Preparative Uses of Aryldiazonium Salts of Complex Fluoro-acids. Part II.[1] Novel Preparations of Fluorenones and Xanthones from Aryldiazonium Tetrafluoroborates

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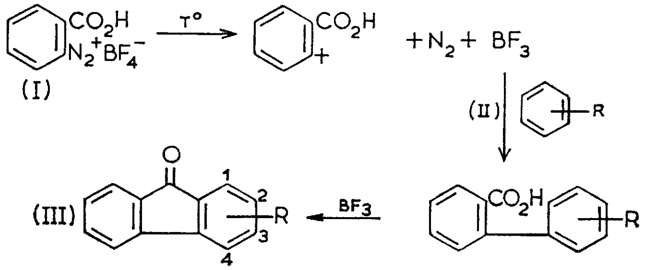
A novel and often convenient preparation of fluorenones and xanthones, the latter in some cases accompanied by 6*H*-dibenzo[*b*,*d*]pyran-6-ones, has been devised by decomposing *o*-carboxybenzenediazonium tetrafluoroborates in aromatic hydrocarbons or phenols respectively. Xanthones have also been prepared by thermolysis of aryldiazonium tetrafluoroborates in salicyclic acid. The mechanism and scope of these reactions are discussed.

THE use of aryl diazonium tetrafluoroborates for the preparation of lightly fluorinated aromatic compounds by the Balz-Schiemann reaction is well established.[2] Because of the availability and stability of these diazonium compounds they have also been utilised for other preparative purposes which are briefly mentioned.

When aryldiazonium tetrafluoroborates react with nucleophiles such as acetic acid or acetic anhydride, aryl acetates are obtained usually in better yields than from other diazonium salts.[3] Hydrolysis of these acetates as a route to phenols is particularly useful when other methods fail, as with *m*-bromo- and *m*-iodophenols.[4] Another valuable application described by Meerwein [5] is the decomposition of diazonium tetrafluoroborates in acetonitrile which gives up to 70% of quinazoline. More recently, diazonium tetrafluoroborates have been used to make aryl azides [6] and have been found to be superior to other diazonium compounds in the preparation of organo-mercury [7] and -lead [8] and particularly organobismuth [9] compounds. To this must be added Bart's method of preparing arylarsonic acids [10] a modification of which gives diarylarsinic acids. Some success in the preparation of analogous compounds of phosphorus [11,12] and antimony [13] from diazonium tetrafluorobotates has been reported.

Nesmeyanov and his school [7] have elegantly demonstrated that aryl diazonium tetrafluoroborates decompose in a solvent predominantly by a heterolytic pathway to generate an aryl carbonium ion, nitrogen, and boron trifluoride. It occurred to us that a molecule of an aryl diazonium tetrafluoroborate is thus a potential source of a carbonium ion and a Lewis acid which, in the right environment, could be utilised for a Friedel–Crafts type cyclisation. Two such ring closures were studied by us; one leading to fluorenones and the other to xanthones.

Fluorenones which by conventional methods require a multistage synthesis are readily formed by the decomposition of *o*-carboxybenzenediazonium tetrafluoroborate in hot aromatic solvents (see Scheme 1).



SCHEME 1

Fluorenones obtained by this method are listed in Table 1. The reaction temperature must be above, or at least near, the decomposition temperature of the diazonium salt, *i.e. ca.* 100°. Reactants boiling below 100° (*e.g.* benzene) require a prolonged period of heating under reflux to bring about breakdown of the diazo-compound. It is obvious that the ketonic linkage is formed by a Friedel–Crafts mechanism with the liberated boron trifluoride acting as catalyst. The internuclear cyclisation is presumably also brought about by a heterolytic process as DeTar has demonstrated [14] for the related formation of fluorenones from 2-diazobenzophenones. In confirmation, we found that when the reaction was carried out in presence of copper powder which is known to favour homolysis of diazo-compounds [15] yields were substantially reduced. The best results were obtained in acetic acid which contained boron trifluoride because the acid presumably promoted the ionic decomposition of the diazo-salt. Benzene and chlorobenzene gave smaller yields than *p*-dimethoxybenzene which is more active towards electrophilic attack.

