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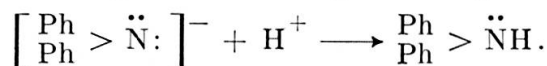
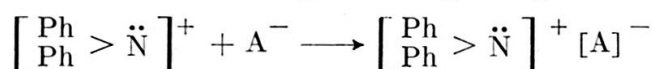
Electron Spin Resonance Studies of the Free Radicals derived from Tetraphenylhydrazine

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INTRODUCTION.

Wieland prepared tetraphenylhydrazine (TPH) for the first time and proposed that [1] when heated in a non-polar solvent like xylene or toluene to about 90° C, TPH dissociates into diphenylamino radicals, and [2] the coloured compounds formed by the action of acids on TPH have a quinonoid structure¹. Weitz and Schwecten observed that TPH does not form salts with acids unless oxidizing agents are present and hence suggested that the action of acids on TPH produces free radicals instead of quinonoid compounds.² Lewis and Bigeleisen held the view that in solution, TPH is in dynamic equilibrium with the positive and negative ions of diphenyl-nitrogen, and when an acid is added, the negative ions are first removed by protonation; the positive ions which accumulate combine with the anions of the acid.³



The technique of electron spin resonance spectroscopy was employed by Hoskins to investigate this problem. He attempted to observe the paramagnetic resonance of diphenylamino radical, which is presumably obtained by heating to 90° C a solution of TPH in toluene.⁴ A five-line spectrum contrary to an expected three-line spectrum was obtained; it will be seen later that an impure sample of TPH gives a five-line spectrum in the solid state and in xylene.

The present investigations on free radicals obtained from TPH, under different conditions, extend Hoskins' attempts to identify the diphenyl-amino radical. The work was undertaken with the expectation that the several radicals obtained from TPH could be distinguished from one another with the help of the $h\nu$ s in their resonance spectra and their g -values.

TECHNIQUES AND MATERIALS.

The spectrometer was similar to a Varian EPR spectrometer (low frequency field modulation) and included a Varian klystron power supply and Varian klystron control unit. A Varian 12" — magnet together with the associated power supply and voltage regulator provided the magnetic field.

A Knöbel-Hahn type transitron proton-resonance oscillator⁵ was employed to measure the magnetic fields and the proton-resonance frequencies were read off on a Hewlett-Packard counter-converter combination. The microwave frequencies were measured accurately using the harmonics of a transfer oscillator⁶. The accuracy of the method was checked with a sample of DPPH. Whereas a speck of DPPH gave inconsistent results due to anisotropic effects, a 0.002 M solution of DPPH in xylene gave a consistent g -value of 2.00347 ± 0.00004 .

Tetraphenylhydrazine: In the first few experiments a sample of TPH kindly sent to us by Dr. M. Vecera was used⁷. The sample, however, had turned green and gave an electron paramagnetic resonance spectrum by itself in the solid state and when dissolved in xylene. The sample was subjected to repeated crystallisations from a mixture of benzene and alcohol but failed to yield a colourless product.

A fresh sample of the material was prepared from Diphenylamine by oxidation with powdered potassium permanganate⁸. On repeated crystallisations from a mixture of benzene and alcohol shining colourless crystals of TPH were obtained; these were dried under vacuum (M.P. 142°C decomp.).

Diphenylbenzidine: Diphenylbenzidine was prepared by the method described by Wieland.⁹

Deuterated acetic acid (CH_3COOD): Deuterated acetic acid (CH_3COOD) was prepared from acetic anhydride and 98% D_2O ¹⁰.

Silver Oxide: Silver oxide was prepared by the oxidation of a solution of silver nitrate with potassium persulphate.¹¹

The other chemicals were obtained commercially and were of "Analar" grade.

RESULTS AND DISCUSSION.

Table I summarizes the data we have obtained on the free radicals we have studied in this series.

I. *Studies on Tetraphenylhydrazine:*

1. On heating a solution of freshly prepared, pure TPH in a non-polar solvent like xylene or toluene to about 90° C, the solution acquired

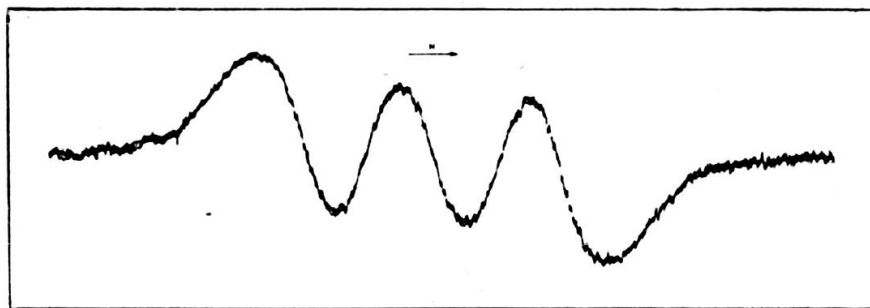


Fig. 1.

Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in xylene heated to 90° C and cooled. The radical is the diphenylamino radical, $\text{Ph} - \text{N} - \text{Ph}$.

a brownish green colour, which it retained on cooling to room temperature. The cooled solution exhibited an electron spin resonance spectrum consisting of three lines with intensities in the ratio 1: 1: 1 (fig. 1). A sample of TPH, which had turned green on keeping, gave, however, a resonance line even in the powder form. The line from the powder exhibited fine structure, which was not very well-resolved, and seemed to consist of at least 5 components. A solution of the same sample in xylene gave a weak, five-line spectrum, which changed to a strong, three line spectrum on heating. It must be pointed out, however, that not all samples of TPH showed visible decomposition on keeping; the samples obtained as colourless crystals after repeated crystallisations were not prone to decomposition on keeping.

The three line spectrum obtained on heating a solution of TPH in a non-polar solvent is attributed to the diphenylamino radical, $\text{Ph} - \dot{\text{N}} - \text{Ph}$,

(sometimes called diphenylnitrogen), whose formation was predicted by Wieland¹. The *hfs* is believed to be due to the hyperfine interaction between the odd-electron and the spin of the N¹⁴ nucleus ($I = 1$), resulting in three equally spaced components with the same intensity.

TABLE I.

Electron Spin Resonance data on Free Radicals derived from and related to Tetraphenylhydrazine

No.	Sample	Number of Components	g-values	Linewidths (gauss) ^a	HFS Separations ^b		Total Spread of the Spectrum	Remarks
					Uncorrected (gauss)	Corrected (gauss) ^c		
I.	<i>Tetraphenylhydrazine (TPH)</i>							
1.	TPH in xylene heated and cooled (fig. 1)	3	2,00549 ± 0,00011	5,5	9,1	10	43	
2.	TPH in xylene, kept for a week	3	2,00537 ± 0,00014	4,0 (approximate)	13	—	39	
3.	TPH in acetic acid, heated and cooled (fig. 2)	5	2,00284 ± 0,00010	3,4	6,1	6.8	41	
4.	(a) TPH in acetic acid, shaken for ten minutes	—	2,00211 ± 0,00010	—	—	—	50	Very weak and poorly resolved.
	(b) TPH in acetic acid, kept for a week	5	2,00285 ± 0,00005	4,2 (approximate)	7,6	—	43	
5.	TPH in acetic acid + PbO ₂ (fig. 3)	5	2,00289 ± 0,00009	—	9,1	—	54	
6.	TPH in Conc. H ₂ SO ₄	5	1,9972 ± 0,0007	—	—	—	39	The radical is very unstable.
7.	(a) TPH in acetic acid + a drop or two of Conc. H ₂ SO ₄ (green) (fig. 4 (a))	6(?)	2,00184 ± 0,00011	—	5,7	—	51	
	(b) TPH in CH ₃ COOD + a drop or two of Conc. H ₂ SO ₄ (green) (fig. 4(b))	—	2,00169 ± 0,00007	—	—	—	43	Very poor resolution

No.	Sample	Number of Components	g-values	Linewidths (gauss) ^a	HFS Separations ^b		Total Spread of the Spectrum	Remarks
					Uncorrected (gauss)	Corrected (gauss) ^c		
II.	<i>Diphenylamine (DPA)</i>							
1.	DPA in acetic acid + PbO ₂	5	2,00289 ± 0,00010	2,9	7	—	37	Similar to fig. 2
2.	DPA oxidized with potassium permanganate and extracted with xylene(fig. 5)	3	2,00416 ± 0,00010	—	—	—	45	
III.	<i>Diphenylbenzidine (DPB)</i>							
1.	DPB in acetic acid + PbO ₂	5	2,00285 ± 0,00010	2,9	6,8	—	39	Similar to fig. 2. The spectrum is asymmetric and consists mainly of 3 lines.
2.	DPB in xylene + AgO or PbO ₂ (fig. 6)	—	—	—	—	—	39	

^a The line-widths refer to distances between points of maximum and minimum slopes and are not corrected for overlap.

^b All the lines [except III (2)] contained hyperfine components which were equally spaced, if overlap was taken into account.

