856. *Free Radicals and Radical Stability. Part XVIII.** *(Halogenophenyl)diphenylmethyls and the Removal of Nuclear Halogen by Silver.*

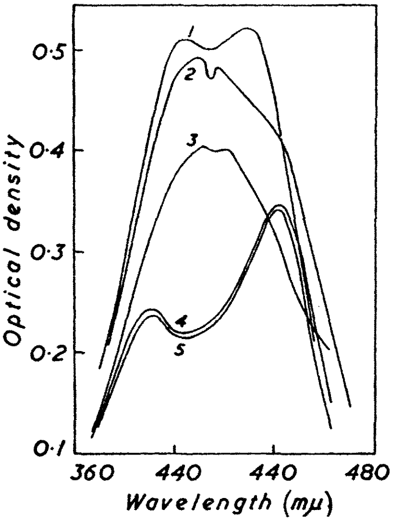
By K. I. Beynon and S. T. Bowden.

In contrast to *para*-substitution, *meta*-substitution by halogen in the triphenylmethyl cation leads to a slight hypsochromic shift in the absorption spectrum.

(*m*-Halogenophenyl)diphenylmethyl chlorides do not form fuchsones, and are reduced to primary radicals which may be isolated in the solid state as the ethanes. The large difference between the values of the unimolecular stability determined by the cryoscopic and the magnetic-susceptibility method is ascribed to incorrect estimation of the diamagnetic contribution in triarylmethyl systems.

Silver removes half of the halogen from (*p*-bromophenyl)diphenylmethyl, but has no action on a radical with *meta*-halogen. This behaviour is interpreted without assuming the existence of a *para*-quinonoid form of the radical.

To ascertain the effects of halogen substituents on the optical properties of the triphenylmethyl cation we have examined the absorption spectra of solutions of the carbinols in sulphuric acid (see Figure). The absorption curves of the *m*-chloro- and *m*-iodo-substituted ions have a peak and a shoulder[1] whereas those of the corresponding fluoro- and bromo-derivatives have two maxima as indicated in Table 1. The slight hypsochromic shift in the spectrum appears to be a characteristic feature of *meta*-substitution, and is in marked contrast to the bathochromic effect accompanying *para*-substitution. The



Absorption spectra in 98% H_2SO_4: (1) *Triphenylmethanol*; (2) (m-*fluorophenyl*)-, (3) (m-*bromophenyl*)-, (4) (3 : 5-*dibromo-2-methoxyphenyl*)-, *and* (5) (5-*bromo-2-methoxyphenyl*)-*diphenylmethanol.*

Table 1.

R in ion CPh_2R	$\lambda_{max.}$ (mμ)	$10^4\varepsilon_{max.}$	R in ion CPh_2R	$\lambda_{max.}$ (mμ)	$10^4\varepsilon_{max.}$
Ph	408, 431	3·8	*m*-C_6H_4I	422	4·1
m-C_6H_4F	410, 418	3·4	2 : 5 : 1-MeO·C_6H_3Br	392, 442, 552	3·0
m-C_6H_4Cl	416	4·0	2 : 3 : 5 : 1-MeO·$C_6H_2Br_2$	392, 442, 555	3·8
m-C_6H_4Br	411, 422	3·4			

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* Part XVII, preceding paper.

[1] Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 470.

substitution of methoxyl in the *ortho*-position of the *meta*-halogenated rings leads to a bathochromic shift and separation of the absorption bands.[2]

The influence of halogen substituents on the basicity of the alcohols and the halochromic properties of the salts is indicated in Table 2. It is evident that *meta*-substitution

TABLE 2.

R in CPh_2R	Basicity	Sulphate	R in CPh_2R	Basicity	Sulphate
Ph	1·0	Yellow	*m*-C_6H_4Br	1·3	Yellow
m-C_6H_4F	1·2	Yellow	*p*-C_6H_4Br	—	Yellowish-red
p-C_6H_4F	1·9	Reddish-yellow	2 : 5 : 1-MeO·C_6H_3Br	1·3	Green
o-C_6H_4Cl	1·2	Yellow	2 : 3 : 5 : 1-MeO·$C_6H_2Br_2$	1·3	Green
p-C_6H_4Cl	1·8	Orange-yellow			

leads to a slight increase in the basicity and that *p*-fluorine is the most effective halogen substituent. The fact that the introduction of methoxyl into a (bromophenyl)diphenylmethanol produces little change in the basicity furnishes a further example of the clashing influences which arise when more than one substituent is present. Of the substituents in triphenylmethyl sulphate, hydroxyl is the most effective in reducing hydrolysis. The *p*-methoxyl group enhances the stability, but in the *meta*-position it has practically the same effect as the fluorine and bromine.

