TABLE II

Supplement compound	Level, micrograms	No. chicks	% Clotting at <10 min.	% Clotting at <15 min.	Average clotting time, min.
None		10			>40
Quinone	1	12	42	58	13.4
Crystalline potassium bisulfite addition	5	10	10	90	10.8
	1.6	13	16	16	29.2
2-Me-1,4-naphthohydroquinone-3-potassium-sulfonate	50	13		8	36.4
	5	13	0		>40
None		8			>40
Quinone	1	10	100	100	7.6
Crystalline sodium bisulfite addition	5	9	78	89	8.7
	3.2	19	84	89	8.4
	1.6	22	27	59	17.0
None		9			>40
Quinone	1	13	61	85	10
2-Me-1,4-naphthohydroquinone-3-sodium-sulfonate	50	22	5	14	
	25	17	0	0	>40
None		10			>40
Quinone	1	9	89	100	7.1
Solution 8, Table I	3.2	8	25	100	10.8
Solution 9, Table I	16	11	64	82	11.3
	8.0	9	33	33	17.0
	2.0	9	11	22	>40
Solution 17, Table I	3.2	12	0	0	>40
None		8			>40
Quinone	1	12	92	100	6.5
Solution 16, Table 1	3.0	10	60	90	9.5

bubbled, the filtered solution was acidified and the precipitated phthiocol purified by sublimation *in vacuo;* yield, 0.07 g.; m. p. 170–172°; no depression in melting point of a mixture with an authentic sample.

Bioassays.—Day old chicks were depleted on the diet of Almquist and Stokstad[4] (modified in that the cod-liver oil was omitted from the diet) for a period of ten to twelve days, or until the clotting time exceeded thirty minutes as measured by the capillary tube method. Injections of the aqueous solutions (0.1 cc.) were made in the leg muscle and, after eighteen hours, the clotting time was ascertained by the capillary tube method. Chicks fed orally with 1 microgram of 2-methyl-1,4-naphthoquinone in Wesson oil were used as positive controls. The claimed concentration of active component in the "Hykinone" solution was used as a basis for the dilution of the solutions injected. The results are summarized in Table II.

(4) Almquist and Stokstad, *J. Nutrition*, **12**, 329 (1936).

Summary

1. The crystalline sodium and potassium bisulfite addition products of 2-methyl-1,4-naphthoquinone have been isolated.

2. The sodium and potassium salts of 2-methyl-1,4-naphthohydroquinone-3-sulfonic acid, isomeric with the corresponding, strongly antihemorrhagic bisulfite addition compounds, have been isolated and shown to have only slight biochemical activity.

3. The structure of the slightly antihemorrhagic salts was established by unequivocal synthesis.

4. Conversion of the primarily-formed bisulfite compounds to the corresponding salts of 2-methyl-1,4-naphthohydroquinone-3-sulfonic acid in heated solutions was established and correlated with the change in biochemical activity of the solution.

5. Precautions in the preparation and use of the bisulfite solutions for medicinal purposes are indicated.

PEARL RIVER, N. Y. RECEIVED FEBRUARY 19, 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH CAROLINA]

The Constitution of Natural Tannins. VIII. Coloring Matters Derived from Anthracene-9-aldehyde

BY ALFRED RUSSELL AND W. B. HAPPOLDT, JR.[1]

Recently, Russell and Speck[2] have shown that coloring matters analogous to benzopyrilium salts but containing naphthalene nuclei can be prepared using the regular procedure—condensation of appropriate aldehydes and ketones by anhydrous hydrogen chloride in dry solvents. It has now been established that related compounds containing anthracene nuclei can be prepared through the condensation of 9-anthraldehyde with various hydroxy-, methoxy-, acetoxy- and benzoyloxy acetophenones. The condensations were effected either by the use of anhydrous hydrogen chloride, or using aqueous alcoholic alkali. With one exception, where a flavanone (Type Formula II) was obtained, the condensation products were chalcones (Type Formula I). To preserve simplicity of nomenclature, the new chalcones have been called 9-anthralacetophenones (*cf.* benzalacetophenones). Analogously, the single flavanone is a hydroxy-2-anthryl-9-benzopyrone. There is included also a single chalcone (III) derived from 9-anthraldehyde and methyl-β-naphthyl ketone.