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[1] C. Sellers and H. Suschitzky, *J. Chem. Soc.* (*C*), 1968, 2317.

[2] H. Suschitzky, 'Advances in Fluorine Chemistry,' Butterworths, London, 1965, vol. IV, p. 1.

[3] H. L. Haller and P. S. Schaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 4954.

[4] H. L. Haller and L. E. Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 143.

[5] H. Meerwein, P. Laasch, R. Mersch, and J. Nentwig, *Chem. Ber.*, 1956, **89**, 224.

[6] U.S.P. 3,123,621/1964.

[7] A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, 1957, **1**, 145.

[8] A. N. Nesmeyanov, K. A. Kocheshkov, and M. M. Nad', *Izvest. Akad. Nauk. S.S.S.R. Otdel. khim. Nauk*, 1945, 522.

[9] A. N. Nesmeyanov, T. P. Tolstaya, and L. S. Isaeva, *Doklady Akad. Nauk. S.S.S.R.*, 1958, **122**, 614.

[10] H. Bart, *Annalen.*, 1922, **429**, 55; C. S. Hamilton and J. F. Morgan, 'Organic Reactions,' Wiley, New York, 1944, vol. 2, p. 415.

[11] G. O. Doak and L. D. Freedman, *J. Amer. Chem. Soc.*, 1951, **73**, 5656.

[12] P. Mastalerz, *Roczniki Chem.*, 1962, **36**, 1093; L. D. Freedman and G. O. Doak, *J. Amer. Chem. Soc.*, 1952, **74**, 2884; L. D. Freedman and J. B. Levy, *J. Org. Chem.*, 1965, **30**, 660.

[13] G. O. Doak, L. D. Freedman, and S. M. Efland, *J. Amer. Chem. Soc.*, 1952, **74**, 830.

[14] D. F. DeTar and D. I. Relyea, *J. Amer. Chem. Soc.*, 1954, **76**, 1680; 1956, **78**, 4302.

[15] D. F. DeTar, 'Organic Reactions,' Wiley, New York, 1957, vol. 9, ch. 7; T. Cohen, A. H. Lewin, and A. H. Dinwoodie, *Tetrahedron*, 1966, **22**, 1527.

Since decomposition of the diazonium salt is instantaneous on contact with the boiling solvent the reaction most likely proceeds in the sequence (I) $\longrightarrow$ (III). This view is supported by the result obtained in the preparation of methylfluorenone from toluene which is known to undergo acylation predominantly in the *para*-position.[16] Thus, if the ketonic linkage were established first 3-methylfluorenone (III; R = 3-Me) should be the major product. In fact a mixture of methylfluorenones was obtained (*cf.* Table 1) containing mainly the 4-methyl-isomer but no 3-methyl compound. Xylene too, gave a mixture of isomeric dimethylfluorenones owing to the not unexpected migration of methyl groups during the reaction.[17] *p*-Dimethoxybenzene produced some 2-methoxyxanthone which arises from demethylation of a methoxy-group by boron trifluoride to give *p*-methoxyphenol followed by reaction of the diazonium compound with the phenol (*cf.* below).

TABLE 1

Fluorenones obtained from the decomposition of *o*-carboxybenzenediazonium tetrafluoroborate (I) and various benzenes

