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THE CHEMISTRY OF HYDRAZYL FREE RADICALS. I. SPECTROPHOTOMETRIC EVIDENCE ON THE STRUCTURE OF α,α-DIPHENYL-β-PICRYLHYDRAZYL AND α,α-DIPHENYL-β-PICRYL-β-OXYHYDRAZYL[1]

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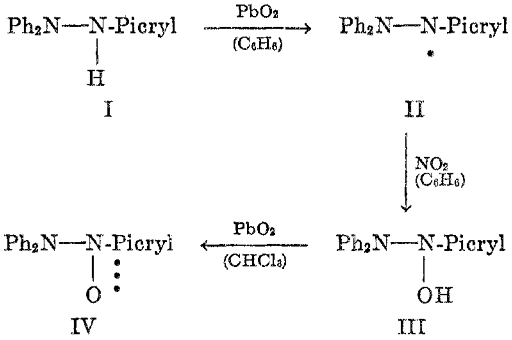
Optical (1) and mass spectroscopic (2) methods have been used to detect free-radical intermediates in the combustion of hydrogen and hydrocarbons. Paneth's lead-mirror technique (3) and its modifications by Rice (4) and co-workers have been applied in the identification of alkyl free radicals. Benington (5) demonstrated the feasibility of interradical reactions to identify gaseous free radicals by the capture of hydrogen atoms, and methyl free radicals, by triphenylmethyl. In continuation of the latter studies, certain hydrazyl-type free radicals were investigated, because of their high degree of dissociation and inertness to molecular oxygen, thereby making such reagents attractive for studies on combustion systems with oxygen as oxidant. This paper is concerned with the characterization and proof of structure of α,α-diphenyl-β-picrylhydrazyl, and some of its derivatives representing adducts with intermediates supposedly formed in the combustion of hydrogen. The intermediates which are most often considered in this combustion process are: hydrogen atoms, H; hydroxy free radical, HO•; hydroperoxy free radical, HOO•; and oxygen atoms, O. The capture of these gaseous constituents by α,α-diphenyl-β-picrylhydrazyl should form identifiable β-substituted, α,α-diphenyl-β-picrylhydrazines.

Oxidation of α,α-diphenyl-β-picrylhydrazine (I) by lead peroxide (PbO_2) in chloroform readily forms α,α-diphenyl-β-picrylhydrazyl (II) (6). Hydrazyl II is a violet-black solid showing paramagnetic properties of a molecule containing one unpaired electron even at liquid air temperatures (7).



$$\begin{tikzcd} \underset{\mathrm{I}}{Ph_2N{-}\underset{\mathrm{H}}{\underset{|}{N}}{-}Picryl} \arrow[r, "PbO_2", "(C_6H_6)"'] & \underset{\mathrm{II}}{Ph_2N{-}\underset{\bullet}{N}{-}Picryl} \arrow[d, "NO_2", "(C_6H_6)"'] \\ \underset{\mathrm{IV}}{Ph_2N{-}\underset{\mathrm{O}}{\underset{|}{N}}{:}{-}Picryl} & \underset{\mathrm{III}}{Ph_2N{-}\underset{\mathrm{OH}}{\underset{|}{N}}{-}Picryl} \arrow[l, "PbO_2"', "(CHCl_3)"] \end{tikzcd}$$

Unlike other compounds of divalent nitrogen, II does not react with nitric oxide, NO, although it absorbs nitrogen dioxide, NO_2, to yield eventually α,α-

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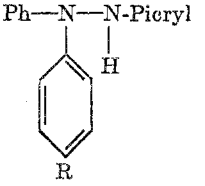
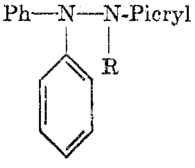
diphenyl-β-picryl-β-hydroxyhydrazine (III). Hydroxyhydrazine III also is oxidized by lead peroxide and forms α,α-diphenyl-β-picryl-β-oxyhydrazyl (IV).

