

172. *Free Radicals and Radical Stability. Part X. The Influence of the Methyl Group on the Stability of Triphenylmethyl.*

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The methyltriphenylmethyls hitherto prepared are so prone to isomerise that the unimolecular stability cannot be ascertained by the usual methods. In a search for methyl-substituted radicals of greater chemical stability, we have prepared diphenyl-*o*-tolylmethyl, which shows a much smaller tendency to isomerise than the corresponding *p*-derivative. In fact, the transformation into the Tschitschibabin type of compound is sufficiently slow to permit of molecular-weight determinations on the free radical system by the cryoscopic method. In benzene the radical is pale yellow, and the solution rapidly absorbs the theoretical amount of oxygen to form a peroxide, which may be isolated in the usual way.

The radical stability in 2% benzene solution at the freezing point is about 20%. The influence of the methyl group is discussed from the standpoint of recent theories of radical stability, and it is shown that the group increases the tendency to dissociation when directly linked to ethane carbon atoms and when present as a nuclear substituent in hexaphenylethane.

GOMBERG (*Ber.*, 1904, **37**, 1632) found that the introduction of a methyl group into the *p*-position of one or more of the phenyl groups in triphenylmethyl gave unstable radicals, which were so prone to isomerise to the Tschitschibabin derivative that it was not possible to apply rigorous methods of molecular-weight determination. Moreover, it was necessary to effect oxidation of the radical at the moment of formation in order to obtain the corresponding peroxide. Expecting that the tendency to isomerise would be diminished if the methyl group were introduced in another position, we have prepared diphenyl-*o*-tolylmethyl by the reduction of the corresponding chloride with molecular silver. The radical is yellow in benzene solution, and the colour is discharged with the formation of a colourless peroxide. For the purpose of ascertaining the extent of isomerisation suffered by diphenyl-*o*-tolylmethyl, the life of the radical was examined by measuring the volume of oxygen absorbed after various intervals. When a solution of diphenyl-*o*-tolylmethyl chloride is reduced by an excess of molecular silver in an atmosphere of oxygen, the gas absorbed amounts to 103—107% of the theoretical value corresponding to true peroxide formation. There is accordingly a further slow oxidation of the peroxide or the accompanying isomeric derivative similar to that found with the methoxytriphenylmethyl compounds. When the radical is prepared in sealed tubes and kept in the dark for periods ranging up to 2 hours, the oxygen absorption still corresponds closely to the theoretical value. This proves that no appreciable isomerisation of the radical into the saturated Tschitschibabin derivative occurs during this period, and molecular-weight determinations may therefore be carried out on the freshly-prepared solutions in accordance with the normal procedure.

The dissociation of hexa-arylethanes into free radicals may be formally envisaged as involving two main processes: (1) the rupture of the ethane linkage and (2) the stabilisation of the resulting free radicals. The earlier theories, which referred mainly to the first process, ascribed the weakening of the ethane linkage to (*a*) steric factors arising from the large size of the aryl groups, or (*b*) the affinity demand of the aryl groups. The steric theory, however, does not give a complete representation of the facts, and there is no strict parallelism between the degree of dissociation and the size of the groups. That steric factors are operative in certain reactions of triarylmethyl derivatives is indicated by other experiments in this laboratory, and Bent and Cuthbertson (*J. Amer. Chem. Soc.*, 1936, **58**, 170) have concluded from measurements of the heat of oxidation and of hydrogenation of triphenylmethyl that the C—C linkage in hexaphenylethane is weaker by about 30 kcal. than in ethane and that the weakening is to be ascribed to steric factors. The affinity-demand theory, as developed by Flürscheim (*J. pr. Chem.*, 1905, **71**, 505) and Zeigler (*Annalen*, 1923, **434**, 34; 1924, **347**, 227), refers the dissociation to the affinity demand of the aryl groups, which is assumed to be so large that little remains for maintaining the ethane linkage. As pointed out by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421), this

theory meets with several difficulties, since the affinity demand of a phenyl group (as indicated by its *op*-orienting power in aromatic substitution) is actually of very moderate order and is greatly exceeded by other groups (*e.g.*, dimethylamino-, methoxyl, etc.) which do not lead to the formation of long-lived radicals.

