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The Reaction of 2,4,6-Tri-*t*-butylphenoxy Radical with Unhindered Phenols

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The products and kinetics for the reaction of 2,4,6-tri-*t*-butylphenoxy radical with 3- and 4-substituted phenols have been determined in benzene at 24 ± 0.5°. The second-order rate constants vary over a range of 10^4, demonstrating the high selectivity of this radical. The value of k_H/k_D for the reaction of the hindered phenoxy radical with 4-phenylphenol-OH and -OD was found to be ≥ 7.5. A critical examination of the σ and σ^+ correlations is presented for this and other free-radical reactions.

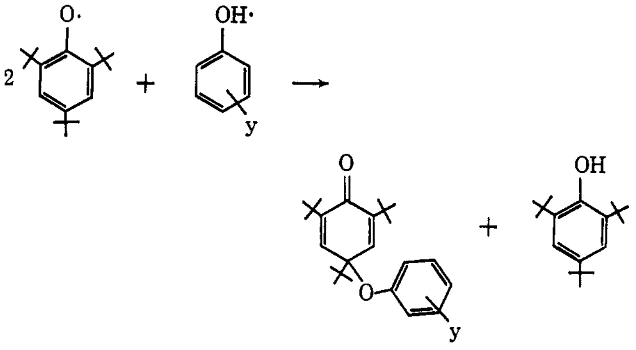
Phenoxy radicals have been proposed as reactive intermediates in a wide variety of chemical systems.[1] The formation of phenoxide polymers has been shown to involve phenoxy radicals in rapid equilibration with oligomers.[2] Such species also are postulated as being reactive intermediates in the retardation of hydrocarbon oxidation by phenolic compounds.[3] The effects of various phenols on enzymatic oxidation has been interpreted as involving phenoxy radicals,[4] and the possible physiological roles of such reactions demand that these intermediates be highly selective in their reactions.

Cook and Norcross[5] reported the rates of disproportionation of 2,6-di-*t*-butyl-4-*sec*-alkylphenoxy radicals and Buchachenko, *et al.*,[6] reported the rates of 2,4,6-tri-*t*-butylphenoxy radical with nitro phenols in concentrated solution. In the present work a systematic study is carried out in order to obtain a knowledge of the relative selectivity of the 2,4,6-tri-*t*-butylphenoxy radical compared with that of other radicals and atoms. Such information should provide a foundation for interpretation of results in more complex systems.

Results and Discussion

Product Analysis.—A reaction which appeared to be most amenable to study is the reaction of the hindered 2,4,6-tri-*t*-butylphenoxy radical with simple phenols variously substituted in the 3 and 4 positions. Previous studies by other workers[7,8] suggested that this reaction occurs with a variety of simple phenols and affords the products in good yields.

An analysis of the products formed in this reaction shows that the quinol ethers and the 2,4,6-tri-*t*-butylphenol are formed in essentially quantitative yields in all the cases studied (Table I). The equation which describes the products and stoichiometry is shown below. We failed to find any evidence for the concurrent formation of phenolic dimers. For every 2 moles of radical, 1 mole of quinol ether and 1 mole of 2,4,6-tri-*t*-butylphenol are formed. This stoichiometry has been previously suggested by others[7] on the basis of yields of quinol ethers and 2,4,6-tri-*t*-butylphenol (45–90%) isolated from particular reaction mixtures. However, it had not been shown that this stoichiometry was true in general nor if phenol dimers were present in any of the reactions studied.



Kinetics.—Rates were measured for the reaction of the hindered 2,4,6-tri-*t*-butylphenoxy radical with various simple phenols in benzene solution. Kinetic measurements were carried out in a mixing stop-flow apparatus since some of the reactions had half-lives of only a few seconds, making batch-type analysis essentially impossible. The blue 2,4,6-tri-*t*-butylphenoxy radical lends itself to kinetic study not only because of its stability in the absence of hydrogen

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(1) For recent reviews, see (a) H. Musso, *Angew. Chem.*, **75**, 965 (1963); (b) A. I. Scott, *Quart. Rev.* (London), **19**, 1 (1965).

(2) G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. Finkbeiner, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

(3) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(4) A. H. Mehler, D. Kertesz, and R. Zito, "Oxygenases," O. Hayaishi, Ed., Academic Press Inc., New York, N. Y., 1962, Chapters 3 and 8.

(5) C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, **81**, 1176 (1959).