Goldschmidt and Renn (6) identified diphenylamine and 1,2,3,5-benzenetetramine in the products of reduction of I and II. No characterizable substances were obtained upon reduction of III, but, because *p*-hydroxydiphenylamine was not isolated, they postulated that the OH group was attached to the β-nitrogen atom and not to the phenyl ring. This conclusion conflicts with their observation that II reacts with bromine and with triphenylmethyl to give ring-substituted adducts such as V, instead of VI. Hence, we sought additional evidence regarding the structure III and, consequently of IV, by means of a spectrophotometric study of these compounds as well as of I and II.



V



VI

R = Br, Ph_3C, or OH

RESULTS

In support of the formulas assigned to these compounds, we have observed that the hydrazine and hydroxyhydrazine show, respectively, a strong NH and OH absorption band in the 3 μ region of the infrared spectrum, whereas the hydrazyl and oxyhydrazyl free radicals do not absorb in this region (Figure 1). This indicates, therefore, that all NH and OH bonds are eliminated in the oxidation of these hydrazine derivatives to the corresponding hydrazyl free radicals. The spectra of diphenylpicrylhydrazine and the related free radical necessitate no explanation, because only the NH bond is involved in these molecules. Diphenylpicrylhydroxyhydrazine, however, can contain one OH group, or one OH and one NH group, depending upon whether or not it has structure III or V. Accordingly, to eliminate NH and OH bonds which absorb in the 3 μ range, a one-electron oxidation process would be required for III and a two-electron change for V.

The interconversion of the hydroxyhydrazine and the oxyhydrazyl is a one-electron process, as is found by titration with standard hydroquinone solution (6). These observations are interpreted best by assigning structures III to diphenylpicrylhydroxyhydrazine and IV to diphenylpicryloxyhydrazyl.

The observed NH and OH absorptions at 3.04 μ in the infrared spectra of I and II are shifted, respectively, 0.25 and 0.34 μ toward longer wavelengths than the values reported for unperturbed NH and OH bonds (8). Such a displacement in these particular NH and OH absorption bands has heretofore been interpreted as a weakening of binding force of these groups through hydrogen bonding in the form of a polymer, a chelate, or a complex with an unlike molecule. The type of hydrogen bonding operative in I is apparently analogous to the six-membered chelate ring through the NH←O—N=O bond, which was suggested as an explanation for a 0.1 μ shift in the spectrum of *o*-nitroaniline (8). A seven-membered ring containing the OH←O—N=O bond as required by III is unknown, although seven-membered chelates have been postulated for derritol (9) and acetylglycine N-methylamide (10). Intramolecular hydrogen bonding in I and III possibly is enhanced by resonance through structures VII and VIII, in which conjugated double bonds appear in the chelate ring. Dimerization is probably insignificant here, since the solutions analyzed were dilute (0.003 *molar*).

