and agitated by inversion to remove gas bubbles (10% resin shrinkage occurred). One half g. of picrate in 100 ml. of 10% aqueous acetone was allowed to flow over the resin at a rate of 30-60 ml./hr. The column was washed with 100 ml. of solvent, the washings and eluate were combined, and the acetone was removed under vacuum. The resulting aqueous phase was filtered, salted out (sodium chloride) and filtered, or "freeze-dried" to obtain pure crystalline alkaloid.

Regeneration of resin. The bright red "spent" resin was transformed *immediately after use* back into Amberlite IRA-400(Cl) by washing with a solution of 50 ml. of concentrated hydrochloric acid in 200 ml. of acetone until no more yellow color was eluted.

Acknowledgments. The author is indebted to Dr. Roy J. Gritter of this department and Professor Carl Djerassi for much helpful advice.

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1-Hydroxy-2,4-Di-*t*-butylphenazine

TOD W. CAMPBELL[1]

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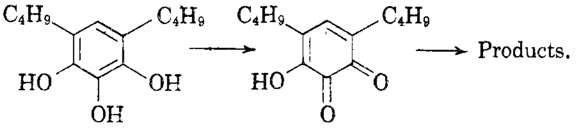
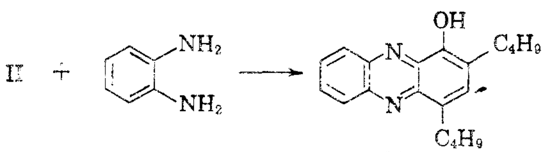
It has been proposed[2] that the oxidation of 4,6-di-*t*-butylpyrogallol in alkaline solution proceeds *via* a highly colored intermediate hydroxy-*o*-quinone:

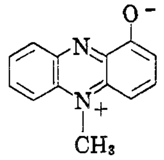


I II

Evidence for such an intermediate *o*-quinone has been obtained by oxidation of di-*t*-butylpyrogallol to an intermediate purple compound, either by air oxidation in alkali or by bromine oxidation in buffered acetic acid solution. The intermediate purple compound coupled with *o*-phenylenediamine to give 1-hydroxy-2,4-di-*t*-butylphenazine (III).

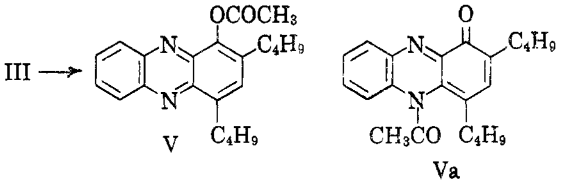


III



IV

This phenazine could not be methylated with dimethylsulfate to a pyocyanine type (IV) derivative.[3,4] It was recovered unchanged from ethereal diazomethane. Acetic anhydride gave an acetyl derivative, V, which from the infrared spectrum had the indicated structure rather than the alternate (Va).



V Va

EXPERIMENTAL

2,4-Di-t-butyl-1-hydroxyphenazine. Ten grams of dibutylpyrogallol[2] was dissolved in 150 ml. of acetic acid containing 15 g. of sodium acetate. To this solution was added 6.5 g. of bromine in 50 ml. of acetic acid. The solution at once developed a brilliant purple color. The mixture was allowed to stand for 15 min. after which 5 g. (10% excess) of *o*-phenylenediamine dissolved in 50 ml. of acetic acid was added. The purple color changed instantly to a brown-orange color. This mixture was allowed to stand for 48 hr. and the acetic acid was evaporated under nitrogen on a steam bath. The solid residue was extracted with 50 ml. of methyl alcohol containing a little concentrated hydrochloric acid. This dissolved most of the brownish orange solid. The product which remained undissolved was then treated with water to remove potassium bromide and the bright orange crystalline residue was dried. This crystalline residue was dissolved in chloroform and the chloroform solution was washed repeatedly with water. The bright orange chloroform layer was retained and the aqueous washings were discarded. Evaporation of the dried chloroform solution gave an orange crystalline solid which was recrystallized from chloroform-methanol mixture. The product was obtained in a yield of 3.2 g. (21%) with a melting point of 170.5°. A deep blue solution resulted when the product was dissolved in alcoholic alkali.

Anal. Calcd. for $C_{20}H_{24}N_2O$: C, 77.9; H, 7.9; N, 9.1. Found: C, 77.4, 77.5; H, 7.76, 7.8; N, 9.1, 9.4.

The same product was obtained by the air oxidation of a mixture of di-*t*-butylpyrogallol and *o*-phenylenediamine. However, the yield was lower and the product difficult to isolate.

2,4-Di-t-butyl-1-hydroxyphenazine acetate. Two hundred milligrams of 2,4-di-*t*-butyl-1-hydroxyphenazine was mixed with 3 cc. of acetic anhydride plus 5 cc. of pyridine. The mixture was boiled 0.5 hr., then cooled and allowed to stand for 48 hr. No crystallization had occurred so the mixture was diluted with water. The gummy material which precipitated was rubbed with a stirring rod to induce crystallization. The solid so obtained was filtered and recrystallized from aqueous methanol. The pale yellow crystalline powder had a melting point of 160.5–162°.

Anal. Calcd. for $C_{22}H_{26}O_2N_2$: N, 8.0. Found: N, 8.3, 8.2.

In alkaline methanol, a blue color developed slowly, indicating slow hydrolysis to the parent compound.

Infrared spectra of the phenazine and its acetate. The spectrum of the parent phenazine showed a relatively sharp —OH band, shifted to 2.95 μ. This indicates internal H-bonding to the adjacent nitrogen. The acetyl derivative showed an ester band at 5.65 μ, and no indication of amide groups. No —OH band was present.

