The Photochemical Decomposition of α, α-Diphenyl-β-picrylhydrazyl (DPPH) in Solution. II. Products of the Photolysis and Its Reaction Mechanism

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In the preceding paper of this series, the kinetic investigation of the photochemical decomposition of DPPH in solution was reported, and there was proposed a reaction mechanism which is compatible with the results of the kinetic experiments[1]. In order to obtain further detailed information on the decomposition mechanism, the reaction products were also investigated. In paper chromatographical analysis, the R_f values of the reaction products were determined; two of the products were found to be identical with those of α, α-diphenyl-β-picrylhydrazine (I) and α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine (II) respectively[2]. Further, by modifying the method of the photolysis, it became possible to obtain a large amount of the reaction products and to separate the reaction products in a relatively large amount on a cellulose column. Thus, two species of the reaction products were identified unequivocally as α, α-diphenyl-β-picrylhydrazine, and α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine by comparison with authentic specimens prepared by a different method.

The third component in the reaction products (III) (an experimental formula $C_{18}H_{10-11}\cdot N_3O_3$) has not yet been identified with any known compound, although a phenazine-type structure is presumed for it. On the basis of its structure and the previous kinetic results, however, it is presumed that this compound originates from excited DPPH; therefore, a reaction mechanism which involves the nitration of DPPH by the excited DPPH is herein proposed, a mechanism which is compatible with the findings of the previous kinetic experiment.

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[1] Part I, This Bulletin, 36, 644 (1963).

[2] Until recently this compound was believed to be α, α-diphenyl-β-hydroxy-β-picrylhydrazine, but it has recently been demonstrated to be α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine by J. A. Weil, K. V. Sane and J. M. Kinkade, *J. Phys. Chem.*, 65, 710 (1961).

Results and Discussion

Separation and Identification of the Reaction Products.—*Separation of the Products by Paper Chromatography.*—As a preliminary investigation, the reaction products were chromatographed on a filter paper. Porier[3] has described the separation of various hydrazyl derivatives by paper chromatography using several eluting solvents. In the present case, however, it was found that the most suitable solvent was a mixture of petroleum ether and carbon disulfide (1 : 1 by volume). The R_f values of the reaction products in the presence or absence of air shown in Tables Ia and Ib, which demonstrate that I and II have the same R_f values as those of α,α-diphenyl-β-picrylhydrazine and α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine respectively.

TABLE Ia. R_f-VALUES OF REACTION PRODUCTS
Decomposition was carried out at 25°C

Solvent	Condition of irradiation	Fraction A	B	C
Benzene	Air present	0.83	0.28	0.04
	Air absent	0.82	0.29	0.04
CCl_4	Air present	0.83	0.29	0.04
	Air absent	0.84	0.27	0.04

TABLE Ib. R_f-VALUES OF REFERENCE SUBSTANCES

	I	II	DPPH
R_f-Value	0.83	0.27	0.84

I : α,α-Diphenyl-β-picrylhydrazine
II : α-Phenyl-α-(p-nitrophenyl)-β-picrylhydrazine

Isolation of the Reaction Products on a Cellulose Column.—Though the separation of the reaction products by paper chromatography is very convenient for the separation of a small amount of the products, it is necessary to obtain a large amount of the products in order to determine the structure of the product III. As a source of light for photolysis, sun-light was substituted for a tungsten lamp in order to complete the photolysis in a short time, and a cellulose column was used to separate a relatively large amount of the reaction products. Benzene was used as a solvent instead of carbon tetrachloride, since the reaction products by sun-light are found to be identical with those obtained under the controlled conditions described in the preceding paper. Three components are isolated on a cellulose column from the reaction products of DPPH, and I and II are confirmed unequivocally to be α,α-diphenyl-β-picrylhydrazine and α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine respectively by infrared spectra and by mixed melting point determinations with the authentic specimens. The structure of III will be discussed in detail later.

The Determination of the Ratios of the Reaction Products.—The method of the separation of the products on a cellulose column described above was also applied in the quantitative estimation of the reaction products. Known amounts of I, II and III were mixed and fractionated on a cellulose column, and the amount of the eluted products was determined by photometry. The visible and ultraviolet absorption spectra of DPPH, I, II and III are shown in Fig. 1, while the results of the quantitative determination of the reaction products are shown in Table II.