The earlier theories of Fry ("The Electronic Conception of Valence and the Constitution of Benzene," London, 1921) and Cole (*Philippine J. Sci.*, 1922, **19**, 681), although they treated the problem of free radicals from the electronic standpoint, were essentially descriptive, and it remained for Burton and Ingold (*loc. cit.*) to propose the first theory which explained the existence of free radicals in terms of a stabilisation process involving charge distribution throughout the molecule. Since the aryl group has an available mechanism for the distribution of any charge on the methyl carbon atom and can thus counteract the instability arising from incompleteness of the valency shell (as in the positive ion, Ph_3C^+) or the instability arising from the incompleteness of electron sharing (as in the negative ion, Ph_3C^-), it can also counteract the two factors when they are present together, as in the neutral radical $\text{Ph}_3\text{C}\cdot$. The stabilisation of the radical was examined from the quantum-mechanical standpoint by Hückel (*Z. Physik*, 1931, **72**, 310; *Trans. Faraday Soc.*, 1934, **30**, 40) and Pauling and Wheland (*J. Chem. Physics*, 1933, **1**, 362). The two treatments, involving the Hund-Mulliken-Hückel method and the Heitler-London-Slater-Pauling method, are based on the premise that the stability of the radical is due to the fact that the increase in the resonance energy of the system after dissociation partially compensates for the energy required to break the C-C link of the original molecule. Incidentally, it may be noted that two assumptions are involved in these theories: (*a*) that the strength of the C-C bond in hexa-arylethanes is the same as that in ethane, and (*b*) that there is a rearrangement of bonds in the free radical to give a planar configuration, although the work of Karagunis and Drikos (*Nature*, 1933, **132**, 354; *Z. physikal. Chem.*, 1934, **26B**, 428) would seem to indicate the contrary.

In a further elaboration of the earlier theory of radical stability, Ingold (*Trans. Faraday Soc.*, 1934, **30**, 52) ascribes the stability of the radical to the degeneracy of the large number of unperturbed forms. Such degeneracy involves loss of energy through resonance, and the resonance energy will be greater the larger the number of unperturbed forms and perturbation mechanisms. The large number of perturbation mechanisms accounts for the existence of Ph_3C^+ and Ph_3C^- as thermodynamically stable ions, while in the neutral radical, $\text{Ph}_3\text{C}\cdot$, the perturbation mechanisms which promote degeneracy of the positive and negative ions are coupled together in the degeneracy of the radical. The efficacy of the degeneracy as a stabilising influence will depend, not only on the number of perturbation mechanisms, but also on the facility with which these mechanisms actually operate.

The problem relating to the influence of alkyl groups on the dissociation of aliphatic-substituted ethanes was first broached by Pauling and Wheland (*loc. cit.*), who assumed that resonance was not possible in these groups and that they increase the tendency to dissociation in virtue of steric factors. This implies that from the resonance standpoint alkyl groups should have no greater influence than hydrogen atoms on the dissociation tendency of an ethane. Subsequently, however, these views were modified by Wheland (*J. Chem. Physics*, 1934, **2**, 474), who assumed that resonance could occur in alkyl groups, and on this basis concluded that butane should be more highly dissociated than ethane. According to these qualitative arguments, therefore, the methyl group is a more effective substituent than a hydrogen atom in promoting the dissociation of this type of ethane derivative into free radicals.

With regard to the influence of a methyl group when present as a nuclear substituent in triphenylmethyl, our results indicate that the unimolecular stability of diphenyl-*o*-tolylmethyl in benzene solution is appreciably greater than that of triphenylmethyl. In this connexion, it has been pointed out by Professor Ingold (private communication) that the methyl group should produce an increase of radical stability because it increases the electron density in that part of the system in which the free radical structure confers additional electron mobility. Mesomerism confers stability since it allows new motions to the electrons, thereby decreasing the electronic zero-point energy in accordance with the uncertainty principle. However, even when the structural theory is qualitatively unambigu-

ous, perfect regularity in the experimental equilibrium figures cannot be expected since these involve heat contents which, for polyatomic molecules, are the sum of contributions from such a large number of partly excited degrees of freedom that it is not possible to predict the totals.

EXPERIMENTAL.