Benzene	Fluorenone	Yield (%)	M.p. (lit. m.p.)	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
1,4-Me_2	1,4-Me_2	10·1	89° (89)[d]					
	2,4-Me_2	2·5	136[a] (153)[e]	86·8	5·9	$C_{15}H_{12}O$		
1,3-Me_2	2,4-Me_2	9·5	136					
	1,3-Me_2	4·5	110 (110)[d]					
1,2-Me_2	1,2-Me_2	2·5	127[b] (127)[f]					
	2,3-Me_2	9·0	109 (110)[g]					
	3,4-Me_2	10·0	117 (117)[h]					
1,4-$(MeO)_2$	1,4-$(MeO)_2$[c]	18·0	166 (165)[i]					
1,4-Cl_2	1,4-Cl_2	0·5	162	62·7	2·5	$C_{13}H_6Cl_2O$	62·7	2·4
Benzene	Fluorenone	2	83 (83)					
1-Cl-4-Me	1-Me-4-Cl	5	118	73·1	4·0	$C_{14}H_9ClO$	73·5	4·0
	1-Me-3-Cl	4	153	73·7	4·2	$C_{14}H_9ClO$	73·5	4·0
1-OH-4-Me	1-OH-4-Me	4·1	122	80·0	5·0	$C_{14}H_{10}O_2$	79·8	4·8
Me-	1-Me	1·0	100 (98)[j]					
	2-Me	4·6	91 (92)[k]					
	4-Me	6·5	93 (91)[l]					

[a] M.p. wrongly reported in lit. Authentic sample gives undepressed m.p. (Calc. for $C_{15}H_{12}O$: C, 86·5; H; 5·8%). [b] Erroneously given as a b.p. in the lit. [c] 2-Methoxyxanthone (10·3%) was also formed. [d] J. F. Dippy and F. R. Williams, *J. Chem. Soc.*, 1934, 1460. [e] J. J. Godfroid, *Bull. Soc. chim. France*, 1964, 2929. [f] E. Bergmonn and R. Ikan, *J. Amer. Chem. Soc.*, 1958, **80**, 5803. [g] C. S. Marvel and C. W. Hinman, *J. Amer. Chem. Soc.*, 1954, **76**, 5435. [h] E. Ritchie, *J. Proc. Roy. Soc. N.S. Wales*, 1946, **80**, 33. [i] C. F. Koelsch and R. N. Flesh, *J. Org. Chem.*, 1955, **20**, 1270. [j] W. C. Lothrop and P. A. Goodwin, *J. Amer. Chem. Soc.*, 1943, **65**, 363. [k] O. Kruber, *Ber.*, 1932, **65***B*, 1382. [l] M. Orchin and E. O. Woolfolk, *J. Amer. Chem. Soc.*, 1945, **67**, 122.

TABLE 2

The chemical shifts (τ-values) in $CDCl_3$ and in benzene and solvent shifts (Δ values) of the methyl protons in the fluorenones

	$CDCl_3$				Benzene				Solvent shift (p.p.m.)			
Fluorenone	1-Me	2-Me	3-Me	4-Me	1-Me	2-Me	3-Me	4-Me	1-Me	2-Me	3-Me	4-Me
1-Me	7·38				7·44				0·06			
3-Me			7·64				8·05				0·41	
4-Me				7·41				7·90				0·49
1,2-Me_2	7·47	7·78			7·51	8·13			0·04	0·35		
1,3-Me_2[a]	7·41		7·62		7·43		7·99		0·02		0·37	
1,4-Me_2[b]	7·41			7·47	7·41			7·89	0·00			0·42
2,3-Me_2		7·73	7·69			8·11	8·17			0·38	0·48	
2,4-Me_2[c]		7·68		7·47		7·89		8·06		0·21		0·59
3,4-Me_2[d]			7·68	7·54			8·09	7·99			0·41	0·45
2-Cl-4-Me				7·45				8·06				0·61
4-Cl-1-Me[e]	7·40				7·58				0·18			
1-OH-4-Me[f]				7·57				8·03				0·46

Aromatic protons: [a] τ 3·26(2H), τ 2·96(4H). [b] τ 3·07(2H), τ 3·21(3H). [c] τ 2·77(1H), τ 3·07(3H). [d] τ 2·53(1H), τ 2·90(2H). [e] τ 2·73(2H), τ 3·03(3H). [f] τ 3·37(2H), τ 2·92(3H).