^c The corrections are made to take into account the overlap between the different hyperfine components; they are approximate and assume a Lorentzian shape for the individual hyperfine components.

2. If a solution of TPH in xylene was not heated, but allowed to remain for about a week, (or if oxygen was bubbled through a fresh, cold solution) the sample changed its colour slightly to a faint brownish hue and gave a weak resonance spectrum similar to figure 1. The g-value also agreed with that of the diphenylamino radical within the limits of experimental error. The role of bubbled oxygen or atmospheric oxygen in this reaction is not well understood; it is possible that the first step in this reaction is oxidation, leading further to the cleavage of the molecules, resulting in the formation of diphenylamino radicals.

3. A solution of TPH in acetic acid, however, showed an entirely different behaviour on heating or on keeping. On heating, it turned

violet and the cooled sample showed a strong paramagnetic resonance absorption consisting of five lines (fig. 2). This 5-line spectrum, which has a g -value that differs distinctly from that of the diphenylamino radical, is believed to be due to the tetraphenylhydrazinium radical ion, $\left[\begin{smallmatrix} \text{Ph} \\ \text{Ph} \end{smallmatrix} > \ddot{\text{N}} - \dot{\text{N}} < \begin{smallmatrix} \text{Ph} \\ \text{Ph} \end{smallmatrix} \right]^+$, a radical similar to DPPH; the hfs arises from the interaction of the electron spin with the nuclear spins of the two equivalent nitrogen atoms. The relative intensities of the hyperfine components also agree qualitatively with the expected ratio 1:2:3:2:1. The experi-

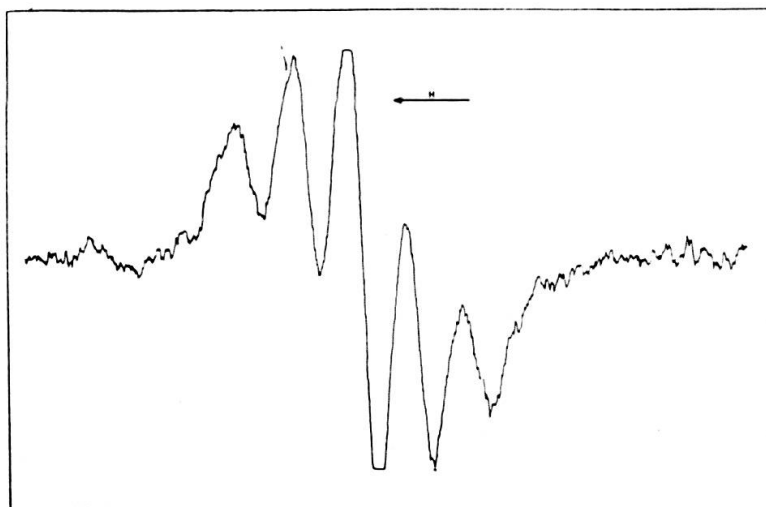
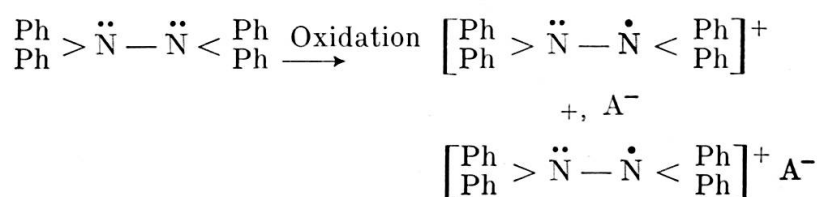


Fig. 2.

Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid heated and cooled.

The radical is the tetraphenylhydrazinium radical, $\left[\begin{smallmatrix} \text{Ph} \\ \text{Ph} \end{smallmatrix} > \ddot{\text{N}} - \dot{\text{N}} < \begin{smallmatrix} \text{Ph} \\ \text{Ph} \end{smallmatrix} \right]^+$.

ment was repeated with $\text{CH}_3\text{COO D}$ and there was no change in the spectrum. Our results support the mechanism proposed by Weitz and Schweten for the behaviour of TPH in acids ²; the tetraphenylhydrazinium radical ion is formed by the removal of an electron from TPH; the resulting cation can then form a salt with the anion of the the acid. A molecule of TPH itself can act as the oxidizing agent:



4. When a freshly prepared solution of TPH in acetic acid was shaken for about ten minutes, the solution took a greenish tinge and showed a very poorly resolved, weak, resonance absorption. The g -value of this differed from those of all the other spectra and the entire spectrum was spread over 50 gauss. A new radical species is formed, the nature of which could not be determined on account of the lack of detailed characteristics of the spectrum.

