6. *Free Radicals and Radical Stability. Part II. The Dimethoxytriphenylmethyls.*

By Sydney T. Bowden.

The influence of the methoxyl group on the thermodynamic stability and other properties of the free radicals 2 : 4′- and 2 : 2′-dimethoxytriphenylmethyls has been studied. The yellowish-red solutions of the radicals in non-ionising solvents undergo rapid oxidation with the formation of soluble peroxides, which suffer a further complex oxidation involving the slow absorption of oxygen. The thermal stability of the corresponding triarylmethyl iodides is much lower than that of triphenylmethyl iodide. In freezing benzene the thermodynamic stabilities of these two compounds are respectively 28% and 41%, but both are appreciably higher in nitrobenzene. The presence of methoxyl groups in triphenylmethyl leads to clashing influences which may be anticipated on the premises of Burton and Ingold's theory, and there is no simple connexion between the stability and the number and orientation of the substituents.

The two radicals have been isolated in the solid state and have a lower melting point than solid triphenylmethyl. Unlike triphenylmethyl, these radicals do not form addition compounds with ether, and it is suggested that the free radical as such is not responsible for the formation of these compounds in the case of hexaphenylethane, since analogous derivatives are obtained with similar saturated substances.

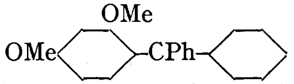
The influence of the methoxyl group on the basicity and halochromic properties of triphenylcarbinol was studied by Baeyer and Villiger (*Ber.*, 1902, **35**, 1189), who found that the introduction of this group into one or more of the phenyl nuclei increased the basicity to an extent depending on the position of the substituent. Actually, the triarylcarbinols are pseudo-bases, which react with hydrogen ion to produce water and the corresponding triarylmethyl cation. The basicity of the carbinol, as measured by the stability of the salt towards hydrolysis, is intimately connected with the electronic condition of the methyl carbon atom, but no information is available as to the deep-seated connexion which must exist between the basicity of the carbinol and the thermodynamic stability of the corresponding neutral, free radical.

The term " stability of the radical " (radical stability) is frequently used in two senses, indicating (*a*) the capacity of existing in the unimolecular state without suffering dimerisation and (*b*) the ordinary chemical stability with reference to reactivity, isomerisation, or disproportionation. The influence of the methoxyl group on the unimolecular stability of radicals has been studied by Gomberg and his co-workers (*J. Amer. Chem. Soc.*, 1923, **45**, 202, 217 ; 1925, **47**, 2387), who obtained the results given in the following table. The values given for the stability actually refer to the percentage dissociation of the corresponding ethane in 2% benzene solution at the freezing point.

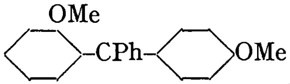
Radical.	Stability, %.	Colour.	Basicity of carbinol.
Triphenylmethyl	5	Yellow	1·0
o-Methoxytriphenylmethyl	27	Yellowish-red	2·0
m-Methoxytriphenylmethyl	12	Reddish-yellow	1·2
p-Methoxytriphenylmethyl	24	Orange-yellow	6·5
2 : 4-Dimethoxytriphenylmethyl	12	Red	11·8
2 : 5-Dimethoxytriphenylmethyl	25	Bright red	—
3 : 4-Dimethoxytriphenylmethyl	22	Yellowish-red	5·9

It is evident that the ability of the radical to exist as a unimolecular entity varies in a remarkable way with the orientation and number of the substituents. The effect of the methoxyl group in the *m*-position is materially lower than in the *o*- and *p*-position, as may be anticipated from Burton and Ingold's theory of radical stability. Whereas the presence of one methoxyl in the *o*- or *p*-position enhances the stability to about 20%, the introduction of a second methoxyl may have but little effect, as in 2 : 5- and 3 : 4-dimethoxytriphenylmethyls, or actually diminish it by half, as in the 2 : 4-dimethoxy-derivative.