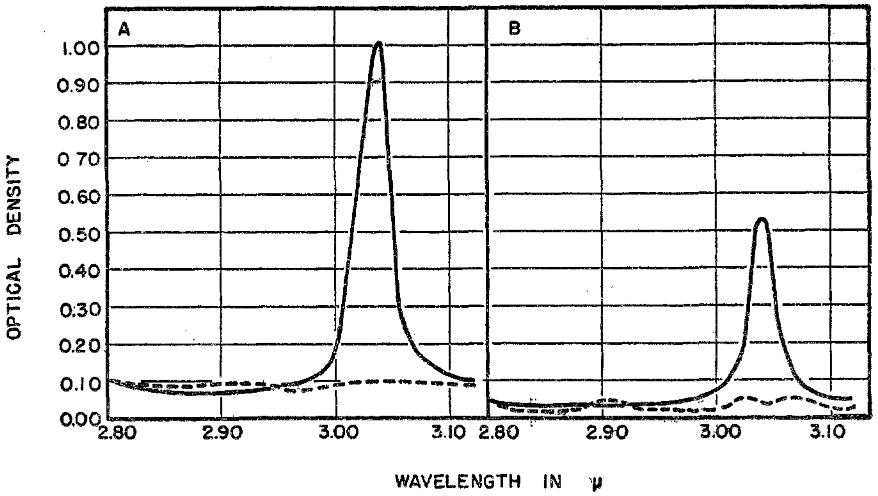
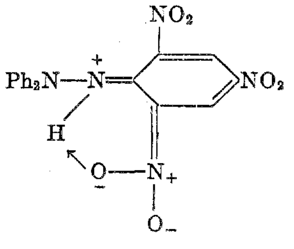
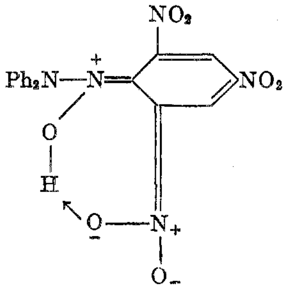


FIGURE 1. INFRARED ABSORPTION SPECTRA (NH AND OH REGION): A, α,α-Diphenyl-β-picrylhydrazine (————) and α,α-Diphenyl-β-picrylhydrazyl (----------); B, α,α-Diphenyl-β-picryl-β-hydroxyhydrazine (————) and α,α-Diphenyl-β-picryl-β-oxyhydrazyl (----------); 0.003 *M* solutions in CCl_4 (2.5-cm. cell)



VII



VIII

The visible and ultraviolet absorption spectra of these compounds also distinguished between the hydrazyl free radicals and the parent hydrazine. As previously observed by Goldschmidt and Graef (11), α,α-diphenyl-β-picrylhydrazyl (II) exhibited two strong absorption bands, one in the visible region at 530 mμ and another in the ultraviolet at 332 mμ (Figure 2). The hydrazine (I) absorbed strongly only in the ultraviolet and gave a maximum at 319 mμ. The absorption band shown by II in the visible light therefore is related to the vibration characteristic of the unpaired electron. The curves presented here differ from those given by Goldschmidt *et al.* in that the observed log ε of 4.16 for II at 530 mμ is higher than the reported value of 3.81. Also, the inflection in the spectrum of I at about 350 mμ shown by these investigators is absent in our spectra. The transition of the hydrazine to the hydrazyl free radical caused the maximum in the ultraviolet to be shifted 13 mμ toward the longer wavelength. This displacement is thought to be caused by charged resonance hybrids like IX–XI. Dipole moment measurements of I and II have indicated that structures IX and X, and related structures through the *ortho* nitro groups, contribute more to the state of the radical than do those like XI to the state of the hydrazine (12).

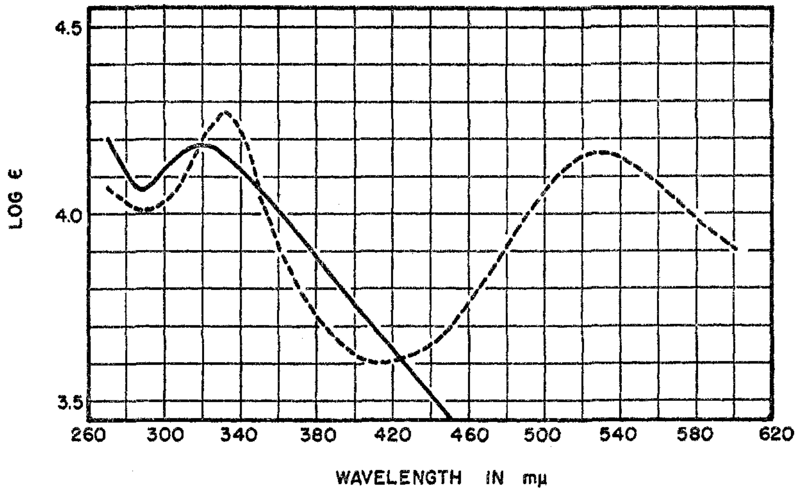
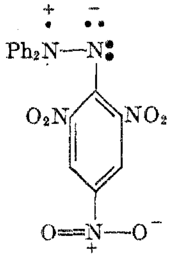
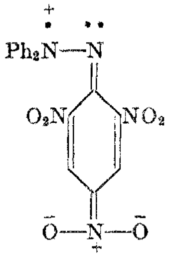