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[1] Present address: E. I. du Pont de Nemours & Company, Wilmington, Del.

[2] T. W. Campbell, *J. Am. Chem. Soc.*, **73**, 4190 (1951).

[3] A. R. Surrey, *Org. Syntheses*, **26**, 36 (1946).

[4] Wrede and Strack, *Ber.*, **62**, 2053 (1929); *Z. physiol. Chem.*, **74**, 181, 184, 185 (1929).

Attempted methylation with diazomethane. Diazomethane was made by adding 2.0 g. of *N*-nitro-*N*-methyl-*N'*-nitroguanidine in portions to 20 g. of 50% potassium hydroxide solution covered by 50 ml. of ether at 0°. The ether layer was removed, washed with water, and placed in a 200-ml. Erlenmeyer flask. Two hundred and fifty mg. of 1-hydroxy-2,4-di-*t*-butylphenazine was added and the solution was allowed to stand overnight. The ether was evaporated and the orange crystalline residue melted without further purification at 169.5 to 170.5°. This material was recrystallized from a chloroform-methanol mixture. It melted sharply at 170.5°. A mixture melting point with 1-hydroxy-2,4-di-*t*-butylphenazine showed no depression.

Methylation with methyl sulfate. Using the method described in *Organic Syntheses*[3] for the preparation of pyocyanine, 200 mg. of the phenazine was warmed at about 110° with 2.0 g. of methyl sulfate for 1 hr. The reaction mixture was poured into a mixture of 10 cc. H_2O, 10 cc. methanol, and 1.5 ml. of 6*N* potassium hydroxide. The resulting dark solid was removed, and dissolved in alkaline methanol to a blue solution, as contrasted to the purple of the starting phenazine. The blue solution was extracted with ether; the color transferred to the ether phase. Gradually the color changed, through green to yellow. The yellow solution gave a faint olive green solution in alkali, and a more intense red in acid. Evaporation of the yellow ethereal solution gave a gum which solidified on standing. This was taken up in boiling methanol, filtered through charcoal, and allowed to crystallize at −10°. An orange, crystalline product was obtained, m.p. 168–169°, which was starting material (20 mg.). The bulk of the product, obtained on dilution with water, was a yellow gum which could not be crystallized.

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An Observation on Chlorination of Normal Hexane with Iodine Monochloride[1]

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Normal hexane is usually considered to be a rather stable solvent, not easily susceptible to halogenations. According to the literature,[2] it acts as a typical "purple" solvent for halogen solutions and the solutions of iodine monochloride in this solvent should have a red-brown color with an absorption maximum in the vicinity of 460 mμ.

In the course of study of iodine monochloride complexes with various Lewis bases, it was decided to use normal hexane as the reaction medium. It was immediately discovered that contrary to the expectations, dilute solutions of iodine monochloride in this solvent had a distinct purple color. Absorption spectra of these solutions were obtained and the resulting absorption curves showed a maximum of 520 mμ which is characteristic of iodine solutions in nonpolar solvents. Although it has become evident that *n*-hexane was not a suitable solvent for the study of iodine monochloride complexes, it was of interest to the authors to establish if the reaction actually occurred between iodine monochloride and *n*-hexane rather than with a reactive impurity in the solvent.

When iodine monochloride is added to the purified *n*-hexane, it dissolved rapidly in the solvent, but the process of dissolution is accompanied by the evolution of a small quantity of a gaseous product, presumably, hydrogen chloride. Although in some instances, the resulting solutions did have, originally, a reddish-brown color, the latter very rapidly turned to purple and showed the characteristic iodine absorption band.

In order to see if we have a photochemical halogenation reaction, iodine monochloride solutions were prepared in a photographic dark room and the absorption spectra were obtained without any previous exposure of the solutions to illumination. In all cases the absorption maxima were shifted toward the iodine peak.

The disappearance of halogen in the *n*-hexane solutions was followed by preparing standard solutions of iodine monochloride in this solvent and titrating the total halogen iodometrically in aliquots of the solutions withdrawn after definite intervals of time. The results of this study are shown in Table I. Since it has been shown that the reaction between iodine monochloride and *n*-hexane can occur in the dark, this series of experiments was done under ordinary illumination.

TABLE I

TITRATION OF IODINE MONOCHLORIDE IN NORMAL HEXANE

Experiment 1		Experiment 2		Experiment 3	
Time, hr.	Normality $\times 10^3$	Time, hr.	Normality $\times 10^3$	Time, hr.	Normality $\times 10^3$
0	3.26	0	5.20	0.3	5.57
1	2.64	1	4.66	1.2	3.68
3	2.12	2	4.09	19.2	2.81
5.5	1.75	18	2.68	44.7	2.75
23.5	1.66	45	2.45	98.5	2.60
100	1.66	69	2.37	260.	2.56
	1.65[a]	90	2.35		2.44[a]
			2.30[a]		

[a] Normality as calculated from absorbance data assuming only I_2 remaining.

It is interesting to note that the limiting concentration of the titratable halogen is either equal to half, or less than half of the original halogen present. After the solutions reached an apparent equilibrium, their adsorption spectra were obtained. In all cases the remaining halogen was the iodine and the calculation of the final concentration from the absorption data agrees well with the titration value.

Since there still remained a possibility that notwithstanding an apparently careful purification of

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[1] Paper XII in the series "Studies on the Chemistry of Halogens and of Polyhalides." Previous paper, *J. Am. Chem. Soc.*, **77**, 4622 (1957).

[2] N. N. Greenwood, *Rev. Pure and Appl. Chem.*, **1**, 89 (1951).