854. *Free Radicals and Radical Stability. Part XVI.* The Properties of Triarylmethanols containing* p-*Hydroxyl Substituents, and the Quinonoidation Theory of Free Radicals.*

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Diphenylquinomethane and the so-called colourless and coloured forms of (*p*-hydroxyphenyl)diphenylmethanol give the same carbonium ion in sulphuric acid, and their hot formic acid solutions evolve carbon dioxide at practically the same rate.

Although American investigators maintain that the product obtained on crystallizing the alcohol from acetic acid is a quinonoid isomer, the present analysis of the absorption spectra of mixtures of colourless alcohol and diphenylquinomethane and the *X*-ray and thaw-melt examination of the solid systems indicate that the colour is due to the presence of the fuchsone. The properties of other triarylmethanols containing *p*-hydroxyl substituents may be accounted for on a similar basis.

If, as indicated, quinonoid forms of these compounds have no independent existence, Gomberg's main evidence in support of the quinonoidation theory of free radicals is no longer valid.

(*p*-HYDROXYPHENYL)DIPHENYLMETHANOL is peculiar in that when deposited from solution in ammoniacal alcohol the crystals are colourless and melt with decomposition at 159—160°, whereas when obtained from 50% acetic acid they are yellow and melt with decomposition at 138—139°. The two products are not polymorphs, and Gomberg *et al.*,[1] and more recently Anderson *et al.*,[2] maintain that the colourless product is the benzenoid alcohol (I) and that the coloured product has the quinonoid structure (II). On the contrary, Ramart-Lucas and Martynoff [3] contend that the coloured product is simply a mixture of the benzenoid alcohol (I) and diphenylquinomethane (III), but their meagre evidence is not entirely convincing.

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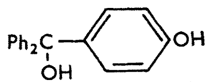
* Part XV, preceding paper.

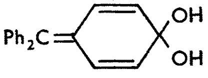
[1] Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 1035; Gomberg and Van Stone, *ibid.*, 1916, **38**, 1577; Gomberg and Sullivan, *ibid.*, 1920, **42**, 1864; Gomberg and Lange, *ibid.*, p. 1874; Gomberg and Anderson, *ibid.*, 1928, **50**, 203.

[2] Anderson, *ibid.*, 1929, **51**, 1889; Anderson and Geiger, *ibid.*, 1932, **54**, 3059; Anderson and Fisher, *ibid.*, 1944, **66**, 594.

[3] Ramart-Lucas and Martynoff, *Bull. Soc. chim. France*, 1941, **8**, 882.

The investigations have been largely concerned with the absorption spectra of the substances in ethereal solution and, while the absorption curves determined in the present


(I)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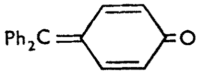

(III)

work are similar to those obtained by previous investigators, it is evident from the following data that the values of $\varepsilon_{max.}$ estimated from the curves given by Ramart-Lucas and Martynoff are substantially lower than those found by us.

Absorption spectra of ethereal solutions.

	$10^{-3}\varepsilon_{max.}$			Absorption max. (mμ)		
	Anderson and Gomberg	Ramart-Lucas and Martynoff	Present work	Anderson and Gomberg	Ramart-Lucas and Martynoff	Present work
Colourless product......	2·2	1·0	2·14	278, 285	278, 285	278, 285
Coloured product	2·2	1·5	2·16	278, 285, 365	278, 285, 365	278, 285, 365
Diphenylquinomethane	30·2	21·4	27·6	260, 365	260, 365	260, 365

If the peak at 365 mμ is due solely to diphenylquinomethane, the concentration of the latter may vary from 0·67 to 0·88%. Our absorption curves for mixtures of colourless (*p*-hydroxyphenyl)diphenylmethanol and the fuchsone are shown in the Figure. The observed values of the optical densities agree closely with those calculated on the basis of Beer's law, and the curve for the mixture containing 99·22% of the colourless alcohol and 0·78% of the fuchsone is indistinguishable from that of the coloured product. We conclude that the coloured product is a mixture and that its composition varies slightly according to the conditions of crystallization.

The alcohol and the coloured product give the same *X*-ray diffraction patterns, the method not revealing less than 5% of diphenylquinomethane. Thermal analysis of mixtures prepared by grinding together the colourless alcohol and diphenylquinomethane indicates that the components form a 1 : 1 compound, but it is not possible to determine the solid solubility at low fuchsone concentrations owing to the thermal instability of the alcohol.