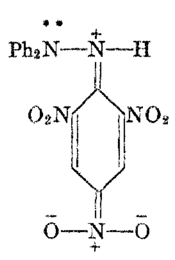
FIGURE 2. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA: α,α-Diphenyl-β-picrylhydrazine (————) and α,α-diphenyl-β-picrylhydrazyl (----------) in chloroform



IX



X



XI

The spectra of hydroxyhydrazine III, and oxyhydrazyl IV (Figure 3) are similar to those obtained for hydrazine I and hydrazyl II. Two bands with maxima at 503 mμ and 362 mμ are noted for the oxyhydrazyl radical and one band at 332 mμ for the hydroxyhydrazine. Resonance structures such as XII and XIII presumably account for the 30 mμ shift of the maxima in the ultraviolet absorption of these compounds, although canonical state XII undoubtedly has the lower energy level. Structure XIV, which arises immediately upon abstracting a hydrogen atom from the hydroxyhydrazine molecule, probably contributes additionally to the stability of the radical. These combined effects are expressed by structure IV, which contains a three-electron bond of the type shown by Waters (13) to describe diphenyl nitric oxide.

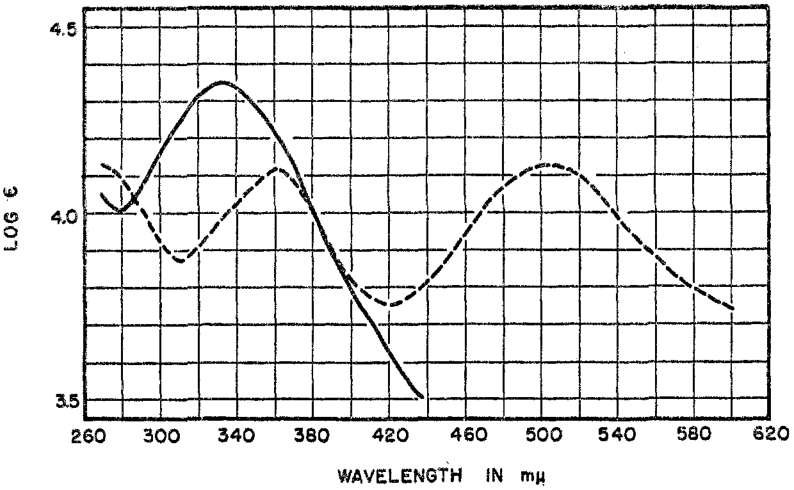
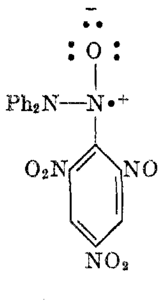
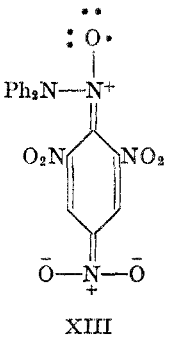


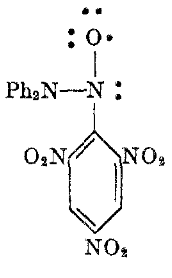
FIGURE 3. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA: α,α-Diphenyl-β-picryl-β-hydroxyhydrazine (————) and α,α-diphenyl-β-picryl-β-oxyhydrazyl (----------) in chloroform



