# 232. Free Radicals and Radical Stability. Part XI. Methyltriphenylmethyls.

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The influence of methyl substituents in triphenylmethyl and its homopolar and ionised derivatives has been studied. The group increases the basicity of the carbinol and the halochromism of the salts, but in lesser degree than methoxyl. Solutions of the sulphates containing methyltriphenylmethyl cations are photosensitive. The rate of thermal decomposition of the methyltriphenylmethyl formates is lower than that of the corresponding methoxyl derivatives, and the reduction of the carbinols to the corresponding methanes is best effected by zinc and acetic acid. The methyl group increases the electrical conductivity of triphenylmethyl chloride in liquid sulphur dioxide and more effectively in the *o*- and *p*-positions than in the *m*-position.

The internal changes suffered by the free radical systems have been examined by methods involving photoelectric and tintometric detection of colour changes, as well as by oxygen-absorption methods. The tendency to isomerise decreases in the following sequence: diphenyl-*p*-tolyl-, diphenyl-*m*-tolyl-, 2 : 5-dimethyltriphenyl-, diphenyl-*o*-tolyl-, triphenyl-methyl.

The new radicals diphenyl-*m*-tolyl- and 2 : 5-dimethyltriphenyl-methyl are orange-yellow, and rapidly absorb nearly the theoretical amount of oxygen with formation of crystalline peroxides and isomeric oxidation products. Solutions of the radicals in benzene rapidly absorb iodine, but the iodides thus formed are dissociated to a greater extent than triphenylmethyl iodide. The radical systems are decolorised in direct sunlight. Molecular-weight determinations show that the methyl substituent increases the unimolecular stability of triphenylmethyl in accordance with the wave-mechanical theory of radical stability.

In continuation of the study of the influence of the methyl substituent in triarylmethyls, we have now examined the behaviour of the three isomeric diphenyltolylmethyls and 2 : 5-dimethyltriphenylmethyl. Motwurf (*Ber.*, 1903, **37**, 3153) had noted that tri-*p*-tolylcarbinol is more basic than triphenylcarbinol and that the three methyl groups are roughly equivalent to one *p*-methoxyl in enhancing the basicity. The results of the present work are included in Table I. It is evident that the methyl group in the *m*-position has nearly the same effect as methoxyl, whereas in the *p*-position it is much less effective in enhancing the basicity of the hypothetical base corresponding to the carbonium salts. Moreover, the methyl substituent does not induce such strong halochromism in these derivatives.

TABLE I.

| | Basicity and halochromism. | | Thermal stability of formate. | |
|---|---|---|---|---|
| | Basicity of carbinol. | Colour of sulphate. | Decompn. temp. | Time (mins.) for 20% decompn. at 77°. |
| Triphenylmethyl | 1·0 | Yellow | 49° | 13·0 |
| *o*-Methoxytriphenylmethyl | 1·97 | Deep red | 48 | 2·0 |
| *m*-Methoxytriphenylmethyl | 1·17 | Orange red | 48 | 12·0 |
| *p*-Methoxytriphenylmethyl | 6·5 | Deep red | 49 | 3·2 |
| *o*-Methyltriphenylmethyl | 1·5 | Orange | 49 | 12·5 |
| *m*-Methyltriphenylmethyl | 1·1 | Orange | 44 | 34·0 |
| *p*-Methyltriphenylmethyl | 1·6 | Orange | 38 | 11·5 |
| 2 : 5-Dimethyltriphenylmethyl | 2·3 | Deep orange | 37 | 12·7 |

Lifschitz and Joffe (*Z. physikal. Chem.*, 1921, **97**, 426) found that colourless solutions of certain triphenylmethane derivatives and especially the leuco-cyanides become coloured on exposure to near ultra-violet light. Since the generation of colour is accompanied by an increase in the electrical conductivity of the solutions, these authors advanced the hypothesis that irradiation induces ionisation of the homopolar derivatives. We find in a similar way that the polar triarylmethyl sulphates are photosensitive and slowly change colour on exposure to direct sunlight. The colour deepens in those solutions containing the triarylmethyl cation, and the change is therefore fundamentally different from that involved in the decolorisation of solutions of the corresponding neutral radicals on irradiation.

