68. *Free Radicals and Radical Stability. Part III. Diphenylpiperonylmethyl and Phenyl-*p*-anisyldiphenylylmethyl.*

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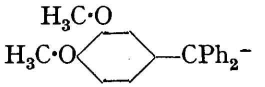
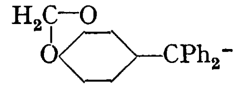
Diphenylpiperonylmethyl has been prepared for the purpose of ascertaining the influence of the methylenedioxy-group on radical stability. The free radical is reddish-orange in non-polar media and has the characteristic properties of the triarylmethyls. It is readily oxidised to the peroxide in air, absorbs iodine at the ordinary temperature, and suffers photochemical decomposition in sunlight. The thermodynamic stability of the radical is lower than that of 3 : 4-dimethoxytriphenylmethyl, and it is evident, therefore, that the stabilising influence of the methylenedioxy-group is less than that of two methoxyl groups in corresponding positions of the aromatic ring.

Phenyl-*p*-anisyldiphenylylmethyl has been prepared in solution, but could not be isolated in the solid state. It is more deeply coloured than Schlenk's diphenyldiphenylylmethyl and is doubtless more stable, but the indirect method of molecular-weight determination could not be applied owing to the difficulty of purifying the corresponding chloride.

In continuation of studies of the influence of the methoxyl group on the stability of the neutral triarylmethyl complex (Part II; this vol., p. 33), we have now examined the influence of the methylenedioxy-group by comparing the stability of the radicals 3 : 4-dimethoxytriphenylmethyl (I) and diphenylpiperonylmethyl (II).

(I.)





(II.)

Diphenylpiperonylmethyl chloride is obtained by the action of acetyl chloride on the corresponding *carbinol*, and may be reduced to the radical by means of mercury or silver. The solution of the radical is yellowish-red, and the colour is discharged on exposure to direct sunlight. The photodecomposition, however, proceeds less rapidly than with triphenylmethyl (Bowden and Jones, J., 1928, 1149). In solution the radical rapidly absorbs oxygen, but the main reaction involving the formation of *peroxide* is followed by a further complex oxidation process, as with the polymethoxytriphenylmethyls. It is evident, accordingly, that the presence of methoxyl groups increases the reactivity of the peroxide towards oxygen. Despite the enhanced susceptibility of the primary peroxide to further oxygen attack, the yield of crystalline derivative is generally higher than that obtained in the oxidation of triphenylmethyl. Gomberg (*Ber.*, 1904, **37**, 3542) has shown that two reactions occur during the oxidation of triphenylmethyl, one involving the production of crystalline triphenylmethyl peroxide and the other the formation of an isomeric derivative, which may be isolated as an oil from the oxidised solution. Since the yield of crystalline polymethoxytriarylmethyl peroxide is higher than that of triphenylmethyl peroxide, it is evident that the presence of methoxyl groups tends to inhibit the reaction leading to the formation of the isomeric derivatives.

The thermodynamic stability of diphenylpiperonylmethyl is slightly lower than that of 3 : 4-dimethoxytriphenylmethyl. In comparison with the effect of two adjacent methoxyl groups, the methylenedioxy-group causes a slight repression of the electromeric effects responsible for the stabilisation of the electronic septet of the methyl carbon atom (Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52).

The influence of the methoxyl group in other free radicals was studied by Ziegler and Ochs (*Ber.*, 1922, **55**, 2257), who found that the substitution of methoxyl groups in the *o*- or *p*-positions of the phenyl nuclei in diphenyl(diphenylallyl)methyl leads to enhanced radical stability. Gomberg and McGill (*J. Amer. Chem. Soc.*, 1925, **47**, 2392) had previously found that phenyl-*o*-anisyl-α-naphthylmethyl exists almost entirely in the unimolecular condition, whereas diphenyl-α-naphthylmethyl is stable to the extent of 60% under similar conditions. Since the substitution of methoxyl groups in the above radicals leads to practically complete stability, it is not possible to estimate the actual contribution of the methoxyl group. In order to obtain a measure of this particular contribution to the stabilising effect, we selected for examination the radical phenyl-*p*-anisyldiphenylylmethyl, so that its stability could be compared with that of Schlenk's diphenyldiphenylylmethyl, which exists in the unimolecular condition to the extent of 15%. Although there was no difficulty in preparing the corresponding *carbinol*, the oily *chloride* could not be crystallised, and so we could not use the indirect method of determining the molecular weight of the radical. The chloride gave a deep red solution of the radical on reduction with silver; and since, in so far as this series is concerned, the colour is displaced towards the red with increasing stability of the radical, it may be inferred that the radical stability is higher than that of diphenyldiphenylylmethyl. Although the radical could not be isolated in the crystalline condition, its presence in solution was proved by measurements of the oxygen absorption and by isolation of the crystalline *peroxide*.