The most striking difference between the alcohol and the coloured product is the more rapid elimination of water from the latter at about 90°. This arises only in the solid state where specific factors governing the formation and growth of nuclei of the solid decomposition product determine the rate of the reaction. If the reaction involves the formation of diphenylquinomethane hydrate as intermediate phase, decomposition of the latter will be induced by nuclei of fuchsone, which are already present in the coloured product. The different thermal behaviour of mixtures of colourless alcohol and diphenylquinomethane prepared by mechanical grinding and the product precipitated from alcoholic solution by water may be explained similarly.

The hydroxyl group exerts an overall inhibitory effect on the reduction of the alcohol in hot formic acid, and since solutions of the colourless alcohol, coloured product, and fuchsone evolve carbon dioxide at practically the same rate, the reactions may be represented:

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH + H{\cdot}CO_2H \rightleftharpoons HO{\cdot}C_6H_4{\cdot}C^+Ph_2 + H{\cdot}CO_2^- + H_2O}$$

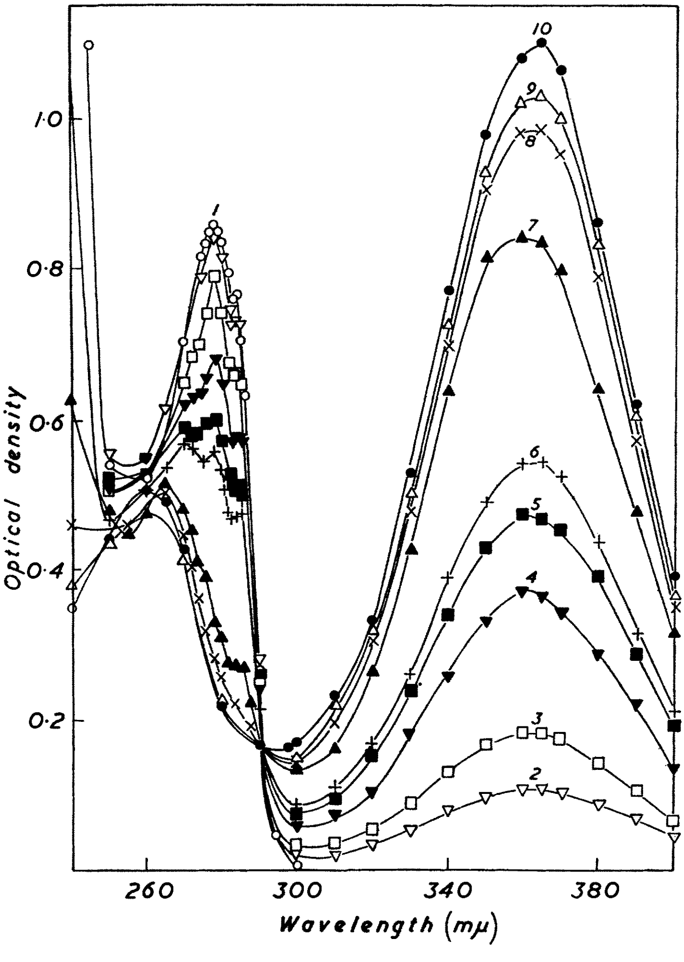
$$\mathrm{O{:}C_6H_4{:}CPh_2 + H{\cdot}CO_2H \leftrightharpoons HO{\cdot}C_6H_4{\cdot}C^+Ph_2 + H{\cdot}CO_2^-}$$

$$\mathrm{HO{\cdot}C_6H_4{\cdot}C^+Ph_2 + H{\cdot}CO_2^- = HO{\cdot}C_6H_4{\cdot}CHPh_2 + CO_2}$$

There is, moreover, no appreciable difference between the basicities of the colourless alcohol and the coloured product as measured by the salt-hydrolysis method.

The coloured products obtained by crystallizing (4-hydroxy-3 : 5-dimethoxyphenyl)-diphenylmethanol and diphenyl-(3 : 4 : 5-trihydroxyphenyl)methanol from 50% acetic acid are mixtures of the alcohol and fuchsone. On the other hand, *X*-ray and chemical analysis reveals that the yellow products obtained by similar treatment of (2 : 4-dihydroxyphenyl)- and (4-hydroxy-2-methylphenyl)-diphenylmethanol are complexes containing acetic acid of crystallization. The properties of the alcohols examined in the present work may thus be explained without recourse to the quinonoidation theory.

