855. *Free Radicals and Radical Stability. Part XVII.** (m-*Hydroxyphenyl*)*diphenylmethanol and the Corresponding Free Radical.*

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(*m*-Hydroxyphenyl)diphenylmethanol does not exhibit thermochromism or form a fuchsone. The carbonium ion is less readily sulphonated than the *ortho*-substituted ion.

(*m*-Hydroxyphenyl)diphenylmethyl chloride, which is stable at room temperature, is reduced by silver to the bright yellow free radical, and the corresponding ethane is the first derivative of this type to be isolated in the solid state.

Although the presence of the hydroxyl group in the radical may lead to the formation of hydrogen-bonded complexes, the observed unimolecular stability is greater than that of (*m*-methoxyphenyl)diphenylmethyl owing to the stronger inductive effect of the substituent.

(*m*-HYDROXYPHENYL)DIPHENYLMETHANOL, which is obtained colourless by recrystallization from alcohol or aqueous acetic acid, is thermally much more stable than the corresponding *ortho*- and *para*-substituted compounds (Parts XV, XVI), and its solutions may be heated to 150° without the development of colour.

The influence of the hydroxyl and methoxyl substituents on the basicity of the alcohol is shown in the annexed Table, where the values are referred to triphenylmethanol as unity. Hydroxyl raises the basicity more than does the methoxyl group,[1] and the effect is most marked with *para*-substitution. The (hydroxyphenyl)diphenylmethanols with excess of metallic sodium in xylene form the disodium derivative $(NaO{\cdot}C_6H_4)CPh_2{\cdot}ONa$,

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* Parts XIII—XVI, preceding papers.

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

and the overall reactivity, measured by the rate of evolution of hydrogen, is in the order: $p > m \gg o$.

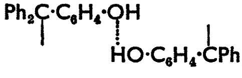
Basicity and halochromism.

Diphenylmethanol	Basicity	Sulphate	Diphenylmethanol	Basicity	Sulphate
(*o*-Hydroxyphenyl)-	2·4	Yellow	(*o*-Methoxyphenyl)-	2·0	Red
(*m*-Hydroxyphenyl)- ...	2·5	Red	(*m*-Methoxyphenyl)-	1·2	Orange-red
(*p*-Hydroxyphenyl)-	30·4	Orange	(*p*-Methoxyphenyl)-	5·6	Red

Formic acid solutions of the (hydroxyphenyl)diphenylmethanols decompose when heated, with evolution of carbon dioxide and formation of the corresponding methane.[2] The relative rates of reduction at 77° conform to the sequence: unsubstituted $\gtrsim o > p > m$. In the early stages of the reaction the *m*-hydroxyl substituent exerts a more favourable influence on the rate of reduction than the *p*-hydroxyl group, but this influence is soon outweighed by an inhibiting effect which leads to a low yield of the triarylmethane. This appears to be a general feature of the behaviour of *m*-substituted triarylmethyl cations, and it is also observed when the substituent is methoxyl or methyl.[1]

(*p*-Hydroxyphenyl)diphenylmethyl chloride cannot be obtained pure because it forms the fuchsone spontaneously, with elimination of hydrogen chloride, and the *ortho*-substituted compound, although obtainable pure, rapidly becomes brown as a result of similar changes.[3] On the other hand, the beautifully crystalline (*m*-hydroxyphenyl)diphenylmethyl chloride is considerably more stable and remains colourless for several weeks in a dry atmosphere. It has the characteristic properties of a triarylmethyl halide, and forms highly coloured addition complexes with ferric chloride and zinc chloride.

Gomberg and Nishida,[3] and Gomberg and Jickling,[4] could not prepare stable solutions of the free radicals (*o*-hydroxyphenyl)diphenylmethyl and (*p*-hydroxyphenyl)diphenylmethyl, but we experienced no difficulty in preparing pure (*m*-hydroxyphenyl)diphenylmethyl by reduction of the chloride in benzene solution with molecular silver. At room temperature in the absence of sunlight the free radical shows little tendency to disproportionate or isomerize, and can be examined by the customary methods. Apart from exhibiting the normal equilibrium between the hexa-arylethane and the free radical, this system presents the unusual feature that the presence of hydroxyl substituents may lead to hydrogen bonding and the formation of complexes such as (I). If this complex functions as an independent entity in solution, its differentiation from the true ethane (II) is not possible by cryoscopy. On the other hand, hydrogen bonding between two or more molecules of the ethane (II) would increase the observed molecular weight. In view of the size of the aromatic groups, however, the concentration of such complexes is probably low and for our present purposes we assume that the observed molecular weight refers solely to the equilibrium between the ethane (II) and the free radical. The radical stability computed on this basis for the system in freezing 2% benzene solution is about 33%, which is roughly twice that found for (*m*-methoxyphenyl)diphenylmethyl (Part XIII). The strong inductive effect of the hydroxyl group stabilises the electron septet in this radical, and doubtless contributes also to the high stability of (3-hydroxy-2-naphthyl)diphenylmethyl.[5]



$$\begin{array}{lll} Ph_2C\cdot C_6H_4\cdot OH & & \\ \quad | \qquad\quad \vdots & & | \\ & HO\cdot C_6H_4\cdot & CPh_2 \end{array}$$