In accordance with the behaviour of the majority of simple triarylmethyl formates, the methyl-substituted derivatives decompose on heating with evolution of carbon dioxide and formation of the triarylmethane. As shown in Table I, the methyl substituent induces a much slower decomposition than the methoxyl group, and as may be expected on electronic grounds, there is a marked difference in the effect of these two groups in the *o*- and in the *p*-position. It is evident, accordingly, that the preparation of methyltriphenylmethanes by heating the carbinols with formic acid is not so efficacious as the process involving the use of zinc and acetic acid. The methyltriphenylmethyl chlorides dissolve in ordinary organic solvents to produce colourless systems, but their solutions in liquid sulphur dioxide are deep orange and exhibit a high electrical conductivity. Measurements at — 10° show that the methyl substituent increases the molecular conductivity in the sequence $p > o > m$.

For the purpose of ascertaining whether the solutions of the neutral radicals suffer internal changes such as isomerisation or disproportionation, we have employed photoelectric and tintometric methods for recording slight changes in the colour of the systems. These methods reveal that isomerisation is slow in triphenyl-, diphenyl-*o*-tolyl-, and 2 : 5-dimethyltriphenyl-methyl, but more rapid with diphenyl-*m*-tolylmethyl. In comparison with these radicals, however, diphenyl-*p*-tolylmethyl is much more susceptible to internal changes of this kind. The orange solutions of diphenyl-*m*-tolyl- and 2 : 5-dimethyltriphenyl-methyl are extremely reactive and are decolorised in air with the formation of colourless peroxides, which are precipitated in the crystalline condition if the oxidation is conducted in ethereal solution. Although the amount of oxygen absorbed by the freshly prepared free radical is nearly quantitative, the yield of peroxide is well below this value owing to the formation of an isomeric oxidation product, which may be isolated as a yellowish-red oil after the oxidation process. This behaviour is also exhibited by triphenylmethyl, which gives a 70% yield of the peroxide together with a yellow oil of unknown constitution. The methyltriphenylmethyls combine with iodine in benzene solution to form equilibrium mixtures of the radical system and triarylmethyl iodide. A comparison of these equilibria with that found in the case of triphenylmethyl shows that the dissociation of the triarylmethyl iodide is slightly increased by the presence of methyl substituents.

The action of direct sunlight on triphenylmethyl leads to decolorisation of the solution and the formation of diphenylbisdiphenylene-ethane and triphenylmethane through autoxidation and reduction (Schmidlin and García-Banús, *Ber.*, 1912, **45**, 1344; Bowden and Jones, J., 1928, 1149). The methyl-substituted radicals undergo a similar reaction and the photosensitivity decreases in the following sequence : diphenyl-*p*-tolyl-, triphenyl-, diphenyl-*m*-tolyl-, diphenyl-*o*-tolyl-, 2 : 5-dimethyltriphenyl-methyl.

Cryoscopic determinations of the molecular weight of diphenyl-*m*-tolylmethyl and 2 : 5-dimethyltriphenylmethyl in benzene show that the dissociation of the corresponding ethanes is greater than that of hexaphenylethane. Although the measured degree of dissociation is higher than might have been expected, there is little doubt that the presence of methyl substituents serves to increase the unimolecular stability of the radical. As pointed out in Part X (this vol., p. 883), this is in harmony with the wave-mechanical theory of radical stability.

## EXPERIMENTAL.

### *Methyltriphenylcarbinols and Halochromic Salts.*

*Diphenyl-*m*-tolylcarbinol.*—The following modifications of previous methods (Acree, *Ber.*, 1904, **37**, 998) were employed. (*a*) The filtered solution of *m*-tolylmagnesium bromide [from *m*-bromotoluene (20 g.), magnesium (3·5 g.), and ether] was slowly treated with an ethereal solution of benzophenone (12 g.), and the mixture heated gently for 4 hours. After decomposition of the triarylmethoxymagnesium bromide with ice and sulphuric acid, the dried ethereal solution was evaporated, and the residue distilled under reduced pressure. The carbinol was obtained as a yellow viscous oil, b. p. 219—223°/2 mm. (*b*) Methyl *m*-toluate (35 g.) was added in small portions to a filtered solution of phenylmagnesium bromide [from bromobenzene (80 g.), magnesium (17 g.), and ether (270 c.c.)], the mixture being vigorously shaken after each addition. After 3 hours' heating on an electric lamp, the reaction mixture was hydrolysed in the usual way. The carbinol was obtained on removal of the ether; it distilled at 220—229°/5 mm. and solidified on standing; recrystallised from ligroin, it was obtained in small colourless crystals, m. p. 65°. This method of preparation is superior to the preceding one with respect to both yield and ease of isolation.