TABLE II. FRACTIONATION OF THE THREE COMPONENTS ON A POWDERED CELLULOSE COLUMN

Eluting solvent	Petroleum ether+CS_2 (2 : 1)		Petroleum ether+CS_2 (1 : 1)	Benzene
Product	DPPH	+I	II	III
Recovery (%)	99	104	103	98

I : α,α-Diphenyl-β-picrylhydrazine
II : α-Phenyl-α-(p-nitrophenyl)-β-picrylhydrazine
III : $(C_{18}H_{10-11}N_3O_3)_n$

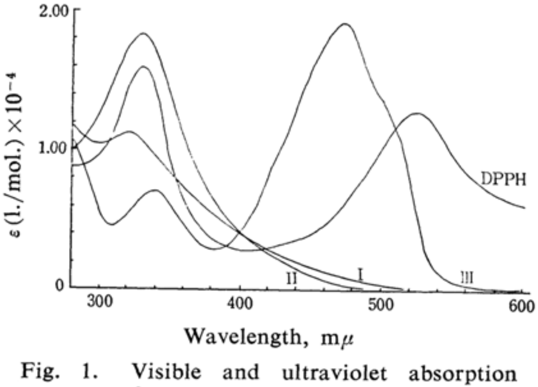

Fig. 1. Visible and ultraviolet absorption spectra of DPPH, α,α-diphenyl-β-picrylhydrazine (I), α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine (II), and unknown compound (III). ε of III is given by assuming its M.W.=317.

The table shows that the method is statisfactory for the present purposes. The recovery of more than one hundred per cent of I and II might be due to errors in photometry caused by some impurities coming from the cellulose, which could not be completely removed even by extracting the adsorbent several times with benzene before its use.

Figure 2 gives the ratios of the reaction

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[3] R. H. Porier, E. J. Kahler and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952).

products in a benzene solution after various periods of the reaction time. Since the ratios of I, II and III do not vary markedly in the course of the decomposition, as is shown in Fig. 2, it may be concluded that no one of these three products is a precursor of the other. The total material balance at the final stage of the reaction may be approximated by saying that four moles of DPPH give approximately one mole of I (slightly more than one mole actually), two moles of II, and one mole of III (really slightly less than one mole). In a carbon tetrachloride solution, similar results were obtained, as is shown in Table III.

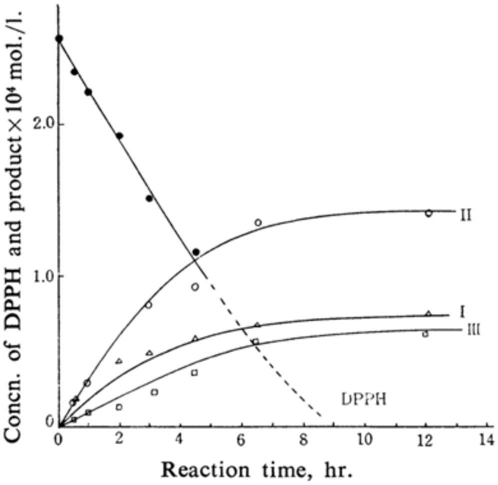

Fig. 2. Concentration-time curves of DPPH products in benzene solution.

I: α, α-Diphenyl-β-picrylhydrazine
II: α-Phenyl-α-(p-nitrophenyl)-β-picrylhydrazine
III: Unknown compound

Investigation of the Structure of III.—*Physical Properties and Molecular Weight.*—The crude substance of III, which was isolated from the decomposition products of DPPH, gives orange-red needles when sublimed at a temperature between 230∼250°C. It does not show a clear melting point, but decomposes gradually when heated above 280°C. In ordinary solvents it is sparingly soluble, but it is soluble in concentrated sulfuric acid or hydrochloric acid to give an orange solution without decomposition, indicating that it has basic property. Elemental analysis shows the chemical composition of $(C_{18}H_{10-11}N_3O_3)_n$. The determination of the molecular weight of III was attempted by various methods: the ebullioscopic method in dimethylformamide, the Rast method in camphor or camphor quinone, and the isothermal distillation method, but they produced no appreciable change in either boiling point or melting point within the possible upper limit of concentration, which is unfortunately very small in the available solvents, but the authors could nevertheless conclude that *n* should be more than three.

