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A STABLE PHENOXY RADICAL INERT TO OXYGEN

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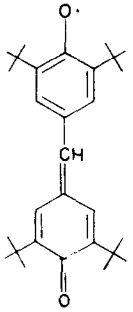
Abstract—The preparation and properties of the stable free radical 2,6-di-t-butyl-4(3,5-di-t-butyl-4-cyclohexa-2,5-dienylideneamino)phenoxy are described.

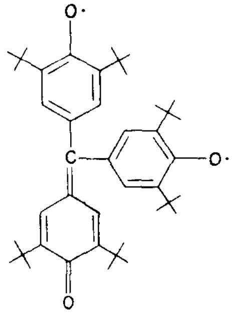
INTRODUCTION

Organic free radicals which can exist in air in the pure state are relatively rare. Diphenyl-picryl-hydrazyl has been known for many years[1] and has been extensively examined. Other types which have been described include picryl-amino-carbazyl,[2] 1,3-dimethyl-1-(phenylimine oxide) butylidene-3-N′-phenyl-N′-oxynitrogen,[3] diphenyl nitrogen oxides,[4] and the general class of substituted *p*-aminophenylamminium salts of which Wurster's blue salts are the most well known.[5]

Recently, the newer class of free radicals prepared from hindered phenols has received a good deal of attention from several groups of investigators.[6] Of the many compounds which have been prepared only two can be described as stable, that is with thermal stability and inertness to oxygen, 2,6-di-t-butyl-4(3,5-di-t-butyl-4-oxocyclohexa-2,5-dieynlidene methyl) phenoxy (I)[7,8] which has acquired the trivial name of galvinoxyl[9] and 2,6,2′,6′-tetra-t-butyl-4,4′(3,5-di-t-butyl-4-oxocyclohexa-2,5-dienylidene methyl) diphenoxy (II)[10] which unfortunately does not have a trivial name.



I



II

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[1] A. N. Holden, C. Kittel, F. R. Merritt and W. A. Yager, *Phys. Rev.* **77**, 147 (1950); S. Goldschmidt *et al.*, *Liebigs Ann.* **437**, 194 (1924).

[2] H. S. Jarrett, *J. Chem. Phys.* **21**, 761 (1953).

[3] T. L. Chu, G. E. Pake, D. E. Townsend and S. I. Weissman, *J. Phys. Chem.* **57**, 504 (1953).

[4] H. Katz, *Z. Phys. Chem.* **87**, 238 (1933); E. Muller, I. Muller-Rodloff and W. Burge, *Liebigs Ann.* **520**, 235 (1935).

[5] S. I. Weissman, *J. Chem. Phys.* **22**, 1135 (1954); L. Michaelis, *Chem. Rev.* **16**, 243 (1935); L. Michaelis and M. P. Schubert, *Ibid.* **22**, 437 (1938).

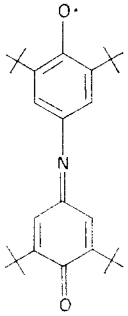
[6] C. D. Cook, D. A. Kuhn and P. Finan, *J. Amer. Chem. Soc.* **78**, 2002 (1956); E. Muller, A. Schick and K. Scheffler, *Chem. Ber.* **92**, 474 (1959); J. K. Becconsall, S. Clough and G. Scott, *Trans. Faraday Soc.* **448**, 459 (1960); G. M. Coppinger, unpublished.

[7] G. M. Coppinger, *J. Amer. Chem. Soc.* **79**, 501 (1957).

[8] M. S. Kharasch and B. S. Joshi, *J. Amer. Chem. Soc.* **79**, 1439 (1957).

[9] P. D. Bartlett and C. Ruchardt, *J. Amer. Chem. Soc.* **82**, 1756 (1960).

[10] N. C. Yang and A. J. Castro, *J. Amer. Chem. Soc.* **82**, 6208 (1960).



III

This paper describes the preparation of a third stable phenoxy radical which has the structure (III).

RESULTS AND DISCUSSION

The synthesis of (III) was accomplished in three separate steps.

The first step, nitrosation, was carried out in the inverse method to avoid the complication of compatible solubility of sodium nitrite and phenol. A small amount of tetra-t-butyldiphenoquinone was obtained as a byproduct.