Acree (*loc. cit.*) stated that diphenyl-*m*-tolylcarbinol is hygroscopic. Since there seemed to be no reason why this compound should differ in this respect from other triarylcarbinols, we have compared its behaviour with that of triphenylcarbinol, known weights of the two carbinols (subjected to identical powdering processes) being exposed to an atmosphere saturated with aqueous vapour, and the increase in weight observed at intervals. The gain in weight, in g. per mol. of carbinol, at room temperature is given below :

| | Diphenyl-*m*-tolylcarbinol. | | Triphenylcarbinol. | |
|---|---|---|---|---|
| Time (days). | Wt. of carbinol, g. | Increase, g. per mol. | Wt. of carbinol, g. | Increase, g. per mol. |
| 0 | 0·9060 | 0 | 0·6830 | 0 |
| 1 | 0·9068 | 0·2543 | 0·6840 | 0·3807 |
| 2 | 0·9081 | 0·6676 | 0·6864 | 1·2940 |
| 3 | 0·9095 | 1·112 | 0·6892 | 2·741 |
| 4 | 0·9109 | 1·558 | 0·6931 | 4·226 |
| 6 | 0·9116 | 1·780 | 0·6935 | 4·378 |
| 7 | 0·9150 | 2·861 | 0·6935 | 4·378 |

It is evident from these results that the *m*-tolyl derivative is actually less hygroscopic than triphenylcarbinol.

*Diphenyl-*p*-tolycarbinol.*—The carbinol, prepared from the magnesium derivative of *p*-bromotoluene and benzophenone by the method described above, was isolated by allowing it to separate slowly from ethereal solution or by direct distillation under reduced pressure (Acree, *loc. cit.*). Recrystallised from ligroin, it melted at 73—74°.

2 : 5-*Dimethyltriphenylcarbinol*.—2 : 5-Dimethylbenzophenone was obtained by a modification of the method of Elbs (*J. pr. Chem.*, 1887, **35**, 472). Dry, freshly distilled *p*-xylene (58 g.), benzoyl chloride (39 c.c.), and carbon disulphide (80 c.c., purified by standing over aluminium chloride) were treated with small quantities of powdered aluminium chloride (81 g.). The mixture was kept for a day and then heated over a lamp heater for 8 hours. The carbon disulphide was removed by distillation, and the well-cooled mass treated with ice and hydrochloric acid. Steam was passed through the mixture for 2 hours to effect complete hydrolysis of the dichloride, and the ethereal extract was dried for a short time over calcium chloride. After removal of the solvent the ketone distilled at 193—196°/20 mm.; yield 55%.

An ethereal solution of the ketone (63 g.) was added to the filtered Grignard reagent prepared from bromobenzene (51 g.) and magnesium (10·7 g.). When the initially vigorous reaction had subsided, the solution was heated on a steam-bath for 4 hours. The mixture was decomposed with ice and sulphuric acid, and the well-washed ethereal solution dried and concentrated. The *carbinol* separated in perfectly white crystals, m. p. 108·5° after recrystallisation from alcohol; yield 60% (Found : C, 87·5; H, 6·8. $C_{21}H_{20}O$ requires C, 87·5; H, 6·95%).

*Halochromic Properties of Methyltriphenylmethyl Derivatives.*—The basicity values of the true bases corresponding to the cations of the triarylmethyl salts were determined by Baeyer's method, and the results are listed in Table I. The slight increase of basicity produced by the methyl substituent is seen by comparing the basicity values with those of the corresponding methoxy-substituted derivatives. In both series, however, the substituent in the *m*-position exerts the minimum influence, and the greatest difference is apparent in the *p*-position.