The Ultraviolet and Infrared Spectra of III.—The ultraviolet spectrum of III indicates a maximum absorption at $\lambda=470\,\mathrm{m}\mu$, and it is

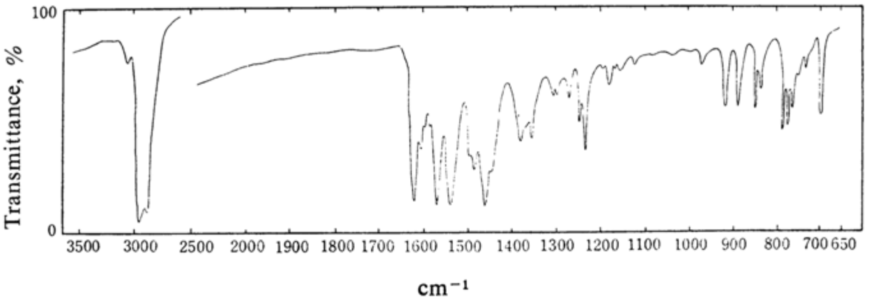

Fig. 3a.

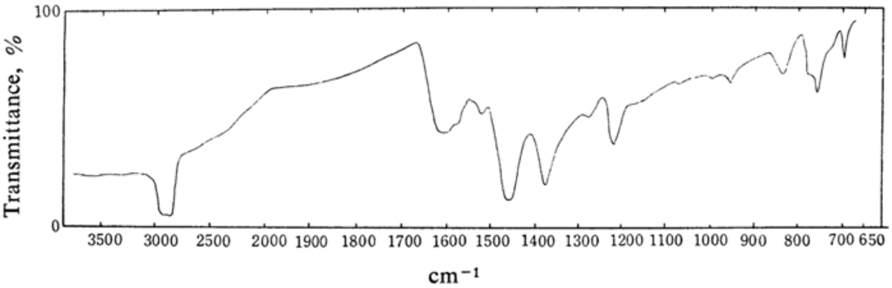

Fig. 3b.

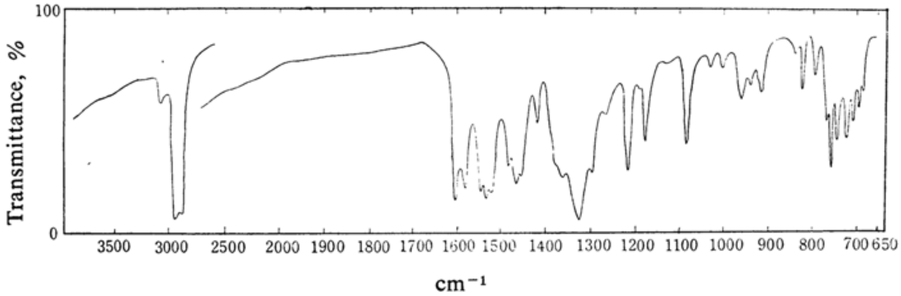

Fig. 3c.

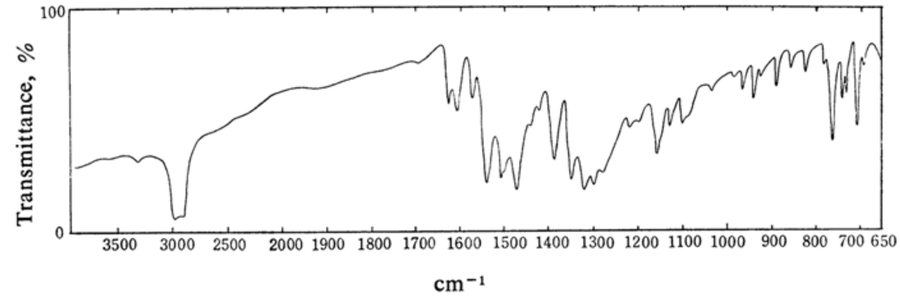

Fig. 3d.

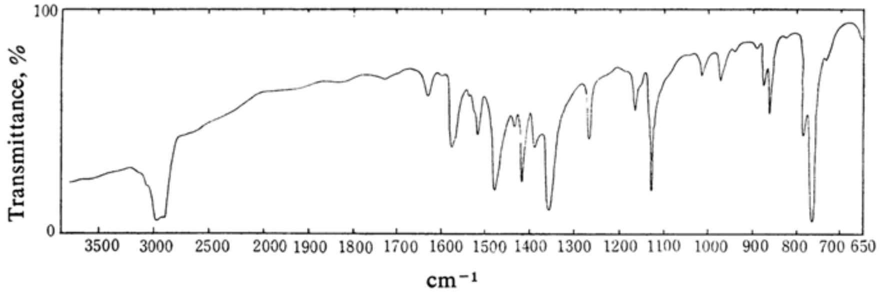

Fig. 3e.