EXPERIMENTAL.

Diphenylpiperonylmethyl.

Diphenylpiperonylcarbinol.—Methyl piperonylate was prepared by a slight modification of Oertley and Pictet's method (*Ber.*, 1910, **43**, 1336). A suspension of the pure acid (25 g.) in methyl alcohol (300 c.c.) was saturated with dry hydrogen chloride and kept overnight in a tightly stoppered bottle. The clear solution was concentrated to half bulk by distillation, and the ester precipitated by pouring the solution into ice-water. After being washed and dried, the ester was recrystallised from methyl alcohol; m. p. 53°; yield 80%.

To a filtered solution of phenylmagnesium bromide (bromobenzene, 38 g.; magnesium, 6 g.), methyl piperonylate (20 g.) in dry ether (70 c.c.) was added during 3 hours. After 6 hours' heating on the steam-bath, the solution was hydrolysed, and bromobenzene and diphenyl removed in steam. The yellow, resinous solid was washed with dilute sodium hydroxide solution and with water, and dried in the air. After successive trituration with carbon disulphide and light petroleum, *diphenylpiperonylcarbinol* was obtained solid, m. p. 105° after repeated crystallisation from alcohol (Found : C, 79·0, 78·75; H, 5·45, 5·35. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%). The halochromic salts are crimson, and the carbinol dissolves in liquid sulphur dioxide to form a pink solution.

Diphenylpiperonylmethane.—The carbinol was reduced by heating with zinc dust and acetic acid; the *methane*, precipitated from the filtered solution by water, crystallised from alcohol in white rosettes, m. p. 65° (Found : C, 83·2; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

Diphenylpiperonylmethyl Chloride.—The above carbinol was covered with a mixture of ether and light petroleum and treated with 2·5 mols. of redistilled acetyl chloride in an apparatus protected against intrusion of moisture. The mixture was boiled for 15 minutes, and the red solution then concentrated to half bulk. Pale yellow crystals of the *chloride* were deposited from the solution cooled in a freezing mixture. After recrystallisation from ether–light petroleum in an atmosphere of dry air, it had m. p. 105° (Found : Cl, 10·8, 10·95. $C_{20}H_{15}O_2Cl$ requires Cl, 11·0%). This chloride was also prepared by passing hydrogen chloride into a benzene solution of the carbinol in the presence of anhydrous calcium chloride, but the product was difficult to purify.

The substance forms a number of halochromic derivatives with certain inorganic halides. The addition *compound* with ferric chloride was prepared by treating an ethereal solution of diphenylpiperonylmethyl chloride with a similar solution of anhydrous ferric chloride. The deep red solution deposited brownish-red crystals, which were washed with ether and dried in a vacuum over soda-lime and paraffin wax; m. p. 145—146° (Found : Cl, 29·1. $C_{20}H_{15}O_2Cl,FeCl_3$ requires Cl, 29·25%). Similarly, the *compound* with zinc chloride was obtained as dark red, extremely hygroscopic crystals (Found : Cl, 22·8. $C_{20}H_{15}O_2Cl,ZnCl_2$ requires Cl, 23·2%), the mercuric chloride *complex* as a dark red, crystalline mass (Found : Cl, 18·1. $C_{20}H_{15}O_2Cl,HgCl_2$ requires Cl, 17·9%), and the stannic chloride *complex* as red crystals (Found : Cl, 36·6. $C_{20}H_{15}O_2Cl,SnCl_4$ requires Cl, 36·7%) (reaction in benzene afforded an oil).

Diphenylpiperonylmethyl Bromide.—Prepared analogously to the chloride, the *bromide* separated from solution in pale yellow crystals, which, recrystallised from light petroleum, had m. p. 121° (Found : Br, 22·2. $C_{20}H_{15}O_2Br$ requires Br, 21·8%). When its ethereal solution was mixed with one of mercuric bromide, a very hygroscopic, dark red addition *compound* was immediately precipitated (Found : Br, 32·6. $C_{20}H_{15}O_2Br,HgBr_2$ requires Br, 33·0%).