The second step consisted of three sequential reactions which were carried through without isolation of the intermediates; this was found to be of advantage because of the instability of VI and VII. The first part of this synthetic path was the well known reduction of the nitroso group to the amine with sodium hydrosulfite. The amine was taken up in ether and the ether replaced with iso-octane. Heating the iso-octane solution of VI under nitrogen brought about the transformation of VI to VII with the evolution of NH_3. This rather strange reaction has previously been reported by Calcott *et al.*[11] to occur with 2,6-diisopropyl-4-aminophenol in the solid state. We were able to confirm that indeed a pure crystalline sample of VI under nitrogen at room temperature does react with the evolution of ammonia to yield VII. Iso-octane solution was chosen for preparative use because it led to fewer side reactions. It is interesting to point out that methanol was used as solvent for this reaction also and that none of the compound IX was detected as a product; VII was obtained in fair yield.

Thus an explanation involving simple displacement or ionization of NH_3 from a protonated amine does not appear to be adequate, for the solvent methanol would be expected to intervene under those conditions and result in IX.

The oxidation of VII to VIII was accomplished by blowing air through the iso-octane solution of VII. Both VI and VII are very sensitive to oxidation by air in the crystalline state as well as in solution. The compound VIII, following purification by recrystallization, was readily oxidized to the stable free radical III with lead dioxide.

The fact that III was a free radical was established in two different ways. Susceptibility measurements* indicated a lower limit of 0·9 mole of unpaired electrons per mole of free radical in the solid state. Electron magnetic resonance spectroscopy revealed a resonance absorption spectrum in iso-octane which, when account of line overlap was

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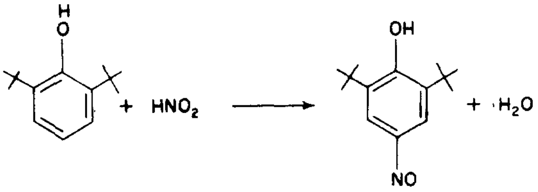
* The magnetic susceptibility measurements were made by R. G. Meisenheimer.

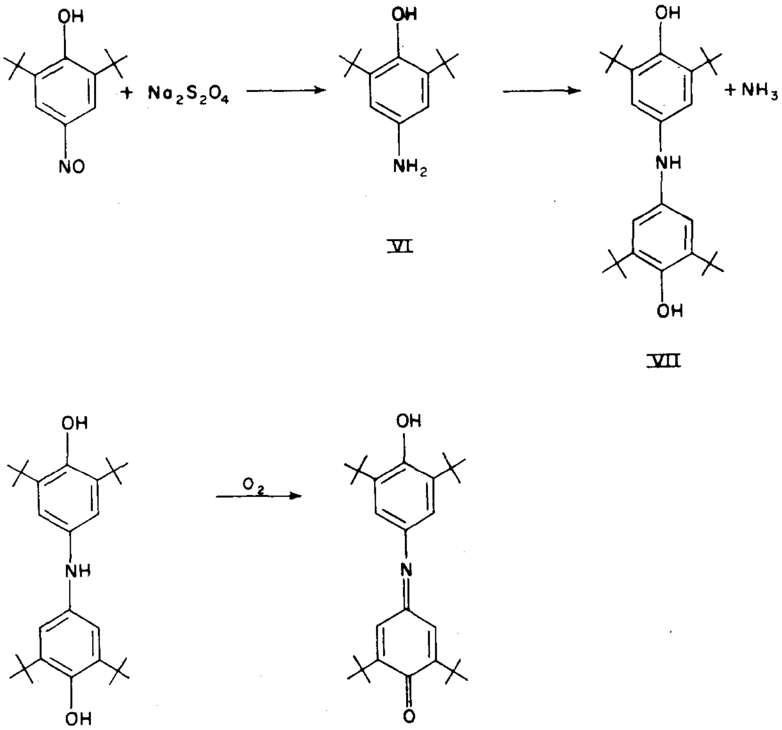
[11] W. S. Calcott, J. M. Tinker and V. Weinmayer, *J. Amer. Chem. Soc.* **61**, 1010 (1939).

1.



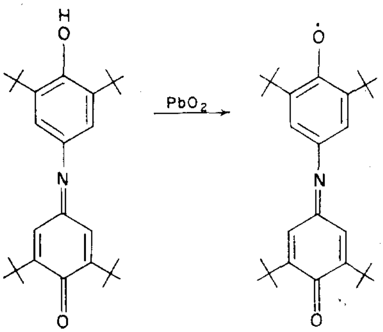
IV V

2.

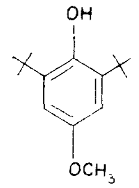


VI VII VIII

3.



