[Contribution from the Battelle Memorial Institute]

THE CHEMISTRY OF HYDRAZYL FREE RADICALS. III. FURTHER EVIDENCE OF THE CONTRIBUTION OF α-GROUPS TOWARD THE STABILIZATION OF α,α-DISUBSTITUTED-β-PICRYLHYDRAZYL FREE RADICALS[1]

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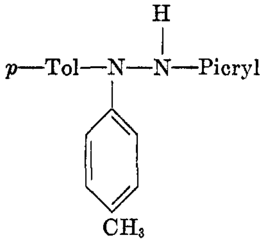
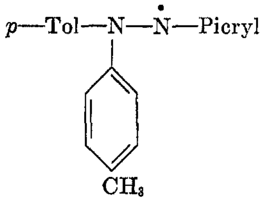
In a previous communication (1), the abnormal reaction of α,α-diphenyl-β-picrylhydrazyl with bromine and triphenylmethyl leading to *para*-substituted diphenylpicrylhydrazines (2) was interpreted through resonance hybrids in which the unpaired electron appeared at the *ortho* and *para* positions of the α-phenyl rings. Further evidence in support of this mechanism has been obtained from an investigation of analogs of α,α-diphenyl-β-picrylhydrazyl in which the α-phenyl groups were replaced by *p*-tolyl and methyl groups. This study has also shown that the introduction of nonresonating groups at the α-nitrogen atom greatly decreases the stability of hydrazyl free radicals.

The procedures developed by Goldschmidt and Renn (2) for the preparation of hydrazyl free radicals, and the modifications of these procedures which we described previously (1) were employed in the synthesis of the hydrazines and hydrazyls here reported.

α,α-Di-(*p*-tolyl)-β-picrylhydrazine (I) was readily oxidized by lead peroxide (PbO_2) to its corresponding hydrazyl free radical (II).



I



II

This hydrazyl is a violet-black solid which forms intense bluish-violet solutions. Although solutions of hydrazyl II remained bluish-violet for more than one week, even in the presence of light, the free radical could not be isolated in the solid state without considerable disproportionation.

The visible and ultraviolet spectra of hydrazine I and hydrazyl II are similar to those shown by the diphenyl analogs (Figure 1, Table I). The *p*-methyl groups in free radical II exerted a slight bathochromic shift in the visible and the ultraviolet absorption bands. This shift can be explained on the basis that the CH_3 groups release electrons and thus impart added stability to resonance structures III to V. Resonance hybrids III to V, which are similar to those considered in interpreting the chemistry of α,α-diphenyl-β-picrylhydrazyl (1),

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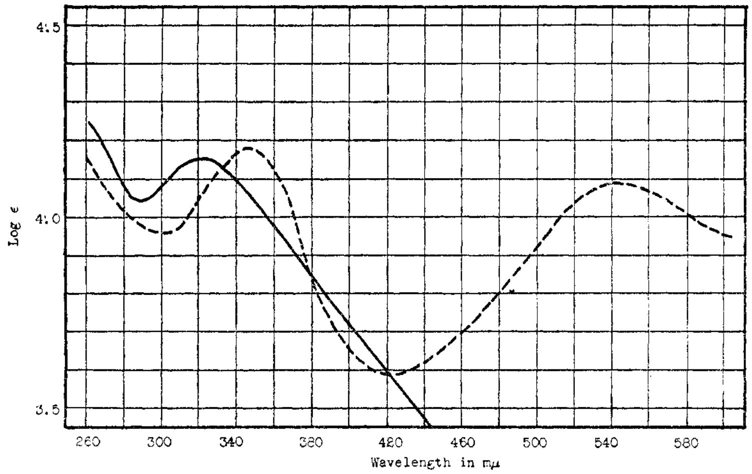
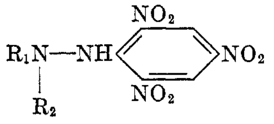
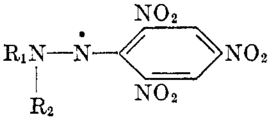


FIGURE 1. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA

α,α-di-(p-tolyl)-β-picrylhydrazine (——) and
α α-di-(p-tolyl)-β-picrylhydrazyl (----) in chloroform

TABLE I

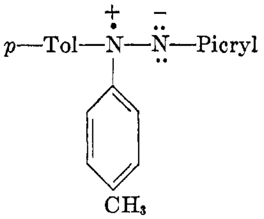
Visible and Ultraviolet Absorption Maxima[a]