Diphenylpiperonylmethyl Peroxide.—An ethereal solution of the chloride was shaken with a large excess of mercury in the absence of air for 6 hours. The orange-red solution was siphoned from the precipitated mercurous chloride, and the free radical oxidised in a current of air. During this process the orange-red colour changed to a pale yellow, and the *peroxide* was precipitated as a white crystalline solid; yield, 65%. After rapid recrystallisation from benzene in an atmosphere of carbon dioxide, it had m. p. 173° (Found : C, 79·05; H, 4·9. $C_{40}H_{30}O_6$ requires C, 79·2; H, 5·0%). The peroxide is moderately readily soluble in benzene, but practically insoluble in alcohol, ether, and light petroleum. Although formic acid dissolves the carbinol with formation of a red solution, no colour is produced in the case of the peroxide. Perchloric acid likewise causes only slight coloration of the peroxide, but with concentrated sulphuric acid a deep red colour is developed comparable with that produced by the carbinol.

Absorption of Oxygen by the Radical.—The amount of oxygen absorbed by the free radical in bromobenzene solution was measured at 18° according to the procedure described previously (Part II, *loc. cit.*). The results of typical experiments, in which the free radical was prepared by reduction of the chloride and bromide severally, are given below.

Experiment 1.

Weight of diphenylpiperonylmethyl chloride, 0·4234 g.; reducing metal, silver; theoretical absorption, 14·7 c.c. (*N.T.P.*).

Time (seconds)	30	50	80	120	160	180	240	300
O_2 absorbed (c.c.)	3·9	5·6	7·8	10·5	12·3	13·1	13·9	14·6
Absorption, %	26·5	38·0	54·2	73·0	84·1	89·4	94·2	99·8

Experiment 2.

Weight of diphenylpiperonylmethyl bromide, 0·7802 g.; reducing metal, mercury; theoretical absorption, 23·8 c.c. (*N.T.P.*).

Time	10 min.	10 days	20 days	40 days
O_2 absorbed (c.c.)	22·5	51·5	59·9	72·0
Absorption, %	97·5	223	259	312

After the initial, rapid oxidation of the radical, the primary peroxide undergoes a slow oxidation process involving the absorption of 2 mols. of oxygen during 10 weeks.

Absorption of Iodine.—The free radical was prepared in air-free benzene by reduction of the chloride by silver in a flask provided with two side-tubes. The vessel was filled under carbon dioxide, and after the side-tubes had been sealed, the mixture was shaken in the dark for 5 hours. The solution was carefully filtered into the titration flask, and the residual mixture of silver and silver chloride well washed with benzene. The radical was treated with a N/15-solution of iodine in benzene until the colour of the iodine was no longer discharged; the 14·0 c.c. of iodine thus required are equivalent to 55·3% of the amount necessary to convert the radical into diphenylpiperonylmethyl iodide. The thermal stability of the iodide is greater than that of some of the corresponding dimethoxy-derivatives, but lower than that of triphenylmethyl iodide.

Radical Stability of Diphenylpiperonylmethyl.—The apparatus employed for the determination of the molecular weight of the radical system was similar to that described previously (Part II; *loc. cit.*) and differed only in dimensions and minor features of design. The cryoscopic constants of the solvents in this apparatus were determined by using pure triphenylmethane as solute. The free radical is orange-red in benzene, but the colour is much more intense in nitrobenzene.

Isolation of the Radical.—A benzene solution of the radical, prepared by reduction of the chloride with molecular silver in the absence of oxygen and light, was filtered into the concentrating apparatus as described previously (Part II). The benzene was evaporated at 40—50°/70 mm. in a slow current of pure carbon dioxide. The residual reddish oil could not be obtained crystalline from acetone or carbon disulphide. The radical was only slightly soluble in light petroleum and would not crystallise from this solvent. When, however, it was dissolved in a small amount of dry ether, crystals of tetraphenyldipiperonylethane slowly separated from the solution cooled in a freezing mixture. After decantation of the mother-liquor, the solid radical was washed with small quantities of cold ether and dried under reduced pressure in a stream of carbon dioxide.

Stability of diphenylpiperonylmethyl.

Molecular weight of tetraphenyldipiperonylethane = 574.
Molecular weight of diphenylpiperonylmethyl = 287.
Benzene, K = 50·9°; nitrobenzene, K = 71·2°.

In benzene.

Solvent, g.	Chloride, g.	Radical concn. %.	Δ.	*M.*	Radical stability, %.	Solvent, g.	Chloride, g.	Radical concn., %.	Δ.	*M.*	Radical stability, %.
17·23	0·2978	1·5	0·151°	518	10·8	17·17	0·2742	1·4	0·137°	528	8·7
	0·4863	2·5	0·243	528	8·7		0·6090	3·1	0·301	533	7·7
	0·6155	3·2	0·306	529	8·5	17·41	0·2643	1·3	0·132	520	10·2
							0·5940	3·0	0·294	525	9·3

In nitrobenzene.

