenoxazoles. However, chrysenequinone reacted with propylamine, butylamine and benzylamine to yield the corresponding 2-substituted chrysenoxazoles as



This reaction is similar to that described by McCoy and Day[6] for phenanthraquinone.

Similarly, 2-phenylchrysenoxazole was prepared by the action of benzylamine on chrysenequinonimine.[7]

Chrysenoxazole (IIa or IIb, R = H) was prepared by the action of diazomethane on chrysenequinonimine (Ia or Ib) by procedure similar to that used for phenanthroxazole[8] and by the action of diazomethane on chrysenequinonemonoxime[7] according to the scheme



In the formation of chrysenoxazole from the imine, the first step is probably the formation of dihydrochrysenoxazole (IIIa or IIIb, R′ = H), which is then oxidized to chrysenoxazole (IIa or IIb, R = H), either by the oxygen of the air or by chrysenequinonimine which may act as a hydrogen acceptor.

An attempt to prepare chrysenimidazole by the action of ammonium acetate and the corresponding aldehyde on chrysenequinone in acetic acid[9] failed and chrysenoxazole was obtained instead. This indicates that, in contrast to phenanthraquinone, one carbonyl group of chrysenequinone is more active than the other; the monoimine (and not the diimine) is first formed and condenses with the aldehyde to yield chrysenoxazole.

(1) It is not known whether Ia or Ib represents the structure of chrysenequinonimine.

(2) German Patent 659,593; *Cent. Blatt.*, **II**, 1491 (1938).

(3) C. W. C. Stein and A. R. Day, THIS JOURNAL, **64**, 2567 (1942).

(4) F. R. Japp and F. W. Streatfeild, *J. Chem. Soc.*, **41**, 157 (1882).

(5) von Bruno Schiedt, *J. prakt. Chem.*, [2] **157**, 203 (1941).

(6) G. McCoy and A. R. Day, THIS JOURNAL, **65**, 1956 (1943).

(7) See A. Schönberg and W. I. Awad, *J. Chem. Soc.*, 72 (1950), for a study of this reaction with phenanthraquinonimine.

(8) A. Schönberg and W. I. Awad, *ibid.*, 651 (1947).

(9) General procedure for the preparation of phenanthrimidazoles; E. A. Steck and A. R. Day, THIS JOURNAL, **65**, 452 (1943).

TABLE I

Chrysenoxazole	Solvent of crystln.	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Color with concd. H_2SO_4
2-Phenyl-[a]	D	268–269[c]	55	$C_{25}H_{15}ON$	87.0	87.2	4.3	4.4	4.1	3.9	Yellow
2-Phenyl-[b]	A[d]		57			86.8		4.6		3.9	
2-Anisyl-[a]	A[d]	258	86	$C_{26}H_{17}O_2N$	83.2	82.8	4.5	4.6	3.7	3.5	Yellow-green
2-(*o*-Chlorophenyl)-[a]	C[d]	212	71	$C_{25}H_{14}ONCl$[e]	79.1	79.7	3.7	3.6	3.7	3.4	Yellow
2-(3,4-Oxymethylene-phenyl)-[a]	A[d]	270–271	80	$C_{26}H_{15}O_3N$	80.2	80.7	3.9	4.1	3.6	3.4	Green-yellow
2-(*p*-Nitrophenyl)-[a]	A[g]	330[f]	66	$C_{25}H_{14}O_3N_2$	76.9	77.2	3.6	4.0	7.2	6.8	Orange-red
2-(*o*-Hydroxyphenyl)-[a]	A[d]	275	86	$C_{25}H_{15}O_2N$	83.1	83.5	4.2	4.3	3.9	4.0	Green-yellow
2-Cinnamyl-[a]	C[d]	244	71	$C_{27}H_{17}ON$	87.3	86.9	4.6	4.6	3.8	4.3	Yellow-green
2-(*m*-Methoxy-*p*-hydroxy-phenyl)-[a]	A[d]	250[h]	66	$C_{26}H_{17}O_3N$					3.6	3.4	Yellow-green
2-(*p*-Aldehydophenyl)-[a]	B	315	21	$C_{26}H_{15}O_2N$	83.6	83.6	4.0	4.0	3.8	3.8	Red-brown
2-(2-Hydroxy-1-naphthyl)-[a]	A[d]	329	94	$C_{29}H_{17}O_2N$	84.7	84.9	4.2	4.0	3.4	3.4	Yellow
2-Ethyl-[b]	E	156	43	$C_{21}H_{15}ON$					4.7	4.8	.....
2-*n*-Propyl-[b]	F	116–117	95	$C_{22}H_{17}ON$	84.9	84.9	5.5	5.6	4.5	4.6	Blue-green[i]
Chrysenoxazole[j]	F	182	50	$C_{19}H_{11}ON$	84.8	85.2	4.1	4.0	5.2	5.1	Brown[i]