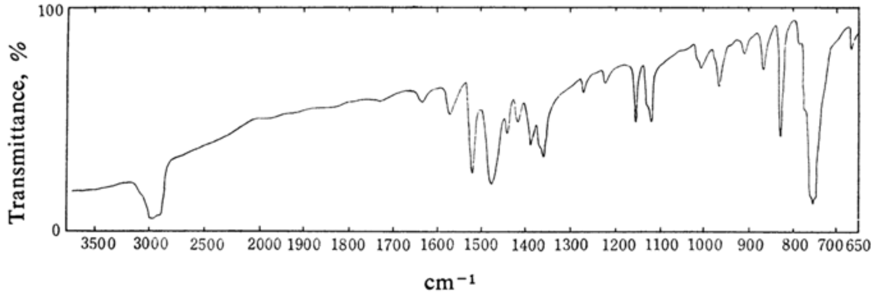

Fig. 3f.

Fig. 3. Infrared absorption spectra of (a) ; III, (b) ; III+HI, (c) : α,α-diphenyl-β-picrylhydrazine, (d) ; 10-phenyl-1,3-dinitro-9,10-dihydrophenazine, (e) ; *N*-oxyphenazine and (f) ; phenazine (in Nujol).

TABLE III. AMOUNT OF THE REACTION PRODUCTS AT THE FINAL STAGE OF THE DECOMPOSITION IN mol./l.×10^5

Solvent	React. temp. °C	React. time hr.	Initial amount of DPPH*	Amount of products* I	II	III	I+II+III	Total yield $\frac{I+II+III}{DPPH}\times 100$
Benzene	25	12	26.0	7.5	14.1	6.2	27.8	107
Benzene	45	12	26.0	7.7	13.2	6.3	27.2	105
CCl_4	25	17	27.7	8.1	14.3	6.0	28.4	103

* Concentration: mol./l.×10^5

to be noted that the maximum is located at longer wavelengths than those of I and II, suggesting that III has a larger conjugate system than I and II.

The infrared absorption spectrum of III, along with those of II, 10-phenyl-1, 3-diniro-9, 10-dihydrophenazine, phenazine and phenazine oxide as reference substances, are shown in Fig. 3.

No characteristic bands corresponding to the stretching vibration of N–H or O–H are observed in the 3000～3500 cm^{-1} region of the spectrum of III. The absorption bands at 1535 cm^{-1} and 1300 cm^{-1} are assigned to the nitro group. A band at 1235 cm^{-1} is difficult to assign to a unique vibration, but it might originate from the asymmetrical stretching vibration of the ether-type bond R–O–R if the supposed structure of III is accepted. α, α-Diphenyl-β-picrylhydrazine, 10-phenyl-1, 3-dinitro-9, 10-dihydrophenazine, and III have a strong band at 695 cm^{-1} in common, a band which is assigned to an out-of-plane bending vibration of the aromatic C–H of mono-substituted benzene. In mono-substituted benzene, we should expect another absorption band near 750 cm^{-1}; Fig. 3a shows two bands at 755 and 767.5 cm^{-1}, but it is not certain which of the two bands is to be assigned to this bending vibration. Figure 3a also shows bands at 835, 845, 882.5 and 915 cm^{-1}, indicating the presence of poly-substituted benzene nuclei in III.

The Reduction of III with Stannous Chloride.—The chemical formula $(C_{18}H_{10-11}N_3O_3)_n$ indicates the presence of one nitro group in one monomer unit, this combination being compatible with the infrared spectrum of III. In order to confirm the presence of this nitro group and simultaneously to investigate the possibility of the presence of any other reducible group or center, such as *N*-oxide or a free radical electron, the quantitative reduction of III with stannous chloride has been carried out. It has been found that three moles of stannous chloride were consumed per one mole of monomer unit of III, confirming the results of the infrared spectrum and elemental analysis. Further, this result shows that no other easily reducible group or center exists in the compound. The authors also concluded that the original hydrazine bond of DPPH is not left intact in the structure of III, since it is generally known that the usual hydrazine bond is split by stannous chloride to give amino compounds.