R_1	R_2	Max. 1		Max. 2	
		mμ	Log ε	mμ	Log ε
α,α-DISUBSTITUTED PICRYLHYDRAZINES  $R_1N{-}NH{-}C_6H_2(NO_2)_3$					
Ph	Ph	319	4.18		
p-Tol	p-Tol	320	4.15		
Ph	CH_3	319	4.14		
CH_3	CH_3	331	4.15		
α,α-DISUBSTITUTED PICRYLHYDRAZYLS  $R_1N{-}\dot{N}{-}C_6H_2(NO_2)_3$					
Ph	Ph	332	4.28	530	4.16
p-Tol	p-Tol	347	4.18	544	4.09
Ph	CH_3	334	4.19	512	3.58
Ph	CH_3[b]	330	4.18		

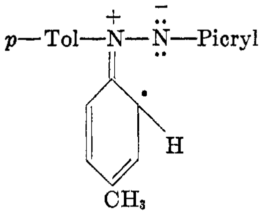
[a] The visible and ultraviolet absorption spectra were determined respectively on 1 × 10^{-4} and 5 × 10^{-5} molar solutions of the hydrazine and hydrazyl compounds with a Cary quartz spectrophotometer. The hydrazyl-free-radical solutions were prepared immediately before the determination.

[b] The spectrum of α-methyl-α-phenyl-β-picrylhydrazyl after standing unprotected from daylight for one hour.

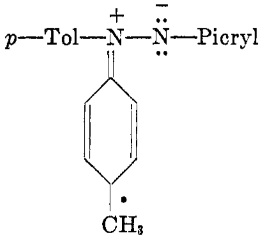
as well as the usual resonance structures through the picryl group, presumably contribute most significantly toward the stabilization of the hydrazyl II.



III

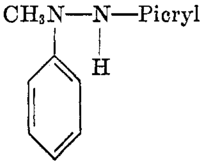


IV

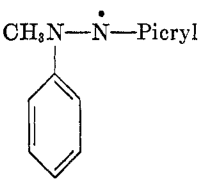


V

The α-methyl-α-phenyl-β-picrylhydrazine VI formed reddish-purple solutions of the hydrazyl free radical VII on shaking with lead peroxide.



VI

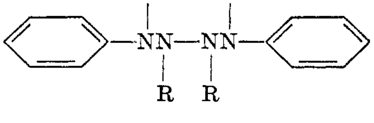


VII

Benzene solutions of the hydrazyl VII were highly unstable for they became orange within one hour after the lead peroxide treatment. The color transition of VII could not be reversed by treatment with lead peroxide.

The spectra of α-methyl-α-phenyl-β-picrylhydrazine (VI) and the corresponding hydrazyl radical (VII) (Figure 2) are typical of compounds of this class (Table I). However, substitution of one of the α-phenyl groups by the nonresonating methyl group caused a hypsochromic shift in both absorption bands and decreased the absorption coefficient of the visible maxima of the free radical VII. These effects must be associated with the fact that the unpaired electron can be distributed through only one phenyl ring, because the spectra of methylphenylpicrylhydrazine is identical with that of diphenylpicrylhydrazine.

Solutions of VII which had faded from a deep reddish-purple color to orange showed only a slight shift in the ultraviolet maxima, but absorption in the visible region had practically disappeared. This color transition indicated that the hydrazyl disproportionated to nonfree-radical products. The close similarity between the ultraviolet absorption spectra of freshly prepared and faded solutions of VII suggested the possibility that the free radical might have dimerized to the tetrazane VIII.