Solvent, g.	Chloride, g.	Radical concn. %.	Δ.	*M.*	Radical stability, %.	Solvent, g.	Chloride, g.	Radical concn., %.	Δ.	*M.*	Radical stability, %.
23·11	0·2430	1·0	0·136	490	16·0	22·04	0·3612	1·5	0·205	506	13·4
	0·5840	2·3	0·320	500	14·8		0·7731	3·1	0·435	511	12·3

The solid was heated in porcelain boats to effect complete removal of solvent. The apparatus consisted of a long horizontal tube closed with rubber stoppers provided with short exit tubes and stopcocks; one end of the tube was connected to the carbon dioxide generator and purification train, and the other end to a suction pump and manometer. The tube was surrounded with a glass jacket through which the vapour from boiling acetone was continuously circulated; the substance was thus maintained at 55—56° without danger of excessive local heating. The pressure was reduced to 20 mm., and carbon dioxide slowly passed through the apparatus for 30 minutes. The loss of weight was not appreciable.

The substance melted at 156° (vac.) and its solution in ether deposited diphenylpiperonylmethyl peroxide, m. p. 169°, on standing in the air.

*Phenyl-*p*-anisyldiphenylylmethyl.*

*Phenyl-*p*-anisyldiphenylylcarbinol.*—*p*-Bromodiphenyl, prepared from *p*-bromoaniline and benzene by Gomberg and Bachman's method (*J. Amer. Chem. Soc.*, 1924, **46**, 2339), was purified by repeated crystallisation from alcohol and finally distilled in an Anschütz apparatus with adequate provision against the intrusion of water vapour.

The Grignard reagent was prepared by strongly activating magnesium powder (2·5 g.) *in situ* with iodine according to Baeyer's method, adding freshly-distilled *p*-bromodiphenyl (19·0 g.) and then distilling the requisite volume of ether (30—40 c.c.) into the apparatus through a long column of sodium wire. Except on one occasion when the reaction set in spontaneously, it was necessary to boil the mixture on an electric heater for 10—12 hours in order to complete the reaction.

The red solution of *p*-diphenylylmagnesium bromide was filtered from the excess of magnesium in a stream of dry air, and treated with the theoretical amount of finely powdered *p*-methoxybenzophenone (Gattermann, Ehrardt, and Maisch, *Ber.*, 1890, **23**, 1204). The ketone was added in small quantities owing to the highly exothermic character of the reaction. The product separated as a brown, gummy mass, which was hydrolysed by prolonged trituration with ice and sulphuric acid. The precipitated solid was combined with the material obtained by evaporation of the ethereal solution, and repeatedly triturated with light petroleum. The pure *carbinol*, recrystallised from ligroin, melted at 78° (Found: C, 84·9; H, 6·1. $C_{26}H_{22}O_2$ requires C, 85·25; H, 6·0%). It formed halochromic salts with strong acids, the sulphate, perchlorate, phosphate, and formate being deep red. It also dissolved readily in liquid sulphur dioxide to form a reddish-orange solution.

Basicity of the Carbinol.—For purposes of comparison we prepared diphenyl-*p*-diphenylylcarbinol, obtained by Schlenk and Weickel (*Annalen*, 1909, **368**, 295) from *p*-diphenylylmagnesium iodide and benzophenone. We, however, used the bromide, and obtained a carbinol of m. p. 106° after recrystallisation from ligroin (Schlenk and Weickel give m. p. 136°). The identity of our product was established by its conversion into the corresponding methane (m. p. 112°), the carbinyl chloride (m. p. 146°), and the peroxide (m. p. 180°), which have the same m. p.'s as those recorded by previous workers.

The basicity of the carbinols was compared with that of triphenylcarbinol by Baeyer's hydrolysis method :

Carbinol.	Basicity.	Colour of sulphate.
Triphenyl	1	Yellow
Diphenyl-*p*-diphenylyl	1·7	Red
Phenyl-*p*-anisyldiphenylyl	9·6	Deep red

The substitution of *p*-methoxyl in triphenylcarbinol raises the basicity value to 6·5.

*Phenyl-*p*-anisyldiphenylylmethane.*—The carbinol (2 g.), zinc dust (2 g.), and glacial acetic acid were heated at 99° for 3 hours, the red colour of the solution being discharged. The filtered solution was poured into water, and the precipitated *methane* crystallised from alcohol; m. p. 92° (Found : C, 88·6; H, 6·35. $C_{26}H_{22}O$ requires C, 89·15; H, 6·3%).