For the purpose of furnishing a simple numerical measure of the halochromism exhibited by carbonium salts, we have specified the colour of the sulphate in terms of Lovibond units. The colour value of a concentrated sulphuric acid solution containing $10^{-5}$ g. of the carbinol per c.c. was determined tintometrically in a cell (1 × 1 cm.) closed with a lightly greased cover-slip to prevent ingress of moisture. The Lovibond units of the sulphates were as follows : triphenylmethyl, 10·5 yellow; diphenyl-*o*-tolylmethyl, 23 yellow; diphenyl-*m*-tolylmethyl, 19·5 yellow; diphenyl-*p*-tolylmethyl, 16 yellow, 0·1 blue; 2 : 5-dimethyltriphenylmethyl, 23 yellow, 3 red, 0·1 neutral. These values show that the methyl group in the *m*-position is less effective in enhancing the halochromism than in the *o*- and *p*-positions. This influence of orientation, however, is still more pronounced in the case of methoxyl substituents.

In view of the fact that colourless solutions of certain triphenylmethane derivatives become coloured on exposure to near ultra-violet radiation (Lifschitz and Joffe, *loc. cit.*), the behaviour of the polar sulphates is of interest. For the purpose of ascertaining whether these derivatives are photosensitive, 0·00005M-solutions of the carbinols in concentrated sulphuric acid were exposed to direct sunlight in sealed tubes, and the colour values observed at intervals by means of a tintometer. The colour change in Lovibond units is given in the following table. Control

*Colour Change in Triarylmethyl Sulphates on Irradiation.*

*Triphenylmethyl sulphate.*

| Time (hours) | 0·75 | 1·5 | 2·0 | 4·0 | 10 |
|---|---|---|---|---|---|
| Colour change | 1 yellow | 3 yellow | 4 yellow | 4 yellow, 0·5 red | 5 yellow, 1 red |

*Diphenyl-*o*-tolylmethyl sulphate.*

| Time (hours) | 0·75 | 1·5 | 10 | 17 |
|---|---|---|---|---|
| Colour change | 0·7 red | 0·8 yellow, 1·1 red | 0·8 yellow, 1·6 red | —9 yellow, 1·7 red |

*Diphenyl-*m*-tolylmethyl sulphate.*

| Time (hours) | 0·75 | 1·5 | 2 | 10 | 17 |
|---|---|---|---|---|---|
| Colour change | 0·2 red | 0·8 red | 1 red | 1·5 red | 2 red |

*Diphenyl-*p*-tolylmethyl sulphate.*

| Time (hours) | 0·75 | 2 | 10 | 17 |
|---|---|---|---|---|
| Colour change | 3·1 yellow | 3·1 yellow, 0·4 red | 3·1 yellow, 1·5 red | 5·4 yellow, 2·4 red |

2 : 5-*Dimethyltriphenylmethyl sulphate.*

| Time (hours) | 10 | 17 |
|---|---|---|
| Colour change | 0·9 red | 1·2 red |

solutions preserved in the dark exhibited little change of colour, and it is evident therefore that these solutions containing triarylmethyl cations are photosensitive. This photochemical effect may account in some measure for the divergences apparent in the recorded absorption spectra of these derivatives.

In this connexion we have examined the photosensitivity of solutions containing the neutral radicals. Freshly prepared 0·5% solutions of the free radicals in benzene were exposed in sealed tubes to direct sunlight. Diphenyl-*p*-tolylmethyl was decolorised in 0·5 min., triphenylmethyl in 2·5 mins., and diphenyl-*m*-tolylmethyl in 4·5 mins. Although solutions of diphenyl-*o*-tolylmethyl and 2 : 5-dimethyltriphenylmethyl lost much of their colour, they were not completely decolorised after 5 hours' irradiation. There appears to be no simple connexion between the photosensitivity of the cation and of the neutral radical.