With a view to obtain further information concerning the factors governing the thermodynamic stability of these systems, free radicals containing substituents in two of the phenyl nuclei have been prepared. For comparison with the apparently anomalous 2 : 4-dimethoxytriphenylmethyl we have synthesised the 2 : 4′-dimethoxy-radical. The colour of the neutral radical in non-polar solvents is orange, but that of the corresponding ion in liquid sulphur dioxide is bright red. The radical exhibits the extreme unsaturation of polymethoxytriarylmethyls, and the colour of the solution is discharged on exposure to air. The absorption of 1 mol. of oxygen is rapid, but this is followed by a further slow absorption owing to the oxidation of the primary *peroxide*. The latter is soluble in benzene but may be obtained as a white crystalline powder. Although the radical itself is prone to undergo isomerisation in the presence of traces of acids, it has been isolated as a pale yellow crystalline solid, m. p. 80° (vac.). Cryoscopic measurements in benzene show that 2 : 4′-dimethoxytriphenylmethyl (II) is much more stable than the 2 : 4-dimethoxy-analogue (I) :



(I.) Radical stability : 12%.



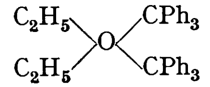
(II.) Radical stability : 29%.

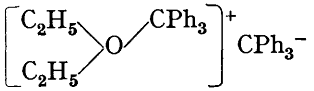
To trace the effect of the number of substituents, the radical 2 : 2′-dimethoxytriphenylmethyl has been prepared in order to compare its stability with *o*-methoxy- and 2 : 2′ : 2″-trimethoxy-triphenylmethyls :

Substituents in CPh_3	*o*-Methoxy-.	2 : 2′-Dimethoxy-.	2 : 2′ : 2″-Trimethoxy-.
Radical stability..................	27%	40%	90—100%

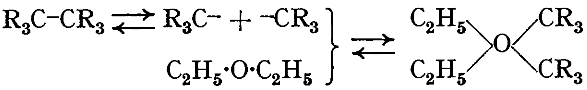
According to Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421), the presence of methoxyl groups in the phenyl nuclei leads to clashing influences and complicating effects. It is clear, however, from the results already available, that the radical stability is not proportional to the number of methoxyl groups. The same lack of proportionality is evident in the successive phenylation of triphenylmethyl, as exemplified in the series of radicals : diphenylyldiphenylmethyl (15%), bisdiphenylylphenylmethyl (80%), trisdiphenylylmethyl (100%).

The ability of triphenylmethyl to form addition compounds with a variety of substances, such as ethers, esters, ketones, aldehydes, etc., has sometimes been regarded as a natural consequence of the extreme unsaturation of the free radical. Gomberg (*Ber.*, 1905, **38**, 1338) found that triphenylmethyl combined with ether to form an addition compound to which the constitution (III) was assigned. This corresponds to the modern oxonium

(III.) 

 (IV.)

formulation (IV), in which the oxygen atom functions in the same way as the oxygen in the ether hydrochlorides. The free radicals 2 : 2′- and 2 : 4′-dimethoxytriphenylmethyl, however, do not form addition compounds with ether, and the question arises as to whether this behaviour is to be referred to the difference in radical stability, the state of the free electron, or to some other cause. The matter has been discussed by Gomberg and Schoepfle (*J. Amer. Chem. Soc.*, 1919, **41**, 1655), who found that diphenyl-α-naphthylmethyl does not form addition compounds with ether. They sought to explain this apparent anomaly by correlating the degree of association or dimerisation of the radical with its capacity to form addition compounds. The radical, in fact, was considered to be so stable as a unimolecular entity that it lacked, not only the property of combining with itself, but also the tendency of uniting with ethers, esters, etc. If we assume that it is the unimolecular radical which combines with ether, then combination must involve a shift in the equilibrium between the bimolecular ethane and the free radical:



The above hypothesis is based on the premise that these equilibria are so related that the greater the amount of hexa-arylethane present in equilibrium with the radical the greater will be the stability of the addition compound formed. It must be urged, however, that the non-polar dimerisation of the radical and the co-ordination of the ether are reactions of fundamentally different types, while the factors governing the dissociation of two such dissimilar systems as $R_3C\cdot CR_3$ and $C_2H_5\cdot O\cdot C_2H_5,R_3C\cdot CR_3$ are of entirely different character.