Diphenyl-o-tolylcarbinol.—A filtered solution of *o*-tolylmagnesium bromide [from *o*-bromotoluene (50 g.) and magnesium (9.5 g.)] was treated with benzophenone (36 g.), and the mixture heated on the steam-bath for 4 hours. After hydrolysis with ice and sulphuric acid, the well-washed ethereal layer was dried over calcium chloride, and concentrated until the carbinol was deposited on standing. After trituration with light petroleum and recrystallisation from ligroin, the carbinol melted at 98°, as recorded by Acree (*Ber.*, 1904, 37, 998) for the distilled material.

The halochromism of diphenyl-*o*-tolylmethyl salts is exhibited in the orange colour of the sulphate, perchlorate, and formate. The basicity of the true base corresponding to the coloured triarylmethyl cation was estimated from the resistance of the sulphate to hydrolysis. The yellow solution of the carbinol (0.0782 g.) in 5 c.c. of glacial acetic acid and 1 c.c. of a 10% glacial acetic acid solution of concentrated sulphuric acid was decolorised by 2.0 c.c. of 75% aqueous alcohol, whereas a similar solution of triphenylcarbinol (0.0743 g.) required 1.3 c.c. If the basicity of triphenylcarbinol is taken as unity, the value for the tolyl derivative is 1.5. Since the basicity of *o*-methoxytriphenylcarbinol is 1.97, it is evident that the methyl group is less powerful than methoxyl in enhancing the basic characteristics of the true base.

Diphenyl-o-tolylmethane.—A solution of the carbinol (1 g.) in formic acid (15 c.c.) was boiled for 6 hours, decolorisation then being nearly complete. On cooling, some of the methane separated in small transparent crystals, which were filtered off. The filtrate was poured into water, and the precipitated oil thoroughly washed with cold water until it hardened. The material, recrystallised from absolute alcohol, had m. p. 82°.

Diphenyl-o-tolylmethyl Chloride.—The dry carbinol (10 g.) in absolute ether (100 c.c.) was shaken at 0° with a few lumps of freshly dehydrated calcium chloride while the solution was being saturated with hydrogen chloride. The triarylmethyl chloride was rapidly deposited, and after recrystallisation from dry ether in an atmosphere of dry air, the almost white crystals melted at 136—137°, as recorded by Bistrzycki and Gyr (*Ber.*, 1904, 37, 1245).

The addition compound with ferric chloride, obtained as a brick-red precipitate by mixing ethereal solutions of the components, had m. p. after purification 137—138° (decomp.) (Found: Cl, 31.06. $C_{26}H_{17}Cl, FeCl_3$ requires Cl, 31.2%). Zinc chloride afforded a similar compound, but this was an oil which failed to crystallise.

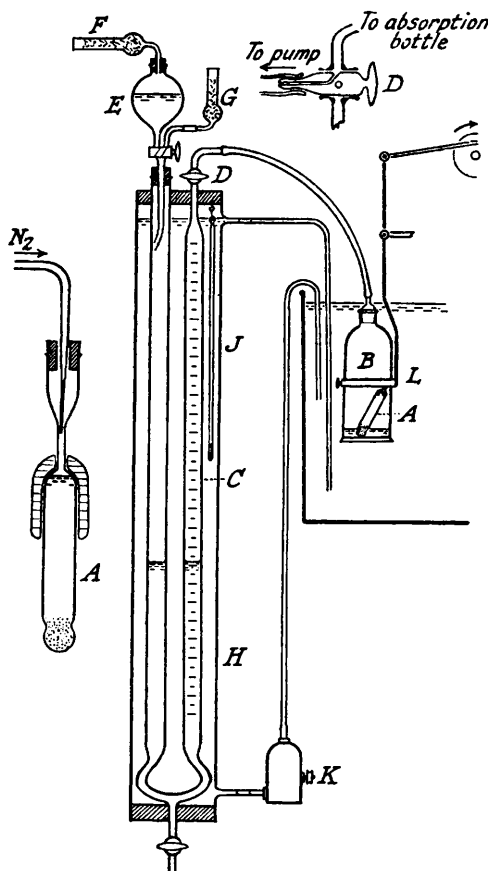
Diphenyl-o-tolylacetic Acid.—Ether (80 c.c.) was distilled from sodium into a reflux apparatus charged with 2 g. of fine magnesium powder, which had been activated *in situ* by Baeyer's method. Pure diphenyl-*o*-tolylmethyl chloride (10.5 g.) was added, and the mixture was then boiled while a stream of dry carbon dioxide was passed through it. After 6 hours the reaction product was treated with 60 c.c. of water and 40 c.c. of hydrochloric acid, and the mixture was boiled for 3 minutes to complete hydrolysis. The crude *diphenyl-o-tolylacetic acid* was separated and dissolved in 10% sodium hydroxide; the solution was filtered, and the acid reprecipitated by addition of hydrochloric acid. Repeated crystallisation from glacial acetic acid gave white crystals, m. p. 226° (Found: C, 83.2; H, 6.2. $C_{21}H_{15}O_2$ requires C, 83.4; H, 6.0%).