Absorption spectra of (p-*hydroxyphenyl*)*diphenylmethanol and mixtures with diphenylquinomethane. Molar % of diphenylquinomethane:* (1) 0; (2) 0·78; (3) 1·56; (4) 4·22; (5) 6·05; (6) 7·33; (7) 28·4; (8) 49·7; (9) 70·4; (10) 100.



Experimental

(p-*Hydroxyphenyl*)*diphenylmethanol*.—The compound was prepared from diphenylmethylene dichloride and phenol.[4] Addition of water to a solution of the alcohol in alcohol containing a drop of 2N-ammonia gave colourless or pale yellow crystals, m. p. 159—160° (decomp.). Similar treatment of the solution in 50% acetic acid led to the separation of yellow crystals, m. p. 137—139° (decomp.).

Thermal decomposition of the alcohol gave diphenylquinomethane, m. p. 168°.[5]

(4-*Hydroxy*-2-*methylphenyl*)*diphenylmethanol*.—Prepared from diphenylmethylene dichloride and *m*-cresol,[6] this alcohol was obtained as colourless crystals, m. p. 114°. The solution in

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[4] Gomberg and Jickling, *J. Amer. Chem. Soc.*, 1915, **37**, 2575.

[5] Baeyer and Villiger, *Ber.*, 1903, **36**, 216.

[6] Gomberg and Johnson, *J. Amer. Chem. Soc.*, 1917, **39**, 1674.

acetic acid on treatment with water deposited yellow crystals of the alcohol–acid complex, m. p. 80—82° (Found: C, 74·5; H, 6·4. Calc. for $C_{20}H_{18}O_2,CH_3{\cdot}CO_2H$: C, 75·4; H, 6·3%).

(2 : 4-*Dihydroxyphenyl*)*diphenylmethanol*.—Hydrolysis of the product from 2 : 4-dihydroxybenzophenone and phenylmagnesium bromide gave the alcohol, m. p. 123°. On addition of water to the solution in 50% acetic acid, the alcohol–acid complex was deposited as yellow crystals, m. p. 115° (Found: C, 72·8; H, 5·6. $C_{19}H_{16}O_3,CH_3{\cdot}CO_2H$ requires C, 71·6; H, 5·7%).

Diphenyl-(3 : 4 : 5-*trihydroxyphenyl*)*methanol*.—A solution of methyl gallate (1 equiv.) in ether was added to phenylmagnesium bromide (4 equiv.), and the mixture was heated and shaken under reflux for 4 hr., then hydrolysed, and after treatment with steam the alcohol was obtained as a dark red solid (18%). Addition of water to the solution of the *alcohol* in 50% alcohol containing a drop of aqueous ammonia gave small yellow crystals, m. p. 183·5—184·5° (Found: C, 74·9; H, 4·9. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). Recrystallization from ammoniacal alcohol yielded dark red needles, m. p. 183—184° (Found: C, 76·8; H, 4·7%). After repeated recrystallization from 50% acetic acid the material was obtained as reddish-brown crystals, m. p. 167° (Found: C, 75·7; H, 5·2%).

(4-*Hydroxy*-3 : 5-*dimethoxyphenyl*)*diphenylmethanol*.—Methyl 4-hydroxy-3 : 5-dimethoxybenzoate[7] (1 equiv.) in ether was added to phenylmagnesium bromide (4 equiv.), and the mixture was heated under reflux for 4 hr., then hydrolyzed and steam-distilled, giving a pale yellow solid (83%). After three recrystallizations from 50% alcohol containing a drop of 2N-ammonia, the *alcohol* was obtained as colourless crystals, m. p. 210—212° (Found: C, 74·9; H, 5·9. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%). Repeated recrystallization from 50% acetic acid gave deep yellow crystals, m. p. 198—199° (Found: C, 74·4; H, 6·1%).