An attempt to widen the scope of the reaction by the use of reactants in which the diazonium and the carboxylate group were on different aromatic nuclei was unsuccessful. Attempts to produce phenanthrones from *o*-aminophenylacetic acid were also unsuccessful since this compound cyclised rapidly to give oxindole under the conditions of diazotisation.

Although yields are generally low our method is more convenient than the conventional fluorenone preparation which uses anthranilic acid.[18] The latter is a multistage procedure involving protection of the amino-group, benzophenone formation with thionyl chloride and aluminium chloride, followed by diazotisation to effect internuclear cyclisation. The new preparation is par-

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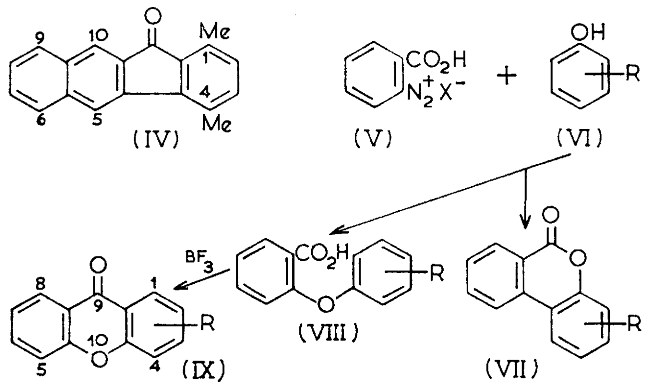
[16] P. H. Gore, ' Friedel–Crafts and Related Reactions,' Interscience, New York, 1964, vol. 3, pp. 36 and 122.

[17] C. C. Price, ' Organic Reactions,' Wiley, New York, 1946, vol. III, ch. 1.

[18] G. Rieveschl and F. E. Ray, *Chem. Rev.*, 1938, **23**, 287.

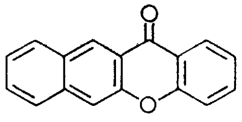
ticularly advantageous for aromatic substrates prone to electrophilic attack (*e.g.* dimethoxybenzene), also for making benzfluorenones, *e.g.* (IV) from 2-carboxy-3-naphthalenediazonium tetrafluoroborate and for 2,4-dimethylfluorenone which is produced in a comparable yield to the more cumbersome literature method.[19] Diazonium hexafluoroantimonates [1] gave similar results to the tetrafluoroborates.

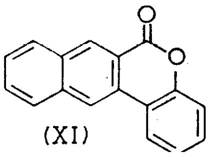
It is known [20] that diazotised anthranilic acid reacts with phenols to give 6*H*-dibenzo[*b*,*d*]pyran-6-ones and *o*-phenoxybenzoic acids (see Scheme 2).

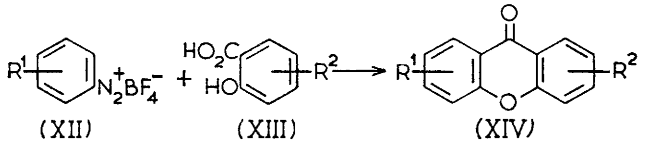


SCHEME 2

When the tetrafluoroborate (V; $X = BF_4$) was pyrolysed in a phenol the liberated boron trifluoride cyclised the intermediate phenoxy-acid (VIII) to xanthone (IX) (Method A). The analogous naphthalene-diazonium compound gave the corresponding benzo-analogues [(X) and (XI)]. Alternatively the diazonium and the phenol group may be switched, *i.e.* a diazonium tetrafluoroborate (XII) can be made to decompose in a salicycic acid (XIII) derivative (Method B) to give a xanthone (XIV) (see Scheme 3).


(X)

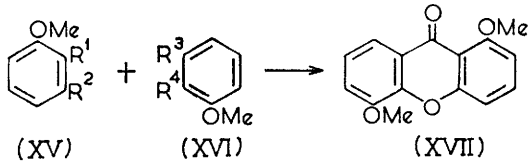

(XI)



SCHEME 3

The results obtained by these two methods are listed (Tables 3 and 4). Invariably small quantities of *o*-fluorobenzoic acid or fluorobenzene, the normal products of a Schiemann decomposition, were found as by-products in the two methods A and B respectively. The use of various solvents (*e.g.* xylene, sulpholane, dimethyl sulphoxide, dimethylformamide, polyphosphoric acid) did not improve the preparation. We also tried dry decomposition of an intimate mixture of the diazonium salt and its substrate but yields were low.