(I)

$HO\cdot C_6H_4\cdot CPh_2\cdot CPh_2\cdot C_6H_4\cdot OH$

(II)

The free radical (*m*-hydroxyphenyl)diphenylmethyl is bright yellow in solution, and there is little loss of colour in the dark in 3 days. In sunlight, however, the solution is rapidly decolorized owing to photodecomposition of the type previously observed with

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[2] Kauffmann and Panwitz, *Ber.*, 1912, **45**, 766.

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

[4] Gomberg and Jickling, *ibid.*, 1915, **35**, 2575.

[5] Gomberg and McGill, *ibid.*, 1925, **47**, 2392.

triphenylmethyl.[6] The radical rapidly absorbs oxygen, and a crystalline peroxide has been isolated.

Although Gomberg and McGill [5] failed to isolate the ethane corresponding to (3-hydroxy-2-naphthyl)diphenylmethyl, we obtained di-*m*-hydroxyphenyltetraphenylethane as pale yellow crystals.

EXPERIMENTAL

(m-*Hydroxyphenyl*)*diphenylmethanol*.—The compound was prepared from phenylmagnesium bromide and methyl *m*-hydroxybenzoate.[7] On treatment of the benzene solution with light petroleum, the alcohol was deposited as colourless crystals, m. p. 148°. In contrast to the behaviour of (*o*-hydroxyphenyl)diphenylmethanol (Part XV), solutions in toluene, diphenyl, naphthalene, or acetic acid do not become coloured at 120°. Unlike (*p*-hydroxyphenyl)diphenylmethanol (Part XVI) the compound is colourless on recrystallization from 50% acetic acid. The basicity (Part XV) of (*m*-hydroxyphenyl)diphenylmethanol is 2·5.

(m-*Hydroxyphenyl*)*diphenylmethyl Chloride*.—(*a*) A few lumps of calcium chloride were added to a solution of the alcohol (2 g.) in ether (20 ml.) and the mixture was saturated at 0° with hydrogen chloride. After 24 hr. the solution was siphoned off and concentrated to half-bulk (guard-tube). The deposited (m-*hydroxyphenyl*)*diphenylmethyl chloride* (30%) was recrystallized from light petroleum in a dry atmosphere, and had m. p. 95—96° (Found: Cl, 12·2. $C_{19}H_{15}OCl$ requires Cl, 12·1%).

(*b*) A solution of the alcohol (2 g.) in acetyl chloride (6 ml.) was heated under reflux in a dry atmosphere for 30 min. (*m*-Hydroxyphenyl)diphenylmethyl chloride (70%) was deposited on allowing the solution to stand in a desiccator.

(m-*Hydroxyphenyl*)*diphenylmethyl Peroxide*.—A saturated solution (4 ml.) of (*m*-hydroxyphenyl)diphenylmethyl chloride was shaken for 20 min. with molecular silver (2 g.) in the absence of oxygen and light. The solution was decanted from silver and silver chloride and allowed to evaporate in the air. The yellow residue was triturated with light petroleum, and the solid was washed with acetone to remove coloured products. The colourless peroxide, m. p. 159°, on analysis gave a low value for C, but could not be purified further by crystallization.

Absorption Spectrum of the Alcohol in Sulphuric Acid.—Absorption spectra were determined by means of a Unicam S.P. 500 spectrophotometer. A $1\cdot46 \times 10^{-5}$M-solution in 98% sulphuric acid had $\lambda_{max.}$ 405 and 435 mμ (ε 40,300); the spectrum changes with time. In 10 days the peak at 405 mμ degenerates to a shoulder; the peak at 435 mμ is displaced to 442 mμ and there is a 13% decrease in $\varepsilon_{max.}$. A $1\cdot05 \times 10^{-5}$M-solution in 80% sulphuric acid had $\lambda_{max.}$ 420 mμ (ε 42,200) and was unchanged for 24 hr.

Thermal Stability of Formic Acid Solutions.—Reduction of the alcohol (0·001 mole) in 98% formic acid (10 ml.) was examined at 76·5° by measuring the rate of evolution of carbon dioxide from the solution: [1]

Triphenylmethanol

Time (min.)	3	8	13	18	23	33	43	63	73
CO_2 (%)	6·15	29·1	43·7	50·7	54·3	58·2	60·9	63·9	64·7

(*m*-Hydroxyphenyl)diphenylmethanol

Time (min.)	5	10	15	20	30	40	50	60	70
CO_2 (%)	8·70	18·5	21·6	25·1	32·0	36·5	38·4	39·8	41·3

The solution was then cooled and treated with water to precipitate (*m*-hydroxyphenyl)-diphenylmethane. Recrystallized from alcohol, the colourless crystals had m. p. and mixed m. p. 105°.