*Reduction of Carbinols.*—The reduction of the carbinols by formic acid, which involves the thermal decomposition of the coloured triarylmethyl formate, was examined by the procedure described in Part VIII (this vol., p. 879), and the results are summarised in Table I. Actually, the methyl group has comparatively little effect on the rate of reduction in the early stages of the reaction; *e.g.*, the rate of evolution of carbon dioxide from a formic acid solution of 2 : 5-dimethyltriphenylmethyl formate at 77° is low and only 35% of the theoretical amount is evolved in one hour. Accordingly, the method is not a suitable one for the preparation of the corresponding methane.

2 : 5-*Dimethyltriphenylmethane* was prepared by boiling the red solution of the carbinol in glacial acetic acid with zinc dust. After 3 hours the colour was discharged, and the filtered solution deposited crystals of the methane on cooling, m. p. 91° after recrystallisation from alcohol; yield, 70% (Found : C, 91·9; H, 7·2. $C_{21}H_{20}$ requires C, 92·65; H, 7·35%).

### *Methyltriphenylmethyl Chlorides.*

*Diphenyl-*m*-tolylmethyl Chloride.*—(*a*) A solution of diphenyl-*m*-tolylcarbinol (10 g.) in dry ether (10 c.c.) was saturated with hydrogen chloride at 0°. For the purpose of absorbing the water generated in the reaction, a small perforated glass basket containing a few lumps of anhydrous calcium chloride was suspended in the solution. After standing overnight in the stoppered flask, the calcium chloride container was withdrawn, and the solution filtered in a stream of dry air. Recrystallised from light petroleum, the hard, white crystals melted at 71° (Found: Cl, 12·3. $C_{20}H_{17}Cl$ requires Cl, 12·1%). (*b*) The finely powdered carbinol (2 g.) was suspended in dry light petroleum (2—3 c.c.) and treated with acetyl chloride (2 c.c.); the mixture was maintained near the b. p. for 15—20 mins. After standing for several days, the triarylmethyl *chloride* was deposited, and was purified as described above. The first method is more convenient for preparation of the pure material.

2 : 5-*Dimethyltriphenylmethyl Chloride.*—A solution of the carbinol (5 g.) in 25 c.c. of dry ether was saturated with hydrogen chloride in the presence of calcium chloride as described above. The triarylmethyl *chloride* separated very rapidly, and was obtained perfectly white after recrystallisation from ether–benzene; m. p. 128·5° (Found: Cl, 11·5. $C_{21}H_{19}Cl$ requires Cl, 11·6%). This chloride forms addition compounds with zinc chloride and ferric chloride, and the halochromism is more pronounced than in the corresponding derivatives of diphenyl-*m*-tolylmethyl chloride.

In the following experiments, the triarylmethyl chlorides were always freshly prepared, and stored in desiccators charged with sulphuric acid or calcium chloride together with soda-lime for the removal of acid vapours and freshly-activated silica gel for the removal of solvent vapours.

*Conductivity in Liquid Sulphur Dioxide.*—The fact that triphenylmethyl chloride dissolves in liquid sulphur dioxide to form a yellow, conducting solution was reported independently by Gomberg (*Ber.*, 1902, **35**, 2402) and Walden (*ibid.*, p. 2018). Although further measurements have been made by Gomberg and his collaborators (*ibid.*, 1903, **36**, 3928; *J. Amer. Chem. Soc.*, 1922, **44**, 1818; 1923, **45**, 206) and by Straus and Dutzmann (*J. pr. Chem.*, 1921, **103**, 66), the data are not sufficiently extensive to permit of any systematic correlation of the effects of various substituents on the conductivity of triarylmethyl chlorides. We have therefore measured the conductivity of the methyltriphenylmethyl chlorides in order to trace the influence of orientation.

The conductivity vessel consisted of a stout, graduated cylinder provided with a stopper through which passed glass tubes holding the electrodes. The stopper also carried a long inlet tube and a short outlet tube with stopcocks for charging the vessel with sulphur dioxide. The platinum electrodes (2 cm. in diameter) were separated by a distance of 5 mm., and the cell constant was determined with 0·02N-potassium chloride.

