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The Use of Tetracyanoethylene for the Qualitative Analysis of Phenols *

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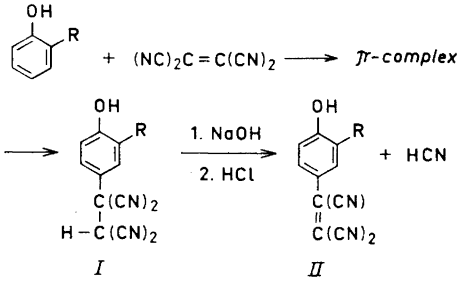
The reaction between tetracyanoethylene (TCNE) and phenols with the formation of coloured *p*-(tricyanovinyl)-phenols has been utilized for the qualitative analysis of phenols. It was found that the mode of reaction was dependant on the structure of the phenol, thereby providing a means for investigating the latter. TCNE also forms coloured complex compounds with phenols, the analytical application of which reaction was also studied. Further, 2,6-dibromoquinone chloroimide (Gibbs reagent) was utilized for establishing the presence or absence of substituents in the position *para* to the phenolic hydroxyl group. The combination of this test with the TCNE tests proved to be valuable for elucidating phenolic structures.

The reaction between tetracyanoethylene (TCNE) and phenols has been dealt with by two of the present authors in some recent papers [1,2]. It has been shown that, under suitable conditions, one mole of TCNE adds on to one mole of certain phenols with the formation of crystalline *p*-(tetracyanoethyl)-phenols (I). These are colourless compounds or eventually slightly coloured. On the addition of alkali followed by acidification they are rapidly converted to the coloured *p*-(tricyanovinyl)-phenols (II) with the expulsion of hydrocyanic acid. The reactions involved may be written as follows:



I *II*

* Paper No. 8 in a series on analytical investigations of phenols and phenol derivatives. For previous papers *cf.* Ref. [1].

The anion of the tricyanovinylphenol is strongly coloured. This fact suggested the possibility of developing a TCNE test for phenols based on the formation of the tricyanovinylphenols.

In a previous investigation [1] it was found that the formation of crystalline *p*-(tetracyanoethyl)-phenols from TCNE and phenols took place only when one or both of the *ortho* positions of the phenol were substituted by suitable groups but other positions in the molecule were free. However, the colour obtained on the addition of alkali to the solution of the two reaction components indicated that a reaction occurred also in many other cases, although no crystalline tetracyanoethylphenols could be isolated. To investigate this problem further a filter paper technique, adapted to small amounts of substance, was worked out and applied to a number of phenols of various structures. The results of the investigation are collected in Tables 1—5 and will be discussed in the following.

TCNE forms coloured π-complexes with aromatic compounds [3]. This fact has been utilized for establishing the position of aromatic hydrocarbons and some of their substitution derivatives on paper chromatograms [4-6]. Phenols also give coloured complexes with TCNE and the colours formed with the material in Tables 1—5 have been examined in order to investigate their usefulness for the qualitative analysis of phenols.

A detailed study of quinone chloroimide as a reagent for phenols was recently made by one of the present authors [7]. In alkaline solution, this reagent almost exclusively attacks at the position *para* to the phenolic hydroxyl group with the formation of blue indophenols. In its specificity for the *para* position it is similar to TCNE which is shown subsequently in this work only to attack at this position. By using the two reagents simultaneously the utility of the TCNE test was increased considerably. The quinone chloroimide employed here was a dibromo derivative of that previously investigated (Gibbs reagent, *cf.* Ref.[8]). Its reaction with a phenol in alkaline solution may be written as follows [9]:

$$\bar{O}-C_6H_5 + ClN=C_6H_2(Br_2)=O + \bar{O}H \longrightarrow \bar{O}-C_6H_4-N=C_6H_2(Br_2)=O + H_2O + \bar{Cl}$$

The test was used merely to establish the presence or absence of substituents in the position *para* to the phenolic hydroxyl group. No other structural influences on the outcome of the test were examined.

EXPERIMENTAL

Material. The material used in this investigation is tabulated in Tables 1—5. It consisted of 131 phenols of various structures. They were arranged in the following order. In Table 1: phenol and alkylphenols * (Nos. 1—36), alkenylphenols (Nos. 37—38) and hydroxymethylphenols (Nos. 39—40). In Table 2: halophenols (Nos. 41—52), monohydroxybenzaldehydes (Nos. 53—55), monohydroxyacetophenones (Nos. 56—57), monohydroxypropiophenones (Nos. 58—59), monohydroxybenzoic acids (Nos. 60—62), esters of monohydroxybenzoic acids (Nos. 63—65) and nitrophenols (Nos. 66—73) In Table 3:

* The last two compounds with substituents in the alkyl groups. If a phenol in addition to alkyl groups also contained functional groups in the aromatic ring its position in the tables was determined by the functional groups in question.

di- and trihydric phenols without and with other substituents (Nos. 74—89), monoesters of dihydric phenols (Nos. 90—91), aminophenols (Nos. 92—96) and ethers of di- and trihydric phenols without and with other substituents (Nos. 97—119). In Table 4: diphenylols (Nos. 120—126) and in Table 5, naphthols (Nos. 127—131).

