complexation, but a lack of correlation between electronic substituent effect on K^+ complexation. No selectivity reversals were observed. The small size of the 15-crown-5 ring and possible 2:1 complexation to K^+ can account for these differing results.

Acknowledgments. K.H.P. acknowledges support of this research by the Robert A. Welch Foundation, Houston, Tex., and the National Institute of Health, MBS Grant 5-S06-RR-08012-04. Stimulating conversations with Dr. M. P. Eastman are also acknowledged.

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Electrochemistry and Radical Ions of 1,3,5-Tri-*tert*-butylpentalene

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Abstract: 1,3,5-Tri-*tert*-butylpentalene has been found to undergo a reversible one-electron oxidation at +0.75 V and a reversible one-electron reduction at −1.45 V vs. SCE. The radical ions were stable at −77 °C and their ESR spectra were obtained. The ESR spectra and redox potentials were found to correlate with simple HMO predictions, and a valence bond treatment indicated the utility of aromatic cyclopentadienyl anions and antiaromatic cyclopentadienyl cations in interpreting the results. A second oxidation or reduction was not observed.

Since pentalene is an 8π-electron system which, unlike cyclooctatetraene (COT), should be planar, its electronic properties and reactivity are of interest. For this reason pentalene has been the focus of much synthetic and theoretical work. The parent ring system defied synthesis for many years until de Mayo[2] and Hafner[3] synthesized some unstable mono- and dialkyl derivatives. Finally, Hafner[4] synthesized 1,3,5-tri-*tert*-butylpentalene (**1**), which is stable. Most calculations have examined the chemical, physical, and electronic properties of pentalene and have compared pentalene with COT.[5] One would like to compare the theoretical predictions with experimental data, but so far this has only been done for the electronic spectra.[3,4]

One method for examining electronic structure is electrochemistry. Not only can redox potentials be obtained and correlated with MO calculations,[6] but the electron spin resonance spectra of the resulting radical ions allows for examination of the HOMO and LUMO. Since these orbitals are involved in chemical reactions, predictions concerning reactivity should be possible. The stability of **1** has enabled us to investigate the electrochemistry and radical ions of a pentalene.

Results

Determination of Redox Potentials. The redox potentials for **1** were determined using several electrochemical techniques. All experiments were performed using acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte, and potentials were referenced to a saturated calomel electrode. Dc polarography at a dropping mercury electrode gave a single wave with $E_{1/2} = -1.46$ V. A plot of log $(i/i_d - i)$ vs. $E - E_{1/2}$ had a slope of -0.059, indicating a reversible one-electron process.[7]

Cyclic voltammetry at a platinum disk gave a reduction couple and an oxidation couple. The oxidation wave was a reversible one-electron process under all conditions with a peak separation of 58 mV and an $E_{1/2}$ of +0.75 V.[8] The reduction couple showed irreversible behavior which resulted from slow charge transfer at Pt and not product instability[8] (Figure 1).

Second harmonic ac voltammetry[9] confirmed these results. Oxidation at platinum at 45 Hz gave a reversible wave with $E_{1/2} = +0.75$ V, a peak separation of 80 mV, and a current ratio of 1.1. The reduction at mercury at 45 Hz gave $E_{1/2} =$

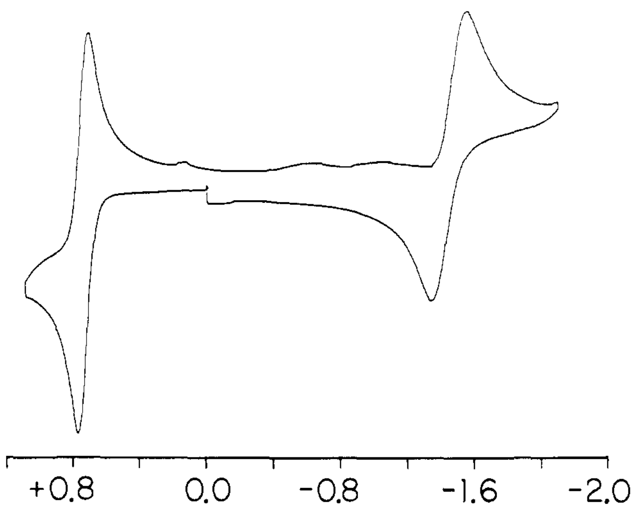
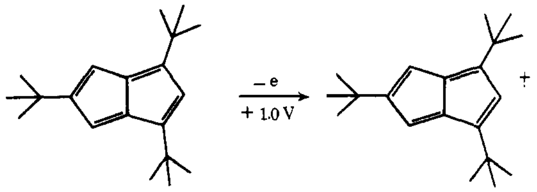


Figure 1. Cyclic voltammogram of **1** in CH_3CN with 0.1 M TBAP at a Pt electrode vs. SCE and a scan rate of 500 mV/s.