R = picryl

VIII

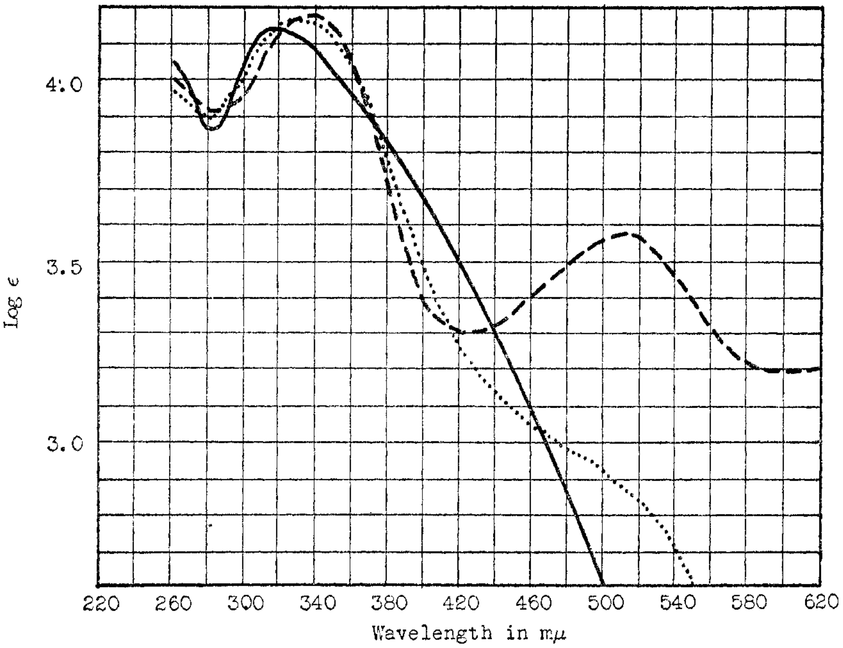


FIGURE 2. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA

α-methyl -α-phenyl -β-picrylhydrazine (——), α-methyl -α-phenyl-β-picrylhydrazyl (– – –), and α-methyl -α-phenyl -β-picrylhydrazyl after standing one hour (······) in chloroform

Although structures of this type should normally undergo thermal dissociation into hydrazyl free radicals, no indication of dissociation was obtained on heating to 100° faded solutions of VII.

The α,α-dimethyl-β-picrylhydrazine did not give evidence of hydrazyl free radical formation by treating its solutions with lead peroxide at temperatures ranging from −70° to 100°. However, the hydrazine must have undergone a marked structural change during this oxidative treatment because the strong absorption band at 311 mμ was not present in the spectra of the PbO_2-treated solution.

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EXPERIMENTAL

N-Nitroso-di-p-tolylamine. The reaction of 59.0 g. (0.3 mole) of crude di-*p*-tolylamine (3), 70 ml. of concentrated hydrochloric acid, and 45 g. of sodium nitrite in 500 ml. of ethyl alcohol and 100 ml. of water at room temperature gave 64.8 g. (94.5%) of reddish-orange crystals. Two recrystallizations from 250 ml. of ligroin finally separated 55.4 g. of gold-colored needles, m.p. 102–103°, (lit., m.p. 102°) (4).

unsym-Di-p-tolylhydrazine hydrochloride. Reduction of N-nitroso-di-*p*-tolylamine by lithium aluminum hydride (5) gave an 80% yield of ethyl alcohol-recrystallized ditolylhydrazine hydrochloride, m.p. 147° with decomposition.

Anal. Calc'd for $C_{14}H_{17}ClN_2$: N, 11.3. Found: N, 10.9.

α,α-Di-(p-tolyl)-β-picrylhydrazine (I). To a warm mixture of 12.6 g. (0.15 mole) of picryl chloride, 12.6 g. (0.15 mole) of sodium bicarbonate, and 200 ml. of ethyl alcohol, 12.4 g. (0.05 mole) of *unsym*-di-*p*-tolylhydrazine hydrochloride in 50 ml. of warm ethyl alcohol was added. After stirring for 30 minutes, the mixture was concentrated to about 100 ml., and 150 ml. of chloroform was added in order to redissolve the small amount hydrazine product which had separated. The residue of sodium chloride and sodium bicarbonate was filtered off and the filtrate was concentrated to about 150 ml. On standing overnight at room temperature, 19.2 g. (91%) of brick-red prisms, m.p. 155–159° separated. Recrystallization from 100 ml. of chloroform and 50 ml. of ethyl alcohol gave 14.4 g. (68%) of lustrous brick-red prisms, m.p. 161° dec.

Anal. Calc'd for $C_{20}H_{17}N_5O_6$: C, 56.8; H, 4.0.
Found: C, 57.0; H, 4.1.