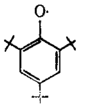
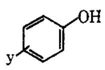
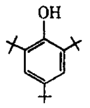
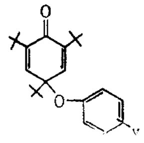
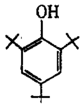
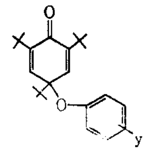
(6) A. L. Buchachenko, M. B. Neiman, O. P. Sukhanova, and Y. G. Mamedova, *Russ. J. Phys. Chem.*, **37**, 113 (1963).

(7) E. Muller, K. Ley, and G. Schlecte, *Chem. Ber.*, **90**, 2660 (1957).

(8) H.-D. Becker, *J. Org. Chem.*, **29**, 3068 (1964).

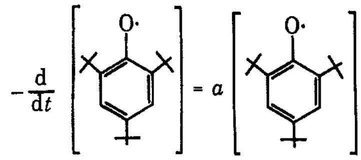
Table I

Summary of Product Analyses for the Reaction of 2,4,6-Tri-*t*-butylphenoxy Radical with 3- and 4-Substituted Phenols

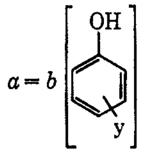
	Concn,[a] mole l.$^{-1}$ of 	Concn,[a] mole l.$^{-1}$ of 	Yield,[b] mole l.$^{-1}$ of 	Yield, mole l.$^{-1}$ of 	Theoretical, mole l.$^{-1}$ of  or 
y = *p*-*t*-Butyl	6.06×10^{-4}	9.865×10^{-4}	3.29×10^{-4}	3.19×10^{-4}	3.03×10^{-4}
	6.06×10^{-4}	7.775×10^{-3}	2.98×10^{-4}	2.89×10^{-4}	3.03×10^{-4}
	6.06×10^{-4}	7.305×10^{-2}	3.36×10^{-4}	3.02×10^{-4}	3.03×10^{-4}
y = *p*-Methoxy	6.14×10^{-4}	2.13×10^{-3}	2.84×10^{-4}	3.02×10^{-4}	3.07×10^{-4}
	6.14×10^{-4}	2.20×10^{-2}	2.93×10^{-4}	2.88×10^{-4}	3.07×10^{-4}
	6.14×10^{-4}	4.24×10^{-1}	2.75×10^{-4}	2.94×10^{-4}	3.07×10^{-4}
y = *m*-*t*-Butyl	3.512×10^{-3}	8.05×10^{-3}	1.58×10^{-3}	...	1.756×10^{-3}
y = *p*-Phenyl	3.512×10^{-3}	8.20×10^{-3}	1.75×10^{-3}	...	1.756×10^{-3}
y = *m*-Carboethoxy	3.512×10^{-3}	5.895×10^{-3}	1.73×10^{-3}	...	1.756×10^{-3}
y = *m*-Cyano	3.512×10^{-3}	1.26×10^{-2}	1.83×10^{-3}	...	1.756×10^{-3}
y = *p*-Carbomethoxy	3.512×10^{-3}	9.7×10^{-3}	1.72×10^{-3}	...	1.756×10^{-3}
y = *p*-Cyano	3.512×10^{-3}	2.33×10^{-2}	1.83×10^{-3}	...	1.756×10^{-3}
y = *p*-Bromo	3.512×10^{-3}	4.21×10^{-3}	1.55×10^{-3}	...	1.756×10^{-3}

[a] Concentrations of reactants after mixing. [b] Corrected for any unreacted 2,4,6-tri-*t*-butylphenol upon generation of the radical.

donors but also because its disappearance can be readily followed spectrophotometrically. The rate of disappearance of the hindered phenoxy radical is a pseudo-first-order process at constant added phenol (Figure 1). Thus



The values of *a* vary linearly with the concentration of added phenol and yield a zero intercept (Figure 2). Then



The rates obtained obey the expression

$$-\frac{d}{dt}[\text{ArO}\cdot] = 2k_1[\text{ArO}\cdot][\text{Ar'OH}]$$

where ArO· = 2,4,6-tri-*t*-butylphenoxyl and Ar'OH = *meta*- or *para*-substituted phenol.

The addition of large amounts of 2,4,6-tri-*t*-butylphenol in amounts up to ten times the molar concentration of radicals had no effect on the value of *a*.

The values of *b* obtained for all the phenols studied are summarized in Table II. The concentrations of unhindered phenols used were such that they were not associated.

The temperature control in our studies was 24 ± 0.5°, but, since the activation energies for our reactions are certainly less than 10 kcal,[9] the resulting error in our rate constants is less than 6%.