−1.45 V, a peak separation of 80 mV, and a current ratio of 0.85. A second oxidation or reduction wave was not seen within the system's limits of +2.0 and −2.8 V.

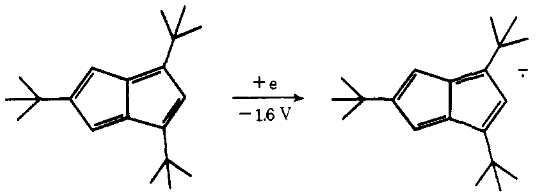
Preparative Scale Chemistry and ESR Spectra. Preparative scale electrolyses were carried out in methylene chloride under argon in a small H cell which was cooled in a dry ice-acetone bath. Oxidation at +1.0 V passed one equivalent of charge and gave an emerald green solution of radical cation **2**, eq 1, whose



(1)

1 **2**

ESR spectrum consisted of a doublet, 8.8 G, with additional fine structure, 0.5 G, Figure 2. Reduction at −1.6 V passed one equivalent of charge and gave a magenta solution of radical anion **3**, eq 2, whose ESR spectrum exhibited a broad triplet,



(2)

1 **3**

6.75 G, with a line width of 2 G, Figure 3.

Dissolution of **1** in concentrated H_2SO_4 produced an orange solution whose weak ESR spectrum was a doublet, 8.8 G, with no resolvable fine structure. Reduction of **1** at a sodium mirror gave a magenta solution which had an ESR spectrum identical with that of electrolytically produced **3**.

A simple comparison between MO predictions and the redox potentials of **1** and COT can be made by relating the orbital energy difference $\Delta MO = LUMO - HOMO$ to $\Delta E = E_{ox} - E_{red}$. Simple HMO calculations on pentalene and COT give the energies listed in Figure 4.[10] Under HMO approximations ΔMO is larger for pentalene than COT which should result in a larger ΔE for pentalene than for COT.

Before comparing ΔE's for **1** and COT, two factors must be considered: the *tert*-butyl groups of **1** and the nonplanarity of COT. The electron-donating *tert*-butyl groups will favor oxidation by stabilizing cation **2** and disfavor reduction by