The Reaction of III with Hydroiodic Acid.—In order to explain the one extra atom of oxygen, in addition to the nitro group, in the chemical formula $C_{18}H_{10-11}N_3O_3$, the presence of ether-type oxygen was supposed, and the reaction of III with hydroiodic acid was carried out in attempt to open the supposed ether bond. When III was treated with hydroiodic acid, it gave a compound containing one atom of iodine for one unit of III, this compound does not, however, seem to be any simple salt nor molecular complex, because it does not liberate iodide ions when treated with alkali. The infrared spectrum of this compound is very different from that of III, but it does not show any band characteristic of N–H or O–H in the 3000～3500 cm^{-1} region. In spite of this finding, we could not, considering the general high resistivity of the aromatic ether bond to hydroiodic acid, discard the possibility of the presence of ether-type oxygen in III.

The Supposed Structure of III.—The whole of the available data described above is still not sufficient to establish the structure of III, particularly since its molecular weight is not yet known, but the following statements on the structure of III may be accepted at the present stage of knowledge:

(1) Three benzene skeletons are preserved, and one of them is of the mono-substituted type.

(2) One nitro group remains in a benzene nucleus which was originally the picryl group, but it is not known which one of the three nitro group (para or ortho) is thus preserved.

(3) The hydrazine-type $\rangle$N–N$\langle$ bond is split during the reaction to form a phenazine-type ring which is considered to be more stable than the hydrazine derivatives.

It is interesting that Wieland[4] found that the

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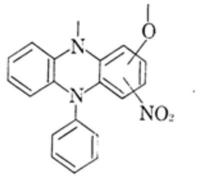
[4] H. Wieland, *Ber.*, **41**, 3478 (1908); **48**, 1078 (1915).

phenazine ring is formed from substituted tetraphenylhydrazines by the action of acid, although the present reaction conditions are different from these in Wieland's experiment.

Summarizing these results, a provisional presentation of the unit structure of III may be shown as follows:



The Material Balance of the Photolysis of DPPH.—According to the experiment determining the ratios of the reaction products, we propose the following stoichiometric relation:

$$4C_{18}H_{12}N_5O_6 \rightarrow C_{18}H_{13}N_5O_6 \text{ (I)}$$
$$+ 2C_{18}H_{12}N_6O_8 + C_{18}H_{10-11}N_3O_3 \text{ (III)}$$

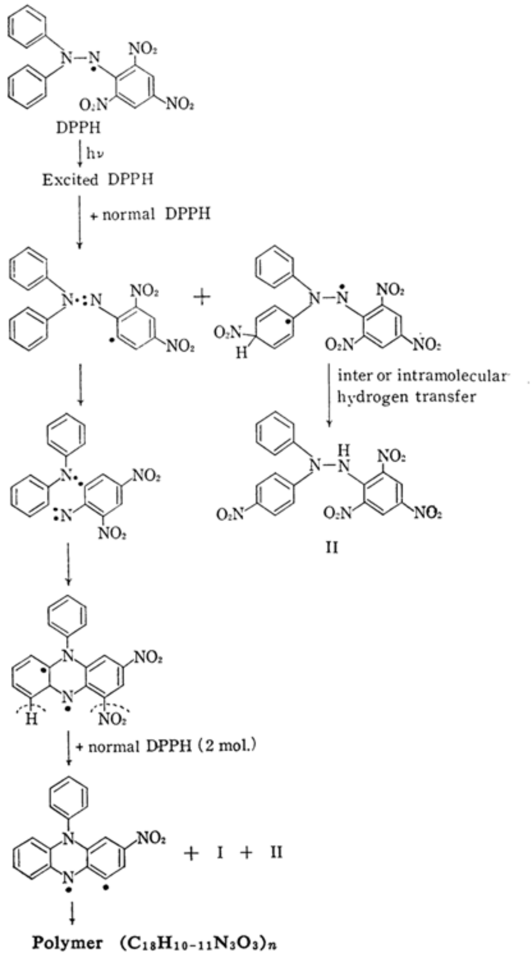
Although there is an excess atom of oxygen on the right hand side, the material balance seems to be fairly statisfactory, considering the accuracy of the quantitative estimation of the reaction products. No definite explanation of the unbalance in the number of oxygen atoms in the above equation is available at present, but it is possible that the oxygen atom is introduced from air or water during the treatment of the reaction products after the irradiation.