Furthermore, it must be borne in mind that triphenylmethyl forms addition compounds, not only with oxygenated derivatives, but with chloroform and even saturated hydrocarbons, such as heptane, *cyclo*hexane, and benzene. Since, moreover, these combinations are also known to occur with the fully saturated triphenylmethane, which combines with benzene to form $CHPh_3,C_6H_6$, it appears that the presence of a free bond in triphenylmethyl is not the essential factor underlying the formation of addition compounds. In the majority of cases, the addition compounds correspond to the union of 2 mols. of the radical with 1 mol. of solvent. It is possible, accordingly, that the unimolecular radical plays no essential part in the formation of addition compound, but that the solvent unites directly with the bimolecular derivative as indicated in the scheme:

$$2Ph_3C- \rightleftharpoons CPh_3\cdot CPh_3 \xrightarrow{C_6H_6} CPh_3\cdot CPh_3,C_6H_6$$

$$CHPh_3 \xrightarrow{C_6H_6} CHPh_3,C_6H_6$$

Of the four radical systems which have been investigated in this connexion, one only is found to form addition compounds of this nature, and it seems clear that the unique behaviour of triphenylmethyl in this respect is not due to the presence of a free electron. The *X*-ray analysis of the crystal structure of the so-called addition compounds may reveal that the two components simply form a crystallographic assemblage.

EXPERIMENTAL.

2 : 4′-*Dimethoxytriphenylcarbinol*.—*p*-Methoxybenzophenone was prepared in 57% yield by adding portions of anhydrous aluminium chloride (150 g.) to a mixture of anisole (135 c.c.), benzoyl chloride (145 c.c.), and carbon disulphide (400 c.c.). After hydrolysis of the product, the ketone was distilled, and obtained as a white solid, m. p. 62°, by crystallisation from ether

(Gattermann, Ehrhardt, and Maisch, *Ber.*, 1890, **23**, 1204). *o*-Iodoanisole (50 g.) (Jannasch and Hinterskirsch, *Ber.*, 1898, **31**, 1710) in dry ether (300 c.c.) was added to magnesium powder (8 g.) previously activated *in situ* by Baeyer's method. The filtered Grignard reagent was treated with freshly distilled methyl benzoate (15 g.), and the mixture heated for 3 hours before being decomposed with ice and sulphuric acid. The brown residue obtained after removal of the ether was dissolved in ligroin, decolorised with charcoal, and finally obtained in white crystals, m. p. 115°. Yield, 44%.

The carbinol was reduced to 2 : 4′-dimethoxytriphenylmethane by boiling with formic acid (Kauffmann and Pannwitz, *Ber.*, 1912, **45**, 766). It melted at 106° and gave no colour with concentrated sulphuric acid.

The salts obtained by treatment of the carbinol with sulphuric, perchloric, phosphoric, and formic acids range from dark brown to purplish-brown; the carbinol also dissolves in liquid sulphur dioxide to form a purple solution.

The determination of the basicity of the carbinol is based on the fact that the coloured solutions of the carbinols in glacial acetic acid–sulphuric acid are decolorised by dilute aqueous alcohol (Baeyer and Villiger, *Ber.*, 1902, **35**, 1189). To obtain comparable results, equimolecular amounts of the carbinols (0·0743 g. of triphenylcarbinol as standard) were dissolved in 5 c.c. of glacial acetic acid and treated with 1 c.c. of a 10% solution of pure concentrated sulphuric acid in glacial acetic acid. To the coloured solution of the triarylmethyl salt, alcohol (75%) was added from a burette until the liquid assumed the colour of a control solution to which the acetic acid–sulphuric acid mixture had not been added. The measurements were carried out at 20° and gave the basicity value 9·9 for 2 : 4′-dimethoxytriphenylcarbinol ($CPh_3 \cdot OH = 1$).

2 : 4′-*Dimethoxytriphenylmethyl Chloride*.—The dry, finely powdered carbinol (2 g.) and sodium-dried light petroleum (5 c.c.) were placed in a flask provided with a ground-glass dropping funnel and a side tube attached to a calcium chloride tube. Acetyl chloride (2 c.c.) was added from the funnel, and the mixture gently simmered. The carbinol dissolved with a red colour, and after 30 minutes the solution was concentrated to half bulk under reduced pressure. The crystals, which were deposited on standing, were washed with light petroleum–benzene to remove most of the colour. The *chloride* was dissolved in the minimum amount of hot benzene, and the solution treated with light petroleum to the point of incipient turbidity. The greyish-white crystals obtained were washed with light petroleum, and dried in a vacuum over soda-lime and paraffin wax. The substance, m. p. 116°, was readily soluble in benzene, but slightly soluble in ether (Found: Cl, 10·4, 10·4. $C_{21}H_{19}O_2Cl$ requires Cl, 10·5%). Treatment of the substance with ethereal solutions of anhydrous ferric, mercuric, or zinc chloride immediately precipitated the addition compounds as dark red oils.