Reagents and methods. Tetracyanoethylene tests. The TCNE reagent consisted of a solution of 50 mg TCNE * in 10 ml methylene chloride. One drop (about 0.02 ml) of a solution of the phenol in acetone containing 100—200 μg of the phenol was put on a filter paper followed by one drop of the TCNE reagent. The colour of the complex developed after some time. One drop of 1.25 N aqueous sodium hydroxide was then placed in the middle of the coloured spot. The colour of the complex vanished and a positive test was denoted by the formation of a coloured ring or spot. The time elapsed until the colour change took place was also noted.

A blank using only the phenol and alkali was run at the same time in order to ascertain whether any colour was developed with alkali alone. If the colour obtained with the TCNE reagent did not deviate from the colour of the blank, the test was designated negative. In the case of nitrophenols, for example, yellow colours were obtained and with di- and trihydric phenols brown colours often resulted. However, in those cases where tricyanovinylphenols were formed, their colours were well recognizable against the dark background.

The TCNE reagent produced a yellow ring on filter paper. The reagent was stable for a long time when protected from moisture. While the colour of the complex faded rather rapidly, the colours of the tricyanovinylphenols were stable for weeks although a slight change in the shade of colour occurred gradually.

2,6-Dibromoquinone chloroimide test. The reagent consisted of a 0.1 % solution of 2,6-dibromoquinone chloroimide in 96 % ethanol. About 200 μg of the phenol was dissolved in 0.2 ml ethanol or acetone and the solution was made alkaline to pH 8 using 0.01 N sodium hydroxide (or 0.1 N in the case of more strongly acidic phenols and hydroxybenzoic acids). One drop of the reagent was added and the change in colour was noted. The test was designated positive in the tables whenever a colour change to blue, blue-green or green took place. If any other colour was observed, it is denoted in the tables.

RESULTS AND DISCUSSION

Tetracyanoethylene tests

Colour of the complex. An examination of the colours listed in Tables 1—5 reveals that the colour of the complex is related to the structure of the phenol. Light colours, *i.e.* light red, pink, orange, yellow, dominated for phenols containing deactivating substituents (*cf.* Table 2) while red, blue and violet colours were generally developed with phenols containing activating substituents (*cf.* Tables 1, 3, 4 and 5). The majority of the tested phenols were positive. However, strongly deactivated phenols gave negative tests as shown by the results with the polyhalophenols (Nos. 51 and 52) and with some nitrophenols in Table 2. Accumulation of several large activating groups might also lead to a negative test (*cf.* No. 33). For the diphenylols the "bleaching" effect of a deactivating group seems to be stronger than for hydroxybenzenes. Thus, the presence of a carboxyl group in each of the benzene rings in diphenyl caused the colour to disappear while the hydroxybenzoic acids yielded coloured spots (*cf.* Nos. 60—63 and 122, 124 and 125). A similar effect was noted for a hydroxydiphenyl ether (No. 102).

Often, when activating and deactivating substituents were combined the deviation from the general shade of colour gave a clue to the structure. To give some examples: the red-violet and blue-violet colours obtained for the

* Obtained from Eastman Kodak Co., USA.

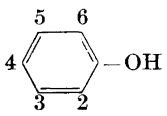
halophenol No. 46 and the ketophenol No. 59 indicate the presence of activating groups as well. The deactivating groups in question may be detected by various methods while alkyl groups are more difficult to trace. The light red colour given by the nitrophenol No. 69 clearly shows that an activating group is present in addition to the nitro group. In the case of the di- and polyhydric phenols, deactivating groups were only recognizable from the colour of the complex when the hydroxyl groups were placed in the *meta* position. For the methoxyphenols in Table 3, a red colour of the complex generally resulted from the presence of more strongly deactivating groups.

The influence of the positions of the substituents on the colour nuance of the complex is not very marked. Certain regularities existed only in the case of the monoalkylphenols. *Ortho* substituted phenols produced a red-violet colour, *meta* substituted a red colour and *para* substituted a violet colour. The size of the alkyl group also had some bearing upon the colour of the complex in that, among the alkylphenols, those with *tert.* butyl groups tended to give greenish colours. It should be noted, however, that several other types of phenols gave greenish complex colours.

The cause of the complex formation between TCNE and aromatic compounds is considered to be a Lewis acid-base type of interaction TCNE acting as the acid and the aromatic compound as the base. The bond is brought about by a partial transfer of π-electrons from the aromatic molecule to orbitals of the TCNE [3]. Merrifield and Phillips [3] have measured the association constants for complex formation between TCNE and some aromatic hydrocarbons and aromatic halogen compounds as well as the wave lengths of maximum absorption (λ_{max}) for the absorption curves in the visible region and the corresponding extinction coefficients. They found that, for the methylbenzenes, there was a progressive increase in the association constants and λ_{max} with increasing methylation. Furthermore, for chloro- and bromobenzene, the association constants and λ_{max} were lower than for the methylbenzenes. Since activating and deactivating groups must be assumed to exert the same influence on the association constants and λ_{max} for complexes between TCNE and phenols as in the case of other TCNE-aromatic complexes, it is obvious that the colour of the phenolic complexes must change with the substituent in the way previously discussed.