The same solution, however, when kept over for about a week turned dark brown and exhibited a strong, five-component, resonance line with a g -value agreeing with that of the tetraphenylhydrazinium radical ion. This radical ion is presumably formed by the atmospheric oxidation of TPH in an acidic medium.

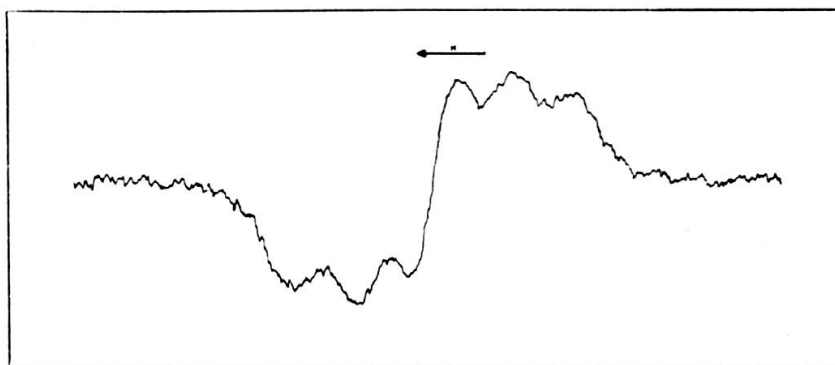


Fig. 3.

Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid treated with PbO_2 .

5. With a stronger oxidizing agent like PbO_2 , however, TPH in acetic acid gave a strong line (fig. 3) whose structure was different from that of the spectrum of the tetraphenylhydrazinium radical ion. Its g -value agrees with that of the hydrazinium radical ion but the hfs spacings are larger, even when they are not corrected for overlap. We have presumably a different radical but with a $>\ddot{\text{N}}-\dot{\text{N}}<$ structure, as is to be expected from a 5-line spectrum. When CH_3COOD was used instead of CH_3COOH , the spectrum showed no change.

6. A powdered sample of TPH, when treated with Conc. H_2SO_4 , showed very rapid colour changes. There was a deep violet colour that lasted for a very short time, followed by a longer blue which finally turned

into pale green. All the colour changes were followed in the paramagnetic resonance spectrometer and only the violet phase showed the presence of free radicals. Initially, the concentration of radicals was very large but decreased very rapidly with no trace of signal after ten minutes. The entire spectrum had to be scanned very rapidly using fast scanning techniques and short time constants. Steady flow techniques were not adopted because of certain experimental difficulties. The g -value measurements were made hurriedly owing to the short-life of the specimen

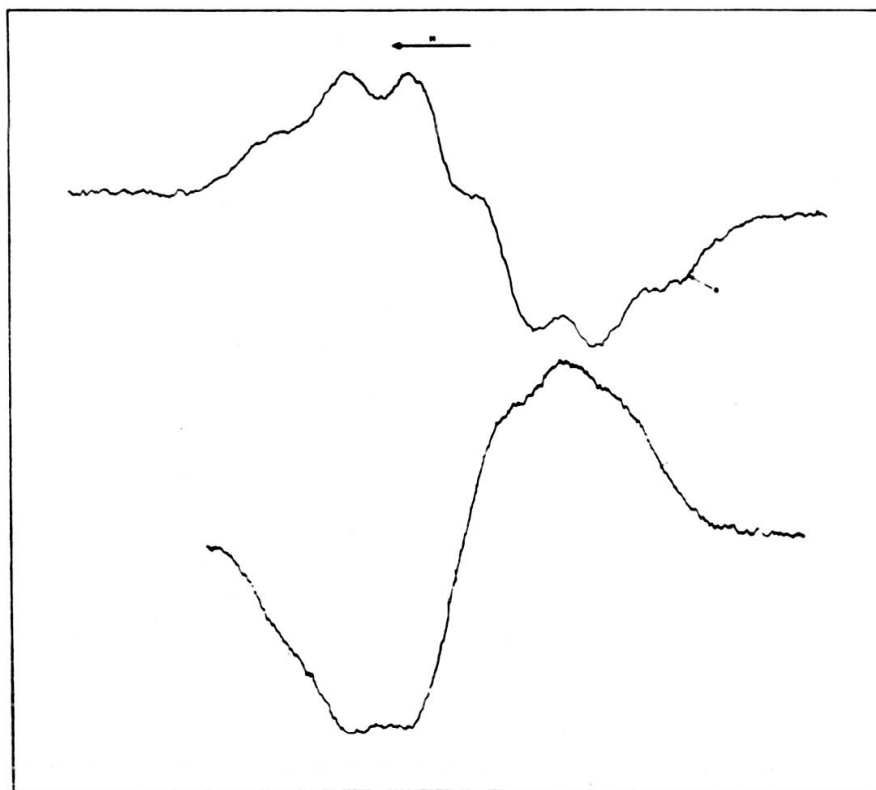
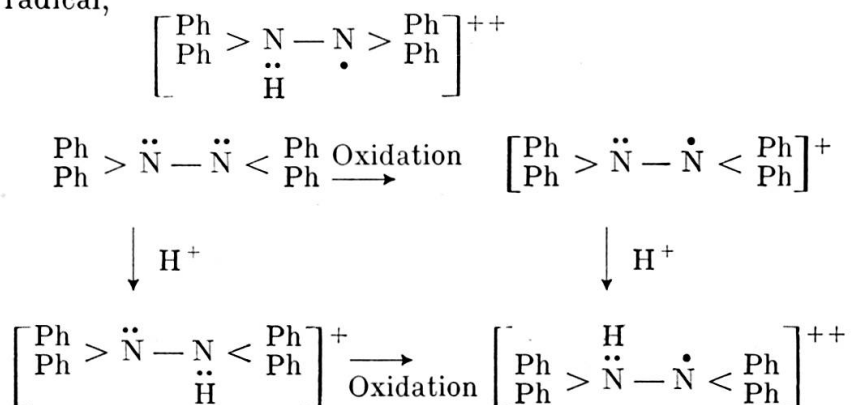