Action of Sodium on the Alcohol.—(*m*-Hydroxyphenyl)diphenylmethanol (0·276 g.) was dissolved in boiling xylene (75 ml.) in the presence of sodium (0·05 g.). The volume of hydrogen evolved (21·2 ml. at N.T.P.) corresponds to the formation of the disodium derivative. The solution remained colourless throughout, and the disodium derivative was deposited on cooling (Found: Na, 13·5.—Calc. for $C_{19}H_{14}O_2Na_2$: Na, 14·4%).

Rate of Reduction [8] *of* (m-*Hydroxyphenyl*)*diphenylmethyl Chloride*.—A solution of the chloride

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[6] Bowden and Jones, *J.*, 1928, 1149.
[7] Baeyer, *Annalen*, 1907, **354**, 167.
[8] Part XII, *J.*, 1940, 1249.

(0·501 g.) in freshly dried bromobenzene (10 ml.) was agitated with molecular silver (1 g.) at 18·5°, and the oxygen absorbed was measured at intervals:

Time (min.)	2	6	10	15	20	30
O_2 absorbed (% at N.T.P.)	43·6	79·1	85·5	89·0	93·0	96·0

Stability of Radical Solutions.—Freshly recrystallized (*m*-hydroxyphenyl)diphenylmethyl chloride (0·05 g.), molecular silver (0·4 g.), and benzene were introduced into a constricted test-tube from which the air had been displaced by dry nitrogen. The tube was sealed, covered with black paper, and shaken for 30 min. to reduce the chloride to the free radical. Two such solutions were prepared, and the optical densities were measured by means of a photoelectric colorimeter with an Ilford OB2 filter. One solution was stored in the dark, while the other was exposed to diffused sunlight. The optical densities (*D*) of the two solutions after various periods are annexed. Benzene solutions of pure (*m*-hydroxyphenyl)diphenylmethyl are thus fairly stable at room temperature in the dark.

Time (hr.)	0	0·5	3	20	24	44	48	72
Temperature (°)	19·5	19·8	19·8	18·0	18·2	19·8	18·8	18·0°
D, dark	32·2	32·4	32·3	31·0	31·0	32·1	13·8	31·1
D, sunlight	38·0	35·0	33·2	32·0	28·0	19·0	14·4	14·7

Dissociation of Di-(m-*hydroxyphenyl*)*tetraphenylethane.*—The degree of dissociation of di-(*m*-hydroxyphenyl)tetraphenylethane in benzene was determined by the indirect cryoscopic method. The chloride was freshly prepared, and both the solvent and the molecular silver were rigorously dried before use. In view of the photosensitivity of the radical, precautions were taken to prevent undue exposure of the solution to light during the measurements. Summarized results are tabulated. After each set of determinations, the solution retained the characteristic colour of the free radical, and gave a normal yield of peroxide on exposure to air.

Degree of dissociation of di-(m-*hydroxyphenyl*)*tetraphenylethane.*

M of radical = 259·3. *M* of the ethane = 518·6.
Cryoscopic const. of benzene = 52·5.
Wt. of solvent = 20·35 g. Wt. of silver = 5·0 g.

Chloride (g.)	Ethane (g.)	Concn. (%)	Δ	*M*	Dissn. (%)	Chloride (g.)	Ethane (g.)	Concn. (%)	Δ	*M*	Dissn. (%)
0·5162	0·4540	2·18	0·303°	386·7	34·1	0·5090	0·4477	2·15	0·302°	382·4	35·6
0·5034	0·4428	2·13	0·292	391·2	32·6	0·6915	0·6082	2·91	0·402	390·3	32·9
0·9388	0·8258	3·90	0·552	386·0	34·4	0·9935	0·8738	4·11	0·567	397·6	30·4

Isolation of Di-(m-*hydroxyphenyl*)*tetraphenylethane.*—(*m*-Hydroxyphenyl)diphenylmethyl chloride (3 g.) in benzene (50 ml.) was shaken with molecular silver (8 g.) for 2 hr. in a Schlenk tube covered with black paper. The solution was filtered into the isolation unit (Part XIV) and evaporated *in vacuo* in a slow stream of carbon dioxide at ≯40°. The residual oil solidified on repeated trituration with light petroleum. The solid was dissolved in the minimum amount of acetone and was cooled with ice until crystallization was complete. The mother-liquor was decanted, and the pale yellow crystals washed with the cold solvent and dried *in situ* in a stream of carbon dioxide. The ethane had m. p. 112—115° (decomp.: vac.).

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