α,α-Di-(p-tolyl)-β-picrylhydrazyl (II). Attempts to isolate in solid form this hydrazyl free radical obtained by shaking a benzene solution of the corresponding hydrazine with lead peroxide led to partly disproportionated products. Studies with this hydrazyl were then made on freshly prepared solutions. Thus, 100 ml. of a 1×10^{-4} molar solution of α,α-di-(*p*-tolyl)-β-picrylhydrazine was shaken with 5.0 g. of lead peroxide and 2.0 g. of anhydrous sodium sulfate for about 30 minutes. The residue was removed by filtration, thereby giving a bluish-purple filtrate containing α,α-di-(*p*-tolyl)-β-picrylhydrazyl.

N-Nitroso-N-methylaniline. Nitrosation of N-methylaniline (6) gave a 96% yield of this nitrosamine, b.p. 121–122° (10 mm.).

α-Methyl-α-phenylhydrazine. Hanna and Schueler (7) obtained this hydrazine in 77% yield by adding N-methyl-N-nitrosoaniline to a solution of lithium aluminum hydride. By adding the lithium aluminum hydride to the nitrosamine, the yield of methylphenylhydrazine, b.p. 105–108° (12 mm.), was increased to 87%. The *benzoyl* derivative melted at 154.5–155.5°.

α-Methyl-α-phenyl-β-picrylhydrazine (VI). To a warm mixture of 9.9 g. (0.04 mole) of picryl chloride and 6.7 g. (0.08 mole) of sodium bicarbonate in 150 ml. of ethyl alcohol, a solution of 4.9 g. (0.04 mole) of α-methyl-α-phenylhydrazine in 25 ml. of ethyl alcohol was added. After stirring the mixture on a steam-bath for 30 minutes, a portion of the solvent was evaporated and the concentrate was allowed to crystallize at room temperature. Brick-red prisms weighing 12.0 g. (90%) and melting with decomposition at 144–148° were thus obtained. Recrystallization of this product from a chloroform-ethyl alcohol solvent mixture gave 9.6 g. of crystals which also melted over a four-degree range, 145–149°. However, by dissolving this product in 50 ml. of warm chloroform, adding 25 ml. of ethyl alcohol, and allowing the solvent to evaporate slowly at room temperature, dark-red microprisms were precipitated. These crystals weighed 7.5 g. and melted with decomposition at 152–152.5° after drying *in vacuo* at 78° [lit., (8), 153°].

Anal. Calc'd for $C_{13}H_{11}N_5O_6$: C, 46.8; H, 3.3.
Found: C, 46.8; H, 3.3.

α-Methyl-α-phenyl-β-picrylhydrazyl (VII). This hydrazyl free radical was found to be very unstable and could not be isolated in the crystalline state. Hence, studies with this radical were made on solutions prepared by the method described above for the preparation of solutions of the ditolyl analog.

N-Nitrosodimethylamine. A solution of 245 g. (3 moles) dimethylamine hydrochloride and 15 ml. of concentrated sulfuric acid in 150 ml. water at 20 to 30°. A yellow oil separated which, upon extracting with ether and distilling, gave 189.5 g. (82%) of N-nitrosodimethylamine, b.p. 148.5–150° at 744 mm. [lit., (9) 149–150° 755 mm.].

unsym-Dimethylhydrazine hydrochloride. This compound was obtained in 88.5% yield by the reduction of N-nitrosodimethylamine with zinc powder and acetic acid (9).

α,α-Dimethyl-β-picrylhydrazine. Picryl chloride (25 g.) was added to a slurry of 9.65 g. of *unsym*-dimethylhydrazine hydrochloride and 33.6 g. of sodium bicarbonate in 500 ml. of ethyl alcohol at room temperature. When the evolution of carbon dioxide had subsided, the mixture was heated on a steam-bath for 90 minutes and then was filtered hot. On cooling the filtrate, 21.6 g. (80%) of orange-red prisms, m.p. 134–135° with dec., was deposited. Recrystallization of this product from 200 ml. of an ethyl alcohol-chloroform mixture (1:1) gave 18.7 g. of large orange-red crystals, m.p. 135.5–136.5°, [lit. (10), 136.5°].

Anal. Calc'd for $C_8H_9N_5O_6$: C, 35.4; H, 3.3.

Found: C, 35.7; H, 3.4.

This hydrazine did not form a hydrazyl free radical by shaking with lead peroxide its 1×10^{-4} molar solutions in toluene at 100°, chloroform at 30°, or ethyl ether at −70°.

SUMMARY

The influence of some α-groups on the stability of α,α-disubstituted-β-picrylhydrazyl free radicals was studied.

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