The colourless alcohol was kept at 150° for 4 hr. Recrystallisation from 1 : 1 ether–benzene gave yellow (3 : 5-*dimethoxyphenyl*)*phenylquinomethane*, m. p. 225—226° (Found: C, 77·2; H, 5·7. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

Reduction of the alcohol by zinc and acetic acid gave (4-*hydroxy*-3 : 5-*dimethoxyphenyl*)*diphenylmethane* which was colourless after recrystallization from alcohol and had m. p. 131° (Found: C, 78·0; H, 5·9. $C_{21}H_{20}O_3$ requires C, 78·8; H, 6·1%).

(3 : 5-*Dihydroxy*-4-*methoxyphenyl*)*diphenylmethanol*.—Methyl 3 : 5-dihydroxy-4-methoxybenzoate[8] (1 equiv.) was gradually added to phenylmagnesium bromide (4 equiv.), and the mixture was heated under reflux for 3 hr., hydrolyzed, and treated with steam. The residual dark red solid was dissolved in ether, and the solution was warmed with " Norit " and filtered. On concentration the *alcohol* was deposited as dark red needles (35%). After three recrystallizations from light petroleum the compound had m. p. 174—175° (Found: C, 75·6; H, 5·3. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

Absorption Spectra of Alcohols and Fuchsones in Ether.—The colourless alcohols and corresponding coloured products were recrystallized at least three times and dried over soda-lime before use, while the fuchsones were purified similarly and dried over silica gel and calcium chloride. The solutions were examined in 10 mm. rectangular cells by means of a Unicam S.P. 500 spectrophotometer. Eastman-Kodak Spectro-grade ethyl ether was the solvent, and evaporation losses were reduced by binding the lid of the cell with tin foil. As far as possible the solutions were kept in the dark, and measurements of the optical density were made in the range 225—500 mμ. The absorption data are summarized in Table 1, where the first value of the maximum extinction coefficient is the mean of two determinations, and the other values refer to solutions prepared from different specimens of the alcohol or fuchsone.

Although the absorption spectra of the so-called colourless and coloured forms of (*p*-hydroxyphenyl)diphenylmethanol are similar in the ultraviolet region, the coloured product exhibits a low absorption peak at a wavelength corresponding to the maximum absorption of the fuchsone. On the basis of Beer's law it may be shown that a mixture containing 99·48% of the colourless carbinol and 0·52% of the fuchsone gives essentially the same absorption band as the coloured product and that the optical density in the ultraviolet region (278 mμ) differs by only 0·8% from that of the colourless alcohol.

A mixture containing 99·48% of colourless alcohol and 0·58% of fuchsone, prepared by grinding the components, melted at 137—158° whereas the " coloured alcohol " had m. p. 137—139°. On the other hand, the yellow crystals obtained by adding water to an alcoholic

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[7] Robinson and Bradley, *J.*, 1928, 1555.
[8] Graebe and Martz, *Ber.*, 1903, **36**, 216.

solution containing the components in the above proportions melted at 136·5—139°, and the m. p. was unchanged on admixture with the "coloured alcohol."

The absorption spectra of various mixtures of (*p*-hydroxyphenyl)diphenylmethanol (m. p. 160·0°) and diphenylquinomethane in ether are shown in the Figure. For each mixture there is very good agreement between the observed values of the optical densities at various wavelengths and those calculated on Beer's law. The curve of a mixture containing 99·22% of colourless alcohol and 0·78% of diphenylquinomethane is indistinguishable from that of the coloured product.

TABLE 1. *Absorption spectra of alcohols, coloured products, and fuchsones in ether.*

Diphenylmethanol	Coloured product	$10^{-4}\varepsilon_{\text{max.}}$	$\lambda_{\text{max.}}$ (mμ)
(*p*-Hydroxyphenyl)-	—	0·216	278, 285
	Yellow	0·221	278, 285, 365
(4-Hydroxy-2-methylphenyl)-	—	0·157	278, 284
	Yellow	0·152	278, 284
(3 : 4 : 5-Trihydroxyphenyl)-	Yellow	1·29	267, 393
	Red	1·31	267, 395
	Brown	1·27	267, 393
(4-Hydroxy-3 : 5-dimethoxyphenyl)-	—	0·162	*268, *285
	Yellow	0·169	*268, *285, 378
Quinomethane			
Diphenyl		2·79	261, 365
(3 : 5-Dimethoxyphenyl)phenyl		2·61	265, 378

* Inflexion.