Hantzsch [21] has shown that ether formation from a diazonium compound and a phenol is a nucleophilic substitution of the former. Since the diazo-compound is seen to pyrolyse on contact with the molten phenol it is feasible that the ether linkage is formed first which will activate the ring for the ensuing Friedel–Crafts acylation. Since two routes can be used for xanthone formation a choice of reactants is available. Even so we found that only simple xanthones are conveniently made by the process since for highly substituted xanthones reactants are not readily available and the reaction products were rather complex. For instance, 1,5-dimethoxyxanthone could be prepared by several routes based on either method (A or B) both of which require one trisubstituted benzene (*e.g.* XV; $R^1 = CO_2H$, $R^2 = OH$, and XVI; $R^3 = H$, $R^4 = N_2^+BF_4^-$) (see Scheme 4).



SCHEME 4

When we tried this route [(XV) and (XVI) as before] however, only a trace of product was obtained. With 2,6-dimethoxybenzoic acid [(XV; $R^1 = CO_2H$; $R^2 =$ OMe) and (XVI) as before] which we thought would partly demethylate under the reaction conditions (BF_3) and thereby become equivalent to 2-hydroxy-6-methoxybenzoic acid, the main product was *m*-dimethoxybenzene derived by decarboxylation. By contrast, 2-hydroxy-6-methoxybenzoic acid reacts with benzenediazonium tetrafluoroborate to give 1-methoxyxanthone (14%).

A number of other observations are noteworthy. When 2,6-dihydroxybenzoic acid is heated with benzenediazonium tetrafluoroborate the expected 1-hydroxyxanthone is not produced because the acid undergoes self-condensation with decarboxylation to form 1,6-dihydroxyxanthone. The use of *o*-carboxybenzenediazonium tetrafluoroborate invariably gave 6*H*-dibenzo[*b*,*d*]pyran-6-ones (VII) in addition to xanthones (*cf.* Table 3). It was expected that boron trifluoride would demethylate the methoxyxanthones formed, but this occurred to only a very small extent. When *p*- or *m*-hydroxyanisole were used as reactant (Method A) the corresponding dimethoxybenzene was formed as a by-product in high yield but none from the *o*-hydroxyanisole. It was shown that passage of boron trifluoride through any one of the molten, isomeric hydroxyanisoles gave a mixture of the corresponding dihydroxy- and dimethoxy-benzenes. The *ortho*-isomer underwent

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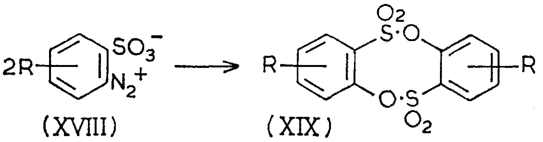
[19] J. J. Godfroid, *Bull. Soc. chim. France*, 1964, 2929.
[20] R. S. Cahn, *J. Chem. Soc.*, 1933, 1400.
[21] A. Hantzsch and E. Jochem, *Ber.*, 1901, **34**, 3337.

this disproportionation only when the temperature was 50° above its melting point.

When we attempted to extend this reaction to diazonium tetrafluoroborates of aniline-*o*-sulphonic acid, however, diazotisation in fluoroboric acid produced only the internal salt which on decomposition in xylene gave the dibenzodioxadithiocin tetroxide (see Scheme 5).