Acetyl chloride converts the (*m*-halogenophenyl)diphenylmethanols into stable chlorides which in non-ionizing solvents are rapidly reduced by molecular silver to the primary radicals. Benzene solutions of (*m*-fluorophenyl)- and (*m*-bromophenyl)-diphenylmethyl retain their colour in the dark for 3 days, and the slight loss of colour which occurs in solutions of the (bromomethoxyphenyl)diphenylmethyls indicates that even in these systems disproportionation is slow under these conditions. This is substantiated by the fact that the solutions absorb nearly the theoretical amount of oxygen, and give normal yields of the peroxides. Although di-*m*-bromophenyltetraphenylethane was obtained only as an oil, we isolated solid ethanes from (*m*-fluorophenyl)-, (5-bromo-2-methoxyphenyl)-, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethyl.

There is a considerable difference of opinion regarding the effect of halogen substituents on the unimolecular stability of triphenylmethyl. We found by the cryoscopic method that di-*p*-fluorophenyltetraphenylethane is dissociated to the extent of 20% in 2% benzene solution,[3] but later Marvel, Johnston, Meier, Mastin, Whitson, and Himel[4] on the basis of magnetic-susceptibility measurements reported that the dissociation in a similar solution at 25° is 3·5%. The fluorine atom in this radical, however, is slowly removed by silver, and a more stringent comparison of the two methods is now possible with the (*m*-halogenophenyl)diphenylmethyls which are not attacked by the metal. For the ethanes corresponding to (*m*-fluorophenyl)- and (*m*-bromophenyl)-diphenylmethyl the dissociation values determined by the magnetic-susceptibility method at 25° are 5·8% and 7·0%, whereas the cryoscopic method gives 46% and 43%, respectively. In view of the precautions taken the large discrepancy is probably due to the incorrect evaluation of the diamagnetic contribution in triarylmethyl systems, as has been pointed out by Selwood and Dobres.[5] According to Marvel, Dietz, and Himel[6] substitution of fluorine, chlorine, or bromine in the *meta*- or *para*-positions or of iodine in the *para*-position of one of the rings of triphenylmethyl does not materially alter the radical stability, but such a conclusion is surprising in view of the known effects of halogen substituents in other systems[7] which would be expected to be less sensitive to inductive and mesomeric effects. The present

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[2] Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 159.

[3] Bowden and Watkins, *J.*, 1940, 1249.

[4] Marvel, Johnston, Meier, Mastin, Whitson, and Himel, *J. Amer. Chem. Soc.*, 1944, **66**, 914.

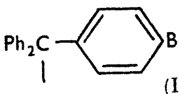
[5] Selwood and Dobres, *ibid.*, 1950, **72**, 3860.

[6] Marvel, Dietz, and Himel, *J. Org. Chem.*, 1942, **7**, 392.

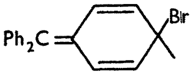
[7] Baddeley and Bennett, *J.*, 1933, 263; Bird and Ingold, *J.*, 1938, 918; Ingold, *Chem. Rev.*, 1934, **15**, 225; Branch, Yabroff, and Bettmann, *J. Amer. Chem. Soc.*, 1934, **56**, 937, 2568; Dippy, *Chem. Rev.*, 1939, **25**, 176.

work, however, indicates that *m*- and *p*-halogen considerably stabilize the unimolecular system, and that similar influences would operate strongly with *ortho*-substituents, whose inhibiting effect on the association to the ethane is ascribed by Marvel *et al.*[6] to steric factors.

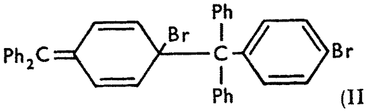
It is now established that nuclear halogen is removed from (halogenophenyl)diphenylmethyl systems by silver. In a further examination of the reaction between (*p*-bromophenyl)diphenylmethyl chloride and the metal, we find that all the chlorine is rapidly lost, and half the total bromine slowly, at room temperature. The theory proposed by Gomberg [8] to account for the latter reaction requires that the halogen is not removed when attached to a benzenoid nucleus but only when the carbon–halogen bond simulates an aliphatic linkage. It is further assumed that the removal of chlorine from (*p*-bromophenyl)diphenylmethyl chloride leads to the benzenoid radical (I) which tautomerizes to



(I)



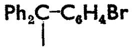
(II)



(III)

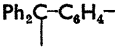
the quinonoid form (II) and that the two modifications combine to produce (III) in which one of the bromine atoms simulates an aliphatically combined halogen, and is thus removable by silver. Implicit in this argument is the supposition that the two structures (I and II) of the primary radical exist as independent entities, but on the basis of the wave-mechanical theory of free radicals [9,10] it is clear that these forms are actually two of the canonical structures which contribute to the existence of (*p*-bromophenyl)diphenylmethyl as a unimolecular entity.