In spite of our efforts to find any other reaction product, gas chromatography failed to detect any such volatile substance as nitrobenzene which might be expected to result from the reaction of excited DPPH with the solvent benzene. It was found, however, that some nitrogen oxide existed in the reaction mixture. When the benzene mixture of the reaction products was extracted with water several times, the Gries test showed the presence of nitrous ions in the water extract, but the amount was very small (about one part to 80 parts of DPPH). Further, it was found that III itself produces some nitrogen oxide, most probably nitrogen dioxide, by irradiating its solution. It is presumed that nitrogen oxide comes from the nitro group of III by irradiation, although the detailed mechanism is not known. The nitrogen oxide found in the original reaction mixture of photolysis of III might be produced by the secondary decomposition of III.

The Reaction Mechanism of the Photolysis of DPPH.—In the absence of further data, it is premature to propose a complete scheme for photolysis of DPPH, but our kinetic investigation described in the preceding paper shows that the experimental rate expression fits the following reaction scheme:

$$\begin{aligned}
&D^* + h\nu && \longrightarrow && D^* \\
&D^* + \text{(solvent)} && \longrightarrow && D \\
&D^* + D && \longrightarrow && D^*D \\
&D^*D && \longrightarrow && A + P_1 \\
&P_1 + D && \longrightarrow && B + P_2 \\
&P_2 + D && \longrightarrow && C + P_3
\end{aligned}$$

The products described here as A and B, are not directly related to the final products identified in the present work, but the authors assume that excited DPPH transfers its two nitro groups to normal DPPH to give α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine. The course through which the original excited DPPH is transformed to III is not yet clearly understood, and it might be difficult to describe the process completely in termes of a classical structure formula. The following scheme must be admitted to be rather speculative, but it is given to show some idea of the reaction mechanism:



Experimental

The Decomposition of DPPH in a Benzene Solution by Sun-light.—One gram of DPPH was dissolved in 1 l. of purified and dried benzene. In order to increase the surface area of the solution exposed to sun-light, the solution was divided into five glass tubes 2 cm. in diameter by 70 cm. in length, and each tube was sealed without evacuation, leaving air in the space above the surface of the solution. They were exposed to sun-light for about twenty days. By the time the decomposition was completed, the color of the solution had become brown red, giving a brown precipitate. The benzene was removed under reduced pressure, and the residue was fractionated by elution chromatography on a powdered cellulose column measuring 9.0 cm. in diameter by 40 cm. in length and containing 400 g. of adsorbent, using a solvent mixture of petroleum ether and carbon disulfide (2 : 1 by volume) as the eluting solvent. After the first fraction, which was α,α-diphenyl-β-picrylhydrazine (I), came out, the ratio of petroleum ether to carbon disulfide was varied from 2 : 1 to 1 : 1 by volume to elute α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine. The last component was eluted with benzene. Each component was readily distinguishable by the color of the zone. The eluting solvents were distilled off under reduced pressure, and the residue was purified in the following way: I was recrystallized from a mixture of chloroform and alcohol (1 : 1 by volume) ; 0.12 g. of brick-red crystals (m. p. 171∼172°C) were obtained. II was purified by recrystallization from an ethyl acetate-alcohol mixture (1 : 2 by volume) ; brick-red crystals, (m. p. 152∼153°C ; weight, 0.21 g.) were obtained. I and II did not depress the melting points of admixture with authentic samples of α,α-diphenyl-β-picrylhydrazine and α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine respectively, and III (0.10 g.) was obtained as a brick-red powder.

The Quantitative Determination of the Reaction Products.—After known amounts of benzene solutions of DPPH, I, II and III were mixed, the solvent was removed by evaporating it under reduced pressure in the dark, and the residue was fractionated on a cellulose column by the method described in the preceding paragraph. The solvents of each fraction were evaporated up to dryness under reduced pressure in the dark, and the residues were dissolved in benzene. From the first fraction the amount of DPPH was determined colorimetrically by absorption at 520 mμ using $\varepsilon=1.28\times10^4$ l./mol., assuming $\varepsilon=0$ for I. The amount of I was obtained from the absorption at 320 mμ minus that of DPPH using $\varepsilon=1.13\times10^4$ l./mol., and $\varepsilon=1.83\times10^4$ l./mol. for I and DPPH respectively. The amounts of II and III were determined by the absorption at 330 mμ ($\varepsilon=1.83\times10^4$ l./mol.) and 470 mμ respectively. The number of moles of III was calculated by assuming its chemical formula to be $C_{18}H_{10}N_3O_3$.