2 : 4′-*Dimethoxytriphenylmethyl Bromide*.—Bromination of the carbinol in light petroleum with 2 mols. of acetyl bromide gave the *bromide* as slightly pink rosettes, m. p. 118° (Found: Br, 20·8. $C_{21}H_{19}O_2Br$ requires Br, 20·9%).

Absorption of Oxygen by 2 : 4′-*Dimethoxytriphenylmethyl*.—The absorption of oxygen by the radical was measured in the Gomberg and Schoepfle apparatus, which was housed in an air-thermostat at 18°. A known weight of pure 2 : 4′-dimethoxytriphenylmethyl chloride and excess of molecular silver were placed in a constricted test-tube, the air displaced by means of nitrogen, and the tube filled with dry bromobenzene to within a short distance of the constriction. The tube, adequately protected with asbestos cord, was quickly sealed in the blowpipe flame, and then shaken in the dark for 4 hours. The tube was placed in the absorption bottle (containing 10 c.c. of bromobenzene), which was connected by pressure tubing to the gas burette. After the apparatus had been charged with oxygen, the tube was broken, and the volume of gas absorbed noted at intervals. The results of a typical experiment are given below, volumes being corrected to *N.T.P.*

Weight of 2 : 4′-dimethoxytriphenylmethyl chloride = 0·677 g. (Absorption corresponding to true peroxide formation = 22·4 c.c.).

Time, hrs.	¼	3	24	48	72	96	120	168	216	240
O_2 absorbed, c.c.	21·6	22·0	25·2	29·8	34·0	41·8	42·8	52·2	65·4	67·0
Absorption, %	96·5	98·3	112	134	151	186	191	233	292	299

2 : 4′-*Dimethoxytriphenylmethyl Peroxide*.—2 : 4′-Dimethoxytriphenylmethyl chloride (2 g.), dissolved in dry benzene–ether, was shaken for 6 hours with a large excess of mercury in a sealed tube adequately protected from sunlight. After standing for some hours to allow complete precipitation of mercurous chloride, the deep orange-coloured solution was siphoned through a

filter, and a current of air drawn through the solution until the colour was almost completely discharged. The resulting pale yellow solution was allowed to evaporate spontaneously, and the thick, yellow residue was washed with ether. By protracted trituration with light petroleum, the oil was converted into a pale yellow solid, which was obtained as a white microcrystalline powder, m. p. 139°, by rapid crystallisation from benzene in an atmosphere of carbon dioxide (Found: C, 78·3; H, 6·0. $C_{42}H_{38}O_6$ requires C, 78·9; H, 6·0); yield, 60%. The *peroxide* is soluble in ether, benzene and carbon disulphide, but practically insoluble in light petroleum. It gives no colour with formic or perchloric acids, whereas the carbinol immediately produces deep red salts. With concentrated sulphuric acid, however, a deep red colour is produced, but less rapidly than with the carbinol itself.

Absorption of Iodine by 2 : 4′-*Dimethoxytriphenylmethyl.*—The solution of the radical was titrated with iodine in the apparatus shown in Fig. 1. The radical was prepared by shaking a benzene solution of the chloride with excess of molecular silver in the sealed glass tube *A* provided with a very thin bottom. This was placed in the sintered-glass filter *B*, and could be broken by lowering the carbon dioxide delivery tube to which the cup *C* is attached. The rubber stopper was fitted with a burette *D* for adding the iodine solution, and also with a delivery tube *E* for the admission of carbon dioxide into the flask *F*. To the delivery tube was fixed a small test-tube *G*, which could be brought under the jet of the burette in order to catch any drops which might fall before the experiment was actually begun. The trap *H* was charged with benzene to prevent backward diffusion of air into the apparatus.

Fig. 1.

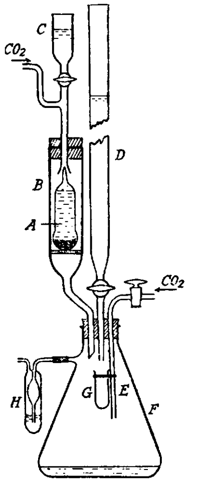
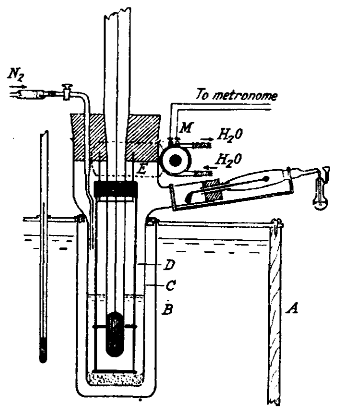


Fig. 2.