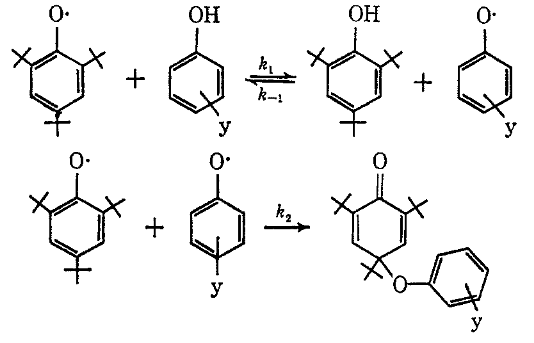
Table II

Summary of Rate Constants Obtained for the Reaction of 2,4,6-Tri-*t*-butylphenoxy Radicals with Unhindered Phenols at 24 ± 0.5° in Benzene

Phenol	*b*, mole^{-1} sec^{-1}[a]
4-Methoxy	6060 ± 235
4-Phenyl	251 ± 20
4-*t*-Butyl	92.5 ± 6.5
4-Bromo	8.70 ± 0.6
4-Carbomethoxy	0.419 ± 0.018
4-Cyano	0.153 ± 0.010
Hydrogen	6.17 ± 0.47
3-*t*-Butyl	20.8 ± 1.9
3,5-Dimethyl	30.7 ± 2.4
3-Carboethoxy	1.19 ± 0.08
3-Cyano	0.163 ± 0.009

[a] The data were treated by the least-squares method and the uncertainties represent standard deviations.

A kinetic scheme which is consistent with the observed rate law is shown in eq 1, −1, and 2 where eq 1 is the



(1)
(−1)
(2)

rate-determining step. Assuming a steady-state concentration of phenoxy radicals the following rate law is derived

$$-\frac{d[\text{B}\cdot]}{dt} = 0 = k_1[\text{A}\cdot][\text{BH}] - k_{-1}[\text{AH}][\text{B}\cdot] - k_2[\text{B}\cdot][\text{A}\cdot] \quad (3)$$

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[9] The activation energy for the reaction of 2,4,6-tri-*t*-butylphenoxy radical with substituted nitrophenols in benzene solution at concentrations displaced completely toward association was found to be 10.3 kcal.[6]

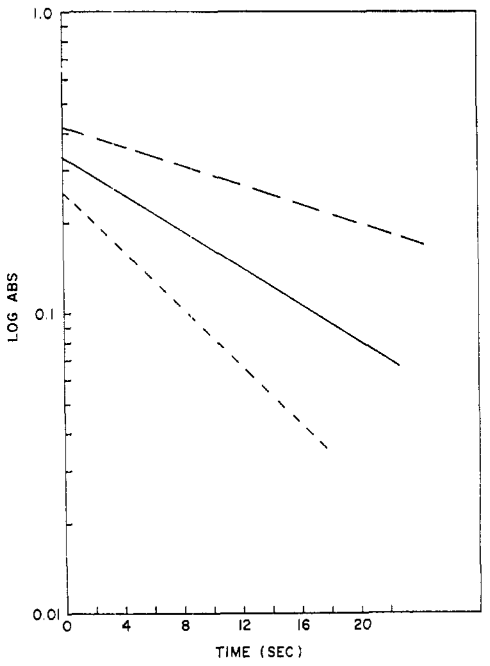
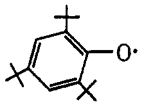
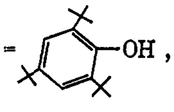
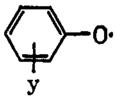
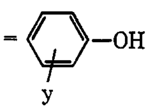


Figure 1.

where

A· = , AH = , B· = 

and

BH = 

then

$$-\frac{d[A\cdot]}{dt} = k_1[A\cdot][BH] + k_2[B\cdot][A\cdot] - k_{-1}[AH][B\cdot] \quad (4)$$

and

$$[B\cdot] = \frac{k_1[A\cdot][BH]}{k_{-1}[AH] + k_2[A\cdot]}$$

Substitution into eq 2 and simplifying yields

$$-\frac{d[A\cdot]}{dt} = k_1[A\cdot][BH] + k_1[A\cdot][BH]\left(\frac{k_2[A\cdot] - k_{-1}[AH]}{k_{-1}[AH] + k_2[A\cdot]}\right)$$

Since the addition of added amounts of 2,4,6-tri-*t*-butylphenol had no effect on the values obtained for b, $k_2[A\cdot] \gg k_{-1}[AH]$ and the experimentally observed rate is obtained where $b = 2k_1$.

