851. *Free Radicals and Radical Stability. Part XIII.* Triphenylmethyls containing* m-*Methoxyl Substituents.*

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The discrepancy between the values of the radical stability determined by the cryoscopic and the magnetic-susceptibility methods is discussed. The former method shows that the stability of (*m*-methoxyphenyl)diphenylmethyl is lower than that of the *ortho*- and the *para*-substituted radical. The presence of more than one substituent leads to clashing influences, and diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl has practically the same stability as (3 : 4-dimethoxyphenyl)diphenylmethyl. The dissociation of triphenylmethyl iodide is also favoured by the presence of methoxyl substituents.

The methoxyl-substituted radicals give a higher yield of peroxide than does triphenylmethyl. In the reaction between a (methoxyphenyl)diphenylmethyl chloride and phenylmagnesium bromide the yield of the tetraphenylmethane is lower for the *meta*-substituted than for the *ortho*-substituted derivative where the effect of steric hindrance would be greater.

The influence of methoxyl substituents in the *ortho*- and *para*-positions of triphenylmethyl has been studied by Gomberg and Nishida,[1] Gomberg and Buchler,[2] Lund,[3] and more recently Marvel, Whitson, and Johnston [4] who confined their study to the effect of orientation on the dissociation of the corresponding hexa-arylethanes. The present work was undertaken to examine primarily the influence of *meta*-substitution by methoxyl on the properties of the free radicals and their saturated derivatives.

The annexed Table shows that the values of the degree of dissociation determined by the cryoscopic method differ considerably from those found by the magnetic-susceptibility method. In discussing these discrepancies Marvel and his co-workers [4] state: "All of the methoxyl substituted hexa-arylethanes were found to be relatively unstable, and the change in magnetic susceptibility with the age of the solution showed that these radicals decompose quickly. The molecular-weight determinations undoubtedly show too high values for the radical because of the presence of disproportionation products in the aged solutions of the ethanes." In so far as the chemical stability of the radical solutions is concerned, the experience of these investigators is at variance with that of other workers. When prepared under conditions which preclude oxidation and photodecomposition and minimise disproportionation and isomerisation, these triphenylmethyls are among the most stable substituted radicals which have yet been prepared. Far from decomposing quickly the radicals prepared in Gomberg's laboratory and at Cardiff exhibited little tendency to undergo these reactions at room temperature, and were kept in the dark for many hours or even days without substantial change. No significant amounts of decomposition products were formed during two hours required for the cryoscopic measurements

Methoxyl-substituted hexaphenylethanes.

	Dissociation of the ethane (%)	
Free radical	Cryoscopic method	Magnetic method
(*o*-Methoxyphenyl)diphenylmethyl	26 (Gomberg and Nishida)	3·8 (Marvel *et al.*)
(*m*-Methoxyphenyl)diphenylmethyl	15 (Present work)	2·6 ,,
(*p*-Methoxyphenyl)diphenylmethyl	24 (Gomberg and Buchler)	4·4 ,,
Di-(*o*-methoxyphenyl)phenylmethyl	40 (Bowden)	7·3 ,,
Tri-(*o*-methoxyphenyl)methyl	100 (Lund)	42 ,,
Tri-(*m*-methoxyphenyl)methyl	13 (Present work)	8·5 ,,
Diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl	23 ,,	—

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* Part XII, *J.*, 1940, 1249.

[1] Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1922, **45**, 190.
[2] Gomberg and Buchler, *ibid.*, p. 207.
[3] Lund, *ibid.*, 1927, **49**, 1346.
[4] Marvel, Whitson, and Johnston, *ibid.*, 1944, **66**, 415.

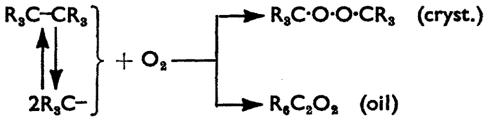
since the volume of oxygen absorbed by the radical system at the end of this period seldom differed by more than 1% from the nearly theoretical value found for the fresh radical. Moreover, the yield of triarylmethyl peroxide obtained by oxidation of the solution after completion of the cryoscopic determinations corresponded closely to that found for the fresh solution. Further, most of the hexaphenylethanes were isolated in the solid state.