The Determination of the Ratios of the Reaction Products in the Course of the Decomposition.—Fifty milliliters of a benzene solution of DPPH (2.60×10^{-4} mol./l.) was irradiated, and 2 ml. of the solution was pipetted out after various periods of time. Each component in the reaction mixture was determined by the method described in the preceding paragraph.

The Purification of the Product III.—The substance III, which was obtained by column chromatography, has a fairly high purity, but further purification can be achieved by sublimation, giving orange needles. A convenient apparatus for it is shown in Fig. 4.

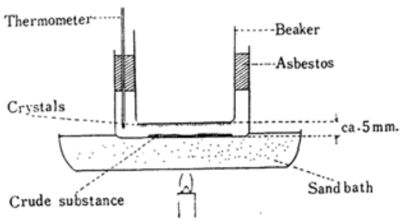


Fig. 4. Apparatus for sublimation of III.

The chemical composition and the visible and ultraviolet absorption spectra after sublimation were consistent with those obtained before sublimation.

Found : C, 68.28 ; H, 3.47 ; N, 13.28. Calcd. for $C_{18}H_{10}N_3O_3$: C, 68.35 ; H, 3.18 ; N, 13.28. $C_{18}H_{11}N_3O_3$: C, 68.13 ; H, 3.49 ; N, 13.24%.

After sublimation ; C, 68.10 ; H, 3.50%.

The Estimation of the Molecular Weight.—The molal elevation constant (K) for dimethylformamide was found to be 18.9°C by using azobenzene. The elevation of the boiling point of the solution of III (0.0171 g.) in dimethylformamide (2.084 g.) was less than 0.10°C, indicating that the number of n is larger than 4.

Because of the low solubility of III in camphor or camphor quinone, as well as because of the coloring of the solutions, the determination of the molecular weight by Rast's method was unsuccessful. The depression of the melting point of a mixture of III (1.3 mg.) with camphor quinone (92.2 mg.) was scarcely observed. If the molecular weight of III is assumed to be about 320, the depression can be expected to be about 2°C in the concentration. When an isothermal distillation method[5] was also applied to III, using benzene as the solvent, the shift of meniscus was hardly noticeable.

The Quantitative Reduction of III with Stannous Chloride in Sulfuric Acid[6].—Nineteen milligrams of III purified by sublimation was suspended in 5 ml. of ethanol which had previously been freed from aldehyde by refluxing it for several hours in a rapid stream of carbon dioxide. When 2 ml. of dilute sulfuric acid (1 : 1 by volume) and 2 ml. of a standard stannous chloride solution (142.1 mg./ml.) were added, the color of III turned reddish violet. During the reduction, a slow stream of carbon dioxide was led into the flask, and the mixture was heated gradually on a water bath. When,

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[5] R. P. Linstead et al., "A Course in Modern Techniques of Organic Chmistry", Butterworths Scientific Publications, London (1955), p. 150.

[6] A. Weissberger et al., "Organic Analysis II", Interscience Publishers, Inc., New York (1954), p. 77.

after half an hour, the reduction had been completed, the contents of the flask were rapidly cooled, diluted with 30 ml. of water, saturated with carbon dioxide, and rapidly titrated against a standard solution of iodine (35.98 mg./ml.), the end point being determined by a pH meter. The difference in the iodine solution between the amount of a blank test and that after the reaction was 1.27 ml., which corresponds to 34.7 mg. of stannous chloride. The theoretical amount of stannous chloride needed to reduce 19.0 mg. of III is 34.2 mg., assuming ing III to have only one nitro group per unit.

The Reaction of III with Hydroiodic Acid.— When a mixture of 10 mg. of III and 0.5 ml. of hydroiodic acid (52%) was heated on a water bath, reaction took place immediately, and the mixture turned black. After heating the mixture of ten minutes, the excess hydroiodic acid was filtered off and the residue was extracted with cold alcohol (95%) several times. The combined alcohol solution was diluted with water to give a dark precipitate which weighed 12.8 mg. when dried at 60°C/2 mmHg for 200 min. The free iodine accompanying the precipitate was completely eliminated in the drying procedure under vacuum.