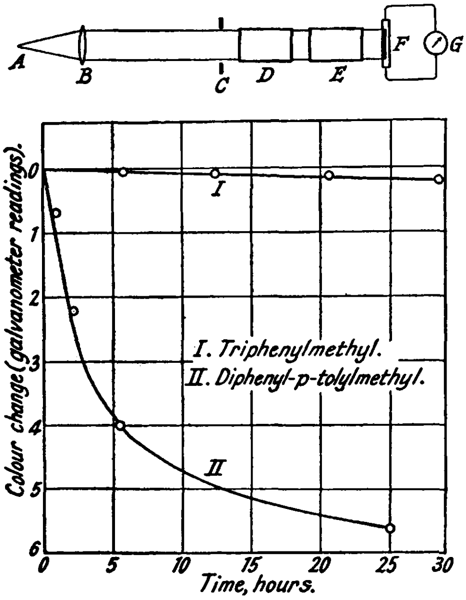
The cell was charged with solvent by immersing it in a freezing mixture at − 15° and leading into the vessel a slow stream of sulphur dioxide dried by passage through a 70-cm. column of fresh phosphoric oxide. After condensation of the requisite volume of liquid, the cell was immersed in a Dewar flask charged with liquid sulphur dioxide at the b. p. (− 10°). The measurements were carried out with a standard conductivity bridge and a shielded valve oscillator (Cambridge Instrument Co.). The results are appended in the following table, where *v* is the dilution in litres and Λ is the equivalent conductivity.

| | | | | | | |
|---|---|---|---|---|---|---|
| Triphenylmethyl chloride | *v* | 963·4 | 274·6 | 94·79 | 29·20 | 20·67 |
| | Λ | 43·19 | 27·92 | 17·74 | 10·88 | 9·65 |
| Diphenyl-*o*-tolylmethyl chloride | *v* | 909·5 | 511·8 | 146·2 | 40·68 | |
| | Λ | 79·12 | 78·12 | 64·12 | 47·46 | |
| Diphenyl-*m*-tolylmethyl chloride | *v* | 997·0 | 329·1 | 106·5 | 38·20 | 26·2 |
| | Λ | 63·98 | 45·04 | 28·04 | 19·37 | 16·9 |
| Diphenyl-*p*-tolylmethyl chloride | *v* | 778·0 | 103·1 | 29·88 | 20·43 | |
| | Λ | 113·0 | 71·25 | 51·02 | 46·61 | |
| 2 : 5-Dimethyltriphenylmethyl chloride | *v* | 578·6 | 222·6 | 88·39 | 30·28 | 22·76 |
| | Λ | 87·52 | 79·56 | 71·68 | 56·54 | 54·94 |

The orange solutions of these methyltriphenylmethyl derivatives are more conducting than the yellow solution of triphenylmethyl chloride, and the influence of orientation may be expressed : $p > o > m$.

### *Methyltriphenylmethyls.*

*Isomerisation of the Free Radicals.*—Solutions of diphenyl-*p*-tolylmethyl lose their colour on standing in the dark (Gomberg, *Ber.*, 1904, **37**, 1632) owing to isomerisation of the radical and formation of colourless, saturated derivatives. In our search for methyl-substituted radicals endowed with greater internal stability, it became necessary to have available a method of investigating the radical in an isolated system. With this end in view we have examined the applicability of photoelectric methods of measuring slight colour changes in free-radical solutions. The apparatus is shown schematically in the diagram, where *A* is a 60-watt Osram lamp, *B* a convex lens, *C* a metal shutter, *D* an optically polished all-glass cell (2 cm. long) containing a standard solution of malachite-green, and *E* a similar cell charged with the free-radical solution (0·5% concn.) under study. The photoelectric cell *F* (Westinghouse " Blue-green " copper–cuprous oxide type) was connected to a sensitive galvanometer *G*. Since the radicals under investigation are yellow or reddish-yellow, light passing through the green-blue filter and the yellow radical solution produces little output from the photoelectric cell. When, however, the radical solution begins to lose colour, the solution will pass more green-blue light, which produces a corresponding output from the cell. Accordingly, the photo-current registered by the galvanometer furnishes a measure of the change of colour. Obviously, if the solution of the radical is stable, the photo-current will remain constant. This method applied to triphenylmethyl showed that this radical does not undergo appreciable isomerisation in benzene at room temperature. The results obtained with diphenyl-*p*-tolylmethyl are represented graphically in the diagram, and it is evident that the methyl group in the *p*-position induces fairly rapid isomerisation of the radical.