XII



XIII



XIV

The absorption spectra of the hydrazine I and the hydroxyhydrazine III in neutral and basic solutions of alcohol demonstrate the acidic properties of these compounds (Figures 4 and 5). The maxima at 425 and 481 mμ are attributed to the ionization of the NH and OH. Only the hydroxyhydrazine is sufficiently ionized in 95% alcohol to retain the absorption band in the visible light. Un-

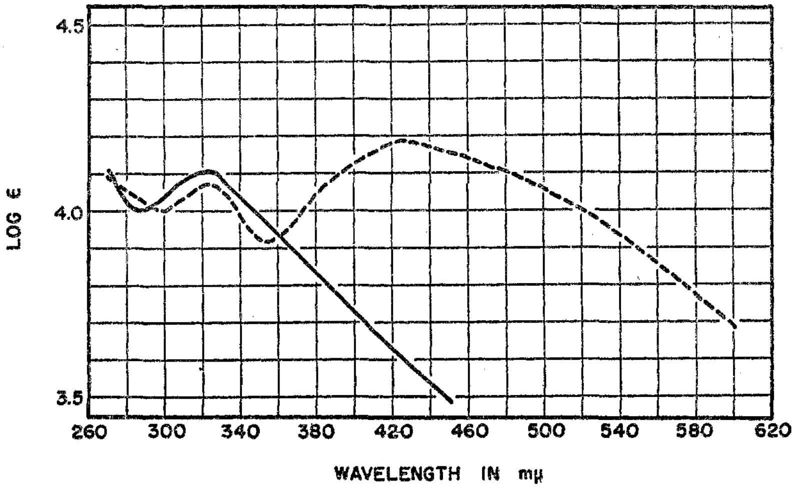


FIGURE 4. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA: α,α-Diphenyl-β-picrylhydrazine in ethyl alcohol (————) and in ethanolic sodium hydroxide (0.01 M) (----------)

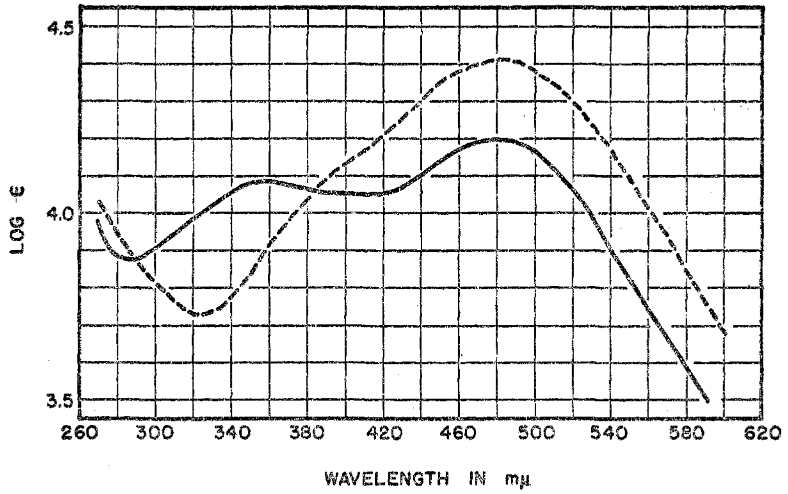
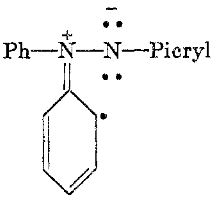


FIGURE 5. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA: α,α-Diphenyl-β-picryl-β-hydroxyhydrazine in ethyl alcohol (————) and in ethanolic sodium hydroxide (0.01 M) (----------)

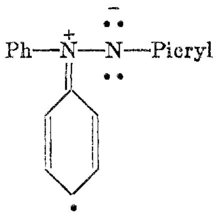
explained, however, is the disappearance of the ultraviolet band in the spectra of the alkaline solution of diphenylpicrylhydroxyhydrazine.

