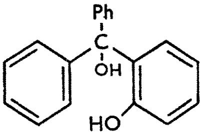
853. *Free Radicals and Radical Stability. Part XV.* The Properties of* (o-*Hydroxyphenyl*)*diphenylmethanol and* (3-*Hydroxy*-2-*naphthyl*)*diphenylmethanol.*

By S. T. Bowden and K. I. Beynon.

The colour developed on heating solutions of (*o*-hydroxyphenyl)- and (3-hydroxy-2-naphthyl)-diphenylmethanol is not due to the formation of the carbonium ion. The phenomenon, previously ascribed to the formation of the *o*-quinonoid isomer, is considered to be due to thermochromism. Decomposition of the alcohols at elevated temperatures is explained in terms of a free-radical mechanism which does not involve formation of quinonoid intermediates.

The hydroxyl substituent in the carbonium ion produces a bathochromic shift in the absorption spectrum, and promotes sulphonation in sulphuric acid. In the reduction of (*o*-hydroxyphenyl)diphenylmethanol in formic acid solution the total amount of carbon dioxide evolved is practically the same as with triphenylmethanol.

Solutions of (*o*-hydroxyphenyl)diphenylmethanol (I) in acetic acid become increasingly brown when heated from about 50° to 110°, and the changes are reversed on cooling; above 110°, however, the alcohol decomposes with elimination of water. Gomberg and Nishida [1] suggested that the development of colour is due to the quinonoid isomer (II), and that elimination of water above 110° leads to the formation of the fuchsone (III) which undergoes immediate conversion into the colourless xanthan (IV). Even if we assume that intramolecular hydrogen bonding [2] stabilizes the quinonoid isomer (II), it is not possible to account for the observed phenomena on this basis. Our preliminary studies of the absorption spectra of hot solutions of the alcohol in acetic acid show that the colour is not due to the carbonium ion and that the phenomenon is a type of thermochromism arising from the broadening of a near-ultraviolet absorption band.[3] The fact that no colour is developed on heating aniline, pyridine, or quinoline solutions is doubtless due to the formation of solvent complexes which do not exhibit thermochromism.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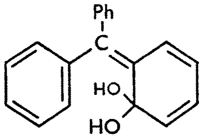
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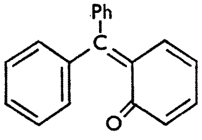
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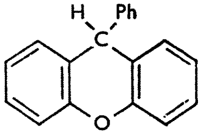
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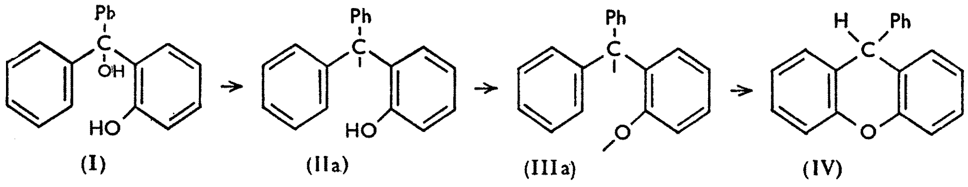

If we accept the above hypothesis, the conversion of the alcohol into the xanthan at >110° must proceed by a mechanism which does not involve the decomposition of a quinonoid isomer. There are many indications of the thermal instability of triarylmethane derivatives: *e.g.*, triphenylmethyl iodide is *ca.* 20% dissociated in 5% benzene

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* Part XIV, preceding paper.

[1] Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1923, **45**, 190.

[2] Davies, *Trans. Faraday Soc.*, 1940, **63**, 333, 1114; Bergmann, " Isomerism and Isomerisation," Interscience Publ. Inc., New York, 1948, p. 18; Albrecht and Corey, *J. Amer. Chem. Soc.*, 1939, **61**, 1087.

[3] Grubbe and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419; Hirshberg and Fischer, *J.*, 1953, 629.

solution at room temperature.[4] Although triphenylmethanol is much more stable, its solution in diphenyl becomes yellow at 240° and the colour persists on cooling to the f. p. It appears, therefore, that the C–OH bond in triphenylmethanol is weaker than has been formerly supposed and that it undergoes homolytic fission at high temperatures to form triphenylmethyl and hydroxyl radicals. If the corresponding weakening of the link in (*o*-hydroxyphenyl)diphenylmethanol is such that homolytic fission sets in at 110°, formation of the xanthan may be explained according to the annexed scheme. Above 110° the hydroxyl group attached to the methane-carbon atom is released as the neutral radical while the residual triarylmethyl (IIa) undergoes redistribution of electron density and approaches the planar configuration. The electronic reorganization leads to a change in the polarity of the O–H link of the ring substituent so that it becomes susceptible to attack by the free hydroxyl with formation of water and the diradical (IIIa). Rearrangement of the latter involves the migration of a hydrogen atom from the *ortho*-position of one of the unsubstituted rings to the methyl-carbon atom to form the xanthan.