The failure of 2,4,6-tri-*tert.*butylphenol (No. 33) to yield a complex colour is consistent with an assumed sandwich structure for the complex between TCNE and aromatic compounds [3]. The large *tert.*butyl groups would hinder the approach of the two molecules close enough for a stable complex to be formed. Evidence of this has been given by Merrifield and Phillips by determining the association constant and spectral characteristics of hexaethylbenzene. Its association constant was found only to be about one fiftieth of that of hexamethylbenzene and its extinction coefficient for maximum absorption was strikingly low in comparison with the values normally obtained. In the case of the two negatively reacting polyhalophenols (Nos. 51 and 52) a deactivation effect as well as a steric effect might be assumed to operate while for, *e.g.*, *o*-nitrophenol deactivation alone is strong enough to decrease the interaction with TCNE and force the absorption of any complex formed down into the ultraviolet region.

Table 1. Results of tests with alkylphenols, alkenylphenols and hydroxymethylphenols.

No.	Phenol 	Tetracyanoethylene tests		2,6-Dibromoquinone chloroimide test
		Colour of the complex	Reaction on the addition of alkali	
1	No subst.	Red	Orange ring (7 sec)	Pos.
2	CH_3(2)	Red-violet	Pink ring (10 sec)	Pos.
3	C_2H_5(2)	Red-violet	Pink ring (4 sec)	Pos.
4	C_3H_7-iso(2)	Red-violet	Pink ring (4 sec)	Pos.
5	CH_3(3)	Red	Pink ring (3 min)	Pos.
6	C_2H_5(3)	Red	Orange-yellow ring (10 min)	Pos.
7	CH_3(4)	Violet	Neg.	Neg.
8	C_2H_5(4)	Violet	Neg.	Pos.(weak)*
9	C_3H_7-iso(4)	Violet	Neg.	Pos.*
10	C_4H_9-*tert.*(4)	Violet	Neg.	Neg.
11	C_5H_{11}-*tert.*(4)	Violet	Neg.	Neg.
12	C_6H_{11}(4)	Violet	Neg.	Pos.(weak)*
13	C_8H_{17}-*tert.*(4)	Violet	Neg.	Neg.
14	CH_3(2,3)	Red-violet-blue	Pink ring (6 min)	Pos.
15	CH_3(2,4)	Blue-violet	Neg.	Neg.
16	CH_3(2)C_4H_9-*tert.*(4)	Green-blue	Neg.	Neg.
17	C_4H_9-*tert.*(2)CH_3(4)	Green-blue	Neg.	Neg.
18	CH_3(2,5)	Red-violet	Red ring (4 sec)	Pos.
19	CH_3(2)C_3H_7-iso(5)	Violet	Pink ring (8 sec)	Pos.
20	C_3H_7-iso(2)CH_3(5)	Violet	Pink ring (10 sec)	Pos.
21	C_4H_9-*tert.*(2)CH_3(5)	Grey-violet	Pink ring (5 sec)	Pos.
22	CH_3(2,6)	Violet	Red ring (2 sec)	Pos.
23	CH_3(2)C_3H_7-*n*(6)	Grey-violet	Pink ring (4 sec)	Pos.
24	C_3H_7-iso(2,6)	Red-violet	Pink ring (3 sec)	Pos.
25	C_4H_9-*tert.*(2,6)	Red-violet	Pink-orange spot (20 sec)	Pos.
26	CH_3(3,4)	Violet	Neg.	Neg.
27	CH_3(3,5)	Red-violet	Neg.	Pos.
28	CH_3(3)C_2H_5(5)	Red-violet	Neg.	Pos.
29	CH_3(2,3,5)	Violet	Neg.	Pos.
30	C_4H_9-*tert.*(2,4)CH_3(5)	Green-grey	Neg.	Neg.
31	CH_3(2,4,6)	Green	Neg.	Neg.
32	C_4H_9-*tert.*(2,6)CH_3(4)	Blue-green	Neg.	Neg.
33	C_4H_9-*tert.*(2,4,6)	Neg.	Neg.	Neg.
34	CH_3(3,4,5)	Green	Neg.	Neg.
35	CH_3COCH_2(2)CH_3(3,5,6)	Violet	Neg.	Pos.
36	$C_6H_5(CH_3)CH$(4)	Violet	Neg.	Neg.
37	CH_3(2)$CH_2{=}CHCH_2$(6)	Red-violet	Pink ring (4 sec)	Pos.
38	$CH_2{=}CHCH_2$(2,6)	Red-violet	Pink ring (5 sec)	Pos.
39	$HOCH_2$(3)	Red	Orange ring (3 min)	Pos.
40	$HOCH_2$(4)CH_3(2,5)	Blue-violet	Red-violet ring (40 sec)	Pos.

* These phenols contained impurities which could not be removed completely.