Diphenyl-o-tolylmethyl Peroxide.—Diphenyltolylmethyl chloride (1 g.) in dry benzene (25 c.c.) was mechanically shaken with molecular silver (8 g.) in a sealed vessel for 10 minutes. The clear yellow solution of the free radical was quickly siphoned from the silver-silver chloride mixture, and then oxidised by the passage of a brisk stream of air until decolorisation was practically complete. The *peroxide* separated as a white, micro-crystalline solid, m. p. 164° after rapid recrystallisation from the same solvent (Found: C, 87.8; H, 6.4. $C_{40}H_{34}O_2$ requires C, 87.9; H, 6.3%). The yield (68%) is almost the same as that of triphenylmethyl peroxide from triphenylmethyl. The peroxide was also prepared in slightly lower yield by the action of mercury on solutions of the chloride.

Absorption of Oxygen by the Radical.—A known weight of the pure triarylmethyl chloride was placed in a constricted test-tube *A* (with a thin, blown-out bottom, as shown in the figure) together with a known excess of freshly dried molecular silver. The air in the tube was displaced by nitrogen, and the vessel then filled almost to the constriction with freshly distilled bromobenzene. The upper part of the tube was insulated with asbestos cord, and a stream of nitrogen was directed into the vessel to prevent intrusion of air while the constriction was

sealed in by means of a small blow-pipe flame. The tube was placed in a light-tight box, and shaken on a rotary machine to effect complete reduction of the chloride.

The tube containing the free radical solution was placed in the bottle *B* together with 10–15 c.c. of bromobenzene. The bottle was provided with a well-ground hollow stopper, which was fixed securely in position with sealing-wax, and connected to the gas burette *C* by means of pressure tubing. The three-way stopcock *D* permitted the apparatus to be alternately exhausted and filled with oxygen, so that no nitrogen was left in the system. Bromobenzene was employed as manometric liquid, and the dropping-funnel *E* and the gas burette were protected from atmospheric moisture by the calcium chloride tubes *F* and *G*, respectively. The burette was enclosed in a glass jacket *H* containing a thermometer *J* for registering the temperature of the water circulated through the system by means of the motor-driven pump *K*.



The absorption bottle was fixed to a metal frame *L* and immersed in a thermostat electrically controlled to within $\pm 0.02^\circ$ of the working temperature. After the attainment of thermal equilibrium, the pressure in the system was equalised to the prevailing atmospheric pressure. The tube containing the free radical was broken by sharply jerking the bottle, and the frame was immediately slipped into position on the shaking mechanism, which was operated by a motor to effect rapid mixing of the oxygen with the free-radical solution. During the oxidation process bromobenzene was run in from the dropping funnel to maintain equality of pressure, and the volume of oxygen absorbed was noted at intervals. A small correction was made for the initial contraction arising from the fact that the nitrogen above the free radical solution in the tube *A* was under reduced pressure as a result of the sealing operation. This correction, as estimated in control experiments on standard tubes of bromobenzene, never exceeded 0.15 c.c. Normally, no correction was made for the vapour pressure of bromobenzene, since this is negligible at the temperature of the experiment.

The apparatus was also employed for following the course of oxidation when the radical is produced in the nascent condition. For this purpose molecular silver and bromobenzene were placed in the absorption bottle and a solution of the chloride in the tube *A*, which was not

constricted or sealed as in the preceding experiments.

The results of typical experiments at 18° are given below.

Experiment 1.

Weight of diphenyl-*o*-tolylmethyl chloride, 0.4570 g.; radical oxidised as formed; theoretical absorption, 17.5 c.c. (N.T.P.).