In view of these considerations and the fact that quinonoid forms of the triarylmethyls have never been isolated, we interpret the reaction as follows: Reduction of (*p*-bromophenyl)diphenylmethyl chloride yields the hybrid radical (IV) in which, for simplicity, the uncoupled electron is represented by a localized free bond. The redistribution of charge density is greatest in *para*- and least in *meta*-positions, and is accompanied by concomitant changes in the polarity of the linkages attaching substituents to the phenyl



$\underset{|}{Ph_2C}{-}C_6H_4Br$

(IV)



$\underset{|}{Ph_2C}{-}C_6H_4{-}$

(V)

$Br{\cdot}C_6H_4{\cdot}CPh_2{\cdot}C_6H_4{\cdot}CPh_2{-}$

(VI)

nuclei. Owing to the enhanced reactivity of the *para*-bromine atom the metal is now able to attack the primary radical with formation of the diradical (V). The latter combines with the primary radical to form the secondary radical (VI), and the ensuing change in the polarity of the C–Br linkage now renders the molecule resistant to attack by the metal. If we assume that combination of the primary radical with the diradical is faster than the reaction between the primary radical and silver, it follows that only half the total bromine will be removed from the system, as is found experimentally.

The free radicals (*m*-fluorophenyl)-, (5-bromo-2-methoxyphenyl)-, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethyl are not attacked by silver at room temperature, and bromine is not removed from (*m*-bromophenyl)diphenylmethyl even when the solution is agitated with the metal at 70° for 3 days. The inertness of *m*-halogen towards silver is to be expected inasmuch as the charge redistribution in the radical does not lead to the requisite activation as it does in the *para*-position.

The present hypothesis is thus able to account for the differences in the reactivity of *para*- and *meta*-substituted radicals towards silver, and for the apparently anomalous behaviour of (*p*-fluorophenyl)diphenylmethyl [3] which cannot be interpreted on the basis of the Gomberg theory.

[8] Gomberg, *J. Amer. Chem. Soc.*, 1914, **36**, 1157.
[9] Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421.
[10] Pauling and Wheland, *J. Chem. Phys.*, 1933, **1**, 362; 1934, **2**, 482.

EXPERIMENTAL

(m-*Fluorophenyl*)*diphenylmethanol*.—To *m*-fluorophenylmagnesium bromide prepared from *m*-fluorobromobenzene (23 g.), magnesium (3·5 g.) and ether (50 ml.), a solution of benzophenone (15 g.) in benzene (50 ml.) was added, and the mixture was heated under reflux for 4 hr. The product was hydrolyzed, and volatile material was removed in steam. The solid residue was dissolved in ether, and the solution was warmed with activated charcoal, filtered, and cooled. The deposited methanol (20 g.) was colourless, and had m. p. 118°; Marvel *et al.*[4] give m. p. 117°.

(m-*Fluorophenyl*)*diphenylmethane*.—The alcohol was heated with zinc dust and acetic acid on a steam-bath for 1 hr., and the filtered solution was poured into water to precipitate the methane. Recrystallized from alcohol, it melted at 95° (Found: C, 87·9; H, 5·7. Calc. for $C_{19}H_{15}F$: C, 87·0; H, 5·7%).

(m-*Fluorophenyl*)*diphenylmethyl Chloride*.—The alcohol (5 g.) was warmed with acetyl chloride (10 ml.) for 1 hr. The chloride was slowly deposited from the cold solution, and after recrystallization from light petroleum in a dry atmosphere, the compound melted at 113·5° in agreement with the recorded value.[4]

(m-*Fluorophenyl*)*diphenylmethyl Peroxide*.—A 10% solution of the chloride in benzene was shaken with molecular silver for 2 hr. in the dark. The yellow solution was decanted and the radical oxidized by exposure to air. The crystalline peroxide was washed successively with light petroleum and boiling acetone, and had m. p. 173°. Marvel *et al.*[4] report m. p. 174°.