Formation of tricyanovinylphenols

The spot test reaction between TCNE and various types of phenols in the presence of alkali will now be considered.

Alkylphenols and alkenylphenols (Nos. 1—38). From the colour tests listed in Table 1 it is seen that, a reaction never took place when the *para* position was occupied. When the *para* position was free a reaction occurred provided that both of the *meta* positions were not occupied. Compounds with both of the *meta* positions filled gave negative tests (*cf.* Nos. 27—29 and 35). A substituent in one of the *meta* positions sometimes retarded the reaction (*cf.* Nos. 5, 6 and 14) while, in other cases, the influence on the development time was negligible (*cf.* Nos. 18—21). The large difference in development time between 2,3-xylenol (No. 14) and 2,5-xylenol (No. 18) is not easily explained. The inability of 3,5-substituted alkyl phenols to react is presumably due to steric hindrance, the bulky tetracyanoethyl group being too large to fit into the gap between the two *meta* situated alkyl groups. Apart from the three *meta* substituted phenols Nos. 5, 6 and 14 there is not any appreciable difference in development time for the positively reacting phenols, nor does the shade of colour show any structural specificity.

Hydroxymethylphenols (Nos. 39—40). A reaction took place when the hydroxymethyl group was placed in the *para* position to the phenolic hydroxyl group. It might be assumed that the hydroxymethyl group is split off in the same way as in the reaction between *para* substituted hydroxymethylphenols and quinone chloroimides (*cf.* Ref.[7] and No. 40). The long development time for *m*-hydroxymethylphenol (No. 39) agrees with that for *m*-cresol (No. 5).

Halophenols (Nos. 41—52). The halophenols tested behaved in much the same way as the alkylphenols. Thus, phenols with a halogen atom in the *para* position were negative and the reaction was retarded for *m*-chlorophenol just as was the case with *m*-cresol. No halophenols with a free *para* position and with halogen in both of the *meta* positions were tested. Undoubtedly, the reaction for such a compound would have been found to be negative.

Monohydroxybenzaldehydes, monohydroxyacetophenones and monohydroxypropiophenones (Nos. 53—59). *Para* and *meta* substituted compounds gave negative tests while *ortho* substituted reacted after about 1 min.

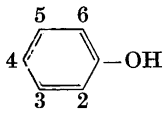
Monohydroxybenzoic acids (Nos. 60—62). Only for *p*-hydroxybenzoic acid was a positive test obtained. This positive reaction is in agreement with the behaviour of *p*-hydroxybenzoic acids in the quinone chloroimide tests (*cf.* Ref.[7] and No. 62).

Esters of monohydroxybenzoic acids (Nos. 62—65). Methyl salicylate (No. 63) was positive while isobutyl salicylate was negative. No phenols with ester groups in the *meta* position were investigated but a negative result is most likely. No reaction took place for compounds with the ester group in the *para* position to the phenolic hydroxyl group.

Nitrophenols (Nos. 66—73). The presence of a nitro group in a phenol precluded any reaction with TCNE.

Di- and trihydric phenols and their monoesters (Nos. 74—91). The reaction of TCNE with these phenols was more erratic than with other types of phenols investigated. The reason for this is presumably that several reaction possibilities

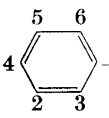
Table 2. Results of tests with phenols mainly containing deactivating groups.

No.	Phenol 	Tetracyanoethylene tests		2,6-Dibromoquinone chloroimide test
		Colour of the complex	Reaction on the addition of alkali	
41	Cl(2)	Red	Pink ring (9 sec)	Pos.
42	Cl(2)CH_3(5)	Red	Pink ring (15 sec)	Pos.
43	Cl(2)CH_3(6)	Red	Pink ring (4 sec)	Pos.
44	Cl(3)	Orange	Pink-orange ring (7 min)	Pos.
45	Cl(4)	Red	Neg.	Neg.
46	Cl(4)CH_3(3)	Red-violet	Neg.	Neg.
47	Cl(2,4)	Light red	Neg.	Neg.
48	Br(2,4)	Red	Neg.	Pos.(weak)*
49	Cl(2,6)	Orange	Pink-orange ring (10 sec)	Pos.
50	Cl(2,4,5)	Orange	Neg.	Neg.
51	Br(2,4,6)	Neg.	Neg.	Neg.
52	Cl(2,3,4,5,6)	Neg.	Neg.	Neg.
53	CHO(2)	Yellow	Orange ring (45 sec)	Pos.
54	CHO(3)	Orange	Neg.	Pos.(weak)
55	CHO(4)	Yellow	Neg.	Neg.
56	$COCH_3$(2)	Pink	Pink-orange ring (1.5 min)	Pos.
57	$COCH_3$(4)	Pink	Neg.	Neg.
58	COC_2H_5(4)	Orange	Neg.	Neg.
59	COC_2H_5(4)CH_3(2,5)	Blue-violet	Neg.	Neg.
60	COOH(2)	Orange	Neg.	Pos.
61	COOH(3)	Light red	Neg.	Pos.
62	COOH(4)	Orange	Orange ring (25 sec)	Pos.
63	$COOCH_3$(2)	Orange	Orange ring (9 min)	Pos.
64	$COOC_4H_9$-iso(2)	Orange	Neg.	Pos.
65	$COOC_6H_5$(4)	Orange	Neg.	Neg.
66	NO_2(2)	Neg.	Neg.	Neg.
67	NO_2(2)COOH(6)	Neg.	Neg.	Neg.
68	No_2(3)	Dirty yellow	Neg.	Neg.
69	NO_2(3)CH_3O(6)	Light red	Neg.	Neg.
70	No_2(4)	Dirty yellow	Neg.	Neg.
71	NO_2(4)COOH(2)	Neg.	Neg.	Neg.
72	NO_2(2,4)	Neg.	Neg.	Neg.
73	NO_2(2,4,6)	Neg.	Neg.	Neg.