Isotope Effect.—An isotope effect was measured for the reaction of the hindered phenoxy radical with *p*-phenylphenol. In order to minimize exchange reactions, it was found necessary to determine the kinetics in the presence of a constant source of deuterium. A successful method[10] for accomplishing this is to run reactions in the presence of D_2O which usually involves a two-phase system. Since this was not possible in our system, a convenient method was devised which consisted of carrying out the reaction in the presence of 0.1% methanol-OD. The rate observed, however, must be compared with rates determined in the presence of undeuterated methanol to compensate for any solvent effect. Figure 3 depicts a plot of the rate of decay of 2,4,6-tri-*t*-butylphenoxy radical *vs.* time at the same concentration of *p*-phenylphenol without methanol, with methanol, and with methanol-OD. Similar plots were obtained for several concentrations of *p*-phenylphenol. The value of k_H/k_D was found to be ≥ 7.5. Therefore a transfer of a hydrogen atom is involved in the rate-determining step. The relatively large isotope effect observed provides evidence for a linear, highly symmetric transition state as shown below.

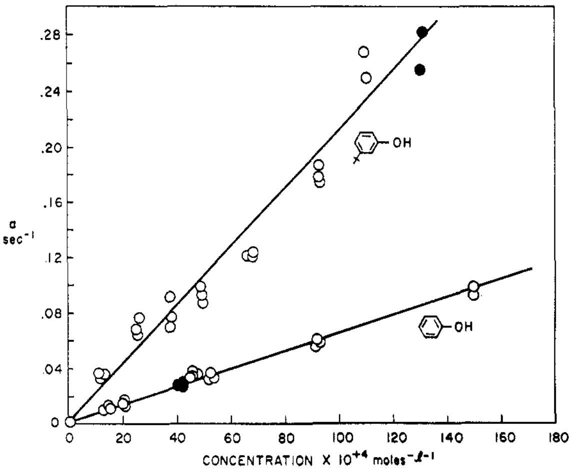


Figure 2.

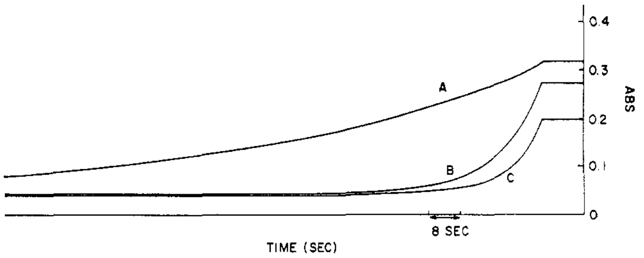
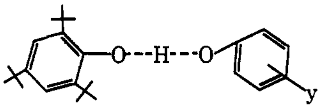


Figure 3.



Correlation of Substituents Effect.—Russell[11a] as well as Howard and Ingold[11b] have recently summarized the available data on the correlations of the rates of free-radical hydrogen abstraction reactions with Hammett σ and/or Brown σ^+ substituent parameters. Owing first of all to its very high selectivity (a variation of 10^4 in rate is observed in the present work) and the large isotope effect (a large degree of bond breaking in transition state), the 2,4,6-tri-*t*-butylphenoxy radical represents an interesting species to subject to such an analysis. A plot of log $2k$ *vs.* Hammett σ and Brown σ^+ values (Figure 4) reveals that neither set of substituent parameters satisfactorily correlates the data. A procedure for analyzing data which do not follow either relationship has been proposed by Taft and Lewis[12] and by van Bekkum.[13] According to this

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[10] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962).

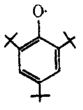
[11] (a) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964); (b) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

[12] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

[13] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

Table III

Summary of Calculated σ–ρ Parameters

Reacn	ρ	No. of 3-substd compd + hydrogen	Calcd σ								Ref
			p-C_6H_5	p-Br	p-Cl	p-t-Bu	p-CN	p-NO_2	p-CH_3	p-OCH_3	
 + phenols	−2.72	5	−0.47	+0.02	...	−0.33	+0.59	...	...	−0.95	This work
DPPH + phenols	−2.22	4[a]	−0.63	...	−0.02	−0.43	...	+0.46	−0.45	−1.4	*c*
BR· + toluenes	−1.75	2	−0.60	...	+0.07	−0.32	+0.60	...	−0.30	...	*d*
t-BuO· + toluenes	−0.77	3	−0.25	−0.2	+0.23	...	+0.68	...	−0.20	...	*e*
Cl· + toluenes	−0.72	4[b]	−0.23	...	+0.20	...	...	+0.70	−0.23	...	*f*
Styryl radicals + styrenes	+0.53	5[a]	...	+0.23	+0.22	...	+0.95	+1.26	...	−0.35	*g*
Polarographic reduction of toluenes	∼+1.0	6[a]	...	...	+0.31	...	...	...	−0.01	−0.1	*h*
Hammett σ	+1.0	...	−0.01	+0.232	+0.227	−0.197	+0.660	+0.778	−0.170	−0.268	
Brown σ^+	−4.45	...	−0.179	+0.150	+0.114	−0.256	+0.659	+0.790	−0.311	−0.778	