The above hypothesis may also be applied to account for the development of colour in acetic acid solutions of (3-hydroxy-2-naphthyl)diphenylmethanol at 80°. In this system, however, the change is not completely reversible, owing to the proximity of the temperature at which colour is developed to that at which decomposition of the alcohol sets in. The latter process involves formation of the corresponding diradical which is converted into the xanthan and coloured products.

The alcohols give rise to carbonium ions in sulphuric acid, and the presence of the *o*-hydroxyl group in the triphenylmethyl and 2-naphthyldiphenylmethyl ions leads to a bathochromic shift in the absorption spectrum. The ions are sulphonated in the 98% acid, and the rates of sulphonation are in the sequence: (*o*-hydroxyphenyl)diphenylmethyl > (3-hydroxy-2-naphthyl)diphenylmethyl > (3-methoxy-2-naphthyl)diphenylmethyl. On the other hand, the presence of the hydroxyl substituent increases the resistance of the triarylmethyl sulphate towards hydrolysis.

In hot formic acid solution the (*o*-hydroxyphenyl)diphenylmethyl cation is reduced to the methane, but, in contrast to the behaviour of the corresponding methoxyl derivative,[5] the favourable influence of the substituent is apparent only in the early stages of the reaction, and the total amount of carbon dioxide evolved is substantially the same as in the reduction of the triphenylmethyl ion.

EXPERIMENTAL

Preparation of Materials.—(*o*-Hydroxyphenyl)diphenylmethanol was prepared by hydrolyzing the product of interaction of phenylmagnesium bromide and methyl salicylate.[6] (3-Hydroxy-2-naphthyl)diphenylmethanol was obtained similarly from methyl 3-hydroxy-2-naphthoate,[7] and was converted into (3-methoxy-2-naphthyl)diphenylmethanol by means of dimethyl sulphate.[8] The alcohols and the solvents employed in the colorimetric experiments were rigorously purified by standard methods.

Action of Heat on Alcohol Solutions.—A solution of the dry alcohol was prepared in a stoppered test-tube provided with a thermometer, stirrer, and calcium chloride guard-tube. The vessel was heated in a bath of glycerol in order to determine the temperature at which the solution became coloured. The temperature at which the colour disappeared on cooling was also noted. The system was then heated to a selected temperature, and the colour of the solution was measured in Lovibond units by means of a tintometer. In Table 1 t represents in the temperature (°c) at which colour appears on heating, t' that at which the colour disappears on cooling the solution, and t'' that at which the colour measurements were made. It is evident that t depends on the nature of the solvent and that t' is generally about 5° lower than t. The solutions of (3-hydroxy-2-naphthyl)diphenylmethanol lost much of their colour on cooling,

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[4] Gomberg, *J. Amer. Chem. Soc.*, 1902, **24**, 597.

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

[6] Baeyer, *Annalen*, 1907, **354**, 167.

[7] Kauffman and Egner, *Ber.*, 1913, **46**, 3782.

[8] Gomberg and McGill, *J. Amer. Chem. Soc.*, 1925, **47**, 2392.

but were not completely decolorized on attaining room temperature. Solutions of either alcohol in aniline, pyridine, or quinoline did not change colour at 120°.

The absorption spectrum of (*o*-hydroxyphenyl)diphenylmethanol in acetic acid at 57° was determined by means of a Unicam S.P. 500 spectrophotometer provided with a water-jacketed cell-holder. The absorption curve shows no maximum in the visible region, and thus differs entirely from that of the solution containing sulphuric acid which has two characteristic peaks. The colour of the former solution, therefore, is not due to the carbonium ion.