The burette was charged with an air-free benzene solution of iodine (N/20), and the flask placed in a shallow porcelain vessel containing water at constant temperature. After displacement of air from the apparatus, the tube *A* was broken, and the solution forced through the filter under pressure of carbon dioxide. The residual silver–silver chloride mixture was thoroughly washed with benzene from the cup *C*. The tube *G* was swung aside by turning *E*, and the iodine solution added drop-wise from the burette. The blue iodine colour was instantly discharged, but after 0·7 c.c. had been added, a permanent brownish solution was obtained. The percentage combination amounted to 1·7%, which is an unusually low value for a triarylmethyl. It follows, therefore, that the thermal stability of 2 : 4′-dimethoxytriphenylmethyl iodide is considerably lower than that of the unsubstituted triphenylmethyl iodide, which is stable to the extent of 80% in benzene at ordinary temperature.

Stability of the Free Radical.—In view of the extreme reactivity of triarylmethyls of this type and their proneness to suffer isomerisation and disproportionation reactions, the molecular-weight determinations were carried out without recourse to the isolation of the material in the solid state. The apparatus (Fig. 2) consisted of a freezing bath *A*, made of wood and provided with a cover of compressed asbestos carrying the fixed air-jacket *B*. The Beckmann tube *C* with a flattened bottom was fitted with a soft rubber stopper through which passed a narrow delivery tube for the admission of nitrogen, and a reliable Beckmann thermometer furnished with a lens, mirror, and electric light for reading purposes. The corrugated, double-ring, platinum stirrer *D* was attached by platinum rods to a platinised iron ring, which moved smoothly over the glass guide-tube *E*, fixed to the underside of the stopper. This device ensured that the stirring conditions were the same in successive experiments. The electromagnet *M* was connected through a variable resistance to a set of accumulators, and an electrical-contact metronome was included in the circuit, so that the rate of stirring could be maintained constant at any desired value. The electromagnet was kept cool by passing a stream of cold water through a coil of lead tubing (telephone wire casing) wound tightly around it. The side-tube of the Beckmann vessel was closed with a rubber stopper through which passed the device for precipitating pellets of the solute into the vessel, and a small trap containing benzene or nitrobenzene served to indicate the speed of the nitrogen stream and prevent backward diffusion of air.

The Beckmann tube, stirrer, stopper, and thermometer were thoroughly dried by passing a stream of rigorously dried, slightly warm air through the apparatus for several hours. The benzene employed as solvent was fractionally crystallised four times, and distilled from sodium wire in a stream of dry nitrogen before use. In the preliminary experiments, the cryoscopic constant of benzene was determined by the use of highly pure specimens of triphenylmethane and triphenylcarbinol. During all the determinations, a slow stream of nitrogen gas passed into the vessel, and all manipulations were conducted without opening it. The nitrogen was drawn from a cylinder, and freed from traces of oxygen by passage over 2 feet of freshly reduced copper gauze maintained at red heat in a small furnace, and a small tube of phosphoric oxide placed before the glass delivery tube served to trap any water vapour which might be carried over from the rubber connexions.

An excess of molecular silver (about 3 g.), dried in a vacuum at 280° for 10 hours and cooled under pure nitrogen, was placed in the Beckmann tube together with a weighed amount of benzene. When four concordant readings of the f. p. had been obtained, pellets of 2 : 4′-dimethoxytriphenylmethyl chloride were precipitated into the liquid. All parts of the pellet press were degreased and dried in a desiccator before use. The mixture in the cryoscopic vessel was stirred at room temperature for 30—40 mins. to effect reduction of the chloride to the free radical. During this operation the vessel was covered with black paper to avoid photochemical decomposition of the radical. The vessel was then immersed in the freezing jacket, and the f. p. of the solution determined in the usual way. In the vicinity of the f. p. the metronome was adjusted for more rapid stirring, and the thermometer was subjected to continuous tapping to avoid sticking of the mercury thread. After the f. p. had been taken, the solution was allowed to acquire room temperature, and the stirring continued for a further 15 mins. before the f. p. was redetermined. The reduction of the chloride was complete when constant f. p.'s were obtained. Further pellets of the chloride were added, and the f. p. after reduction determined according to the same procedure.