Although the low values of dissociation reported by Marvel and his co-workers [4] may be due to isomerization, leading to derivatives analogous to *p*-diphenylmethyltetraphenylmethane, they probably arise from an inherent defect in the application of the magnetic-susceptibility method to determine the concentration of free radical in solution. In a critical study of the method Selwood and Dobres [5] point out that their own results with triarylmethyl systems can be explained on the basis of an underestimation in the diamagnetic correction of 65—120% and an increase of 195—300% in the principal molecular susceptibility normal to the plane of the rings. These values are large, and there is no means of estimating the electronic currents in the resonating bonds attaching the aryl nuclei to the methyl-carbon atom. There is no doubt that the published values of the radical stability are far too low, and until the difficulties inherent in the magnetic-susceptibility method are resolved we prefer to rely on the simpler and more direct cryoscopic method. According to Marvel and his co-workers,[4] steric factors are responsible for the high unimolecular stability of triphenylmethyls containing *o*-methyl or *o*-methoxyl groups. This conclusion, however, is based solely on the questionable data furnished by the magnetic-susceptibility method. Although steric influences may operate to some extent in preventing association of the radical to the ethane or in lengthening the central C–C bond,[6] the cryoscopic results indicate that these effects are small with substituents such as methyl and methoxyl. If we refer the greater unimolecular stability of the substituted radicals to the increase in degeneracy arising from the modification of the inductive and mesomeric effects,[7] we would expect the stability of (*m*-methoxyphenyl)diphenylmethyl to be higher than that of triphenylmethyl but lower than that of the *o*- and *p*-derivatives. This is substantiated by the annexed cryoscopic results. In other respects (*m*-methoxyphenyl)diphenylmethyl is similar to the *o*- and *p*-derivatives. It absorbs rapidly a mole of oxygen with complete decolorization of the solution. The oxidation of a triarylmethyl radical generally involves the formation of a crystalline peroxide and an oily, isomeric product:

(Methoxyphenyl)diphenylmethyls.

Radical	M. p. (decomp.) of the ethane	Dissociation of the ethane (%)	Colour of solution	Absorption of O_2 (%) *	Absorption of I_2 (%) *
Triphenylmethyl	145°	2—4	Yellow	99·9	80
(*o*-Methoxyphenyl)diphenylmethyl	117—121	26	Yellow-brown	93·6	64
(*m*-Methoxyphenyl)diphenylmethyl	120—124	16	Orange-yellow	99·1	60
(*p*-Methoxyphenyl)diphenylmethyl	145—150	24	Orange-yellow	100·9	60

* Of theoretical.



and it is evident that the first reaction is favoured by the presence of the methoxyl group since the yield of peroxide is 15% higher than that of triphenylmethyl peroxide. The radical also combines with iodine until an equilibrium is established, and, as might be expected on the basis of the behaviour of the corresponding ethanes, the degree of

[5] Selwood and Dobres, *J. Amer. Chem. Soc.*, 1950, **72**, 3860.
[6] Ziegler, *Annalen*, 1942, **551**, 127.
[7] Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; *Trans. Faraday Soc.*, 1934 **30**, 52.

dissociation of the three (methoxyphenyl)diphenylmethyl iodides in benzene at room temperature is substantially higher than that of triphenylmethyl iodide.

The influence of methoxyl substituents on the stability of a triarylmethyl is not additive, and it is not possible to predict its value from a knowledge of the number and orientation of the substituents. The stability of di-(*o*-methoxyphenyl)phenylmethyl is 40% but the stabilities of the 2 : 4- and the 3 : 4-derivative are 29% and 12%, respectively. Although tri-(*o*-methoxyphenyl)methyl is reported to be almost completely unimolecular in solution,[3] the present results indicate that the stability of the corresponding tri-*meta*-derivative differs little from that of the monosubstituted radical. The same inhibitory influence of *meta*-substituents is apparent in the radical diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl with a stability of 23%, which does not differ appreciably from that of (3 : 4-dimethoxyphenyl)diphenylmethyl.

The difficulty experienced in synthesizing tetraphenylmethane is generally ascribed to steric hindrance,[8] and the hydrocarbon is formed in only 2—5% yield by the action of phenylmagnesium bromide on triphenylmethyl chloride. In the analogous reaction between the Grignard reagent and (*m*-methoxyphenyl)diphenylmethyl chloride we find that the yield of (*m*-methoxyphenyl)triphenylmethane is 20%, which is lower, however, than the yield of (*o*-methoxyphenyl)triphenylmethane in whose formation steric hindrance would be expected to be more strongly operative.