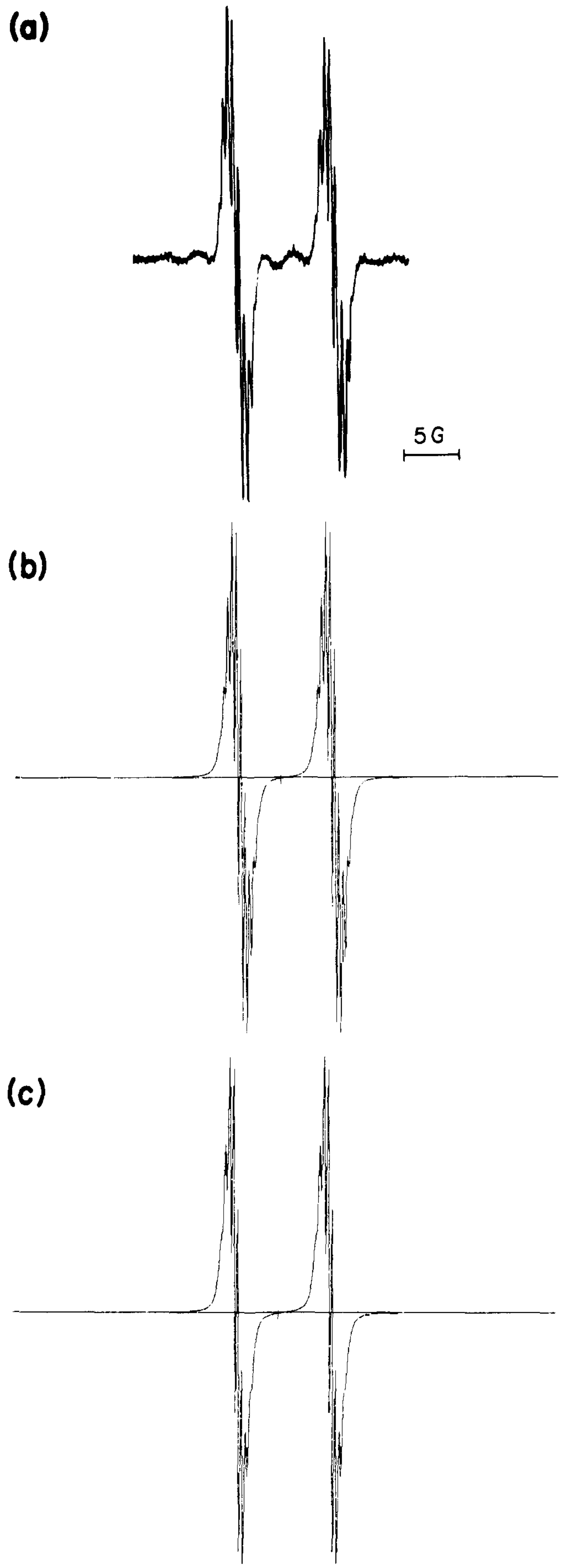


Figure 2. (a) ESR spectrum of **2** generated electrochemically in CH_2Cl_2; (b) computer simulation using 11 equivalent protons; (c) computer simulation using nine equivalent protons.

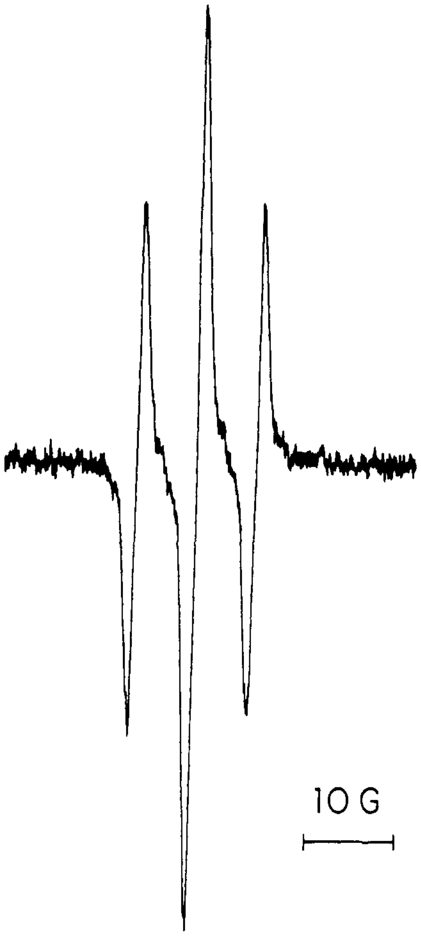


Figure 3. ESR spectrum of 3 generated electrochemically in CH_2Cl_2.

destabilizing anion **3** so that the potentials for **1** are negative with respect to those expected for pentalene. However, ΔE will depend upon the difference in shifts of these potentials. Since the ESR spectra indicate that the *tert*-butyl groups interact more strongly with **2** than **3** (vide infra), the oxidation potential should be shifted more than the reduction potential which means that ΔE for **1**, 2.20 V, must be smaller than ΔE for pentalene.

COT is not planar, whereas its radical ions are planar (or at least nearly so).[11] This stereochemical change has been the subject of several electrochemical studies,[12] and the conclusion is that some of the electrochemical energy is used to flatten the ring. NMR measurements give a $\Delta G^{\ddagger}$ of 14 kcal (0.60 V) for double bond isomerization in COT.[13] Since ESR spectra show that the radical ions have delocalized structures, it is reasonable to assume that the ions are as flat as the transition state for isomerization. Thus, 0.60 V of the redox potentials is used to flatten the ring.[14] The redox potentials for COT, previously determined to be +1.40 and −1.70 V,[16] become +0.80 and −1.10 V with a ΔE of 1.90 V when this 0.60 V correction is applied. Thus, ΔE for pentalene, which must be larger than ΔE for **1**, must also be larger than ΔE for COT, as predicted by HMO theory.