TABLE 1. *Colour of alcohol solutions.*

	(*o*-Hydroxyphenyl)diphenylmethanol (5%)					(3-Hydroxy-2-naphthyl)-diphenylmethanol (2·5%)			
				Lovibond units				Lovibond units	
Solvent	*t*	*t′*	*t″*	red	yellow	*t*	*t″*	red	yellow
Acetic acid	55	50	100	8·9	9·0	80	100	0	3·3
Me benzoate	110	100	120	0·1	0·1	150	150	3·0	7·0
n-Pentyl ether	85	80	85	1·0	2·0	—	—	—	—
Benzophenone	90	85	95	2·3	5·0	90	130	0	1·3
Benzene	55	55	80	3·0	4·5	70	80	0	0·4
o-Xylene	—	—	—	—	—	120	135	0	0·6
Diphenyl	64	—	100	13·5	9·0	85	100	0	1·1
Naphthalene	60	50	100	15·0	9·9	100	115	0·5	3·0

Action of Sodium on (o-*Hydroxyphenyl*)*diphenylmethanol*.—A solution of the alcohol (0·276 g.) in boiling xylene (75 ml.) was treated with metallic sodium (0·50 g.) in a vessel attached to a gas-burette for measuring the volume of hydrogen evolved. The gas evolved in 40 min. corresponded to the replacement of the hydrogen atoms of both hydroxyl groups. The suspension of the ***disodium derivative*** was removed from unchanged metal and kept in a dry atmosphere. The deposited crystals were filtered off, washed with xylene and light petroleum, and dried over silica gel and paraffin wax in a vacuum-desiccator (Found: Na, 13·7. $C_{19}H_{14}O_2Na_2$ requires Na, 14·4%).

Absorption Spectra of Carbonium Ions.—The absorption spectra of sulphuric acid solutions of the alcohols were determined at room temperature, and the main features are indicated in Table 2. The absorption curve of (*o*-hydroxyphenyl)diphenylmethanol in acetic acid containing 1% sulphuric acid differed from that of the compound in 98% sulphuric acid, and in the latter solution sulphonation was complete before measurements could be undertaken. The stabilities of the ions in 80% sulphuric acid were found to conform to the sequence: (3-methoxy-2-naphthyl)diphenylmethyl > (3-hydroxy-2-naphthyl)diphenylmethyl > (*o*-hydroxyphenyl)diphenylmethyl.

TABLE 2. *Absorption spectra of carbonium ions.*

Carbonium ion	Concn. of acid (%)	$\lambda_{max.}$ (mμ)	$10^{-4} \times \varepsilon_{max.}$	Remarks
(*o*-Hydroxyphenyl)diphenyl-	98	370, 440	3·20	No change in 24 hr.
(3-Hydroxy-2-naphthyl)diphenyl	98	440, 480	4·63	Rapid change
	80	426, 490	—	No change in 24 hr.
(3-Methoxy-2-naphthyl)diphenyl	98	432, 473	4·81	Slight change in 1 week

Basicity of Alcohols.—The basicity of the hypothetical base as measured by the stability of the triarylmethyl sulphate towards hydrolysis was determined by a modification of the method of Baeyer and Villiger[9] of two solutions of the alcohol (0·0003 mole) in acetic acid (5·0 ml.); one served as a control while the other was treated with a 10% solution of sulphuric acid in acetic acid (5 ml.) to convert the alcohol into the coloured sulphate. The latter was titrated with a 75% aqueous solution of ethyl alcohol, and the colour change was followed by means of a photoelectric colorimeter, whose scale had been previously adjusted to zero by means of the control solution. Addition of the aqueous solution was continued until the optical density of the carbinol solution attained a constant value which was generally zero. The basicity of triphenylmethanol being taken as unity, the results were: (*o*-hydroxyphenyl)-, 2·4; (3-hydroxy-2-naphthyl)-, 3·9; (3-methoxy-2-naphthyl)-, 1·3.

[9] Baeyer and Villiger, *Ber.*, 1902, **35**, 489.

Reduction of Alcohols in Formic Acid.—The rate of evolution of carbon dioxide from a solution of the alcohol (0·001 mole) in 98% formic acid (10 ml.) at 76·5° was measured in the apparatus previously described.[8] The behaviour of triphenylmethanol was examined under similar conditions with the tabulated results.

Triphenylmethanol.

Time (min.)	3	8	13	18	23	33	43	53	73
CO_2 (%)	6·15	29·1	43·7	50·7	54·3	58·2	60·9	62·6	64·7

(o-*Hydroxyphenyl*)*diphenylmethanol.*

Time (min.)	5	10	15	20	25	30	40	50	70
CO_2 (%)	22·1	39·9	45·4	48·7	52·2	54·4	58·2	60·0	61·8

The favourable influence of the hydroxyl group is evident in the early stages of the reaction but this effect is not sustained as in the case of the methoxyl group in the *o*-position.[5] The solution of the (*o*-hydroxyphenyl)diphenylmethyl derivative deposited the methane, m. p. and mixed m. p. 124° (from alcohol), on treatment with water.

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[10] Baeyer, *Annalen*, 1907, **354**, 178.