(1) From a dissertation submitted to the Faculty of the University of North Carolina in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

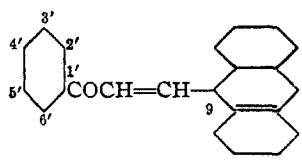
(2) Russell and Speck, THIS JOURNAL, **63**, 851 (1941).

TABLE I

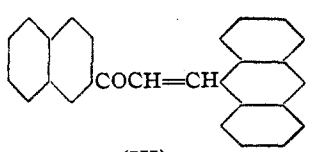
CHALCONES R-ANTHRALACETOPHENONE

R-	Procedure	Color	Cryst. form	M. p., °C.	Solvent recryst.	Yield, %	Formula	Mol. wt. Calcd.	Mol. wt. Found	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
9-	A	Bright y.	Needles	122–123	95% ethanol	68	$C_{23}H_{16}O$	308	298	89.58	89.73	5.23	5.71
2′-Benzoyloxy-9-	A	Bright y.	Prisms	151	Benzene	68	$C_{30}H_{20}O_3$	428	430	84.11	83.91	4.67	4.89
2′-Hydroxy-9-	[a]	Orange	Plates	159–160	Acetone-alc.	44	$C_{23}H_{16}O_2$	324	332	85.19	85.53	4.95	5.04
3′-Hydroxy-9-	A	Deep o.	Needles	202	Alcohol	63	$C_{23}H_{16}O_2$	324	330	85.19	85.48	4.95	4.95
4′-Hydroxy-9-	A	Light o.	Needles	241–242	95% alcohol	71	$C_{23}H_{16}O_2$	324	321	85.19	85.30	4.95	4.94
2′,6′-Dibenzoyloxy-9-	A	Yellow	Prisms	224	Benzene	27	$C_{37}H_{24}O_5$	548	533	81.02	80.76	4.38	4.42
2′5′-Dibenzoyloxy-9-	A	Bright y.	Prisms	171	95% ethanol	55	$C_{37}H_{24}O_5$	548	541	81.02	81.03	4.38	4.38
2′,5′-Diacetoxy-9-	A	Light y.	Plates	146	Alcohol	36	$C_{27}H_{20}O_5$	424	421	76.41	76.25	4.71	4.69
2′,5′-Dihydroxy-9-	A	Deep red o.	Plates	228.5	Alcohol	50	$C_{23}H_{16}O_4$	340	334	81.17	80.92	4.71	4.77
2′,4′-Diacetoxy-9-	A	Bright y.	Plates	188	Acetone-alc.	41	$C_{27}H_{20}O_5$	340	337	76.49	77.12	4.71	4.77
2′,4′-Dihydroxy-9-	B	Red o.	Prisms	199	MeOH-H_2O	40	$C_{23}H_{16}O_4$	340	344	81.17	80.56	4.71	4.81
2′,3′,4′-Tribenzoyloxy-9-	A	Canary y.	Prisms	161–162	Acetic acid	48	$C_{44}H_{28}O_7$	668	660	79.04	79.00	4.19	4.22
2′,4′-Dimethoxy-9-	A	Deep y.	Prisms	139	Acetone-alc.	36	$C_{25}H_{20}O_3$	368	371	81.52	81.49	5.43	5.34
2′,6′-Dimethoxy-9-	A	Light y.	Prisms	202	Benzene	70	$C_{25}H_{20}O_3$	368	369	81.52	80.85	5.43	5.25
4′-Phenyl-9-	A	Bright y.	Prisms	212–213	Benzene	68	$C_{29}H_{20}O$	384	389	90.61	90.89	5.20	5.23
III	A	Bright y.	Needles	163	Acetone-alc.	80	$C_{27}H_{18}O$	358	368	90.47	90.35	5.06	5.05
(Flavanone) 7-hydroxy-2-anthryl-9-benzopyrone	A	Cream	Needles	212–220	EtOH-H_2O	59	$C_{23}H_{16}O_3$	340	336	81.17	80.58	4.71	4.75

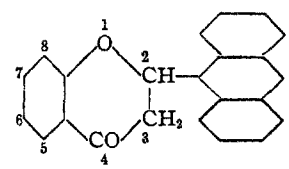
[a] This compound could be obtained only in very small quantities by direct condensation.