The Molecular-weight Estimation of the Reaction Product. — When the reaction product (27.8 mg.) of III with hydroiodic acid was dissolved in bromoform (6.322 g.), the depression of the melting point was 0.005°C. As the molal depression constant for bromoform is 14.4°C, the molecular weight was calculated to be 1270, which means that III is a trimer of ($C_{18}H_{10}N_3O_3I$, mol. wt. 443). In such a case, the depression should be not so large as to enable us to determine the molecular weight precisely, but it may be concluded that the number of n for $(C_{18}H_{10}N_3O_3I)_n$ is larger than 3.

The Determination of Nitrous Ions[7]. — DPPH (10.46 mg. 27 μ mol.) was dissolved in distilled dry benzene (100 ml.) and irradiated for 13 hr., according to the procedure described in the preceding paper, until the decomposition of DPPH had been completed. The reaction mixture was extracted several times with distilled water (in total 100 ml.) until the extract did not show the presence of nitrous ions. The extract was then brought to reaction with Griess' reagent and the amount of nitrous ion was determined colorimetrically, using a calibration curve obtained by an experiment with a known amount of sodium nitrite. The extract was found to contain 10^{-3} mg. of nitrous ions per 100 ml.

The benzene solution of the reaction mixture, which had been completely extracted with water and which was free from nitrous ion, was then divided into two parts; one of these was kept in the dark, and the other was irradiated for another 9 hr.

When the solutions were extracted with distilled water (in total 50 ml.), the one kept in the dark showed a scarcely positive Griess test, but the irradiated one contained 3.3×10^{-3} mg. (0.07 μmol.) of nitrous ions per 50 ml. of solution. The former was fractionated on a cellulose column into three components, and each component was then dissolved in benzene (50 ml.) as before. When these benzene solutions had been further irradiated for 9.5 hr., nitrous ions were detected only in the solution of III. The change in the absorption spectra of III before and after the irradiation was shown in Fig. 5.

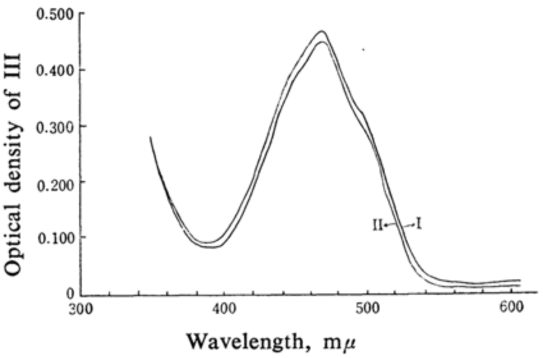

Fig. 5. Change in the absorption spectra of III before and after the irradiation.
I: Immediately after the isolation
II: After irradiation for 9.5 hr.

The other experiment, in which DPPH (10.50 mg.) (27 μ mol.) was dissolved in benzene (100 ml.) and irradiated for 22 hr., showed that the amount of nitrous ions was at most 17.25×10^{-3} mg. (0.37 μ mol.), which corresponds approximately to one part to twenty parts of III, assuming that III is produced in the yield of about 25 per cent from DPPH. Since the photochemical decomposition of III seems to be very slow, the low yield of nitrous ions and the high yield of III in the original reaction mixture of the photolysis of DPPH is understandable.

Summary

1. DPPH in a benzene solution was decomposed by sun-light on a relatively large scale in the presence of air, and the prducts were separated on a cellulose column. The products were identified as α,α-diphenyl-β-picrylhydrazine (I), α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine (II), and a third component (III) with a chemical composition of $(C_{18}H_{10-11}N_3O_3)_n$ (the n is greater than 3).

2. The method of separation by means of a cellulose column was applied in the quantitative estimation of the reaction products. The ratios of the products in the course of the decomposition were determined. From the ratio at the final stage, the over-all reaction can be written as follows:

$$4\ \text{DPPH} \rightarrow \text{I} + 2\,\text{II} + \text{III}$$

3. The physical and chemical properties of the third component have been described, and a possible structure for III has been proposed.

4. From the material balance and the

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[7] M. B. Shin, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 33 (1941).

chemical compositions of the reaction products, it is presumed that the early stage of the decomposition of DPPH induced by light is an intermolecular nitration of DPPH.

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