Fig. 4.

- (a) Derivative of electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid treated with a drop of sulphuric acid;
(b) CH_3COOD is used as the solvent instead of CH_3COOH .

and a precision greater than ± 0.0007 could not therefore be attained. The g -value was smaller than the free electron value of 2.0023 and this spectrum also consisted of 5-components. Both the powdered TPH and the conc. H_2SO_4 were cooled to about -5°C before mixing to prolong slightly the life of the free radical phase. We have not understood the nature of the free radical we have observed in this case.

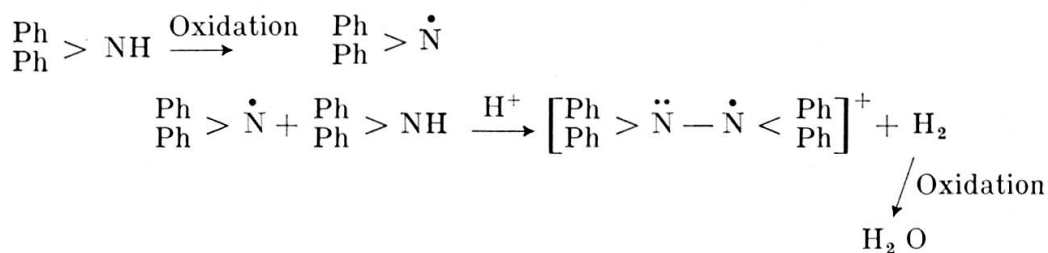
7. The spectrum obtained after the addition of a drop of concentrated sulphuric acid to a freshly prepared solution of TPH in acetic acid was, however, very much different from those discussed earlier (fig. 4(a)). When sulphuric acid was added to the acetic acid solution, there was a flash of violet colour quickly followed by blue, turning slowly into green. The violet phase was too short-lived for resonance studies and the blue phase exhibited no resonance. The green phase had a paramagnetic resonance spectrum, whose central portion showed a flat on the derivative curve indicating a trough rather than a peak at the centre of the line. Since the hyperfine interaction with nitrogen alone ($I = 1$) cannot under any conditions give a trough at the centre, it had to be concluded that some *hfs* due to protons also was being observed. (In the other spectra where the observed *hfs* has been attributed solely to nitrogen nuclei, any *hfs* due to protons might be unresolved). To confirm this, the experiment was repeated with CH_3COOD instead of CH_3COOH and the resulting spectrum (figure 4(b)) showed no trough at the centre. The trough at the centre was, therefore, caused by hyperfine interaction with the protons derived from the carboxyl group of acetic acid; and the deuteration of the carboxyl group led to a peak instead of a trough, as expected from a nucleus with $I = 1$. The *g*-values of the deuterated and undeuterated species agree with each other, though they differ from the *g*-values of the other radicals and fall below the free electron value. The spectrum of the deuterated species was split into five main lines and the spectrum of the undeuterated species apparently into six. The five main lines might be due to a larger nitrogen splitting over which smaller proton or deuteron splittings are superimposed. From the fact that some of the *hfs* is derived from the proton abstracted from the carboxyl group of acetic acid, we are led to believe that the free radical is in all probability, the protonated tetraphenylhydrazinium radical,



