[Contribution from Battelle Memorial Institute]

THE CHEMISTRY OF HYDRAZYL FREE RADICALS. IV. CHROMATOGRAPHIC STUDIES WITH α,α-DIPHENYL-β-PICRYL HYDRAZYL AND SOME OF ITS β-DERIVATIVES[1]

R. H. POIRIER and F. BENINGTON

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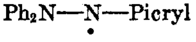
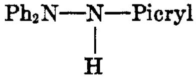
The successful capture and identification of hydrogen atoms and methyl free radicals by triphenylmethyl (1) led to the consideration of other free-radical reagents for the detection of free-radical intermediates in the combustion of hydrogen and hydrocarbons. Prior to making studies on combusion systems with oxygen as oxidant, hydrazyl-type free radicals were investigated because of their inertness to molecular oxygen at ambient temperatures. A previous communication[2] was concerned with the characterization and proof of structure of α,α-diphenyl-β-picrylhydrazyl (I) and its probable reaction products with hydrogen atoms (II), oxygen atoms (III), and hydroxy free radicals (IV).



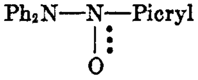
$\mathrm{Ph_2N{-}\underset{\bullet}{N}{-}Picryl}$

I



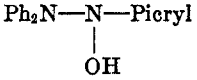
$\mathrm{Ph_2N{-}\underset{\underset{H}{|}}{N}{-}Picryl}$

II



$\mathrm{Ph_2N{-}\underset{\underset{O}{|:}}{N}{-}Picryl}$

III



$\mathrm{Ph_2N{-}\underset{\underset{OH}{|}}{N}{-}Picryl}$

IV

Since mixtures of these products would presumably be encountered in combustion studies, a method for their separation and identification was sought. This paper describes the development of a chromatographic technique for resolving such mixtures into individual fractions which are amenable to spectrophotometric analysis. The reactivity of III toward tertiary hydrogen atoms is also discussed.

As a preliminary step in this investigation, the infrared and ultraviolet spectra of I–IV were examined to establish whether or not mixtures of these compounds could be analyzed directly by spectrophotometric methods. As shown in Figure 1, the infrared spectra would only be useful in differentiating I and II from III and IV. The 9μ absorption band of the oxy- and hydroxy-hydrazine compounds could serve in this characterization. The hydrazines II and IV could be distinguished from the corresponding hydrazyls by their NH and OH absorption bands at 3.04μ (2). Further differentiation of the hydrazyl components from the

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[2] Paper I, Poirier, Kahler, and Benington, *J. Org. Chem.*, **17**, 1437 (1952); Paper II, Benington, Shoop, and Poirier, *J. Org. Chem.*, **18**, 1506 (1953); Paper III, Poirier and Benington, *J. Org. Chem.*, **19**, 1157 (1954).