DISCUSSION

The abnormal reactions of II with bromine and triphenylmethyl leading to ring-substituted diphenylpicrylhydrazines (V) were explained by Goldschmidt and Renn (6) through a rearrangement process in which the entering group migrates from the β-nitrogen atom to the benzene nucleus. This mechanism seems inaccurate, because it is very improbable that the large triphenylmethyl molecule can penetrate the reactive sphere of the highly hindered β-nitrogen atom. A more reasonable course of reaction exists if it is assumed that resonance hybrids XV and XVI are possible extensions of IX (14). Thus, when II is attacked by an

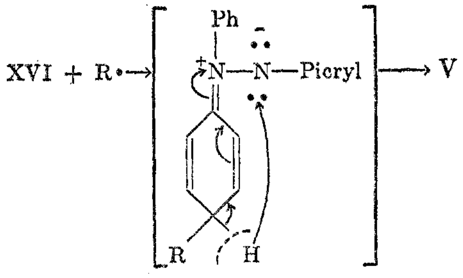


XV



XVI

atom or a free radical too large to penetrate the reactive sphere of the β-nitrogen atom, such groups could add to XV or XVI, followed by release of the displaced proton and finally by electron shifts. Since the *ortho* positions in the α-phenyl rings are also hindered, additions to the *para*-carbon atom of these rings are most important in reactions of II with bromine and triphenylmethyl.



(R = Br or Ph_3C)

Nitrogen dioxide becomes attached to the β-nitrogen by the oxygen, perhaps because the NO_2 molecule is nearly linear (angle of 132° ± 2°) (15) with a transverse radius only slightly greater than the covalent single-bond radius of oxygen.

Similar resonance structures involving the displacement of the unpaired electron through the α-phenyl rings can be written for oxyhydrazyl IV, but the reactions of this free radical are interpreted by means of structures XII–XIV. For example, IV readily abstracts the tertiary hydrogen atom in methylcyclopentane, and also reacts with the methylcyclopentyl free-radical residue, or fragments of this residue, to form O—R adducts which were not completely characterized. In addition, IV reacts very sluggishly with bromine, for the N—O—Br group is difficult to form. It appears, therefore, that the β-oxygen atom lies outside the sphere of steric influence of the picryl group.

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C. D. Smith and Mr. F. R. Wetsel, who obtained the infrared and ultraviolet absorption spectra, and to Drs. J. F. Foster and G. A. Lutz for their suggestions and criticisms.

EXPERIMENTAL

The procedures employed in the syntheses of α,α-diphenyl-β-picrylhydrazyl and its related compounds were modified slightly from those developed by Goldschmidt and Renn (6). *All melting points were determined on a Fisher-Johns apparatus and are uncorrected.* A Beckman model IR-2 single-beam spectrophotometer, equipped with a lithium fluoride monochromator, was used to obtain the infrared spectra of carbon tetrachloride solutions of the compounds. The visible and ultraviolet spectra of chloroform and alcohol solutions of the compounds were determined with a Cary quartz spectrophotometer. Solutions of the hydrazyl and oxyhydrazyl free radicals were prepared immediately before the determination.

α,α-Diphenyl-β-picrylhydrazine. A solution of 22.0 g. (0.1 mole) of *unsym*-diphenylhydrazine hydrochloride in 250 ml. of absolute ethyl alcohol at room temperature was treated first with 21.0 g. (0.25 mole) of sodium bicarbonate, then with 24.8 g. (0.1 mole) of picryl chloride. After the evolution of carbon dioxide had subsided, the mixture, which then had become red, was boiled gently for 15 minutes. An equal volume of chloroform was added and the solid residue was filtered off while the mixture was still warm. The filtrate was washed with two 250-ml. portions of water, was concentrated on a steam-bath to about 150 ml., and was diluted with 150 ml. of warm absolute ethyl alcohol. On standing at room temperature overnight, brick red prisms which weighed 37.1 g. (97%) and melted at 169–171° separated. When 30 g. of this product was recrystallized from a solvent mixture composed of 90 ml. of chloroform and 60 ml. of ethyl alcohol, 27.6 g. of small brick red needles, m.p. 171–172°, was obtained. The mother liquor, upon concentrating to one-half its volume, gave an additional 2.3 g. of long, spear-like, red needles, m.p. 174–176°.