[a] 3-Methoxyphenol omitted from calculations. [b] *m*-Phenoxytoluene omitted from calculations. [c] J. S. Hogg, D. H. Lohmann, and K. E. Russell, *Can. J. Chem.*, **39** (1961). [d] R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963). [e] R. D. Gilliom and B. F. Ward, Jr., *ibid.*, **87**, 3944 (1965). [f] Reference 11. [g] "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 135. [h] A. Streitweiser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1649).

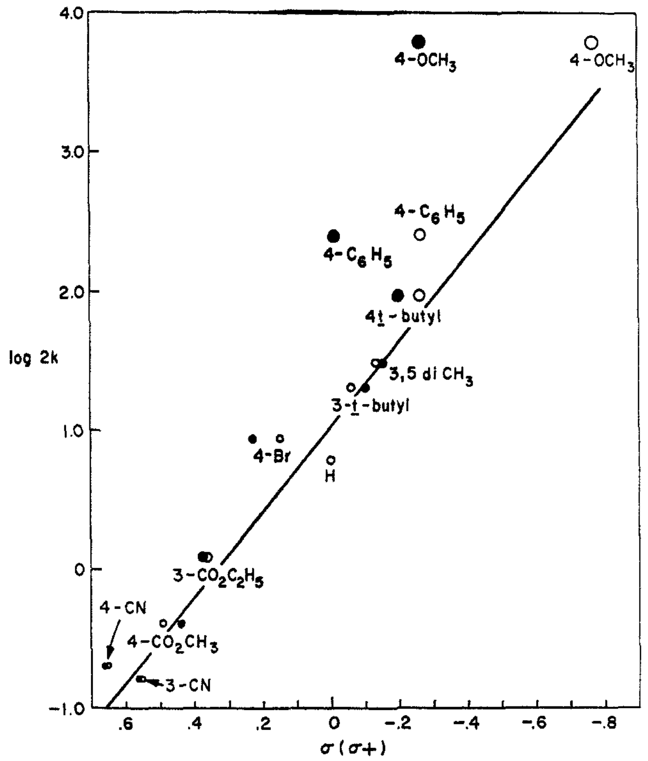


Figure 4.

procedure the ρ value for a reaction is determined by a plot of log k/k_H for a number of 3-substituted compounds. A correlation is considered successful if the values of σ for these substituents do not vary by more than ±0.1 unit from the best line drawn through the points. Applying this criterion to the data of the present work yields a value of ρ equal to −2.72 (solid line in Figure 4). This value represents the largest ρ value reported to date for a free-radical hydrogen abstraction reaction. The compounds which deviate most strongly from this correlation line are the 4-phenyl-, 4-bromo-, and 4-methoxy-substituted phenols.

In Table III is presented the limited amount of available data for hydrogen abstraction reactions from substituted phenols, styrenes, and toluenes where the rate data for at least two 3-substituted compounds and hydrogen are available. The procedure of van Bekkum and Taft has been applied and an effective σ constant necessary to place the point on the correlation line defined by the *meta* compounds has been calculated. Although deviations of the calculated σ from either Hammett σ or Brown σ^+ parameters of ±0.1 unit cannot be considered significant, there is a definite trend which indicates that nearly all 4 substituents accelerate the reactions. It is also apparent that the more selective the radical (the larger the ρ value), the greater the deviations.

Gilliom and Ward[14] have recently reported a similar deviation for hydrogen abstraction from 4-phenyltoluene by Cl·, Br·, and *t*-butoxy radicals. Streitweiser and Perrin[15] in their study of the polarographic reduction of benzyl chlorides observed wide deviations for all 4-substituted compounds. Both groups suggested that radical stabilization of the transition state by interaction with substituents at the 4 position was of extreme importance in their reactions. The possible importance of such effects has been recently demonstrated by Martin, *et al.*,[16] who reported the stabilization energies of monosubstituted methyl radicals from electron-impact measurements. The large value found for OCH_3, +20 kcal mole^{-1}, compared with a value of +25 kcal mole^{-1} for phenyl supports such interpretations.