* This substance contained impurities which could not be removed completely.

exist in this case. This fact was indicated by the formation of more than one colour in certain instances (*cf.* Nos. 74, 77, and 90). In the normal reaction, involving attack of TCNE *para* to the phenolic hydroxyl group, at least theoretically, more than one tricyanovinyl compound is possible for di- and trihydric phenols. TCNE is further a mild oxidizing agent [10], which could give rise to coloured oxidation products. It has also been shown that TCNE can react with ketones having hydrogen alpha to the carbonyl group, forming α-tetracy-

Table 3. Results of tests with di- and trihydric phenols, their esters and ethers, aminophenols and quaiacyl derivatives.

No.	Phenol 	Tetracyanoethylene tests		2,6-Dibromoquinone chloroimide test
		Colour of the complex	Reaction on the addition of alkali	
74	OH(2)	Blue-violet	Violet spot (1 min) + red ring (4 min)	Neg.
75	OH(2)CH_3(5)	Blue	Neg	Neg.
76	OH(2)CHO(4)	Red	Neg.	Neg.
77	OH(2)COOH(4)	Violet	Red + violet ring (1.5 min)	Neg.
78	OH(3)	Red-violet	Orange spot (2 sec)	Pink
79	OH(3)CH_3(5)	Red-violet	Neg.	Pink
80	OH(3)CHO(4)	Orange	Pink ring (2 min)	Pos.
81	OH(3)$COCH_3$(6)	Light red	Pink-orange ring (4 min)	Pos.
82	OH(3)COOH(5)	Light red	Light brown ring (3 min)	Red-violet
83	OH(3)COOH(6)	Light red	Pink-orange ring (2.5 min)	Red
84	OH(4)	Blue	Violet ring (2.5 min)	Neg.
85	OH(4)CH_3O(2)	Green-blue	Green ring (20 sec)	Neg.
86	OH(4)COOH(2)	Violet	Neg.	Neg.
87	OH(2,3)	Red-violet	Brown-red ring (2 min)	Neg.
88	OH(2,3)COOH(5)	Red-violet	Neg.	Neg.
89	OH(3,5)	Light red	Pink spot (2 sec)	Pink
90	$OCOCH_3$(2)	Red-violet	Violet spot (8 sec) + red ring (30 sec)	Neg.
91	$OCOCH_3$(3)	Red	Brick-red spot (6 sec)	Pink
92	NH_2(2)	Yellow-green	Light brown ring (2 min)	Pos.
93	NH_2(3)	Red-violet	Orange ring (1 sec)	Violet
94	$N(CH_3)_2$(3)	Blue	Red spot (1 sec)	Pos.
95	$N(C_2H_5)_2$(3)	Grey-blue	Red brown spot (1 sec)	Pos.
96	NH_2(4)	Green-yellow	Neg.	Neg.
97	CH_3O(2)	Violet	Cerise ring (1 sec)	Pos.
98	C_6H_5O(2)	Red.	Pink ring (15 sec)	Pos.
99	CH_3O(4)	Blue	Neg.	Pos.
100	$C_6H_5CH_2O$(4)	Blue	Neg.	Pos.
101	C_6H_5O(4)	Red-violet	Neg.	Pos.
102	*o*-$HOOCC_6H_4O$(4)COOH(2)	Neg.	Neg.	Neg.
103	CH_3O(2,6)	Blue-violet	Red-violet ring (1 sec)	Pos.
104	CH_3O(2)CH_3(4)	Blue-green	Neg.	Pos.(weak)*
105	CH_3O(2)CH_2=$CHCH_2$(4)	Blue	Neg.	Neg.
106	CH_3O(2)CH_3CH=CH(4)	Blue-grey	Neg.	Neg.
107	CH_3O(2)HOOCCH=CH(4)	Blue	Dark blue ring (1 sec)	Pos.**
108	CH_3O(2)$HOCH_2$(6)	Grey-blue	Cerise ring (2 sec)	Pos.
109	CH_3O(2)Br(5)	Blue-violet	Violet ring (4 min)	Pos.
110	CH_3O(2)CHO(4)	Light red	Neg.	Neg.
111	CH_3O(2)CHO(5)	Red	Neg.	Pos.
112	CH_3O(2)CHO(6)	Red	Pink ring (10 sec)	Pos.
113	CH_3O(2)$COCH_3$(4)	Red	Neg.	Neg.
114	CH_3O(2)COC_2H_5(4)	Red	Neg.	Neg.
115	CH_3O(2)$COCH_3$(5)	Red	Neg.	Pos.
116	CH_3O(2)COOH(4)	Green-grey	Pink ring (35 sec)	Pos.
117	CH_3O(2)$COOCH_3$(4)	Red	Neg.	Neg.
118	CH_3O(2,5)CH_2OH(4)	Blue-violet	Wine-red ring (40 sec)	Pos.
119	CH_3O(2,6)COOH(4)	Red	Wine-red ring (5 sec)	Pos.