(XVIII) (XIX)

SCHEME 5

These compounds are usually prepared by elimination of water, hydrochloric acid, or some other small molecule from the appropriate derivative of an aromatic *o*-hydroxysulphonic acid.[22]

EXPERIMENTAL

Preparation of 1,4- *and* 2,4-*Dimethylfluorenones*.—*o*-Carboxybenzenediazonium tetrafluoroborate [23] (7·11 g.) was added to a refluxing mixture of *p*-xylene (30 ml.) and boron trifluoride–acetic acid complex (30 ml.). The mixture was cooled and the acetic acid layer was run off and diluted with water and then extracted with benzene. The benzene extracts were added to the xylene layer which was then extracted with 3N-sodium hydroxide. On acidification of this extract, *o*-fluorobenzoic acid was precipitated (3·61 g., 85%).

The xylene solution was evaporated under reduced pressure to leave a yellow oil which solidified. Chromatography on alumina with high-boiling point light petroleum gave the following two products. 1,4-Dimethylfluorenone (0·68 g., 10·1%) which recrystallised from light petroleum (b.p. 60—80°) and had m.p. 89° (lit.,[24] m.p. 89°) (Found: C, 86·1; H, 5·8. Calc. for $C_{15}H_{12}O$: C, 86·5; H, 5·8%) and 2,4-dimethylfluorenone (0·15 g., 2·4%) which recrystallised from light petroleum (b.p. 100—120°) and had m.p. and mixed m.p. 136° (Found: C, 86·8; H, 5·9. Calc. for $C_{15}H_{12}O$: C, 86·5; H, 5·8%). Other fluorenone preparations are listed in Table 1.

The above reaction was also carried out under the following conditions to determine maximum yields. (Percentage yields of the two isomers 1,4-dimethyl and 2,4-dimethyl, are given in parentheses.)

(1) The *p*-xylene was saturated with boron trifluoride prior to the decomposition (4·6%; 1·6%). (2) Nitrogen was blown through the *p*-xylene during the decomposition (5·1%; 1·2%). (3) Copper powder was added to the *p*-xylene before the reaction (2·3%; —). (4) Acetic acid–boron trifluoride complex was added to the *p*-xylene before reaction (10·1%; 2·4%). (5) Polyphosphoric acid was added to the *p*-xylene before the reaction (8·9%; 2·9%). (6) When nitrobenzene was used as a solvent the reaction failed.

When 2-carboxy-3-naphthalenediazonium tetrafluoroborate (prepared in the usual way; decomp. temp. 126°) and *p*-xylene were made to react 1,4-*dimethylbenzo*-[6,7-b]-*fluorenone* (IV), m.p. 178° (21%) was obtained (Found: C, 88·3; H, 5·6. $C_{19}H_{14}O$ requires C, 88·3; H, 5·5%). The n.m.r. resonances in $CDCl_3$ were at τ 1·86 (10-H), 2·1 (5-H), 7·37 (1- and 4-Me) with the other aromatic protons between τ 2 and 3. In benzene the 1-, and the 4-Me-group appeared at τ 7·31 and 7·73 respectively.

Preparation of Xanthones.—*Method A. Reaction of* o-*carboxybenzenediazonium tetrafluoroborate and a phenol.* A typical procedure for xanthone preparation was as follows: *o*-Carboxybenzenediazonium tetrafluoroborate (7·31 g.) was dropped onto hot *p*-hydroxyanisole (25 ml.) which caused decomposition of the diazonium salt and left a very dark mixture. The reaction mixture was cooled and poured into cold water (200 ml.) with stirring; 4N-sodium hydroxide (200 ml.) was then added and the mixture was extracted with chloroform. For investigation of the alkaline solution (Solution 1) see below. The solvent layer was dried and the chloroform was removed under reduced pressure to leave a dark oil. This was heated with 4N-sodium hydroxide for 1 hr. after which the mixture was extracted with chloroform. For investigation of this alkaline solution (Solution 2) see below. The oil obtained by evaporation of the chloroform extract was chromatographed on alumina with benzene to yield the following fractions: *p*-Dimethoxybenzene (5·34 g., 19·15%), m.p. and mixed m.p. 56°. (Its i.r. spectrum was identical to that of an authentic sample) and 2-methoxyxanthone (1·27 g., 18·1%), m.p. and mixed m.p. 131°. Its i.r. spectrum was identical to that of an authentic sample.