(m-*Bromophenyl*)*diphenylmethanol*.—This compound has been obtained as an oil by several workers.[6, 11] A solution of phenylmagnesium bromide [from bromobenzene (93 g.), magnesium (25 g.), and ether (200 ml.)] was filtered and concentrated to about one-third bulk. After addition of benzene (100 ml.) and then freshly distilled methyl *m*-bromobenzoate (30 g.) in benzene (100 ml.), the solution was boiled for 4 hr., decomposed with ice and dilute sulphuric acid, and distilled in steam. The residual alcohol was treated with charcoal in ether and recovered as an oil which solidified during 6 months, and after several recrystallizations from light petroleum was colourless, m. p. 62·5° (Found: C, 65·0; H, 5·4; Br, 24·6. Calc. for $C_{19}H_{15}OBr$: C, 67·3; H, 4·5; Br, 23·6%).

(m-*Bromophenyl*)*diphenylmethyl Peroxide*.—Prepared in the same way as the corresponding fluorine compound, this melted at 172°; Gomberg and Van Slyke [11] report m. p. 170°.

(5-*Bromo-2-methoxyphenyl*)*diphenylmethanol*.—The *alcohol*, prepared from methyl 5-bromo-2-methoxybenzoate [12] and phenylmagnesium bromide, had m. p. 123° (from light petroleum) (Found: C, 65·0; H, 4·8; Br, 21·9. $C_{20}H_{17}O_2Br$ requires C, 65·1; H, 4·6; Br, 22·0%). It gave the *methane*, m. p. 100° (Found: C, 67·4; H, 4·7; Br, 21·9. $C_{20}H_{17}OBr$ requires C, 68·0; H, 4·9; Br, 22·6%), *chloride*, m. p. 116° (Found: Cl, 9·2. $C_{20}H_{16}OClBr$ requires Cl, 9·2%), and *peroxide*, m. p. 153° (Found: C, 64·5; H, 4·4; Br, 19·7. $C_{40}H_{32}O_4Br_2$ requires C, 65·2; H, 4·3; Br, 21·7%).

(3 : 5-*Dibromo-2-methoxyphenyl*)*diphenylmethane*.—The alcohol [13] was reduced by the general method. The methane (from alcohol) had m. p. 89° (Found: C, 55·1; H, 3·5; Br, 37·9. Calc. for $C_{20}H_{16}OBr_2$: C, 55·6; H, 3·7; Br, 37·0). The *chloride*, recrystallized from light petroleum–acetyl chloride, had m. p. 111·5—112° (Found: Cl, 7·7. $C_{20}H_{15}OClBr_2$ requires Cl, 7·6%).

Absorption Spectra of the Triarylmethyl Cations.—Solutions of the alcohols in 98% sulphuric acid [(*m*-fluorophenyl)-, 1·44, (*m*-bromophenyl)-, 1·18, (5-bromo-2-methoxyphenyl)-, 1·12, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethanol, 0·91 × 10^{-5} mole/l.] were examined by means of a Unicam S.P. 500 spectrophotometer (see Figure, and Table 1). The curves for the two methoxyl-substituted derivatives show an additional peak at 592 mμ corresponding to optical density 0·08. There was no change in the spectra in 24 hr. in the dark.

Basicity of the Alcohols.—The basicities recorded in Table 2 were determined by Baeyer and Villigers's method.[14]

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[11] Cone and Long, *J. Amer. Chem. Soc.*, 1906, **28**, 524; Gomberg and Van Slyke, *ibid.*, 1911, **33**, 181; Tschitschibabin, *Ber.*, 1911, **44**, 458.

[12] Hirwe and Patil, *Proc. Indian Acad. Sci.*, 1939, **5***A*, 321.

[13] Kauffmann and Egner, *Ber.*, 1913, **46**, 3786.

[14] Baeyer and Villiger, *Ber.*, 1902, **35**, 1189.

Reduction of (m-*Halogenophenyl*)*diphenylmethyl Chlorides.*—A solution of (*m*-fluorophenyl)-diphenylmethyl chloride (0·428 g.) in bromobenzene (10 ml.) with molecular silver (3·0 g.) at 19° absorbed 1 mol. of oxygen in <15 min. (*m*-Bromophenyl)diphenylmethyl chloride is also rapidly and completely reduced to the free radical under these conditions.

Stability of the Radical Solutions.—No change in optical density (photoelectric colorimeter) occurred when benzene solutions were kept in the dark for 3 days. The volume of oxygen absorbed showed that there was no appreciable disproportionation or isomerization during the period (2—3 hr.) required for the molecular-weight determinations.