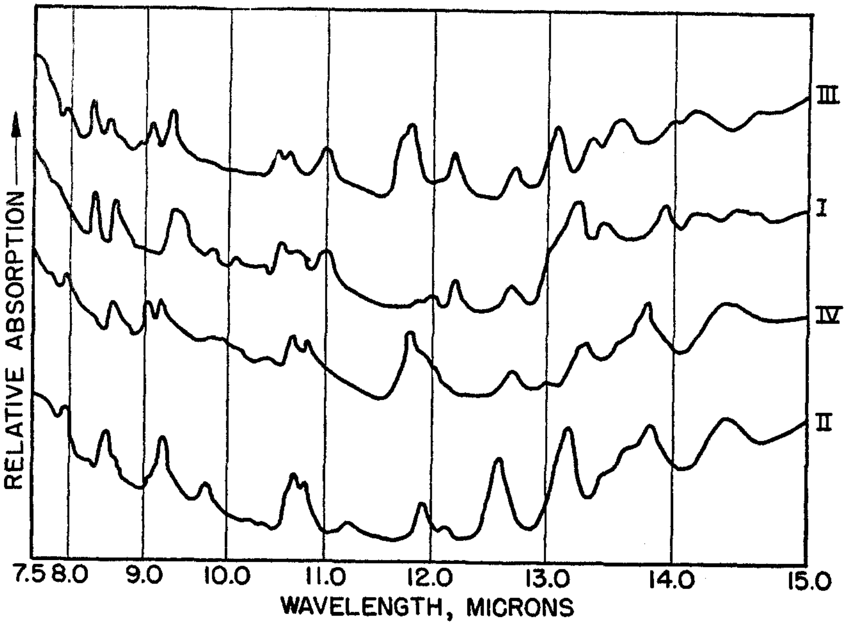


FIGURE 1. INFRARED ABSORPTION CURVES FOR I, II, III, AND IV

hydrazines could be made by use of the characteristic absorption maxima of I and III at 527 and 502 mμ, respectively, in the visible region of the spectra (2). The spectra of these compounds in the ultraviolet region are too similar to be useful for identification and analytical purposes. In view of the apparent limitations of the spectrophotometric (light-absorption) procedures for the direct analysis of mixtures of I–IV, means were sought for resolving such mixtures into individual components, prior to spectrophotometric analysis.

Initial attempts to separate hydrazyl I from hydrazine II by chromatography on activated alumina led to extensive disproportionation of I. However, weaker adsorbents such as sugar, starch, and cellulose did not significantly attack either the hydrazyl or oxyhydrazyl free radicals. Consequently, attention was directed toward separating binary and ternary mixtures of I–IV by paper chromatographic techniques.

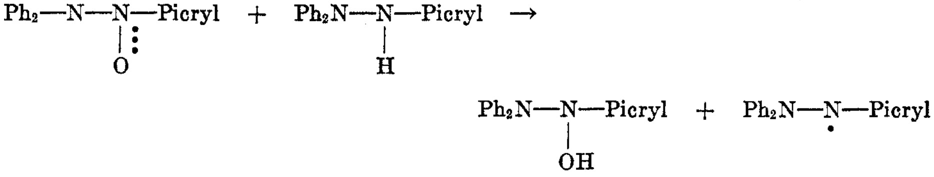
The R_f values of I–IV were determined by capillary ascension chromatography on strips of filter paper using saturated hydrocarbons as the mobile phase. The R_f values thus obtained indicated that mixtures I–IV could be resolved into individual components by this method (Table I). Although *n*-hexadecane exhibited greater resolving power than the other hydrocarbons which were examined, long periods of time were necessary to effect satisfactory resolution of chromatograms. Since prolonged contact of the hydrazyl constituents with the paper could lead to significant disproportionation of these agents, *n*-hexane and petroleum ether (b.p. 35–55°) were found more useful as the mobile phase than the higher molecular hydrocarbons.

TABLE I

R_f VALUES OF α,α-DIPHENYL-β-PICRYLHYDRAZYL (I), AND ITS β-HYDRO (II), β-OXY (III), AND β-HYDROXY (IV) DERIVATIVES

SOLVENT	R_f Values			
	I	II	III	IV
n-Hexane	0.62	0.48	0.02	0.11
n-Decane	.53	.38	.015	.13
n-Hexadecane	.56	.36	.01	.16
Petroleum ether, b.p. 35–55°	.55	.35	.025	.125
Petroleum ether, b.p. 60–75°	.72	.58	.065	.25
Mineral oil	.56	.41	.036	.14
Cyclopentane	.84	.70	.10	.36
Cyclohexane	.76	.75	.075	.28

Binary mixtures of I with either II, III, or IV were completely resolved into separate zones by *n*-hexanes. Binary mixtures of III and IV were best separated by using cyclopentane as the mobile phase. Ternary mixtures of I, II, and IV were similarly resolved into three zones by *n*-hexane. However, a mixture consisting of I, II, and III gave only two colored zones, one intense purple and the other orange; these phases were identified by both their R_f values and ultraviolet absorption spectra as the hydrazyl I and the hydroxyhydrazine IV. Apparently, oxyhydrazyl III is sufficiently reactive to abstract the β-hydrogen atom of II to form the more stable hydrazyl I and the hydroxyhydrazine IV.



$$\underset{\text{III}}{Ph_2\text{—N—}\underset{\overset{|\,\vdots}{O}}{N}\text{—Picryl}} + \underset{\text{II}}{Ph_2N\text{—}\underset{\overset{|}{H}}{N}\text{—Picryl}} \rightarrow \underset{\text{IV}}{Ph_2N\text{—}\underset{\overset{|}{OH}}{N}\text{—Picryl}} + \underset{\text{I}}{Ph_2N\text{—}\underset{\bullet}{N}\text{—Picryl}}$$