EXPERIMENTAL

(m-*Methoxyphenyl*)*diphenylmethanol*.—The compound was prepared in 50% yield from *m*-methoxyphenylmagnesium iodide or bromide and benzophenone, but was more conveniently obtained from phenylmagnesium bromide and methyl or ethyl *p*-anisate.[9, 4] Recrystallized from alcohol or ether, it melted at 88°.

Treatment of a cold solution of the alcohol in acetic anhydride with slight excess of 70% perchloric acid gave deep violet crystals of the *perchlorate*, m. p. 110° (Found: ClO_4, 26·5. $C_{20}H_{17}O_5Cl$ requires ClO_4, 26·7%).

(m-*Methoxyphenyl*)*diphenylmethane*.—The alcohol (1 g.), glacial acetic acid (15 c.c.), and zinc dust (1 g.) were heated on the steam-bath for 3 hr. On concentration of the filtered solution the methane (0·7 g.) was deposited, and having m. p. 86° (from alcohol), not changed on admixture with a specimen prepared by reduction of the alcohol with formic acid.[10]

(m-*Methoxyphenyl*)*diphenylmethyl Chloride*.—(*a*) The compound was prepared by Marvel *et al.*[4] by refluxing a benzene solution of the alcohol with excess of acetyl chloride for several hours, and had m. p. 89—90° after recrystallisation from ethyl acetate. Since the alcohol reacts rapidly with acetyl chloride in ether–light petroleum, we adopted the following procedure. Acetyl chloride (0·25 mole) was added to a solution of the alcohol (0·1 mole in 1 : 1 ether–light petroleum), and the mixture was simmered gently for 15 min. (*m*-Methoxyphenyl)diphenylmethyl chloride was slowly deposited on storage in the cold, and had m. p. 88° after recrystallization from the same solvent mixture.

(*b*) A 10% solution of the alcohol in ether was saturated with hydrogen chloride and kept over calcium chloride in a stoppered vessel for 24 hr. The filtered solution was concentrated to one-third of its bulk, and the deposited (*m*-methoxyphenyl)diphenylmethyl chloride was filtered off in a stream of dry air. Recrystallized from ether–light petroleum, the compound had m. p. 88° (mixed m. p. with the alcohol, 75—76°) (Found: Cl, 11·4. Calc. for $C_{20}H_{17}OCl$: Cl, 11·5%). This method does not yield such a readily purified product as method (*a*).

(m-*Methoxyphenyl*)*triphenylmethane*.—A filtered solution of phenylmagnesium bromide [from bromobenzene (9·0 g.) and magnesium (1·4 g.)], boiling under nitrogen, was treated with (*m*-methoxyphenyl)diphenylmethyl chloride (5·0 g.) during 1 hr. After 12 hours' heating the cooled solution was acidified and treated with steam to remove volatile material. The solid residue was washed with water, dried, dissolved in the minimum amount of benzene, treated with an equal volume of light petroleum, and kept for several days. The deposited (*m*-methoxyphenyl)triphenylmethane (20·4%) was obtained colourless after two recrystallizations from

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[8] Gomberg, *J. Amer. Chem. Soc.*, 1914, **36**, 1144.

[9] Baeyer and Villiger, *Annalen*, 1907, **354**, 171.

[10] Kauffmann and Panwitz, *Ber.*, 1912, **45**, 770.

glacial acetic acid, and had m. p. 163° [Found: C, 88·9; H, 6·5%; *M* (Rast), 346. $C_{26}H_{22}O$ requires C, 89·1; H, 6·3%; *M*, 350].

(m-*Methoxyphenyl*)*diphenylmethyl*.—The free radical was prepared by agitating a 10% benzene solution of the chloride with rigorously dried molecular silver under carbon dioxide with exclusion of light. The yellow solution was transferred into the standard type of isolation apparatus,[11] and the solvent removed at 45°, the pressure being finally reduced to 20 mm. The residual oil was dissolved in the minimum amount of warm acetone, and cooled to −10°. Di-*m*-methoxyhexaphenylethane was deposited as very pale yellow crystals, which were washed with small amounts of cold light petroleum and then dried *in situ* at 50° in a stream of carbon dioxide; it had m. p. (in vacuum) 120—124° (decomp.).

The volume of 0·99 mol. of oxygen was absorbed by bromobenzene solutions. The benzene solution rapidly absorbed iodine to form (*m*-methoxyphenyl)diphenylmethyl iodide, and at 18° equilibrium was established when the amount of combined iodine corresponded to 60% of the theoretical value.