* This substance contained impurities which could not be removed completely

anoethyl ketones [10,11]. Since some of the di- and trihydric phenols exist in a tautomeric equilibrium with ketone forms, an addition of TCNE to these can not wholly be excluded. It has yet to be investigated which reactions actually take place.

However, the results obtained for the di- and trihydric phenols can in many cases be explained on the basis of a normal TCNE-phenol reaction. Thus, the strong reactions given by resorcinol (No. 78) and phloroglucinol (No. 89) might be due to the fact that a position *para* to a hydroxyl group also is activated by *ortho* situated hydroxyl groups. It must be concluded that the steric hindrance from one or two *ortho* situated hydroxyl groups is negligible. On the other hand, no reaction took place when the position of attack of TCNE was situated between a hydroxyl and a methyl group (*cf.* No. 79). The influence of formyl, acetyl and carboxyl groups on the outcome of the test is, for the *meta* dihydric phenols, in agreement with previous experience (*cf.* above). The light brown colour formed for No. 82 is presumably not connected with tricyanovinylation of the phenol.

For two of the *ortho* dihydric phenols, a violet as well as a red colour was developed. It might be speculated that these colours are due to the formation of mono- and bis-(tricyanovinyl)-phenols. However, provided that substitution only takes place at the position *para* to the phenolic hydroxyl group, it could be argued that, for steric reasons, the formation of the latter compound is less likely to occur. The two tricyanovinyl groups would namely be placed adjacent to each other in the bis-(tricyanovinyl)-phenol. The negative reaction of No. 75 indicates that no substitution takes place *ortho* to a methyl group, which result diverges from that previously obtained for monohydric phenols (*cf.* No. 5). The colour formation with the two *para* dihydric phenols obviously can not be due to a normal TCNE-phenol reaction.

The tests given by the two esters (Nos. 90 and 91) were rather similar to those of the corresponding dihydric phenols (Nos. 74 and 78).

Aminophenols (Nos. 92—96). Only *m*-aminophenols gave the characteristic colour reaction, which was especially strong for the N,N-dialkylaminophenols (Nos. 94 and 95). A tricyanovinylation is possible at the *para* position to the hydroxyl group or at the *para* position to the amino group [12]. A reaction between TCNE and hydrogen in the amino group has also been shown to take place in neutral solution, giving rise to white or yellow N-tricyanovinylamines [12]. It might be that a competition between these reactions makes the reaction for *m*-aminophenol weaker than for the two phenols without hydrogen at the nitrogen atom.

Monoethers of dihydric phenols and 2,6-dimethoxyphenol (Nos. 97—103). Phenols with the ether groups in the ortho position gave a positive test while no reaction took place for *para* substituted compounds. This is in contrast to the positive tests given by these phenols with 2,6-dibromoquinone chloroimide. No phenol with the ether group in the *meta* position is included in this section but a positive test was obtained for compound No. 118 in the next section.

Phenols Nos. 104—119. This section comprises phenols, the majority of which contain a methoxy group in the *ortho* position and, in addition to this substituent, various other groups. The last two compounds contain two methoxy groups.

The results obtained with the previously investigated material were wholly confirmed here. For example, the reaction was negative when the position *para* to the phenolic hydroxyl group was filled by an alkyl, alkenyl, formyl, acetyl or propionyl group, but positive in the case of a hydroxymethyl or carboxyl group. The positive reaction of ferulic acid (No. 107) is in agreement with the behaviour of this compound towards quinone chloroimides [7,13]. It was further found that the reaction was retarded when a bromine atom was placed in the *meta* position (No. 109) and wholly inhibited when the same position was filled by a formyl or acetyl group (Nos. 111 and 115).

Diphenylols (Nos. 120—126). The positive reaction of *p*-hydroxydiphenyl (No. 123) was undoubtedly due to the presence of impurities. The reaction was considerably weakened on repeated recrystallizations. As previously found for hydroxybenzoic acids, the presence of carboxyl groups *ortho* to the phenolic hydroxyl groups made the test negative (*cf.* Nos. 122 and 125). The negative reaction of No. 126 agrees with the result obtained with 5-methylpyrocatechol (No. 75). In the latter case, the presence of a methyl group *ortho* to the position attacked by TCNE hindered the reaction. In the case of the diphenylol the positions of attack are flanked by a methyl group and by the other half of the diphenylol molecule.