The alkaline mixture (Solution 1) was treated with carbon dioxide to liberate phenols which were then extracted with chloroform. The resulting chloroform solution was chromatographed on silica and eluted with benzene to give a little *p*-methoxyphenol and 2-hydroxyxanthone (0·08 g., 1·2%), m.p. and mixed m.p. 239°. On acidification of the hydrogen carbonate solution a little *o*-fluorobenzoic acid was obtained.

The second alkaline mixture (Solution 2, *cf.* above) was acidified and then extracted with chloroform. The solvent layer after separation and evaporation gave 2-methoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (1·8 g., 26%), m.p. 118° (lit.,[25] m.p. 119—120°). Its i.r. spectrum showed a band at 1715 cm.$^{-1}$ (C=O).

Yield and details of other xanthones and 6*H*-dibenzo-[*b*,*d*]pyran-6-ones prepared by method A are given in Table 3.

2-Carboxynaphthalene-3-diazonium tetrafluoroborate was decomposed in hot phenol to give benzo[2,3]xanthone, m.p. 202° (lit.[26] m.p. 202°) (16%), and the 5*H*-benzo[*b*]-naphtho[3,2-*d*]pyran-5-one (XI) (16%), m.p. 186° (Found: C, 81·6; H, 4·4. $C_{17}H_{10}O_2$ requires C, 81·1; H, 4·5%).

Method B. Reaction of a benzenediazonium tetrafluoroborate and a salicyclic acid. The decomposition was carried out as in Method A and after the reaction mixture had been cooled, the products were poured with stirring into dilute sodium hydroxide solution. The xanthone was either precipitated or was extracted with chloroform and purified by recrystallisation from ethanol or light petroleum (b.p.

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[22] R. Anschutz, *Ber.*, 1912, **45**, 2378; *Annalen.*, 1918, **415**, 64; G.P. 711,710/1941.

[23] J. F. Dippy and F. R. Williams, *J. Chem. Soc.*, 1934, 1460.

[24] J. Colonge and H. Daunis, *Bull. Soc. chim. France*, 1961, 2238.

[25] J. W. Cook, G. T. Dickson, J. Jack, J. D. London, J. McKeown, J. MacMillan, and W. F. Williamson, *J. Chem. Soc.*, 1950, 139.

[26] W. Dilthey and F. Quint, *J. prakt. Chem.*, 1934, **141**, 306.

100—120°). The products were identified by comparing melting points and infrared spectra with those of authentic samples. Yields of xanthones prepared by method B are given in Table 4.

TABLE 3

Method A: Xanthones and dibenz[*b,d*]α-pyrones obtained from *o*-carboxybenzenediazonium tetrafluoroborate (I) and a phenol (R·C_6H_4·OH)

R·C_6H_4OH R	Xanthone Yield (%)	M.p. (lit. m.p.)	Dibenz-α-pyrone Yield (%)	M.p. (lit. m.p.)
H	Xanthone (20·6)	174(174)	Dibenzo[*b,d*] pyran-one (27)	92° (92·5) [f]
4-Me	2-Me (20·3)	121(121) [c]	2-Me (31)	134(135) [f]
2-Me	4-Me (14)	128(126) [c]	4-Me (40)	126 [a]
4-MeO	2-MeO (18)	130(131) [c]	2-MeO (26)	118(120) [g]
2-MeO	4-MeO (8)	176(173) [c]	4-MeO (24)	166(167) [f]
3-MeO	3-MeO (8)	129(128) [d]	1- and 3-MeO (13·8) [b]	
2,3-$(MeO)_2$	3,4-$(MeO)_2$(10)	160(156) [e]		

[a] Found: C, 80·1; H, 4·75. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%). It showed a band at 1720 cm.$^{-1}$ (C:O). [b] The mixture was inseparable by chromatography. Analysis was correct for $C_{14}H_{10}O_3$. [c] F. Ullmann and M. Zlokasoff, *Ber.*, 1905, **38**, 2111. [d] F. Ullmann and W. Denzler, *Ber.*, 1906, **39**, 4332. [e] G. Venkat Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 1953, **37***A*, 710. [f] R. S. Cahn, *J. Chem. Soc.*, 1933, 1400. [g] J. W. Cook, G. T. Dickson, J. Jack, J. D. London, J. McKeown, J. MacMillan, and W. F. Williamson, *J. Chem. Soc.*, 1950, 139.