III



IX

taken, consisted of 3 sets of 5 absorption lines of relative intensities 1,4,6,4,1. This is consistent with the assignment of structure III to the free radical. With the odd electron delocalized through the resonance system, interaction of the magnetic moment of the electron with the nitrogen nucleus will give rise to three lines of equal intensity each of which will be split into five lines through interaction of the free electron with the four equivalent ring hydrogens.[12] Within the limits of the method, III was shown to exist entirely as a free radical both in the solid state and in solution by comparison of its total resonance absorption with that of samples of galvinoxyl and of diphenylpicrylhydrazyl.

The stability of the free radical III has been demonstrated by the fact that samples stored in air have remained unchanged after a period of three years.

EXPERIMENTAL

2,6-*Di-t-butyl-4-nitrosophenol*

One mole of 2,6-di-t-butylphenol was dissolved in 1 l. of ethanol containing 0·55 mole H_2SO_4. Into this solution was poured over a period of 1 hr a solution of 1 mole of sodium nitrate in 200 ml of water. The reaction temperature was maintained at 0°C. A half-liter of water was added to precipitate the nitrosophenol. Purification was accomplished by recrystallization from ethanol–water. Yield 75–80%, m.p. 208·9°C. (Found: C, 71·5; H, 9·1; N, 5·89. Calc. for $C_{14}H_2NO_2$: C, 71·5; H, 8·7; N, 5·95%).

2,6-*Di-t-butyl-4-aminophenol*

The nitrosophenol, 0·5 mole was dissolved in 1 l. of ethanol and the solution was heated to 50–60°C. To this solution a concentrated solution of sodium hydrosulfite was added slowly until the reaction mixture was colorless. The solution was made basic with sodium carbonate and the amino phenol extracted with ether. The ether was removed and the aminophenol was recrystallized from iso-octane. Yield 60–65%, m.p. 103–107°C. (Found: C, 76·1; H, 10·5; N, 6·3. Calc. for $C_{14}H_{23}NO$: C, 76·0; H, 10·4; N, 6·3%).

Care was necessary in the isolation of this compound because it underwent rapid oxidation in contact with air. In the crystalline state, ammonia was evolved and it was possible to isolate VII as a product of this reaction. The product VII in turn was rapidly oxidized to VIII in the presence of air.

2,3′,5′,6-*Tetra-t-butylindophenol*

The aminophenol from the reduction of the nitrosophenol was taken up in ether and the ether replaced by iso-octane. The iso-octane was heated at reflux temperature under nitrogen for 36 hr or until ammonia was no longer evolved. The temperature of the solution was reduced to room temperature and oxygen was bubbled through the solution for 4 hr. Part of the iso-octane was removed until crystallization occurred. The compound VIII was then purified by recrystallization from iso-octane. Yield 60–75%, m.p. 132–133°C.

(Found: C, 79·5; H, 9·8; N, 3·2. Calc. for $C_{28}H_{43}NO$: C, 79·4; H, 9·8; N, 3·3%).

3,5,3′,5′-*Tetra-t-butyl-4-′-dihydroxydiphenylamine* VII

Compound VIII was reduced quantitatively to VII with hydrogen and a platinum or charcoal

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[12] D. J. E. Ingram, *Free Radicals*. Academic Press, New York (1958).

catalyst in methanol solution. (Found: C, 78·6; H, 10·3; N, 3·4. Calc. for $C_{28}H_{45}NO$: C, 78·6; H, 10·5; N, 3·3%).

2,6-*Di-t-butyl*-4-(3,5-*di-t-butyl*-4-*cyclohexa*-2,5-*dienylideneamino*)-*phenoxy* III

A solution of 10 g of VIII in 100 cm^3 of ethyl ether was stirred with a suspension of 20 g of lead dioxide for 2 hr at room temperature. The lead oxides were removed by filtration. The free radical III was recovered by evaporation of solvent and was recrystallized from iso-octane. Yield 70–80%, m.p. 135–136°C. (Found: C, 79·7; H, 9·6; N, 3·46. Calc. for $C_{28}H_{44}NO$: C, 79·5; H, 9·5; N, 3·31%).

The electromagnetic resonance measurements were made with a 9400 Mc spectrometer employing 400 c modulation. The solution of free radicals were carefully degassed before examination. The splittings were A_H 1·13 ± 0·05 gauss, A_N 2·25 ± 0·05 gauss. The spectroscopic splitting factor was 2·0024 ± 0·0010.*

* We are indebted to Dr. J. D. Swalen for the measurement of these splittings.