Anal. Calc'd for $C_{18}H_{13}N_5O_6$: C, 54.7; H, 3.3; N, 17.7.
Found: C, 54.7; H, 3.3; N, 17.5.

α,α-Diphenyl-β-picrylhydrazyl. This hydrazyl free radical was prepared by shaking for two hours a mixture of 5.1 g. (0.013 mole) of α,α-diphenyl-β-picrylhydrazine, 5.1 g. of anhydrous sodium sulfate, and 31.4 g. of lead peroxide (PbO_2) in 100 ml. of purified benzene. The solid residue was removed from the dense violet solution by filtration through a fine-grain paper. The filtrate was evaporated to dryness by passing a stream of dry nitrogen over the solution (evaporation *in vacuo* was equally effective). The dark-colored residue (95 to 97%) gave large, dark-violet prisms, m.p. 127–129° (dec.), when recrystallized from a benzene-ligroin solvent mixture (2:1 by volume).

Anal. Calc'd for $C_{18}H_{12}N_5O_6$: C, 54.85; H, 3.05; N, 17.75.
Found: C, 54.8; H, 3.1; N, 17.0.

α,α-Diphenyl-β-picryl-β-hydroxyhydrazine. Through a solution of 5.0 g. (0.0127 mole) of α,α-diphenyl-β-picrylhydrazyl in 250 ml. of benzene, dry nitrogen dioxide gas was passed for 30 minutes. The oxide of nitrogen gas was conveniently generated by heating gradually to 360° lead nitrate intermixed with sand. During this treatment, the solution turned brown and a small amount of a brick-red solid separated. The reaction mixture then was concentrated to about 50 ml. by gently warming under a vacuum. The solid substance which precipitated weighed 4.6 g. (89%). It was purified by solution in 40 ml. of ethyl acetate and 60 ml. of ethyl alcohol followed by slow evaporation of the solution at room temperature. In this manner well defined brick-red prisms melting at 153° after softening at about 140° were obtained.

Anal. Calc'd for $C_{18}H_{13}N_5O_7$: C, 52.6; H, 3.15; N, 17.0.
Found: C, 52.7; H, 3.0; N, 16.9.

α,α-Diphenyl-β-picryl-β-oxyhydrazyl. Diphenylpicrylhydroxyhydrazine, 1.5 g. (0.0037 mole), was converted to the oxyhydrazyl free radical by reaction with 18.0 g. of lead peroxide and 6.0 g. of anhydrous sodium sulfate slurried in 37.5 ml. of chloroform. After two hours, the mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The dark residue weighed 1.15 g. (77%), and, when recrystallized from ethyl acetate, gave dark-green crystals, m.p. 196° (dec.) after softening at 193°. This product and several samples from other preparations did not give satisfactory carbon, hydrogen, and nitrogen values. Goldschmidt and Renn (6) also reported a similar discrepancy in nitrogen values. The formation of products arising from the rupture of the N-N bond is a reasonable explanation for these anomalous assays.

Anal. Calc'd for $C_{18}H_{12}N_5O_7$: C, 52.75; H, 2.92; N, 17.05.
Found: C, 49.4; H, 2.6; N, 19.5.

SUMMARY

1. α,α-Diphenyl-β-picrylhydrazine and α,α-diphenyl-β-picryl-β-hydroxyhydrazine and the corresponding hydrazyl free radicals have been characterized by infrared, visible, and ultraviolet absorption methods.

2. A mechanism has been proposed for the abnormal addition of free radical groups to the α,α-diphenyl-β-picrylhydrazyl free radical.

Columbus 1, Ohio

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