Thermal Decomposition of the Formate.—Employing a modification of the method of Kauffmann and Panwitz (*Ber.*, 1912, **45**, 766; *Rec. Trav. chim.*, 1930, **49**, 665), we made preliminary experiments to compare the rates of decomposition of phenyl-*p*-anisyldiphenylylmethyl formate and the corresponding diphenyldiphenylylmethyl ester. When the deep red solution of phenyl-*p*-anisyldiphenylylcarbinol in formic acid was maintined at 99°, carbon dioxide was evolved at a rate corresponding to a unimolecular reaction until 53% of the theoretical amount had been evolved. The colour of the solution was partly discharged during this process, and after 2 hours the decomposition had proceeded to the extent of 65%. The cold solution precipitated the methane as a gummy solid; m. p. 92° after recrystallisation from alcohol. The product was identical with that obtained by direct reduction of the carbinol with zinc and acetic acid. Neither product gave a trace of colour with anhydrous formic acid.

The solution of diphenyl-*p*-diphenylylcarbinol in formic acid behaved in a similar way, but the thermal decomposition of the formate proceeded at a slightly lower rate in the early stages of the reaction. Although the colour was not completely discharged after 2½ hours' heating at 99°, the cold solution deposited the methane in 70% yield. The m. p. of the product, after recrystallisation from alcohol, was identical with that given by Schlenk and Weickel (*loc. cit.*), who employed zinc and acetic acid for the reduction.

In so far as the early stages of the reaction are concerned, it is evident that the presence of *p*-methoxyl leads to a slight increase in the rate of thermal decomposition of the formate.

*Phenyl-*p*-anisyldiphenylylmethyl Chloride.*—The carbinol (5 g.), light petroleum (15 c.c.), and acetyl chloride (5 c.c.) were gently heated for ½ hour in an apparatus fitted with guard-tubes of calcium chloride. The deep red solution deposited the required chloride as a thick oil on cooling, but this showed no tendency to crystallise. Several variations of the general procedure, involving the use of acetyl chloride alone and in benzene, failed to yield a solid product. Inoculation with the partly isomorphous crystals of the methane and the carbinol was likewise unsuccessful, and it appeared that the substance exhibits the non-crystallisability characteristic of certain *p*-methoxy-derivatives of the triphenylmethane group. The thick, highly viscous oil was dissolved in benzene, and the solution gently warmed in a current of carbon dioxide to remove the excess of acetyl chloride. To the concentrated solution, light petroleum was added to produce incipient turbidity. The precipitated oil was washed, and dried over soda-lime and paraffin wax (Found : Cl, 8·8. $C_{26}H_{21}OCl$ requires Cl, 9·2%). The material was not sufficiently pure for use in the determination of the molecular weight of the radical by the indirect method. *Phenyl-*p*-anisyldiphenylylmethyl chloride* gave the following addition compounds when its ethereal solution was treated with the appropriate chloride in ether: *ferrichloride*, a dark brown, finely divided solid (Found : Cl, 25·5. $C_{26}H_{21}OCl,FeCl_3$ requires Cl, 25·9%); *mercurichloride*, a bright red solid (Found : Cl, 16·9. $C_{26}H_{21}OCl,HgCl_2$ requires Cl, 16·3%).

*Phenyl-*p*-anisyldiphenylylmethyl Peroxide.*—The chloride (5 g.) was dissolved in dry ether and shaken with excess of molecular silver in a tightly stoppered vessel for 3 hours in the dark. The intensely wine-red solution of the free radical was treated as in the preparation of the other peroxide (p. 304), but the peroxide remained in solution. The solvent was rapidly removed in a stream of warm air, and the residual gummy mass repeatedly triturated with small portions of light petroleum until it was converted into a grey powder. This was dissolved in a small quantity of warm benzene, and the cooled solution treated with light petroleum. After recrystallisation from the same mixture, the *peroxide* melted at 166° (Found: C, 85·0; H, 5·8. $C_{52}H_{42}O_4$ requires C, 85·5; H, 5·8%).

*Isolation of Phenyl-*p*-anisyldiphenylylmethyl.*—The chloride (4 g.) was repeatedly washed with dry light petroleum and stored for 36 hours in a vacuum desiccator charged with soda-lime and paraffin wax. It was dissolved in 50 c.c. of pure, sodium-dried benzene, and reduced as described on p. 305. The red syrup obtained after evaporation of the benzene from the deep red solution was readily soluble in warm ether, but was deposited as an oil on cooling. The radical dissolved readily in acetone and carbon disulphide, and more slowly in light petroleum, but could not be crystallised from either of these solvents.

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