X-*Ray Diffraction Measurements.*—Preliminary experiments showed that the extent of conversion of colourless alcohol into coloured product during the measurements is small.

(a) *Powder photographs.* The diffraction patterns of the two specimens are identical with respect to the position and relative intensity of the bands. Similar remarks apply to (4-hydroxy-3 : 5-dimethoxyphenyl)diphenylmethanol. With diphenyl-(3 : 4 : 5-trihydroxyphenyl)-methanol, however, the diffraction pattern of the red product is different from those of the yellow and brown products, which are practically identical.

(b) *Single-crystal method.* Single crystals of the colourless and coloured products were examined by means of the Unicam single crystal goniometer (Stubbins), with Cu-K_α radiation for 1 hr. The unit cells were identical: $a = 8{\cdot}6$, $b = 10{\cdot}6$, $c = 15{\cdot}4$ Å, $\beta = 100°$.

Thermal Analysis of Mixtures.—A preliminary study was made with mixtures of triphenylmethanol and diphenylquinomethane. In the first method, weighed amounts of the two components were intimately mixed by fusion before thermal analysis, but in the second method the mixtures were prepared by mechanical grinding. The thaw points and melt points of mixtures prepared by the two methods are in Table 2. The data obtained by method 1 show that the components form a 1 : 1 compound with congruent m. p. 126°, and that the two eutectic mixtures containing 30·5% and 60·5% of the fuchsone melt at 120° and 115°, respectively. Although the thaw points and melt points of mixtures prepared by method 2 may differ by several degrees from those found for mixtures prepared by method 1, the data indicate the main features of the solid–liquid equilibria.

TABLE 2. *Triphenylmethanol and diphenylquinomethane.*

Method 1

Diphenylquinomethane (molar %)	0	9·6	23·7	38·4	40·0	50·0	53·3	57·5	62·5	75·9	78·4	100
Thaw point	162°	120°	120°	120°	120°	126°	115°	115°	116°	115°	115°	168°
Melt point	162°	151°	130°	123°	123°	126°	125°	121°	122°	149°	152°	168°

Method 2

Diphenylquinomethane (molar %)	0	10·0	25·0	35·0	50·0	55·0	70·0	90·0	100
Thaw point	162°	121°	121°	121°	124°	116°	116°	116°	168°
Melt point	162°	144°	126°	122°	125°	125°	144°	158°	168°

The system (*p*-hydroxyphenyl)diphenylmethanol and diphenylquinomethane can be investigated by method 2 only as the alcohol decomposes in the solid state to form the fuchsone and water. The temperatures corresponding to thaw points and melt points accordingly depend on the rate of heating, and in the present experiments the tubes containing the mixture were rapidly heated by immersion in a bath at 120°, and the temperature then raised at a rate of 0·3° per min. Table 3 shows that the two components form a 1 : 1 compound (m. p. 146°) and that the two eutectic mixtures containing 27·5% and 65·0% of diphenylquinomethane melt at 137° and 138°, respectively. The compound had been prepared previously by maintaining (*p*-hydroxyphenyl)diphenylmethanol at 90°, and its m. p. is reported to be 150° by Baeyer and Villiger [5] and 144° by Ramart-Lucas and Martynoff.[3] Owing to thermal instability of the alcohol the present method could not be applied to determine the limits of solid solubility in the system. It is possible, however, that a solid solution of diphenylquinomethane in the alcohol is produced when a solution of the components in ethanol at ordinary temperatures is treated with water.

TABLE 3. (p-*Hydroxyphenyl*)*diphenylmethanol and diphenylquinomethane.*

Diphenylquinomethane (molar %)	0	5·0	10·0	25·0	30·0	40·0	50·0	60·0	75·0	90·0	100
Thaw point	161°	137°	137°	138°	136°	137°	138°	138°	139°	138°	168°
Melt point	161°	154°	148°	142°	139°	145°	146°	142°	145°	160°	168°

Rate of Elimination of Water.—The rate of elimination of water in boiling organic liquids was measured in an entrainment-distillation apparatus. (*p*-Hydroxyphenyl)diphenylmethanol and the coloured product are completely soluble in boiling *iso*propyl ether (b. p. 69°), and the two solutions lost water at practically the same rate. On the other hand, the colourless alcohol and the coloured product are insoluble in *n*-hexane, and with this liquid the rate of elimination of water from the coloured product was almost double that from the colourless one, in harmony with Gomberg's observations [1] of a similar difference in the decomposition rates at 90°.