Cryoscopic measurements were also carried out in nitrobenzene, which was purified by fractional distillation and fractional freezing, and the cryoscopic constant was determined by using triphenylmethane as solute. The results of the molecular-weight determinations in these solvents are recorded below.

Radical Stability of 2 : 4′-Dimethoxytriphenylmethyl.

Molecular weight of 2 : 4′ : 2″ : 4‴-tetramethoxyhexaphenylethane = 606.
,, ,, 2 : 4′-dimethoxytriphenylmethyl = 303.
Cryoscopic constants : benzene = 52·5; nitrobenzene = 75·3.

Solvent.		Weight of chloride, g.	Concn. of radical, %.	Δ.	*M*.	Radical stability, %.
C_6H_6	18·60 g.	0·3341	1·6	0·181°	472	28·4
		0·5049	2·4	0·266	479	26·8
	18·78 g.	0·3180	1·7	0·190	467	29·8
		0·5121	2·7	0·295	485	24·8
	18·77 g.	0·3352	1·8	0·195	481	26·0
		0·4199	2·2	0·252	466	30·1
$PhNO_2$	23·0 g.	0·3640	1·6	0·261	456	32·6
		0·5563	2·2	0·354	461	29·2
	23·2 g.	0·4321	1·9	0·312	451	34·5
		0·5697	2·5	0·399	464	31·0

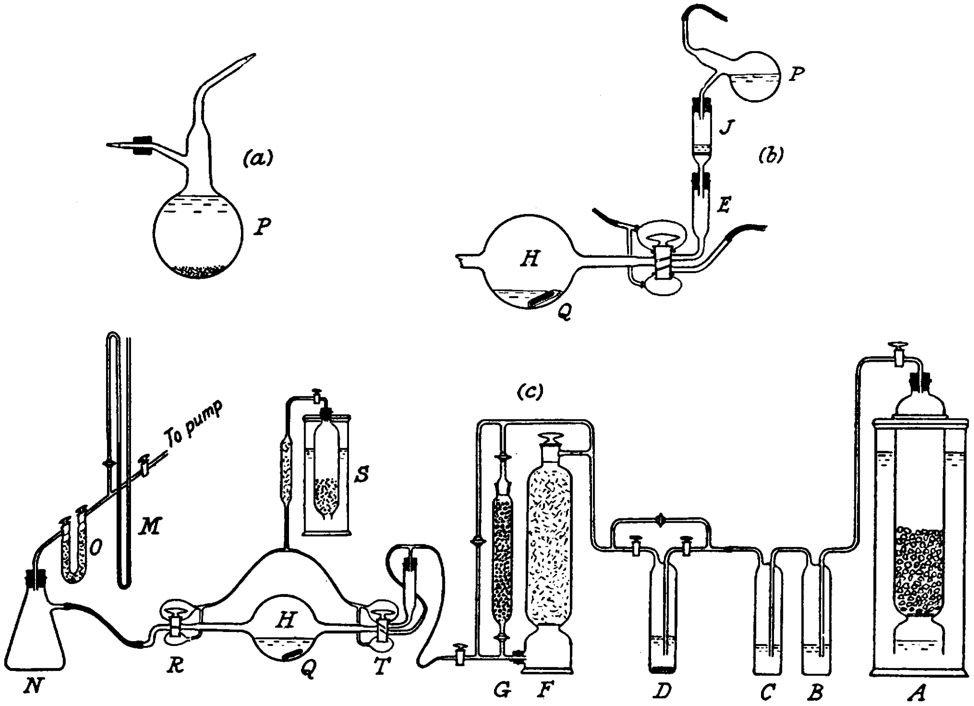
2 : 4′-Dimethoxytriphenylmethyl chloride dissolves in benzene to give a colourless solution, but a red colour is produced in nitrobenzene. The colour, however, becomes greatly intensified with increasing concentration of the radical, and a 2·5% solution is deep blood-red.

Isolation of the Radical.—Freshly recrystallised 2 : 4′-dimethoxytriphenylmethyl chloride (4 g.) and three times the calculated amount of molecular silver were placed in the flask *P* [Fig.