III II IV I

The tendency for α,α-diphenyl-β-picryl-β-oxyhydrazyl to abstract active hydrogen atoms was also observed in its reactions with methylcyclopentane. Attempts to obtain R_f values of III using a sample of cyclohexane that contained methylcyclopentane as an impurity revealed the activity of III toward certain tertiary hydrogen atoms. When a dilute solution of III in methylcyclopentane and benzene was allowed to stand at room temperature for three days, the intense reddish-purple color, which is characteristic of solutions of the oxyhydrazyl free radical, was replaced by a pale reddish-orange color. Separation of the reaction products by chromatography either on paper or on a column of potato starch led to the isolation of three main fractions. Characterization of these fractions was made by a study of their infrared and ultraviolet spectra. Table II summarizes the significance of the major absorption bands of these spectra.

The absorption bands at 310 and 370 mμ for Fraction A correspond to those

TABLE II

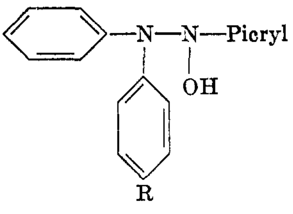
SPECTRAL CHARACTERIZATION OF THE REACTION PRODUCTS OF α,α-DIPHENYL-β-PICRYL-β-OXYHYDRAZYL AND METHYLCYCLOPENTANE

FRACTION	SOLVENT PERCOLATE	SPECTRAL PROPERTIES	
		Infrared[a]	Ultraviolet[b]
A	Petroleum ether (b.p. 35–55°)	Strong OH band at 3.0μ, with aromatic C—H band at 3.8–3.9μ, and some aliphatic C—H absorption at 3.45μ.	Strong band at 370 and 265 mμ.
B	Chloroform	Weak OH band but strong C—H band at 3.8–3.9μ, fairly strong aliphatic C—H band at 3.45μ, and a relatively weak CH_2 absorption at 6.8 μ.	Fairly sharp maxima at 330 mμ and a stronger band at about 250 mμ.
C	Ethyl alcohol-chloroform (50–50)	Strong OH band at about 3.0 μ; no aromatic C—H absorption; but strong aliphatic C—H band at 3.45 μ and relatively strong CH_2 absorption at 6.8μ.	A shoulder at about 310 mμ and strong absorption less than 250 mμ.

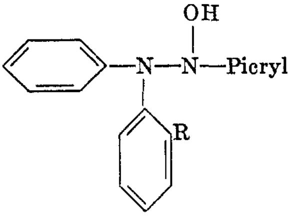
[a] Infrared spectra of all three fractions were determined on mineral oil mulls.

[b] Ultraviolet spectra were obtained on chloroform solutions of Fractions A and B and on an ethyl alcohol solution of Fraction C.

for oxyhydrazyl III (310 and 365 mμ); however, the absence of the 530 mμ maxima, which characterizes III as a free radical, distinguishes A from III. Strong OH and some aliphatic CH absorption in the infrared region of the spectra suggests that Fraction A is an analog of IV, presumably one with methyl or methylcyclopentyl substituents attached to one of the α-phenyl rings, (*e.g.* V and VI), in preference to an oxygen substituted analog (VII). Less outstanding features of the infrared spectra also support this postulate.



V



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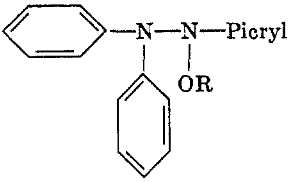


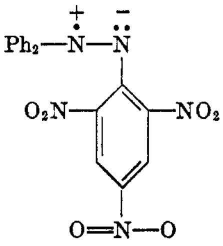
VII

The ultraviolet spectrum of Fraction B with maxima at 250 and 330 mμ compares favorably with the spectrum of III whose maxima in the ultraviolet region are 245 and 332 mμ. However, the absence of the OH band, the presence of fairly strong aliphatic CH absorption at 3.45μ, and weak CH_2 absorption at 6.8μ in the infrared spectra identifies Fraction B as an O-alkyl analog of III, such as VII. A small amount of a product similar to Fraction A perhaps accounts for the presence of the weak OH absorption band.