Correlation between the ESR spectra and MO predictions can be performed using the McConnell equation:[17,18]

$$a_i^{H} = \rho_i^{\pi} Q \qquad (3)$$

which relates the calculated spin densities, ρ_i^{π}, to the observed proton hyperfine coupling constant, a_i^{H}. For alternant hydrocarbons this procedure works very well and affords Q values varying from 23 to 33 with cations having larger values than anions. For nonalternant hydrocarbons the correlations are not as good, possibly due to the variable electron density in the neutral molecules, e.g., azulene.[18,19]

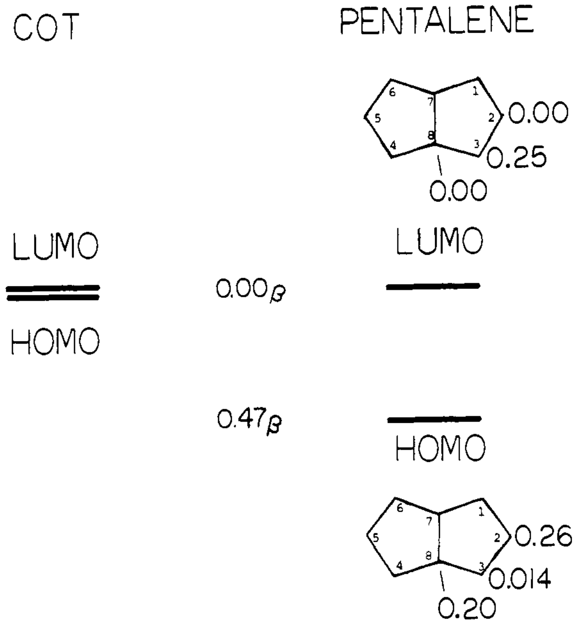


Figure 4. HOMO and LUMO energies for COT and pentalene, and the spin densities, $\rho = \sigma^2$, for the HOMO and LUMO of pentalene.

Simple HMO calculations for pentalene give electron densities shown in Figure 4. The nodes of the LUMO restrict coupling in **3** to positions 1, 3, 4, and 6, positions bearing two *tert*-butyl groups and two hydrogens as substituents. These two equivalent hydrogens give rise to the observed triplet, the small, unresolved coupling to the *tert*-butyl groups manifesting itself only as line broadening.[20] From the hydrogen coupling constant of 6.75 G, we calculate a Q value of 27 for **3**. The coefficients of the HOMO place most of the unpaired electron density in **2** at positions 2, 5, 7, and 8. Since 7 and 8 are quaternary centers, the coupling will be at positions 2 and 5 bearing a hydrogen and *tert*-butyl substituent. In the ESR spectrum of **2**, the doublet splitting of 8.8 G, due to the hydrogen at position 2, gives a Q value of 34. The observed hyperfine splitting of 0.50 G arises from two sources. A splitting of this magnitude is typical for *tert*-butyl groups in radical cations.[21] However, calculated spectra using the nine protons from the *tert*-butyl group at position 5 do not sufficiently reproduce the experimental spectrum. The small density at positions 4 and 6 with a Q value of 34 would give these hydrogens a coupling constant of 0.50 G also. Simulated spectra using all 11 protons fit the original very well (Figure 2). Hyperconjugation to the *tert*-butyl groups at positions **1** and **3** is not observed due to the small spin density at those positions.

It is difficult to assess the accuracy with which HMO theory or other theories predict these ESR spectra, since in each case there is only one well-defined coupling constant. For the same reason, the possibility of negative spin densities at the nodal carbons cannot be ruled out, and the 0.5 G splitting in **2** and some broadening in **3** may result from negative densities. Calculations more suited to open shell compounds might bring these effects to light.