(I) 9-Anthralacetophenone



(III)



(II) 2-Anthryl-9-benzopyrone

In physical properties, the 9-anthraldehyde chalcones closely resemble those of the benzene series but have much higher melting points. They are crystalline solids ranging in color from light yellow to deep orange, the depth of color depending partly on the number and partly on the orientation of the free hydroxyl groups present in the molecule. The acetoxy-, benzoyloxy- and methoxy derivatives are all light yellow in color. As might be expected, the new chalcones are somewhat soluble in alcohol or acetone, the solubility decreasing with the number of free hydroxyl groups. The benzoyloxy derivatives are somewhat insoluble in alcohol or acetone but more soluble in benzene. The results are summarized as far as possible in Table I.

Experimental

Preparation of Intermediates

N-Methylformanilide.—This anilide was prepared by the method of Fieser and Jones[3] from monomethylaniline and 85 to 90% formic acid.

9-Anthraldehyde was prepared according to the method of Fieser, Hartwell, and Jones[4] by condensing methylformanilide and anthracene by means of phosphorus oxychloride in an *o*-dichlorobenzene solution. In a private communication with Wood, he recommended omission of the solvent. This resulted in improved yields and a considerable saving of time.

Ortho, meta and para hydroxyacetophenones, quinacetophenone, resacetophenone, gallacetophenone and 2,6-dihydroxyacetophenone[5] were prepared in the laboratory. Acetophenone and methyl-β-naphthyl ketone were Eastman products.

The benzoates of these phenolic ketones were prepared in pyridine solutions containing benzoyl chloride in excess of the theoretical quantity required for all of the hydroxyl groups present in the phenol and the acetates, when used, by standard methods. The methyl esters were also made by the usual methods.

The Hydrogen Chloride Condensation.—Procedure A. This method was employed for the preparation of most of the compounds of this series, and the experimental procedure followed was that of Russell and Clark.[6] For this condensation, equimolar quantities of 9-anthraldehyde and the appropriate ketone were dissolved in slightly more than the minimum amount of anhydrous ethyl acetate (previously dried over calcium chloride, distilled, and stored over dry sodium sulfate). Upon saturation with dry hydrogen chloride, the solution usually turned a deep red, and in some cases the product would separate on standing overnight. The solutions were usually allowed to

(3) Fieser and Jones, *Org. Syn.*, **20**, 66 (1940).

(4) Fieser, Hartwell, and Jones, *ibid.*, **20**, 11 (1940); Bost and Wood, *ibid.*, **20**, 11 (1940).

(5) Russell and Frye, *ibid.*, **21**, 22 (1941).

(6) Russell and Clark, THIS JOURNAL, **61**, 2056 (1939).

stand for two or three days, although in some instances the reaction was complete after a twenty-four hour period. If the solid products did not separate from the mother liquor, the ethyl acetate was removed by evaporation on a steam-bath under a hood. Trituration of the residue with cold alcohol caused crystallization in such cases.

7-Hydroxy-2-anthryl-9-benzopyrone.—When 2.06 g. (0.01 mole) of 9-anthraldehyde and 1.36 g. (0.01 mole) of resacetophenone were dissolved in ethyl acetate and treated with dry hydrogen chloride, the solution remained quite clear. However, after standing overnight, a solid material separated; this was collected and recrystallized from ethyl alcohol and water (charcoal) to give light cream needles. Since this product was too light in color to be the chalcone, ring closure must have occurred to give the corresponding flavanone (*cf.* Russell and Clark[6]); yield, 2 g. (59%). *Anal.* Calcd. for $C_{23}H_{16}O_3$: C, 81.17; H, 4.71; mol. wt., 340. Found: C, 80.58; H, 4.75; mol. wt., 336.