Degree of Dissociation of the Ethanes.—The indirect cryoscopic method [15] (benzene solutions of the radicals) gave the results in Table 3. The solvent (20·35 g.) ($K = 52·5°$) was introduced into the cryoscopic vessel by means of a pipette. 5·0 g. of molecular silver were employed in each series of determinations.

Isolation of Halogenohexaphenylethanes.—Preparation of the free radical and isolation of the corresponding ethane from solution were carried out as described in Part XIV. Di-(*m*-fluorophenyl)tetraphenylethane was a yellowish-brown solid, m. p. 117—121° (decomp.). Di-(*m*-bromophenyl)tetraphenylethane was a brown oil, but gave the solid peroxide. Di-(5-bromo-2-methoxyphenyl)tetraphenylethane crystallized at −68°; it was yellowish-brown and melted at 135—139° (decomp.). Di-(3 : 5-dibromo-2-methoxyphenyl)tetraphenylethane separated as pale orange-yellow crystals, m. p. 138—142° (decomp.).

TABLE 3.

(m-*Fluorophenyl*)*diphenylmethyl.* M of radical = 261·3. M of ethane = 522·6.

Chloride (g.)	Radical (g.)	Δ	M	Dissocn. of ethane (%)
0·5092	0·4483	0·315	367·2	42·3
0·7968	0·7015	0·490	369·3	41·5
0·5592	0·4923	0·353	359·8	45·3
0·7636	0·6716	0·501	345·8	51·1
0·5232	0·4607	0·326	364·7	43·3
0·7620	0·6710	0·501	345·5	51·3

(m-*Bromophenyl*)*diphenylmethyl.* M of radical = 322·2. M of ethane = 644·4.

Chloride (g.)	Radical (g.)	Δ	M	Dissocn. of ethane (%)
0·7451	0·6714	0·395	438·5	47·0
1·0227	0·9127	0·535	444·4	44·5
0·6003	0·5409	0·303	460·6	39·9
0·8947	0·8060	0·467	445·2	44·7
0·8665	0·7807	0·436	461·9	39·5
0·9464	0·8527	0·497	442·6	45·6

Action of Silver on (*Halogenophenyl*)*diphenylmethyls.*—Bromobenzene solutions containing known amounts of the (halogenophenyl)diphenylmethyls were agitated with molecular silver as usual: the volume of oxygen absorbed and amount of silver halide formed were measured periodically.

In agreement with Gomberg and Blicke [16] we found that with (*p*-bromophenyl)diphenylmethyl absorption fell in 7 days to about 50% of the original value while the radical lost half its halogen.

In experiments with (*m*-fluorophenyl)diphenylmethyl, four specimens were used. The tubes were charged under dry nitrogen with a known weight of the chloride, molecular silver (1·00 g.), and dry bromobenzene (9 ml.), then sealed, covered with black paper, and agitated (see Table 4). The contents of the last four tubes were examined for silver fluoride by the following procedure. Steam was passed through the mixture to remove bromobenzene, and the residual mass was boiled with water (150 ml.) before filtration. The filtrate was reduced to small bulk. Addition of lead chloride did not precipitate lead chlorofluoride, and the zirconium–alizarin test for fluoride was negative. Therefore, fluorine is not removed by silver and the fall in oxygen absorption is due to disproportionation or isomerization of the radical.

TABLE 4.

Time	Sample	Chloride (g.)	O_2 absorbed (%)	Time	Sample	Chloride (g.)	O_2 absorbed (%)
20 min.	A	0·4006	99·9	8 hr.	D	0·3894	98·5
1 hr.	A	0·3998	100·8	17 hr.	C	0·5230	97·0
4 hr.	B	0·3854	100·9	74 hr.	C	0·3392	96·5
4 hr.	C	0·3426	98·4	6 days	C	0·5828	95·8
4 hr.	A	0·3602	98·5	10 days	B	0·3916	94·9

[15] Part II, *J.*, 1939, 33.

[16] Gomberg and Blicke, *J. Amer. Chem. Soc.*, 1923, **45**, 1768.

In similar experiments (*m*-bromophenyl)-, (5-bromo-2-methoxyphenyl)-, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethyl lost no halogen in 7 days at room temperature. The fluorescein and the fuchsin test for bromide showed that the halogen is not removed from (*m*-bromophenyl)diphenylmethyl at 70° in 3 days.

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