A valence bond description also provides an excellent rationale for the spin localization. In Figure 5 are given the resonance structures for **3** with the unpaired electron located at the three unique positions in pentalene. The most important contributor should be **3c** which allows for formation of an aromatic cyclopentadienyl anion and results in localization of the unpaired electron at positions 1, 3, 4, and 6 in **3**, the same positions as predicted by HMO theory. The three corresponding resonance structures for **2**, are also shown in Figure

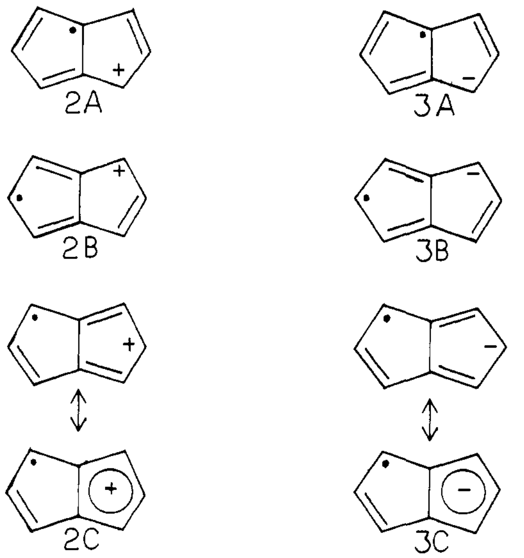


Figure 5. Valence bond structures for pentalene radical ions with the unpaired electron localized at the three unique positions.

5. In this case the important contributors should be **2a** and **2b,** for they avoid the antiaromatic cyclopentadienyl cation present in **2c.** This would place the unpaired electron in **2** at positions 2, 5, 7, and 8, analogous to the prediction of HMO theory. Thus, the spin density patterns observed reflect the stability of aromatic cyclopentadienyl anions and the instability of antiaromatic cyclopentadienyl cations and show a unique situation to exist for the radical ions of **1: 2** and **3** couple to mutually exclusive sets of protons. This is an excellent example of the nonexistence of the pairing theorem for nonalternant hydrocarbons.[5b]

If the valence bond argument is extended to chemical reactions, one predicts that nucleophilic reaction will occur at positions 1, 3, 4, and 6 to form a cyclopentadienyl anion and that electrophilic attack will occur at positions 2 and 5 to avoid the antiaromatic cyclopentadienyl cation. The latter prediction is the same as that made by the reactivity indices q_r, electron density, and L_r^+,[10,22] cation localization energy; and, since noncrossing holds, the prediction should be valid.

One last point to consider is the absence of a second oxidation or reduction potential for **1** within our limits of +2.0 and −2.8 V. Since a second oxidation is not observed for COT which is more easily oxidized than **1** and the dication generated would be a fused pair of cyclopentadienyl cations, the absence of a second oxidation is not surprising.

A second reduction of **1** to give the dianion, a naphthalene analogue is not observed, in spite of the facts that COT undergoes two reductions[16] and dilithium pentalenide is known.[23] The *tert*-butyl groups in **1** will shift the second reduction potential negatively. Also, the lithium dianion is probably ion paired whereas our electrolyte contains the noncoordinating tetra-*n*-butylammonium cation. In this case it is interesting to note that sodium reduction of **1** gave no evidence for dianion formation. Sodium does not coordinate as well as lithium and the *tert*-butyl groups probably hinder this coordination. Since the second reduction potential is more negative than −2.7 V, the difference in reduction potentials is greater than 1.2 V, which is extremely large for aromatic hydrocarbons.[6] We have no explanation for this behavior.

Experimental Section

Materials. Acetonitrile (Fisher reagent grade) was distilled from $KMnO_4$-Na_2CO_3, followed by distillation from P_2O_5 under nitrogen. Just prior to use, it was redistilled from P_2O_5 under nitrogen. Methylene chloride was distilled from P_2O_5 under nitrogen just before use. Dimethoxyethane was distilled from $LiAlH_4$, followed by distillation from Na-benzophenone under nitrogen and used immediately. Tetra-*n*-butylammonium perchlorate was prepared from an aqueous solution of the corresponding bromide by addition of an excess of 70% $HClO_4$. The precipitate was dissolved in ethyl acetate, washed with 5% $NaHCO_3$ and brine, then dried over $MgSO_4$. The solution was concentrated and hexane added to force out the salt. The TBAP was recrystallized three times from distilled ethyl acetate-hexane and dried for 10 h at 100 °C in vacuo.

1,3,5-Tri-*tert*-butylpentalene from Professor Hafner was stored in sealed ampules under argon which were opened just before use.