II. *Studies on Diphenylamine:*

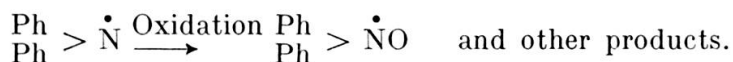
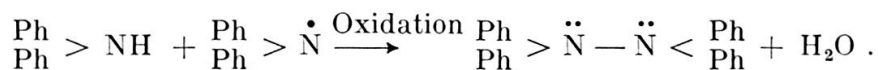
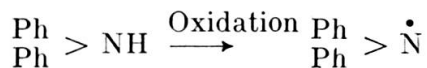
The paramagnetic resonance studies were extended to a few reactions of diphenylamine and diphenylbenzidine, to ascertain whether diphenylamine and diphenylbenzidine, would, under suitable conditions, yield the same radicals as those obtained from TPH.

1. Diphenylamine was subjected to oxidation with PbO_2 in a polar medium, viz., acetic acid. The resonance spectrum of the resulting mixture exhibited five components and the g-value, the line widths of the components and $h\nu$ s spacings agreed with those of the free radical obtained by heating a solution of TPH in acetic acid (i.e. similar to the spectrum of fig. 2). When deuterated acetic acid was used, there was no change in the spectrum. It is possible that the same radical, tetraphenylhydrazinium ion, is derived in the following manner:



2. If, however the oxidation is carried out with PbO_2 or AgO in xylene, a non-polar solvent, the resulting solution gave a very weak, broad resonance spectrum, whose characteristics could not be easily discerned. Since TPH is usually prepared by the oxidation of diphenylamine with powdered potassium permanganate in acetone this system was subjected to resonance studies. A solution of diphenylamine in acetone was shaken for about ten minutes with powdered potassium permanganate at room temperature and the acetone was evaporated with a jet of nitrogen. The residue—which on crystallization from a benzene-alcohol mixture yields TPH—was extracted with xylene in the cold and the xylene extract was examined in the spectrometer; a well resolved three-line spectrum was found (fig. 5). This spectrum, resembled the spectrum of the diphenylamino radical (fig. 1) in its line-width and over-all spread, but had a different g-value. The mother liquor from the crystallisation of the crude TPH also gave a similar spectrum. The mechanism for the formation of TPH is presumed to be the oxidation of diphenylamine into diphenylamino radicals, leading further to the formation of TPH. Since the spectrum

we have observed cannot be attributed to the diphenylamino radical, the radical formed might be due to the successive oxidation of the diphenylamino radical:



The presence of three *hfs* components in the spectra is indicative of this free radical containing only one nitrogen atom. The spectrum reported

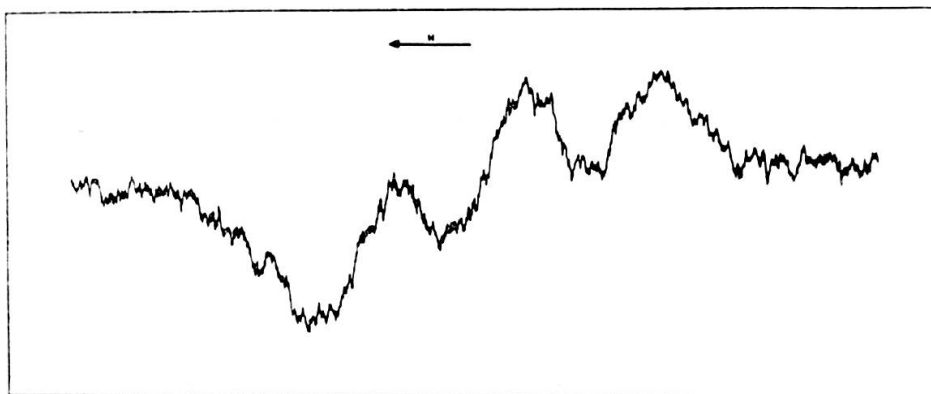


Fig. 5.