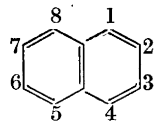
Naphthols (Nos. 127—131) reacted much as might be expected. However, the strong test given by *α*-naphthol (No. 127) in comparison with 1,5-dihydroxynaphthalene (No. 130) is somewhat puzzling. The reaction of 1,3-dihydroxynaphthalene (No. 129) agrees with that of resorcinol (No. 78). It is of interest that *β*-naphthol and 2,7-dihydroxynaphthalene (Nos. 128 and 131) gave negative tests since these compounds were positive with 2,6-dibromoquinone chloroimide.

Table 4. Results of tests with diphenylols.

No.	Phenol	Tetracyanoethylene tests		2,6-Dibromoquinone chloroimide test
		Colour of the complex	Reaction on the addition of alkali	
120	OH(2)	Red-violet	Pink ring (4 sec)	Pos.
121	OH(2,2′)	Red	Pink-orange ring (10 sec)	Pos.
122	OH(2,2′)COOH(3,3′)	Neg.	Neg.	Pos.(weak)
123	OH(4) *	Blue	Weak pink ring (1.5 min)	Pos.
124	OH(4,4′)COOH(3,3′)	Neg.	Neg.	Neg.
125	OH(3,3′)COOH(4,4′)	Neg.	Neg.	Pos.(weak)
126	OH(2,2′,3,3′)CH_3(4,4′)	Blue-violet	Neg.	Red.

* This phenol contained impurities which could not be removed completely.

Table 5. Results of tests with naphthols.

No.	Phenol 	Tetracyanoethylene tests		2,6-Dibromoquinone chloroimide test
		Colour of the complex	Reaction on the addition of alkali	
127	OH(1)	Grey-blue	Violet spot (1 sec)	Pos.
128	OH(2)	Blue	Neg.	Pos.
129	OH(1,3)	Grey-green	Red spot (1 sec)	Pink
130	OH(1,5)	Blue-grey	Green ring (1 min)	Pos.
131	OH(2,7)	Blue-violet	Neg.	Pos.

2,6-Dibromoquinone chloroimide tests

As previously mentioned, the 2,6-dibromoquinone chloroimide reagent was mainly used to ascertain whether the position *para* to the phenolic hydroxyl group was vacant or filled. The results obtained here are on the whole in close agreement with the experience gained with quinone chloroimide in a previous investigation [7]. The conclusions arrived at in the quoted paper are also valid here, *i.e.* the 2,6-dibromoquinone chloroimide test is applicable in determining whether the position *para* to a phenolic hydroxyl group in a monohydroxybenzene is free or filled by an alkyl, aryl, halogen, formyl, keto or ester group but not applicable in ascertaining whether the *para* position is free or occupied by a hydroxymethyl, carboxyl, alkoxy, aralkoxy or aryloxy group or by a β-carboxyvinyl group.

Further, the 2,6-dibromoquinone chloroimide test is not applicable to nitrophenols and to di- and polyhydric phenols as well as their monoesters. From the results listed in Table 3 it is seen that, 1,2- and 1,4-dihydric phenols and 1,2,3-trihydric phenols gave a negative test, which means that no colour change was observed on addition of the 2,6-dibromoquinone chloroimide reagent *. For the 1,3-dihydric phenols a colour change took place, sometimes to red, pink or red-violet, sometimes to the bluish nuances associated with a positive test. This mode of reaction of the di- and trihydric phenols is somewhat different from their behaviour towards quinone chloroimide. In that case reddish or brownish colours generally resulted (*cf.* Ref.[7]).

There is a marked difference in the development time for the two quinone chloroimide reagents. In the experiments with quinone chloroimide, the time, elapsed until the first appearance of any colour, ranged from seconds to several hours. In the present case, in the positive reactions, the colour was often developed in less than 10 sec and only in a few cases the development time was longer than 1 min. The greater activity of the 2,6-dibromoquinone chloroimide reagent can be ascribed to the presence of the two bromo atoms which increase the electrophility of the reagent. The short development

* An exception was provided by the diphenylol No. 126 which gave a red colour.

time is a distinct advantage in a qualitative test but, on the other band, there is a decrease in the sensitivity to changes in the structure.

The tests given by the diphenylols containing carboxyl groups were rather weak (*cf. Nos.* 122 and 125). This fact indicates a stronger deactivation than in the case of the hydroxybenzoic acids and should be compared with the inability of these compounds to produce any complex colour with TCNE. Among the naphthols, the positive reactions of β-naphthol and 2,7-dihydroxynaphthalene are noteworthy (*cf.* Nos. 128 and 131). It means that substitution occurs *ortho* to the phenolic hydroxyl groups, presumably in the reactive 1- and 8-positions which are known to be readily attacked by electrophilic reagents (*cf.* Ref.[14]). The failure of TCNE to yield tricyanovinylnaphthols with the compounds in question can be ascribed to steric hindrance. TCNE was, for example, previously in this work found not to attack a position flanked by a methyl group and a hydroxyl group (*cf.* No. 79).