The exceptions to this "trend" are the 4-cyano and 4-carbomethoxy from the present work and the 4-nitro substituents from the diphenylpicrylhydrazyl radical data. In both cases the substrata are substituted phenols. Russell[11] has suggested that, in the case of phenols or amines, where the nonbonding electrons are involved in resonance, conformations are involved in which the –OH or –NH bond is copolanar with the benzene ring and such conformations make

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[14] See Table III, footnote *e*.

[15] See Table III, footnote *h*.

[16] R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966).

resonance of the incipient radical difficult since it lies in an orbital perpendicular to this plane.

It has been well established that many free-radical reactions are subject to polar effects and a $\sigma\rho$ treatment would appear to be a useful tool to describe their magnitude. This effect should be measurable by a study of 3-substituted compounds in the same reaction series. The possibility would then exist for the isolation of polar and radical stabilization effects which manifest themselves in the 4-substituted compounds. However, as Table III demonstrates, there is an incredible lack of appropriate data in the literature at present. To give a detailed description of the polar character of the transition state for a free-radical reaction in the absence of sufficient data on 3-substituted compounds is in the authors' opinion tenuous.

Experimental Section

Prepurified nitrogen (a product of the Liquid Carbonic Division of General Dynamics) was passed through a tube containing copper filings at 400° before use. The Celite (503) was a gift from Johns-Mansville, Inc. The Methanol-OD was obtained from the New England Nuclear Corp. The spectrophotometric cell, designed specifically for flow reactions, was manufactured by Pyrocell Manufacturing Co., Westwood, N. J. The solvents were of Spectrograde quality. All of the phenols used were crystallized to constant melting point and showed no extraneous impurities on vapor phase or thin layer chromatography. All melting points were corrected.

Product Analysis.—A complete product analysis was carried out for the reaction of 2,4,6-tri-*t*-butylphenoxy radical with *p*-methoxyphenol and *p*-*t*-butylphenol in benzene. For the reactions involving the other unhindered phenols, only the amount of 2,4,6-tri-*t*-butylphenol formed was determined.

The reactions were carried out in a mixing step-flow apparatus as shown in Figure 5. Table I lists the concentrations of reagents used. The 2,4,6-tri-*t*-butylphenoxy radical was generated by passing solutions of 2,4,6-tri-*t*-butylphenol over a column of PbO_2–Celite (4:1). The exact radical concentration was determined from its extinction coefficient at 6300 mμ (ε 410) and also by treating solutions of the radical with oxygen and subsequently analyzing for bis(1,3,5-tri-*t*-butyl-2,5,cyclohexadien-4-one) peroxide *via* infrared, utilizing the absorbance at 6.0 μ (ε 400) and 6.1 μ (ε 468) in CCl_4. The amount of any unreacted 2,4,6-tri-*t*-butylphenol could also be determined from the infrared spectra from its absorbance at 2.7 μ (ε 243).

Aliquots of the reaction mixtures were diluted with benzene and washed with 10% sodium hydroxide[17] (six times) and water (three times). The benzene was removed *in vacuo* at 25°. The residue was dissolved in an appropriate volume of CCl_4 and the infrared spectra were obtained. The sodium hydroxide washings were neutralized with dilute hydrochloric acid and extracted several times with chloroform. The chloroform solutions were concentrated and used directly for vapor phase or thin layer chromatography.

The absorbance at 6.0 and 6.1 μ was used for the analysis of the quinol ethers and the absorbance at 2.7 μ was used for the analysis of 2,4,6-tri-*t*-butylphenol. All of the compounds obeyed Beer's law. The method of analysis was checked on prepared mixtures of the pure compounds which also had undergone base treatment.

Analysis of the base-insoluble portion of the reaction mixtures shows the quinol ethers and the 2,4,6-tri-*t*-butylphenol to be formed in essentially quantitative yields (Table I). Thin layer chromatography did not show any other products to be present.

The base-soluble portion of the reaction mixtures upon vapor phase or thin layer chromatography showed only unreacted unhindered phenol to be present. Even when the concentration of unhindered phenol was 50 or 100 times the concentration of 2,4,6-tri-*t*-butylphenoxy radical, there was no indication of phenolic dimers.

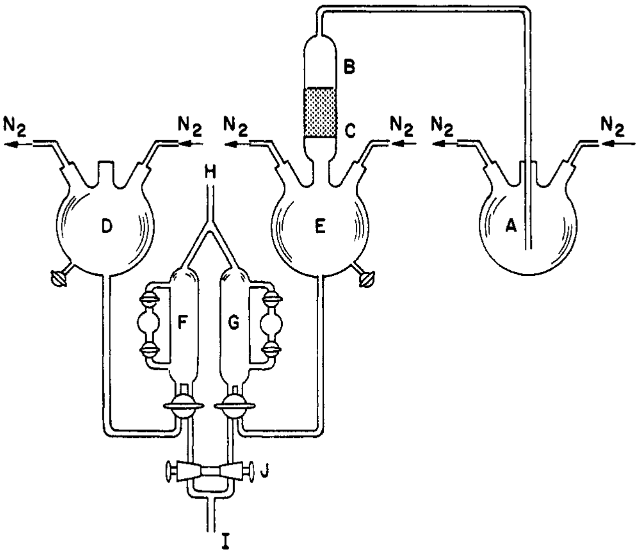

Figure 5.