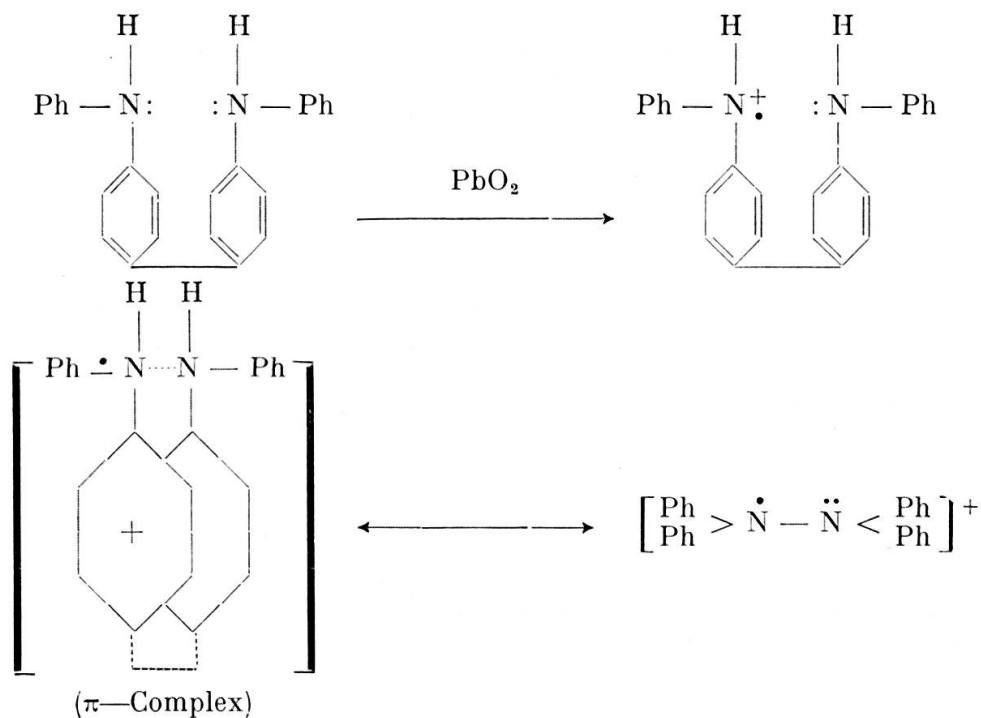
Derivative of the electron spin resonance spectrum of the xylene extract of the residue obtained by the oxidation of diphenylamine with potassium permanganate in acetone and evaporating the acetone.

by Hoskins for the radical obtained by passing oxygen through a hot solution of diphenylamine in a mixture of toluene and alkaline alcohol, and presumed to be diphenyl nitric oxide, $\text{Ph} > \ddot{\text{NO}}$,⁴ does not agree with our spectrum and the *g*-values are also different. The nature of the free radical we have observed here is, therefore, not well understood.

III. Studies on Diphenylbenzidine.

1. Diphenylbenzidine behaved in a manner analogous to diphenylamine when treated with acetic acid and PbO_2 (similar to the spectrum of fig. 2). The five line resonance spectrum did not undergo any change when

deuterated acetic acid, CH_3COOD , was used instead of CH_3COOH . In this case also we believe that the tetraphenylhydrazinium radical is obtained in the following manner:



A similar π -complex is at present believed to be the transition state in the benzidine rearrangement¹². The two aromatic rings fold on each other and the energy difference before and after the folding is extremely small¹²; and the formation of the tetraphenylhydrazinium radical through a π -complex transition state may be compared to the reverse of the benzidine rearrangement.

2. In a non-polar solvent like xylene, the oxidation of diphenylbenzidine with PbO_2 or AgO , resulted in an asymmetric paramagnetic resonance spectrum (fig. 6). It is likely that more than one radical is formed and the measurement of g -value has very little meaning due to the ambiguous nature of the spectrum. If the spectrum could be interpreted as consisting of a less intense line superimposed on a stronger three-line spectrum, the g -value of the three component species is 2.0030 ± 0.0005 , which does not agree with the g -value of the diphenylamino radicals. The radical formed is perhaps $\text{Ph} - \dot{\text{N}} - \text{Ph} - \text{Ph} - \text{NH} - \text{Ph}$. Though a bi-radical of the type $\text{Ph} - \dot{\text{N}} - \text{Ph} - \text{Ph} - \dot{\text{N}} - \text{Ph}$ could also give a three-line spectrum, the formation of the bi-radical is considered unlikely because