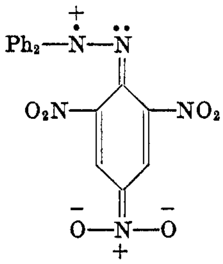
Both the ultraviolet and infrared spectra of Fraction C differed from those of the diphenylpicrylhydrazine compounds studied in this program. The shoulder at 310 mμ presumably arises from trace amounts of Fraction B products. On the basis of the strong OH band at 3.0μ, the absence of aromatic CH absorption, and the presence of strong aliphatic CH and CH_2 adsorption at 3.45 and 6.8μ, respectively, this fraction was associated with naphthenic-type compounds. Methylcyclopentanols, which can possibly be derived from the oxidation of methylcyclopentane by III, could easily account for this fraction.

DISCUSSION

Intermolecular association with the adsorbent appears to exert a greater effect on the chromatographic behavior of these hydrazine and hydrazyl compounds than does their inherent ionic character. Dipole moment measurements



VIII



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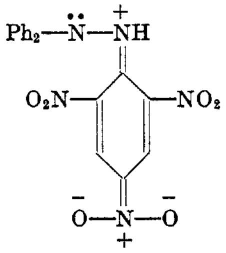

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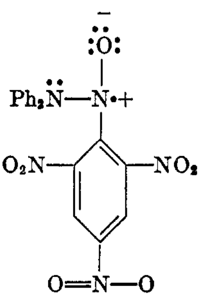

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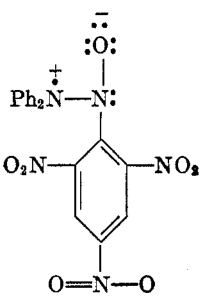

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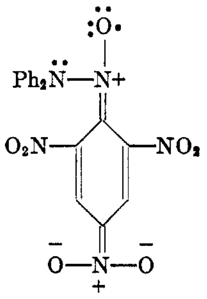
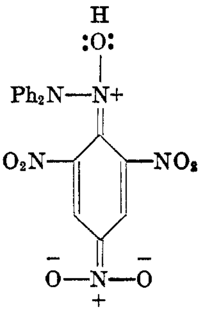


XIII



XIV

of I and II have indicated that structures VIII and IX, and related structures formed through the *ortho* groups, contribute more to the energy state of the radical than do those like X to the energy state of the hydrazine (3). Although no dipole measurements have been made on the oxyhydrazyl III and the hydroxyhydrazine IV, it is probable that ionic structures XI, XII, and XIII impart greater ionic character to III than does structure XIV to IV. On the basis of these ionic considerations, the mobility of the apparently more polar hydrazyl compounds in nonpolar solvents would have been expected to be less than that of the less polar hydrazine counterpart. Therefore the greater mobility of the hydrazyl radicals I and III than the corresponding hydrazines II and IV is explained in terms of hydrogen bonding between the hydrazines and the hydroxyl oxygen of the cellulose molecules. Consequently, the intramolecular hydrogen bonding previously shown to exist in hydrazine II and hydroxyhydrazine IV (2) must be of lower energy than the intermolecular bonding of II and IV with the cellulose OH groups.

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EXPERIMENTAL

The preparation of α,α-diphenyl-β-picrylhydrazyl and its β-hydrogen, β-oxy, and β-hydroxy derivations was described in a previous communication (2). The hydrocarbon solvents which were used to develop the chromatographs were washed with concentrated sulfuric acid, dried over calcium chloride, distilled, and stored over sodium. Ascending chromatograms were run on Whatman No. 1 paper strips at room temperature. The chromatograms were prepared from 1×10^{-3} molar solutions of the materials in dry, ethanol-free chloroform. The intense color of the materials permitted visual identification of the chromatographs. Quantitative analysis of each band was possible by recovering the chromatographed substance with a known volume of chloroform and comparing the optical density of such eluates with that from standard solutions (Figure 2). These concentration curves were derived from the spectra of standard chloroform solutions of the materials using a Cary quartz spectrophotometer. The infrared spectra of mineral oil mulls of I–IV were determined with a Beckman model IR-2 single-beam spectrophotometer and are presented without correcting for background interference.

Initially, the R_f values for each compound in the different solvents were determined on 2 x 18-cm. paper strips. The chromatograms were prepared using 0.10 ml. of 1×10^{-3} molar solutions of the compounds so that a band 4 to 5 cm. wide and about 1 cm. from one end of the paper strip was formed. The R_f values were calculated from the distance of migration of the foremost point of the origin to the leading edge of the spot after the solvent had ascended 6, 7, and 8 cm. above the point of application of the compound. Table I summarizes the results of these determinations. Later, separations of binary and tertiary combinations of hydrazyl I and its derivatives II–IV were made from similarly prepared chromatograms using *n*-hexane and petroleum ether (b.p. 35–55°) as resolving solvent. However, cyclopentane gave a more efficient separation of the oxy (III) and hydroxy (IV) derivatives.