(m-*Methoxyphenyl*)*diphenylmethyl Peroxide*.—Marvel *et al.*[4] give no preparative details, but state that the compound has m. p. 156—157°. We prepared the compound by passing air through a 10% ethereal solution of the radical until the colour was discharged and the peroxide was precipitated, or by allowing a benzene solution of the radical to evaporate spontaneously in the air, and then triturating the residue with ether and light petroleum. The solid was recrystallized from 1 : 1 benzene–ligroin, or by dissolving the compound in xylene at 50° and rapidly cooling the solution to 0°. It was thus obtained as a colourless powder, m. p. 163° (Found: C, 82·8; H, 6·0. Calc. for $C_{40}H_{34}O_4$: C, 83·2; H, 5·9%). The average yield (85%) is substantially higher than that found for triphenylmethyl peroxide (70%).

Tri-(m-*methoxyphenyl*)*methanol*.—The compound, m. p. 119·5° (from alcohol) (cf. ref. 9), was obtained in 48% yield from *m*-methoxyphenylmagnesium iodide and methyl *m*-anisate.

Tri-(m-*methoxyphenyl*)*methane*.—A 10% solution of the alcohol in glacial acetic acid was boiled with zinc dust for 6 hr. Addition of water to the filtered solution precipitated the *methane*, which after three recrystallizations from alcohol melted at 103° (Found: C, 78·7; H, 6·7. $C_{22}H_{22}O_3$ requires C, 79·0; H, 6·6%).

Tri-(m-*methoxyphenyl*)*methyl Chloride*.—Marvel *et al.*[4] prepared the compound by prolonged boiling of a benzene solution of the alcohol with excess of acetyl chloride, but a cleaner product was obtained by the following method. A 15% solution of the alcohol in ether at 0° was saturated with hydrogen chloride, and set aside for 12 hr. in a stoppered vessel with a glass basket containing fused calcium chloride immersed in the liquid. The trimethoxytriphenylmethyl chloride was deposited as a colourless solid which melted at 123—124° after recrystallization from 1 : 1 benzene–ether (Found: Cl, 9·6. Calc. for $C_{22}H_{21}O_3Cl$: Cl, 9·6%).

Tri-(m-*methoxyphenyl*)*methyl*.—Agitation of the chloride (1 g.) in bromobenzene (10 ml.) with 5 times the theoretical amount of molecular silver led to complete reduction in 20 min. at room temperature with formation of a yellowish-red solution. Removal of the solvent from a 15% benzene solution of the radical in the isolation apparatus gave the ethane as a yellowish-red oil which did not crystallize.

A freshly prepared solution of the radical absorbed 0·98 mol. of oxygen in 5 min., and 0·97 mol. in the dark in 2 hr. There was a further absorption of a similar amount in 8 days owing to further oxidation. The *peroxide* was isolated by passing air through a 15% benzene solution of the radical until most of the solvent was removed, triturating the residue with light petroleum, and rapidly recrystallizing the product from benzene under carbon dioxide. It had m. p. 153—154° whereas Marvel *et al.*[4] found m. p. 155—156° (Found: C, 75·4; H, 6·1. Calc. for $C_{44}H_{42}O_8$: C, 75·6; H, 6·1%).

Diphenyl-(3 : 4 : 5-*trimethoxyphenyl*)*methyl Chloride*.—The compound was prepared by a modification of Bogert and Isham's method.[12] A suspension of diphenyl(3 : 4 : 5-trimethoxyphenyl)methanol (5 g.) in ether (50 ml.) containing a few lumps of calcium chloride was saturated with hydrogen chloride. After 12 hr. the deep red solution was filtered and concentrated to one-third of its bulk in a dry atmosphere. The chloride deposited on cooling had m. p. 110° after recrystallisation from ether. The *ferric chloride addition compound* was obtained as a dark red precipitate on mixing ethereal solutions of the components. After being washed with ether

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[11] Gomberg and Schoepfle, *J. Amer. Chem. Soc.*, 1917, **39**, 1659.

[12] Bogert and Isham, *ibid.*, 1914, **36**, 514.

and kept over soda-lime and silica gel in an evacuated desiccator, it had m. p. 140° (Found: Cl, 29·4. $C_{22}H_{21}O_3Cl,FeCl_3$ requires Cl, 29·3%). The addition compounds with zinc and mercuric chlorides were dark red oils.