3(*a*)], and the air displaced with pure carbon dioxide. The vessel was charged with sodium-dried benzene (70—80 c.c.) under a stream of carbon dioxide, and the two arms sealed in the blow-pipe flame. The mixture was shaken for 4—6 hours on a rotary shaking machine in the dark.

A file mark was made near the end of each arm, and the vertical tube broken inside a rubber tube connected to a carbon dioxide generator. The other tube was then opened similarly and attached to the sintered-glass filter-tube *J*, which was fixed to the cup *E* of the concentrating apparatus *H* [Fig. 3(*b*)]. By partly evacuating the apparatus (previously filled with carbon dioxide), the reddish-yellow solution of the radical was drawn at a regulated speed through the filter into the bulb *H*. The flask and filter attachments were removed, and a carbon dioxide delivery tube fixed to the cup *E*. The apparatus at this stage is shown in Fig. 3(*c*) : *A* is a carbon dioxide generator containing Carrara marble and air-free hydrochloric acid, and *B* and *C* are wash-bottles containing silver nitrate and potassium permanganate, respectively. The vessel *D* contains triphenylmethyl (triphenylmethyl chloride, benzene, and mercury) to absorb traces of free oxygen from the carbon dioxide. This vessel was provided with three stopcocks, so that the solution could be cut out of the gas circuit during the final drying process. The tower *F* was charged with calcium chloride, which was rendered anhydrous and air-free by heating in an atmosphere of carbon dioxide. The small absorption tube *G* contained freshly activated silica gel, and was brought into the circuit during the final stages of the preparation in order to adsorb the benzene vapour carried over from the calcium chloride tower.

FIG. 3.



The stopcocks *R* and *T* of the concentrating apparatus *H* were fitted at the top and bottom with small rubber balloons, which were kept inflated with carbon dioxide from the auxiliary generator *S*. Although the hot benzene vapours rapidly remove the lubricant from the stopcocks, this device entirely prevents the intrusion of air during the isolation and drying of the free radical. The flask *N* served to receive the mother-liquor and washings after crystallisation of the solution, and communicated *via* the calcium chloride tube *O* with a manometer *M* and a suction pump.

Before the parts of the concentrating apparatus were sealed together, the inside of the bulb *H* was roughened by means of carborundum in order to avoid superheating and promote gentle evaporation of the solution. A further innovation was the mercury-filled scratcher *Q* which consisted of a small glass tube weighted with mercury and roughened on the outside by means of a carborundum wheel. When the apparatus was gently oscillated, the scratcher proved exceedingly efficacious in inducing crystallisation of the radical.

The benzene solution of the radical was evaporated in a small water-bath at 40—45° under a pressure of about 70 mm. in a slow stream of carbon dioxide. Every care was taken to avoid excessive heating in view of the disproportionation which triarylmethyls suffer at higher temperatures. After concentration of the solution to small bulk, the radical separated as a thick, reddish-yellow oil. Attempts to crystallise the radical from acetone and light petroleum (introduced through the cup *E*) were unsuccessful, but when the oil was covered with anhydrous ether (4 c.c.), heated to 30° to effect solution, and then cooled to 0°, it separated slowly as a pale yellow, crystalline solid. After standing for several hours, the yellowish-red mother-liquor was decanted through *R* into the receiver *N* The crystalline material, after being washed with small portions of cold ether, was similar in appearance to solid triphenylmethyl. The substance was dried *in situ* under reduced pressure in a slow stream of carbon dioxide. During this process the triphenylmethyl reagent in *D* was cut out of the circuit, and the gas led into the apparatus through the silica gel adsorbent.

The apparatus was broken midway between the bulb *H* and the stopcock *R*, and the substance transferred under a stream of carbon dioxide into a tube, which was then sealed. Under the microscope 2 : 4′ : 2″ : 4‴-tetramethoxyhexaphenylethane appeared as a mass of small plates, m. p. 80° (vac.).

To test the capacity of the radical to form addition compounds, the material was crystallised from ether at 0°, dried *in situ* at room temperature, and the solvent removed at 56° under 70 mm. in a stream of carbon dioxide for ½ hour. The loss in weight was not appreciable, and the m. p. of the substance was unchanged.