of the greater stability of its diamagnetic quinonoid form,

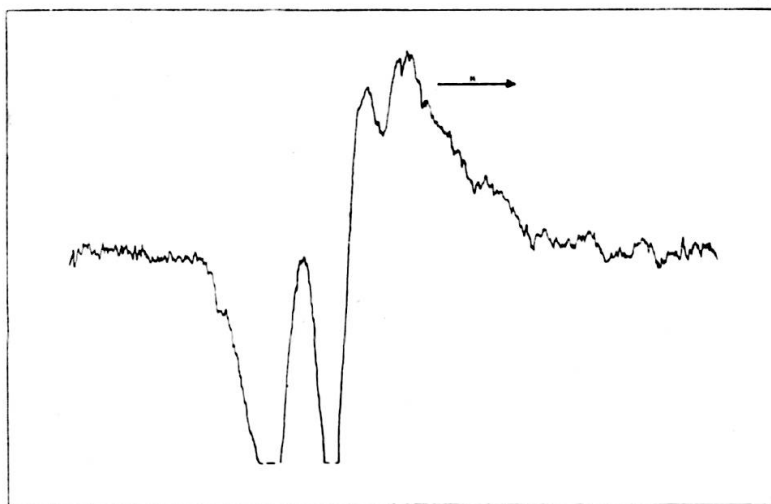
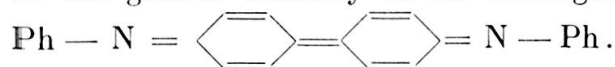


Fig. 6.

Derivative of the electron spin resonance spectrum of a solution of diphenylbenzidine in xylene oxidized with Pb O_2 .

ACKNOWLEDGEMENTS.

The authors are grateful to Dr. M. Vecera, Research Institute for Organic Syntheses, Pardulice-Rybitvi, Czechoslovakia, for providing them with a sample of TPH and for initiating this problem. They also wish to thank Mr. K. V. Lingam for help in obtaining the electron spin resonance spectra of some of the free radicals studied and Dr. S. S. Dharmatti for numerous helpful discussions.

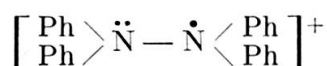
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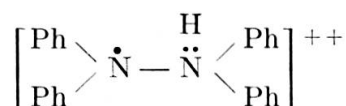
Abstract.

The Free radicals derived from tetraphenylhydrazine, diphenylbenzidine and diphenylamine under different conditions have been investigated with ESR techniques. The identification and differentiation between the radicals were done on the basis of their g -values and the line-widths and hyperfine structure exhibited by their spectra. The formation of the diphenylamine radical, $\text{Ph} - \dot{\text{N}} - \text{Ph}$, by the thermal dissociation of tetraphenylhydrazine in non-polar solvents has been confirmed. The same radical is obtained when tetraphenylhydrazine is subjected to atmospheric oxidation in a non-polar solvent. The tetraphenylhydrazine radical ion,



is formed (1) when a solution of tetraphenylhydrazine in acetic acid is subjected to prolonged atmospheric oxidation, (2) when a similar, freshly prepared solution is heated and (3) when diphenylamine or diphenylbenzidine is subjected to oxidation in an acetic acid medium.

It is believed that the protonated hydrazinium radical,



results if an acetic acid solution of tetraphenylhydrazine is treated with a few drops of concentrated sulphuric acid.

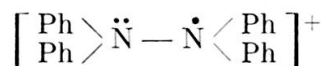
During the course of this investigation, the g -value of a 0.002 M solution of DPPH in xylene was measured 2.00347 ± 0.00004 .

Résumé.

Nous avons étudié au moyen des techniques de résonance électronique les radicaux libres dérivés de la tétraphénylhydrazine, de la diphenylbenzidine et de la diphenylamine dans différentes conditions.

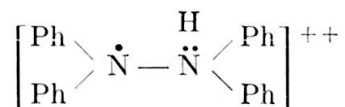
L'identification des radicaux et leur différenciation sont faites au moyen des valeurs de g , des largeurs de raies et de la structure hyperfine présentée par les spectres. La formation de radicaux de diphenylamine $\text{Ph} - \dot{\text{N}} - \text{Ph}$ par dissociation thermique de la tétraphénylhydrazine dans des solvants non polaires a été confirmée. Ce même radical est obtenu quand la tétraphénylhydrazine est

soumise à une oxydation atmosphérique dans un solvant non polaire. Le radical ionique tétraphénylhydrazine



est formé (1) quand une solution de tétraphénylhydrazine dans l'acide acétique est soumise à une oxydation atmosphérique prolongée; (2) quand une solution semblable fraîchement préparée est chauffée et enfin (3) quand la diphenylamine ou la diphenylbenzidine sont soumises à une oxydation en milieu acide acétique.

On croit que le radical hydrazinium protoné



se forme quand on ajoute à une solution acide acétique de tétraphénylhydrazine quelques gouttes d'acide sulfurique concentré.

Au cours de ces recherches, on a mesuré pour le facteur g d'une solution 0,002 M de DPPH dans du xylène, la valeur $2,00347 \pm 0,00004$.