A simpler and more convenient method of detecting constitutional changes in the radical system is furnished by tintometric observations of the colour of the solution. In applying this method, the radical solution was prepared by reduction of a benzene solution of the pure triarylmethyl chloride by molecular silver in a sintered-glass filter through which a stream of oxygen-free nitrogen passed upwards. When reduction was complete, the stream of nitrogen was diverted to the top of the filter so that the solution was forced into a constricted tube, which was then sealed in a small blowpipe flame. The solution was kept in the dark until required for examination. The colour values in Lovibond units are recorded in the following table.

| | Colour of original solution. | | Colour after 4 days. | |
|---|---|---|---|---|
| | Yellow. | Red. | Yellow. | Red. |
| Triphenylmethyl | 9·9 | 2·5 | 9·9 | 2·4 |
| Diphenyl-*o*-tolylmethyl | 29·9 | 3·5 | 29·9 | 2·5 |
| Diphenyl-*m*-tolylmethyl | 29·9 | 2·9 | 11·0 | 2·2 |
| Diphenyl-*p*-tolylmethyl | 10·0 | 3·4 | 2·0 | 0·2 |
| 2 : 5-Dimethyltriphenylmethyl | 29·9 | 5·0 | 29·9 | 2·4 |

This method can be used for estimating the rate of isomerisation and for ascertaining whether the molecular weight of the radical system can be determined by the application of ordinary cryoscopic methods. The results indicate that isomerisation is most rapid in the case of diphenyl-*p*-tolylmethyl; with the exception of the *m*-derivative, the other radicals isomerise relatively slowly.

*Reaction with Oxygen.*—The volume of oxygen absorbed by freshly prepared solutions of the radicals in bromobenzene was determined at 20° by means of the apparatus described in Part X. The results of typical experiments are given below, volumes being corrected to *N.T.P.* The rate of absorption is similar to that found for triphenylmethyl, but the total amount absorbed is slightly lower.

*Diphenyl*-m-*tolylmethyl.*

Weight of diphenyl-*m*-tolylmethyl chloride = 0·404 g.

| Time (secs.) | 15 | 50 | 70 | 100 | 160 | 240 | 900 |
|---|---|---|---|---|---|---|---|
| $O_2$ absorbed, c.c. | 4·7 | 8·5 | 11·3 | 12·1 | 12·9 | 13·1 | 14·4 |
| Absorption, % | 30·4 | 55·0 | 73·1 | 78·1 | 83·4 | 84·7 | 93·0 |

2 : 5-*Dimethyltriphenylmethyl.*

Weight of 2 : 5-dimethyltriphenylmethyl chloride = 0·497 g.

| Time (secs.) | 15 | 40 | 60 | 120 | 360 |
|---|---|---|---|---|---|
| $O_2$ absorbed, c.c. | 8·8 | 12·7 | 15·7 | 17·6 | 17·7 |
| Absorption, % | 48·5 | 69·9 | 86·4 | 96·9 | 97·5 |

*Diphenyl*-m-*tolylmethyl Peroxide.*—An ethereal solution of the chloride was shaken with excess molecular silver in a sealed tube protected from light. When reduction was complete, the clear orange solution of the free radical was rapidly siphoned into another vessel, where it was oxidised by a current of air. Although the solution was not completely decolorised as in the case of triphenylmethyl, the *peroxide* was deposited in fine white crystals, m. p. 155°; yield 36% (Found: C, 88·1; H, 6·4. $C_{40}H_{34}O_2$ requires C, 87·9; H, 6·2%).

2 : 5-*Dimethyltriphenylmethyl Peroxide.*—The solution of the chloride was reduced by excess mercury as described above. On oxidation of the radical, the solution was rapidly decolorised, and the *peroxide* was precipitated as a fine powder; purified by rapid recrystallisation from hot carbon disulphide, it melted at 157°; yield 78% (Found: C, 87·9; H, 6·6. $C_{42}H_{38}O_2$ requires C, 87·8; H, 6·6%).