Isolation of Products.—Products were isolated for the reactions of 2,4,6-tri-*t*-butylphenoxy radical with *p*-methoxyphenol and *p*-*t*-butylphenol. Aliquots of the reaction mixtures were diluted with benzene and washed with sodium hydroxide and water. The solvent was removed at 25° under reduced pressure and the compounds were separated by fractional crystallization. In each case, the 2,4,6-tri-*t*-butylphenol was separated by dissolving the residue in a small amount of absolute ethanol. The quinol ethers were then isolated from the mother liquors by further concentration and subsequent recrystallization from appropriate solvents. The quinol ethers were found to be identical with authentic samples synthesized by other methods.

Preparation of Authentic Samples. 4-(4-*t*-Butylphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one.—4-(2,3-Dichloro-5,6-dicyano-4-hydroxyphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one[18] (490 mg, 1 mmole) was added to a solution of 150 mg (1 mmole) of 4-*t*-butylphenol in 10 ml of dry methanol under N_2. The deposition of a yellow solid began almost immediately. Stirring was continued for 0.5 hr. After the mixture chilled at 0° for 1 hr, the solution was filtered. Bright yellow flakes, mp 95.5–96° (lit.[17] mp 94–95°), were obtained from methanol in 343-mg yield (83.8% of theory); infrared showed 6.0 μ (ε 288) and 6.1 μ (ε 330) (CCl_4).

4-(4-Methoxyphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one.—This compound was also prepared *via* the DDQ adduct using 490 mg (1 mmole) of 4-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one and 124 mg (1 mmole) of *p*-methoxyphenol as described above. Pale yellow flakes were obtained from methanol (270 mg, 70.5% of theory), mp 78.5–79.5° (lit.[8] mp 77–78°); infrared showed 6.0 μ (ε 289), 6.1 μ (ε 353) (CCl_4).

Bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) Peroxide.—2,4,6-Tri-*t*-butylphenol (262 mg 1 mmole) was added to a slurry of 0.5 g of lead dioxide in 100 ml benzene. The mixture was stirred vigorously for 20 min and then filtered. The filter cake was washed with benzene and the resultant blue filtrate was allowed to react with air. The yellow solution was evaporated and the residue was crystallized from alcohol. Bright yellow prisms (0.255 g, 92% of theory) were obtained, mp 146–147.5° (lit.[19] mp 148–149°).

Rate Measurements.—The kinetic measurements were carried out in an all-glass mixing stop-flow apparatus, as shown in Figure 5. A Cary spectrophotometer with a variable-speed chart recorder was used to record the decay of the radical with time. The radical was generated by passing solutions of 2,4,6-tri-*t*-butylphenol over a column of PbO_2–Celite (4:1). The rates were measured by following the decay of the 2,4,6-tri-*t*-butylphenoxy radical in the visible at 6300 mμ (ε 410) or at 4000 mμ (ε 2050) at constant added phenol. The absorbance at 4000 mμ was found to be more convenient for concentrations of radical $<5 \times 10^{-4}$ *M*. In the concentration range studied,

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(17) The unhindered phenols must be removed since they interfere with the infrared analysis in CCl_4; even at low concentrations of unhindered phenol the absorbance at 6.0 and 6.1 μ is markedly diminished.

(18) H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

(19) H. S. Blanchard, *ibid.*, **25**, 264 (1960).

solutions of the radical obeyed Beer's law. The maximum rate of flow through the spectrophotometric cell (volume, 0.1 cc) was 12 ml/min at 300 mm. Solutions of the pure radical could be kept in the cell for periods up to 1 hr with no detectable change in radical concentrations.