2 : 2′-*Dimethoxytriphenylmethyl.*

2 : 2′-*Dimethoxytriphenylmethyl Chloride.*—The carbinol was prepared in 44% yield by Baeyer's method (*Annalen*, 1907, **354**, 181) from *o*-anisylmagnesium iodide and methyl benzoate, and had m. p. 115°. It was converted into the chloride by means of acetyl chloride (2·5 mols.) in light petroleum, the dark brown solution being gently boiled for 1 hour. The *chloride* separated from light petroleum in rosettes, and after recrystallisation from ether–benzene, melted at 95° (Found: Cl, 10·3, 10·4. $C_{21}H_{19}O_2Cl$ requires Cl, 10·5%). It is readily soluble in benzene, but slightly soluble in ether and light petroleum. It reacts immediately with ethereal solutions of ferric and mercuric chlorides to form highly coloured addition compounds.

2 : 2′-*Dimethoxytriphenylmethyl Peroxide.*—Reduced solutions of the chloride in non-polar solvents are deep orange in colour. The solution of the radical absorbed 1 mol. of oxygen with great rapidity, but this was followed by a further slow absorption owing to oxidation of the peroxide. The peroxide, which is soluble in the ordinary organic solvents, was obtained by triturating with light petroleum the oil obtained by the rapid evaporation of the radical solution in the air. By rapid recrystallisation from benzene in an atmosphere of nitrogen or carbon dioxide, the *peroxide* was obtained as a white, finely divided solid, m. p. 110° (Found: C, 78·4; H, 6·2. $C_{42}H_{38}O_6$ requires C, 78·9; H, 6·0%); it gives a very slight coloration with concentrated formic, perchloric, and phosphoric acids, but immediately forms a deep brown colour with sulphuric acid.

Stability of the Radical.—The molecular weight of the radical system in benzene and nitrobenzene was determined by the indirect method described previously.

Radical Stability of 2 : 2′-*Dimethoxytriphenylmethyl.*

Molecular weight of 2 : 2′ : 2″ : 2‴-tetramethoxyhexaphenylethane = 606.
„ „ 2 : 2′-dimethoxytriphenylmethyl = 303.

Solvent.		Weight of chloride, g.	Concn. of radical, %.	Δ.	*M*.	Radical stability, %.
C_6H_6	19·89 g.	0·2867	1·4	0·174°	433	39·8
		0·4360	2·2	0·266	434	39·9
	19·23 g.	0·2794	1·3	0·165	417	45·2
		0·5360	2·5	0·303	433	39·8
	19·46 g.	0·3844	2·0	0·246	422	43·4
		0·5228	2·7	0·328	431	40·7
$PhNO_2$	22·5 g.	0·4046	1·6	0·311	390	55·5
		0·5401	2·1	0·410	395	53·5
	23·09 g.	0·4104	1·8	0·349	384	57·6
		0·5498	2·4	0·453	397	52·7

The chloride dissolves in benzene to form an almost colourless solution, but in nitrobenzene the colour is deep brown. As with the 2 : 4'-isomer, the stability of the radical is appreciably higher in nitrobenzene.

Isolation of 2 : 2'-*Dimethoxytriphenylmethyl.*—The reddish-yellow solution of the radical, prepared by reducing freshly recrystallised 2 : 2'-dimethoxytriphenylmethyl chloride (4 g.) with molecular silver (5 g.), was filtered under carbon dioxide into the concentrating apparatus, where the solvent was evaporated at 40—50° under 70 mm. The gummy residue dissolved readily in dry ether (3 c.c.) at room temperature. When the solution was cooled to −15°, it deposited the radical as small, pale yellow crystals. The solid, after being washed thrice with cold ether–light petroleum, and dried for 1 hour in a stream of carbon dioxide, had m. p. 88° (vac.). It dissolved readily in non-polar solvents to give yellowish-red solutions, but the deep brown colour in liquid sulphur dioxide was so intense that a 2-cm. layer of the solution appeared almost black.

When the solid was dried at 55° under 70 mm. of carbon dioxide, it turned pink and caked together in the course of 45 mins. The brittle mass thus obtained melted at 85—86° (vac.). The radical did not form an addition compound with ether under the above conditions of crystallisation.

The absorption of iodine by benzene solutions of the radical amounted to 25% of the theoretical value for complete absorption. Although this is much higher than the value found for 2 : 4'-dimethoxytriphenylmethyl, the results indicate that the polymethoxytriphenylmethyl iodides are thermally less stable than triphenylmethyl iodide, so the equilibrium in the former case is largely in favour of the radical.

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