Action of Boron Trifluoride on p-*Methoxyphenol*.—Boron trifluoride was passed through molten *p*-methoxyphenol (3 g.) at 120° for 0·5 hr. The mixture was cooled and then distilled under reduced pressure; the lower boiling fractions distilled in the range 80—130° and solidified when cooled. The distillate was stirred with 3N-sodium hydroxide and then extracted with chloroform. Evaporation of the solvent yielded *p*-dimethoxybenzene (0·4 g.), m.p. 56°.

The alkaline solution was acidified and extracted with chloroform to give unchanged *p*-methoxyphenol (1·05 g.).

The residue from the distilling flask was dissolved in the minimum amount of ethyl acetate–chloroform (1 : 1) and chromatographed on silica with chloroform; hydroquinone (0·45 g.), m.p. 169°, was obtained as the main fraction.

Decomposition of 2-Diazoniumbenzene Sulphonate.—A mixture of analine-*o*-sulphonic acid (8·5 g.) dissolved in 2N-sodium hydroxide (10 ml.) was cooled to 0° and sodium nitrite (3·5 g.) was added to the well stirred solution; the mixture was then poured into a slight excess of 2N-sulphuric acid. In time the diazo-compound separated as crystals (7·66 g., 84·5%), decomp. temp. 106°. The diazonium salt of 4-aminotoluene-3-sulphonic acid was similarly prepared (58·5%), decomp. temp. 150°.

TABLE 4

Method B: Xanthones obtained from a benzenediazonium tetrafluoroborate (R·C_6H_4·$N_2^+BF_4^-$) and a salicyclic acid

R·C_6H_4·N_2BF_4	Salicyclic acid	Xanthone	Yield (%)	M.p. (lit. m.p.)
H	Salicyclic acid	Xanthone	18·8	
4-Me	,,	2-Me-	21·4	
4-MeO	,,	2-MeO	19	
4-F	,,	2-F	20·6	154(157) [b]
H	3-Me	4-Me	1·8	
H	3,5-Pr^i_2	Failed		
H	Thiosalicyclic	Thioxanthone	6	206(209) [c]
H	6-OH	1,6-$(OH)_2$ [a]	12	250(252) [d]
H	6-MeO	1-MeO	16	

[a] Product from selfcondensation of 2,6-dihydroxybenzoic acid. [b] F. L. Allen, P. Koch, and H. Suschitzky, *Tetrahedron*, 1959, **6**, 315. [c] E. G. Davis andS. Smiles, *J. Chem. Soc.*, 1910, **97**, 1290. [d] H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 430.

2-Diazo-benzene sulphonate (7·66 g.) was decomposed in refluxing *p*-xylene overnight. The *p*-xylene solution decanted from the tar produced, was evaporated under reduced pressure to leave dibenzo[1,5,2,6]dioxadithiocin 6,12-bisdioxide as a white solid which was purified by washing with a little benzene followed by sublimation (0·98 g., 11·2%), m.p. 237° (lit.,[22] m.p. 237°). It showed bands at 1391, 1162, and 1190 cm.$^{-1}$ (–SO_2) (Found: C, 46·2; H, 2·5. Calc. for $C_{12}H_8O_6S_2$: C, 46·1; H, 2·6%). The 2,8-dimethyl derivative (5%) was obtained from 5-methylaniline-2-sulphonic acid by a similar procedure. It had m.p. 274° (lit.,[21] m.p. 279°) and showed bands at 1386 and 1173 cm.$^{-1}$ (SO_2).

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