*Reaction with Iodine.*—Titration of the free-radical solution with a standard solution of iodine in benzene under an atmosphere of nitrogen at 19° showed that diphenyl-*m*-tolylmethyl absorbed 40·5% and 2 : 5-dimethyltriphenylmethyl 59·5% of the theoretical value for one atomic equivalent. The corresponding absorptions for other radicals are: triphenylmethyl 70%, *m*-methoxytriphenylmethyl 60%, and 2 : 5-dimethoxytriphenylmethyl 53%. If, therefore, we assume that the rate of isomerisation of the methyl-substituted radicals is not increased by the presence of iodine, it follows that the methyltriphenylmethyl iodides are dissociated to a greater extent than the iodides of triphenylmethyl and the methoxytriphenylmethyls.

*Unimolecular Stability of the Radicals.*—The molecular-weight determinations were carried out according to the procedure described in Part X with due regard to the precautions for minimising isomerisation.

*Diphenyl*-m-*tolylmethyl.*

Molecular weight of tetraphenyldi-*m*-tolylethane = 514.
,, ,, diphenyl-*m*-tolylmethyl = 257.
Benzene, *K* = 52·5°.

| Solvent, g. | Weight of chloride, g. | Concn. of radical, %. | $\Delta$. | *M*. | Unimolecular stability, %. |
|---|---|---|---|---|---|
| 18·1 | 0·5306 | 2·8 | 0·312° | 433·4 | 18·6 |
| — | 0·6754 | 3·3 | 0·410 | 419·9 | 22·4 |
| 18·0 | 0·5536 | 2·8 | 0·342 | 412·6 | 24·6 |

### 2 : 5-*Dimethyltriphenylmethyl.*

Molecular weight of 2 : 5 : 2′′′′ : 5′′′′-tetramethylhexaphenylethane = 542.
,, ,, 2 : 5-dimethyltriphenylmethyl = 271.

| Solvent, g. | Weight of chloride, g. | Concn. of radical, %. | Δ. | *M*. | Unimolecular stability, %. |
|---|---|---|---|---|---|
| 18·0 | 0·2551 | 1·3 | 0·151° | 433·2 | 25·2 |
| | 0·4301 | 2·1 | 0·253 | 436·0 | 24·9 |
| | 0·5153 | 2·5 | 0·304 | 434·7 | 24·8 |
| 18·1 | 0·3032 | 1·5 | 0·179 | 434·5 | 24·8 |
| | 0·4496 | 2·2 | 0·257 | 448·8 | 20·8 |
| 18·1 | 0·5696 | 2·8 | 0·331 | 441·6 | 22·8 |
| | 0·7954 | 3·9 | 0·471 | 433·3 | 25·2 |

At the conclusion of the determinations the solution was filtered from silver and silver chloride and oxidised by a current of air. The fact that 2 : 5-dimethyltriphenylmethyl was recovered in the form of peroxide in even higher yield (average 77%) than triphenylmethyl under similar conditions indicates that the radical does not suffer appreciable isomerisation during the period required for the cryoscopic measurements. As expected from the preliminary experiments, the results for diphenyl-*m*-tolylmethyl were more variable and the yield of peroxide was lower.

*Isolation of the Associated Radicals.*—The bright yellow solution of diphenyl-*m*-tolylmethyl in benzene was transferred to the isolation apparatus described in Part II (J., **1939**, 33), and evaporated to small bulk at 40° under reduced pressure in a slow stream of carbon dioxide. The concentrated solution showed no tendency to crystallise on cooling, and the radical remained as a yellow oil on removal of the solvent. The oil dissolved readily in warm acetone, ether, and light petroleum, but the solutions did not crystallise even after prolonged application of the devices normally employed for inducing crystallisation of radical solutions. The ethereal solution was finally treated with oxygen in order to obtain the peroxide. In similar experiments with 2 : 5-dimethyltriphenylmethyl, the radical was isolated as a light red oil, which gave the peroxide on oxidation.

The fact that the radicals showed little tendency to crystallise is reminiscent of the behaviour of certain methoxytriphenylmethyls which, though isolated only as oils, are chemically stable and may be investigated in solution by the usual physicochemical methods.

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