A mixture of 0.5 ml. of a 1×10^{-3} molar solution of the oxyhydrazyl III and 0.5 ml. of methylcyclopentane (prewashed with sodium hydroxide solution and distilled) was allowed to stand in the dark until the color of the hydrazyl had disappeared (4 to 6 hrs.). The whole reaction mixture was then deposited as a band 6.0 cm. wide on a strip of paper 3 x 55 cm. Ascension chromatography with *n*-hexane as solvent resolved this chromatogram into three separate bands. After 48 hrs. the uppermost band was orange, 0.5 cm. in width and

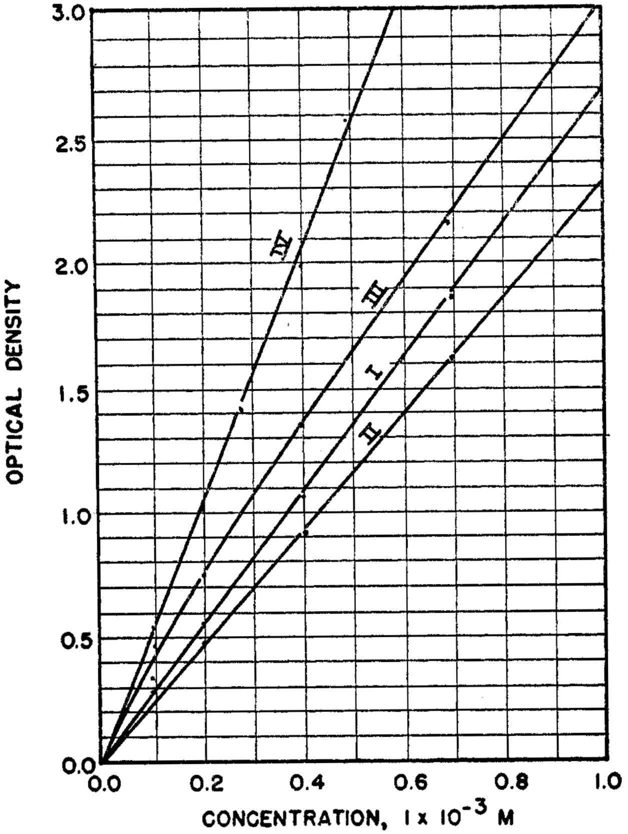

FIGURE 2. CONCENTRATION CURVES FOR CHLOROFORM SOLUTIONS OF I AT 332 mμ, II AT 320 mμ, III AT 362 mμ, AND IV AT 332 mμ

had migrated 36 cm. from the point of application. Immediately below this zone was a more diffused yellow band, about 5 cm. in width and 35.0 cm. from the origin. The third band consisted of a yellow zone which had not moved from the initial location of the chromatogram.

In order to obtain these products in amounts sufficient for spectrophotometric studies, a solution of 100 mg. of III in 100 ml. of cyclopentane and 50 ml. of benzene was allowed to react at room temperature for three days. During this time the color of the mixture changed from dense reddish-purple to pale reddish orange. The mixture was evaporated to dryness in a stream of dry nitrogen gas. The orange residue was dissolved in 100 ml. of a 50:50 benzene-petroleum ether solvent mixture and the solution thus formed was chromatographed on a 2.7 x 100-cm. column of potato starch. Successive percolation with 250 ml. of petroleum ether (b.p. 35–55°), 250 ml. of chloroform, and 150 ml. of a 50:50 chloroform-ethyl alcohol mixture gave three fractions. Interpretation of the ultraviolet and infrared absorption spectra of these products is summarized in Table II.

SUMMARY

1. The resolution of mixtures of α,α-diphenyl-β-picrylhydrazyl and its β-hydro-, β-hydroxy- and β-oxy-derivatives by chromatographic techniques is described.

2. The ionic character of α,α-diphenyl-β-picrylhydrazyl and its derivatives is used to explain chromatographic behavior.

3. The course of the reaction between α,α-diphenyl-β-picryl-β-oxyhydrazyl and methylcyclopentane is discussed.

Columbus 1, Ohio

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