Action of Sodium.—Solutions of (*p*-hydroxyphenyl)diphenylmethanol and the coloured product in boiling xylene were treated with metallic sodium, and the volume of hydrogen evolved was measured at intervals. The gas was evolved at practically the same rate from the two systems and the total volume corresponded to the formation of the disodium derivative. During the experiments there was partial decomposition of the alcohol into water and diphenylquinomethane, and the solution became coloured owing to interaction of the latter with the metal. The insoluble disodium derivative obtained as a white powder after washing of the precipitated mass with anhydrous xylene was difficult to free from the adherent liquid (Found: Na, 12·8, 13·5. Calc. for $C_{19}H_{14}O_2Na_2$: Na, 14·4%).

Absorption Spectra of Carbonium Ions.—The alcohols were recrystallized at least three times and kept in a desiccator with soda-lime and paraffin wax for 48 hr. before use. The compounds were dissolved in 98% sulphuric acid ("AnalaR") so that the concentration of the solution was 10^{-5} mole/l. In order to ascertain whether the compounds are sulphonated under these conditions, the absorption spectrum was determined within 15 min., and again after 24 hr. in the dark. The main features of the absorption spectra are summarized in Table 4 together with the basicity values determined by the modified Baeyer method (Part XV). It is evident that *p*-substitution of hydroxyl in triphenylmethyl leads to a bathochromic shift in the absorption of the ion, and contributes strongly to the stability of the sulphate twards hydrolysis.

TABLE 4. *Absorption characteristics of sulphuric acid solutions.*

Substance	$\varepsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$ (mμ)	Basicity
Diphenylquinomethane	4·20	401, 464	—
(2 : 4-Dihydroxyphenyl)phenylquinomethane	—	370, 477	—
Triphenylmethanol	3·84	408, 431	1·0
(4-Hydroxy-2-methylphenyl)diphenylmethanol	3·43	432, 473	—
(3 : 5-Dihydroxy-4-methoxyphenyl)diphenylmethanol	3·11	405, 489	21·2
(4-Hydroxy-3 : 5-dimethoxyphenyl)diphenylmethanol	3·24	400, 505	4·5
(*p*-Hydroxyphenyl)diphenylmethanol: colourless	4·30	401, 464	30·4
yellow	4·25	401, 464	30·7
(3 : 4 : 5-Trihydroxyphenyl)diphenylmethanol: red	3·26	398, 498	16·3
yellow	3·64	398, 498	—
brown	3·04	398, 498	—

Reduction in Formic Acid.—The reduction of (*p*-hydroxyphenyl)diphenylmethanol and diphenylquinomethane in formic acid was examined by measuring the rate of evolution of gas.[9]

[9] Part VIII, *J.*, 1940, 874.

The results in Table 5 refer to the reduction of 0·001 mole of the compound in 98% formic acid (10 ml.) at 76·5°. When carbon dioxide was no longer evolved from the solution of (*p*-hydroxyphenyl)diphenylmethanol, the system was cooled and treated with water. The deposited methane was recrystallized from alcohol, and did not depress the m. p. of a specimen prepared by means of zinc and acetic acid.

TABLE 5. *Reduction in formic acid.*

Triphenylmethanol									
Time (min.).........	3	8	13	18	23	33	43	53	73
CO_2 (%)	6·2	29·1	43·7	50·7	54·3	58·2	60·9	62·6	64·7
(*p*-Hydroxyphenyl)diphenylmethanol									
Colourless product									
Time (min.).........	5	10	20	25	30	40	60	80	110
CO_2 (%)	3·2	8·3	18·9	24·0	29·0	38·6	51·7	61·6	68·1
Coloured product									
Time (min.).........	5	10	15	20	30	40	60	80	110
CO_2 (%)	2·8	7·5	12·9	18·9	28·7	37·6	51·1	61·1	68·5
Diphenylquinomethane									
Time (min.).........	10	15	20	25	30	40	60	80	100
CO_2 (%)	4·7	10·5	15·9	21·9	27·9	36·1	51·0	59·8	65·6

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