Diphenyl-(3 : 4 : 5-*trimethoxyphenyl*)*methyl*.—The solvent was removed from a 15% solution of the radical in benzene in the isolation apparatus, at 45° under reduced pressure in a stream of carbon dioxide. The residual orange-yellow oil, when dissolved in the minimum amount 1 : 4 acetone–light petroleum and cooled to −10°, deposited the pale yellow ethane, m. p. 154—155° (decomp.; vac.). In liquid sulphur dioxide and dimethyl sulphate it formed crimson solutions. It rapidly absorbed 0·96 mol. of oxygen in non-ionizing solvents, but some yellow colour remained; further slow absorption took place.

Diphenyl-(3 : 4 : 5-*trimethoxyphenyl*)*methyl Peroxide*.—A 10% solution of diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl chloride was shaken with a large excess of mercury in a sealed tube for 4 hr. in the dark. Air was passed through the filtered solution for 20 min. The *peroxide* was precipitated as a yellow powder, and was obtained as colourless crystals, m. p. 175°, by rapid recrystallization from hot benzene (Found: C, 75·5; H, 6·1. $C_{44}H_{42}O_8$ requires C, 75·6; H, 6·1%).

Dissociation of the Ethanes.—The degree of dissociation was determined by the indirect cryoscopic method with the customary precautions to avoid isomerization, disproportionation, and oxidation during the preparation of the radical and the subsequent measurements.[13] The solvent employed was benzene; *K*, 52·5°.

Solvent (g.)	Chloride (g.)	Radical (g.)	Δ	*M*	Dissocn. of ethane (%)
(m-*Methoxyphenyl*)*diphenylmethyl*.					
M of radical = 273·3; *M* of the ethane = 546·5.					
18·10	0·3080	0·2726	0·166°	478·9	14·1
	0·5570	0·4930	0·302	476·1	14·8
	0·7429	0·6573	0·405	469·7	16·4
18·11	0·2882	0·2549	0·156	474·0	15·3
	0·4483	0·4259	0·266	466·0	17·3
	0·7460	0·6894	0·420	476·2	14·7
	0·8204	0·7552	0·460	475·8	14·9
18·10	0·2548	0·2255	0·139	470·6	16·1
	0·5038	0·4459	0·279	463·6	17·7
	0·6908	0·6114	0·377	470·3	16·0
	0·7740	0·6850	0·420	473·2	15·5
18·47	0·4373	0·3871	0·231	476·6	14·7
	0·6304	0·5580	0·268	470·2	16·0
	0·7838	0·6938	0·327	479·2	14·1
Diphenyl-(3 : 4 : 5-*trimethoxyphenyl*)*methyl*.					
M of radical = 333·3; *M* of the ethane = 666·6.					
18·13	0·2604	0·2351	0·125	544·6	22·2
	0·5238	0·4730	0·259	528·8	26·0
	0·7409	0·6691	0·363	538·8	23·0
	0·8941	0·8074	0·441	530·8	23·7
18·47	0·2536	0·2290	0·123	529·3	25·2
	0·4421	0·3992	0·210	540·5	22·6
	0·6634	0·5991	0·313	544·3	21·7
18·47	0·2724	0·2460	0·131	538·8	24·8
	0·4794	0·4329	0·226	544·6	22·5
	0·6966	0·6290	0·328	546·3	21·9

Solvent (g.)	Chloride (g.)	Radical (g.)	Δ	*M*	Dissocn. of ethane (%)
Tri-(m-*methoxyphenyl*)*methyl*.					
M of radical = 333·3; *M* of the ethane = 666·6.					
18·10	0·1970	0·1780	0·089°	580·3	14·8
	0·4304	0·3890	0·188	600·1	11·1
	0·6993	0·6320	0·308	597·8	11·5
18·10	0·2379	0·2150	0·107	582·8	14·4
	0·7767	0·7020	0·333	602·4	10·7
18·10	0·4769	0·4309	0·209	598·2	11·4
	0·6662	0·6020	0·290	604·9	10·2
18·48	0·5987	0·5411	0·265	580·3	14·9
	0·8212	0·7420	0·356	592·3	12·5
18·48	0·6407	0·5790	0·279	589·6	13·1
21·10	1·018	0·9196	0·412	583·3	14·3

After each set of determinations, the solution was quickly filtered from silver and silver chloride, and the radical converted into peroxide by passing air through the solution or allowing the latter to evaporate in the atmosphere. The yield of peroxide was practically the same as that obtained by oxidation of the freshly prepared solutions.

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[13] Bowden, *J.*, 1939, 37.