A, benzene; B, *n*-butyl alcohol; C, benzene–benzine (40–60°); D, xylene; E, methyl alcohol–benzene; F, methyl alcohol. [a] Prepared from chrysenequinonimine and the aldehyde. [b] Prepared from chrysenequinone and the amine. [c] Ref. 4, m.p. 259–265°; ref. 5, m.p. 286°. The compound prepared by Schiedt's procedure (ref. 5) melted at 268°. The mixed melting points were not depressed. [d] Violet fluorescence in benzene solution. [e] Calcd.: Cl, 9.4. Found: Cl, 8.9. [f] Ref. 5, m.p. 318°. [g] Green fluorescence in benzene solution. [h] Ref. 5, m.p. 240°. [i] Color faded. [j] Prepared from diazomethane and chrysenequinonimine. Admixture with the product prepared from chrysenequinonemonoxime and diazomethane gave no depression of m.p.

Experimental[10]

Chrysenequinonimine.—Chrysenequinone (2 g.) in chloroform (about 75 ml.), was mixed with saturated anhydrous alcoholic ammonia (100 ml.), and left for 12 hr. in a dry atmosphere at room temperature. During this time, most of the imine separated out and was filtered. The filtrate was concentrated under reduced pressure to give another crop of the imine. The two crops were crystallized from chloroform (containing a little anhydrous alcoholic ammonia) as orange needles, m.p. 186°, yield 2.0 g. It gave a reddish-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{18}H_{11}ON$: C, 84.0; H, 4.3; N, 5.4. Found: C, 83.5; H, 4.0; N, 6.07.

Preparation of 2-Arylchrysenoxazoles from Chrysenequinonimine.—Chrysenequinonimine (1 mole), aldehyde (2 moles) and a few drops of the piperidine catalyst in a suitable amount of absolute ethyl alcohol or benzene were refluxed for 2 hr. The product was filtered after cooling and crystallized from a suitable solvent. The results are summarized in Table I. A similar experiment was carried out without piperidine; on cooling of the solution, only the unchanged imine separated as shown by m.p. and mixed m.p. determinations.

Preparation of Chrysenoxazoles from Chrysenequinone.—Chrysenequinone (0.2 g.) and the amine (few drops) were refluxed in benzene (20 ml.) for 2 hr. The benzene was driven off and the residue triturated with methyl alcohol for the ethyl, and benzine (40–60°) for the propyl derivative. The precipitate was recrystallized from the appropriate solvent.

(10) Microanalyses were carried out by Alfred Bernhardt, Germany. Melting points are not corrected.

Chrysenequinonimine treated with benzylamine in this manner yielded 2-phenylchrysenoxazole, m.p. and mixed m.p. 268–269°.

Action of Diazomethane[11] on: (a) Chrysenequinonimine.—The imine (0.2 g.) was suspended in ether, cooled in an ice-bath treated with an excess of ethereal diazomethane solution and left overnight. The ether was then evaporated and chrysenoxazole recrystallized.

(b) Chrysenequinonemonoxime.[12]—Chrysenoxazole was prepared in the same way from the monoxime; on admixture with the product obtained from chrysenequinonimine and diazomethane gave no depression of the melting point.

2-*p*-Methoxyphenylchrysenoxazole.—Chrysenequinone (1 g.), ammonium acetate (5 g.) and anisaldehyde (0.5 g.) were dissolved in glacial acetic acid (about 100 ml.) and refluxed for 2 hr. The mixture was then cooled and diluted with an equal volume of water. The deposit was filtered, washed with a little water, dried and recrystallized from benzene with activated charcoal. The compound was proved to be 2-*p*-methoxyphenylchrysenoxazole by m.p. and mixed m.p. determinations.

Anal. Calcd. for $C_{26}H_{17}O_2N$: C, 83.2; H, 4.5; N, 3.7. Found: C, 83.6; H, 4.4; N, 4.0.

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(11) F. Arndt, *Org. Syntheses*, **15**, 3 (1935).

(12) von C. Graebe and F. Honigsberger, *Ann.*, **311**, 272 (1900).