Table 6. Summary of results of tests with certain monohydric phenols.

Substituent group	Results of tests		Position of substituent group *		
	Tetracyanoethylene tests **	2,6-Dibromoquinone chloroimide tests	*Para*	*Meta*	*Ortho*
Alkyl Alkenyl Halogen	Neg.	Neg.	+	− −	− −
	Neg.	Pos.	−	+ +	− −
	Retarded	Pos.	−	+ −	− −
	Retarded	Pos.	−	− + (3)	− + (2)
	Pos.	Pos.	−	− + (5)	− + (2)
	Pos.	Pos.	−	− −	+ +, + − or − −
Hydroxymethyl	Pos.	Pos.	+	− −	− −
	Pos.	Pos.	−	− −	+ −
	Retarded	Pos.	−	+ −	− −
Formyl Acetyl Propionyl	Neg.	Neg.	+	− −	− −
	Neg.	Pos.	−	+ −	− −
	Pos.	Pos.	−	− −	+ −
Carboxyl	Pos.	Pos.	+	− −	− −
	Neg.	Pos.	−	+ −	− −
	Neg.	Pos.	−	− −	+ −
Ester	Neg.	Neg.	+	− −	− −
	Neg.	Pos.	−	+ −	− −
	Pos. or neg.	Pos.	−	− −	+ −
Ether	Neg.	Pos.	+	− −	− −
	Pos.	Pos.	−	+ −	− −
	Pos.	Pos.	−	− −	+ + or + −
	Pos.	Pos.	−	− + (5)	− + (2)

* + Means that a position is filled, − that it is vacant. The numbers refer to the position in the aromatic ring.

** Reaction on the addition of alkali.

Analytical use

The analytical application of TCNE and 2,6-dibromoquinone chloroimide is partly evident from the previous description. However, to point out the utility of a combination of the two reagents a scheme for their use in the structural investigation of phenols will be outlined in the following.

The analytical application of TCNE is twofold: (1) The colour of the complex formed between TCNE and phenols gives information about the general type of phenol present. Light colours are generally associated with deactivated phenols and stronger colours with slightly deactivated or activated phenols. It also happens that no complex colour is developed, either as a result of strong deactivation or due to steric hindrance from bulky substituents in the aromatic ring. This matter has been fully discussed above (*cf.* p. 711).

(2) The second application of TCNE arises from its ability to react with phenols at the position *para* to the phenolic hydroxyl group with the formation of coloured *p*-(tricyanovinyl)-phenols. This reaction is to a considerable degree influenced by substituents at the *meta* and *ortho* positions to the phenolic hydroxyl group and, a negative test does not necessarily mean that the *para* position in filled.

The 2,6-dibromoquinone reagent like TCNE attacks at the position *para* to the phenolic hydroxyl group * and a positive test is obtained whenever this position is vacant, except for nitrophenols and di- and polyhydric phenols. In addition, phenols with certain substituents at the *para* position give a positive test. It means that a negative test is always associated with a filled *para* position except for nitrophenols ** and di- and polyhydric phenols. While the 2,6-dibromoquinone chloroimide test mainly gives information about the *para* position it is possible by applying it together with the TCNE test also to obtain information about other positions in the aromatic ring.

In order to facilitate the evalutation of the results, a summary of some of the tests is given in Table 6. In this list, only monohydric phenols of the hydroxybenzene type are included. Further, except for alkyl, alkenyl, halogen and ether groups, only one substituent group is considered to be present, because no experience has been gained in this work on the behaviour of, *e.g.*, phenols with two carboxyl groups or two formyl groups. Concerning di- and polyhydric phenols and their monoesters, aminophenols, nitrophenols, diphenylols and naphthols, Tables 2—5 should be consulted. The previous tables also give information about the colour of the complex compounds formed between TCNE and phenols.

The results obtained with phenols having several substituent groups of different types indicate that, to a certain extent, informations may be obtained about the reaction of phenols not studied in this work by combining the results listed in Table 6. For example, no monohydric phenol with more than one carboxyl group should be expected to give a positive TCNE test nor a 2,6-dimethyl-4-hydroxybenzoic acid. It is questionable whether a 3-hydroxymethyl-5-methylphenol will be positive in the TCNE test and the same applies to a 3,5-dimethoxyphenol.

* *Cf.*, however, certain naphthols p. 720.

** Other types of strongly deactivated phenols might also be expected to give a negative test.

The present investigation has, we believe for the first time, furnished a simple method for investigating the positions *meta* to a phenolic hydroxyl group. It is thought that, by including the present tests in the scheme previously proposed for the identification of phenols [7], the possibilities of obtaining rapid information about their structural details will be increased. Because of its twofold effect, the TCNE reagent should also be useful for tracing phenols separated by various chromatographic procedures. A paper chromatogram could, for example, first be sprayed by a solution of TCNE and the complex colours formed examined. After that, it could be treated by dilute aqueous alkali when the colours of the tricyanovinylphenols would develop. It is our intention to further investigate this application of TCNE.

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