2',4'-Dihydroxy-9-anthralacetophenone.—Procedure B. (This was the only case in which alkaline condensing agents were used.) In a nitrogen atmosphere 10.3 g. (0.05 mole) of 9-anthraldehyde and 6.8 g. (0.05 mole) of resacetophenone were dissolved in 350 cc. of methyl alcohol containing 15 g. of potassium hydroxide. The solution was refluxed for seven hours, and during this period the color changed from orange to deep red. One-half of the alcohol was then removed by distillation. The solution was cooled and made acid with 50% acetic acid. The chalcone which separated was removed by filtration. After several recrystallizations from methanol and water (charcoal) bright red-orange prisms of pure chalcone were obtained; yield, 7 g. *Anal.* Calcd. for $C_{23}H_{16}O_3$: C, 81.17; H, 4.71; mol. wt., 340. Found: C, 80.56; H, 4.81; mol. wt., 344.

Summary

1. Through the condensation of 9-anthraldehyde with various hydroxylated acetophenones there has been prepared a series of 9-anthralacetophenones. These are colored materials analogous to the simpler benzalacetophenones but are more brilliant and deeper in color.

2. In one case a hydroxy-2-anthryl-9-benzopyrone, analogous to the 2-phenylbenzopyrones (flavanones), was obtained.

3. Condensation of 9-anthraldehyde with methyl beta-naphthyl ketone gives a bright yellow product analogous to benzalacetophenone (chalcone).

4. It is established that the familiar syntheses of the simpler natural coloring matters (chalcones and flavanones) can be extended to the preparation of analogous compounds containing at least one anthracene nucleus.

CHAPEL HILL, N. C. RECEIVED JANUARY 23, 1942

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Addition Polymerization Catalyzed by Substituted Acyl Peroxides

BY CHARLES C. PRICE, ROBERT W. KELL AND EDWIN KREBS

The suggestion of Staudinger[1] that, under certain conditions, addition polymerization proceeds by means of a chain reaction involving successive addition of monomer molecules to an active free radical intermediate is now widely accepted.[2]

$$R\cdot + CH_2{::}CHX \longrightarrow R{:}CH_2{:}CHX\cdot \longrightarrow R(CH_2CHX)_nCH_2CHX\cdot$$

The nature of various processes which might initiate such a chain reaction has been a matter of considerable speculation.[2,3] Schulz and Wittig have shown, however, that the free radicals formed from dissociation of tetraphenylsuccinonitrile[4] or from the decomposition of benzene azotriphenylmethane ($C_6H_5N{=}NC(C_6H_5)_3$)[5] are capable of catalyzing the polymerization of styrene.

(1) Staudinger, *Trans. Faraday Soc.*, **32**, 323 (1936).

(2) See, *e. g.*, Flory, THIS JOURNAL, **59**, 241 (1937); Mark and Raff, "High Polymeric Reactions," Interscience Publishers, New York, N. Y., 1941.

(3) Irany, THIS JOURNAL, **62**, 2690 (1940).

(4) Schulz and Wittig, *Naturwissenschaften*, **27**, 387, 456 (1939).

(5) Schulz, *ibid.*, **27**, 659 (1939).

Several investigators[6] have recently suggested that catalysis by acyl peroxides is due to their thermal decomposition to active free radicals,[7] a mechanism which has been found to be in complete accord with the kinetics of the peroxide-catalyzed polymerization of *d-s*-butyl α-chloroacrylate.[8]

$$(RCO_2)_2 \longrightarrow RCO_2\cdot + R\cdot + CO_2$$

If these free radicals are responsible for the initiation of the polymerization, the polymer molecules so formed should contain fragments from the catalyst. The presence of these fragments in polystyrene and polymethyl methacrylate has now been established by carrying out the polymerizations in the presence of peroxides containing an atom or group, the presence of

(6) Norrish and Brookman, *Proc. Roy. Soc.* (London), **171A**, 147 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1087 (1939); Kamenskaya and Medvedev, *Acta Physicochem., U. S. S. R.*, **13**, 565 (1940).

(7) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(8) Price and Kell, THIS JOURNAL, **63**, 2708 (1941).