Time (mins.)	1	2	3	4	5	10	15
O ₂ absorbed (c.c.)	8.9	12.4	13.4	17.4	18.1	18.5	18.7
Absorption, %	39.4	70.9	87.8	99.4	103.4	105.3	106.8

Experiment 2.

Weight of chloride, 0.5000 g.; radical oxidised after life of 20 minutes; theoretical absorption, 19.2 c.c. (N.T.P.).

Time (mins.)	1	2	3	4	5	8	18
O ₂ absorbed (c.c.)	15.2	17.8	18.4	18.7	18.9	19.4	20.1
Absorption, %	79.6	93.3	96.1	97.9	98.8	101.6	105.2

Experiment 3.

Weight of chloride, 0.5095 g.; radical oxidised after life of 2 hours; theoretical absorption, 19.5 c.c. (N.T.P.).

Time (mins.)	1	2.5	3.5	5	10	22
O ₂ absorbed (c.c.)	15.5	17.9	18.8	19.3	19.5	20.0
Absorption, %	79.1	91.8	96.3	99.0	99.9	102.6

It is evident from Expt. 1 that diphenyl-*o*-tolylmethyl chloride is very rapidly reduced to the free radical by the specimen of molecular silver used in this work. The high values of the oxygen absorption after the free radical had stood at room temperature for periods ranging from 20 minutes to 2 hours show that little, if any, isomerisation into saturated compounds occurs under these conditions. These findings therefore justify the application of molecular-weight methods involving ordinary cryoscopic procedure provided that the operations be not unduly prolonged. The fact that the absorption of oxygen in each of the above experiments finally exceeds 100% indicates that in addition to the primary oxidation of the radical there is a slower oxidation process involving the peroxide or its precursor, CPh₂(C₆H₄Me)•O•O. This feature, however, is also exhibited in the oxidation of methoxytriphenylmethyls which are known to suffer little if any isomerisation.

*The Radical Stability of Diphenyl-*o*-tolylmethyl.*—The degree of dissociation of tetraphenyldi-*o*-tolylethane was determined by the indirect method in which the radical is formed *in situ* in the cryoscopic vessel. In view of the nature of this particular radical, special precautions were taken with regard to the dryness of the apparatus and materials in order to ensure that the system was as free as possible from traces of hydrogen chloride, since this is known to induce isomerisation of hexa-arylethanes. The freshly-prepared molecular silver, after being washed with alcohol and ether, was dried by heating to 270° in vacuum for 12 hours, and was then cooled under pure nitrogen. An excess of silver larger than customary was placed in the cryoscopic vessel in order to effect more rapid completion of the reduction at the lower temperatures. The benzene employed as solvent was distilled (under nitrogen) over a column of sodium wire immediately before use, and the pure chloride was kept over solid potassium hydroxide and activated silica gel. The material was made into pellets in a rigorously dried pellet press which was manipulated in a desiccated chamber.

*Radical Stability of Diphenyl-*o*-tolylmethyl.*

(M.W. of monomer = 257; M.W. of dimeride = 514. Benzene, $K = 52.5$.)						
Wt. of solvent, g.	Wt. of chloride, g.	Radical concn., %.	Δ .	M .	Radical stability, %.	
18.13	0.4654	2.3	0.278°	426	20.7	
	0.6369	3.1	0.376	431	19.3	
18.10	0.2038	1.0	0.122	426	20.7	
	0.7672	3.7	0.442	442	16.3	
18.11	0.4136	2.0	0.252	419	22.7	
	0.5667	2.8	0.340	425	21.0	

As a further check on the measurements, the solution of the free radical at the end of each experiment was filtered (under carbon dioxide) from the silver-silver chloride mixture, and rapidly oxidised by the passage of a stream of air. The yield of diphenyl-*o*-tolylmethyl peroxide amounted to 63—65% of the theoretical value. This corresponds closely to the yield obtained in control experiments involving oxidation of the freshly made radical, and is, moreover, almost identical with that obtained in the oxidation of triphenylmethyl itself. The results of the oxygen absorption experiments, together with those relating to the yield of peroxide from the cryoscopic solutions, enable us to place considerable reliance upon the validity of the molecular-weight determinations in so far as they indicate the general order of the degree of dissociation of the ethane.

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