The rate of disappearance of the 2,4,6-tri-*t*-butylphenoxy radical is a pseudo-first-order process as demonstrated by plotting the logarithm of the absorbance *vs.* time. Figure 1 illustrates the decay of the hindered phenoxy radical at three different concentrations of 3-*t*-butylphenol. Good first-order plots were obtained for all of the unhindered phenols studied. Initial concentrations of radical were in the range 1–20 × 10^{-4} mole $l.^{-1}$. Phenol concentrations were chosen to give convenient rates of reaction, 5 × 10^{-4}–100 × 10^{-4} mole $l.^{-1}$, except for *p*-cyano- and *m*-cyanophenol where concentrations up to 200 × 10^{-4} mole $l.^{-1}$ were used.[20]

The rate of the reaction of 2,4,6-tri-*t*-butylphenoxy radical with *p*-methoxyphenol was too fast to measure by this method, but was readily determined by esr. The esr spectrometer was of conventional design, operating at 9600 MHz and employing 100-kHz field modulation. The esr cavity was cylindrical and was operated in the TE 011 mode. The data were read into a Varian C-1024 time-averaging computer. The reactions were carried out in the mixing stop-flow apparatus as described. The solutions were mixed at a point 4 cm above the esr cavity and allowed to flow through a signal free quartz tube, 2-mm bore, clamped on the axis of the cavity. Immediately upon attainment of equilibrium, the flow was stopped and the computer scan was simultaneously initiated (5-sec scan time). The spectrometer time constant was 0.01 sec.

Isotope Effect.—The kinetics were carried out as described above, except that the solutions of *p*-phenylphenol contained 0.1% (by volume) methanol-OD. Similar experiments were done in the presence of 0.1% undeuterated methanol.

Acknowledgment.—The authors are indebted to Dr. T. Cole for assistance with the esr measurement and to Mr. J. Beers for his enthusiastic approach to the solution of our glass blowing problems.

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[20] Hydrogen bonding was not detected at these concentrations from infrared spectroscopy.

Conformational Preferences in Diastereomers. II

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An nmr study of the coupling constants of protons located at the two asymmetric centers in two systems is reported. In the 1,2-diphenyl-1-propyl system, increasing the size of the substituent leads to large coupling constants for both the *erythro* and *threo* isomers. A correction for electronegativity changes is made and the rotamer populations are compared with *A* values. In the substituted dihalopropane system, the use of dipole moment data in conjunction with the nmr data positively identifies the predominant rotamers. A large discontinuity is reported upon changing the substituent from isopropyl to *t*-butyl.

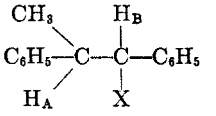
The observation that the vicinal coupling constant determined in nmr spectra is related to the dihedral angle[1] described by the H–C–C–H bonds has opened up a wide field of inquiry into the conformational preferences of large organic molecules.[2]

The observed vicinal coupling constant is a weighted mean derived from the populations of the two *gauche* rotamers (each J_{AB} = 1–3 cps) and the *trans* rotamer (J_{AB} = *ca.* 11–13 cps).

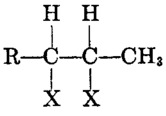
The effect of moving from one substituent to a more electronegative substituent has been shown to decrease the vicinal coupling constant.[3–6]

Bond-angle deformations also affect the vicinal coupling constant.[1,7] For example, cyclopropyl and cyclobutyl systems show somewhat anomalous coupling constants.[8,9]

With these reservations in mind, the conformational preferences of two new sets of diastereomers were studied, the 1,2-diphenyl-1-propyl system[10,11] (I) and



I



$$R-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}-CH_3$$

II

the substituted dihalopropane system (II). Once again the size of the substituents was systematically varied.

Results and Discussion

1,2-Diphenyl-1-propyl Series.—Table I records the nmr chemical shifts and coupling constants of the system in question. The variation in chemical shifts of the vicinal protons is small and will not be considered further. However, in the *erythro* series the chemical shift of the methyl substituent consistently falls at *ca.* 1.2 ppm. In the *threo* series this group appears at *ca.* 1.5 ppm. Examination of molecular models shows that the methyl group in the *erythro* isomer lies slightly above the plane of the two phenyls and probably suffers partial shielding due to the aromatic ring current. This effect is much less apparent in the *threo* model.

Partial nmr spectra of *threo*- and *erythro*-III are shown in Figure I.

The vicinal coupling constants listed in Table I show a fairly steady increase with increasing size of the substituent X. For example, when X is chloro the *erythro* isomer exhibits a coupling constant of 8.7 cps. This increases to 9.7 for bromo and 10.5 cps for iodo.

Discussion of conformational preferences will be aided by reference to Newman projections shown in

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[2] (a) A survey of the literature has been given in part I of this series: C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966); (b) D. J. Pasto, C. Cumbo, and J. Frazer, *J. Am. Chem. Soc.*, **88**, 2194, 2201 (1966); (c) M. Buza and E. I. Snyder, *ibid.*, **88**, 1161 (1966).

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