Instrumentation. Polarographic experiments were performed using a Princeton Applied Research (PAR) Model 174A polarographic analyzer with a PAR 172A drop timer and a Houston Instruments Omnigraphic 2000 X-Y recorder. Second harmonic voltammograms were obtained using a PAR 174/50 ac polarographic interface to integrate the above equipment with a PAR 122 lock-in amplifier and a Hewlett-Packard HP-3300A function generator.[24] Cyclic voltammetry and preparative electrolyses were performed using a PAR 175 universal programmer, a PAR 173 potentiostat/galvanostat with a PAR 176 current-to-voltage converter, a PAR 379 coulometer, and a Tektronix 5103N storage oscilloscope with two 5A23N amplifiers.

Electron spin resonance spectra were obtained on a Varian E-9 spectrometer with a low-temperature probe. All spectra were run on samples contained in Pyrex, capillary ESR tubes. Computer simulations were calculated on an IBM 360 computer with a Gould plotter using a program based on that of Stone and Maki.[25]

Electrochemical Experiments. For analytical use, a three-electrode cell was made from a 25-ml, three-neck, round-bottom flask by adding a gas bubbler and a gas outlet. The platinum working electrode was a 0.25 cm^2 disk (Beckmann No. 39273) sealed in glass. The platinum wire auxiliary electrode was isolated in a single-fritted compartment. The saturated calomel reference electrode was isolated in a double-fritted compartment which was connected to the bulk solution by a 2-mm capillary. The solutions were degassed by bubbling with argon.

Preparative electrolyses were carried out in an H-type cell with the working and auxiliary compartments separated by a fritted buffer compartment. The working electrode was platinum gauze, the auxiliary electrode was a platinum wire, and a silver wire in the working compartment served as a pseudo reference. The cell was cooled in a dry ice-acetone bath, and the working compartment was continuously flushed with argon. All experiments used solutions containing 0.1 M TBAP as supporting electrolyte in methylene chloride.

Chemical Oxidations and Reductions. 1 was dissolved in concentrated sulfuric acid which gave an orange solution. An ESR spectrum of this solution was then run at room temperature. A vacuum tube with a side arm was used for chemical reductions. Into the side arm was placed a freshly cut piece of sodium, and **1** was placed in the bottom of the main tube. The tube was attached to the high vacuum line, evacuated, and the sodium gently heated to form a mirror. Dimethoxyethane was vacuum transferred from Na-benzophenone into the tube. The tube was warmed to room temperature, stirred to dissolve **1**, then cooled to −77 °C in dry ice-acetone. The solution was brought into contact with the sodium mirror and a magenta color developed immediately. After 20 min, argon was let in and samples removed for determination of the ESR spectrum at −77 °C.

Acknowledgments. The gift of tri-*tert*-butylpentalene from Professor K. Hafner is greatly appreciated. I wish to thank Professor Ronald Breslow for suggesting the problem and providing helpful discussions. Financial support from the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

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Intramolecular Interaction of Free Radicals with Peroxides. Reactivity of Di-*tert*-butyl *p*-Benzenediperacetate and *tert*-Butyl *p*-Vinylphenylperacetate

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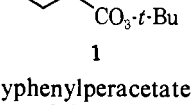
Abstract: Di-*tert*-butyl 1,4-benzenediperacetate (**15**) reacts in cumene with rates and activation parameters ($k_1 = 8.83 \times 10^{-4}$ s^{-1} at 100.3 °C, $\Delta H^* = 26.9$ kcal/mol, $\Delta S^* = -1.0$ eu) that require a mechanism involving rate-determining two-bond scission to form the *tert*-butyl *p*-benzylperacetate radical (**12**). The observed products are consistent with a scheme whereby **12** undergoes couplings and further reactions without the intervention of *p*-xylylene as an intermediate, but the formation of this latter species cannot be rigorously excluded. *tert*-Butyl *p*-vinylphenylperacetate (**17**) reacts in cumene with rates and activation parameters ($k_1 = 1.48 \times 10^{-3}$ s^{-1} at 100.3 °C, $\Delta H^* = 27.8$ kcal/mol, $\Delta S^* = 2.5$ eu) also requiring initial two-bond scission. The products from **17** are derived from radical couplings of the *p*-vinylbenzyl radical. The reaction of **17** with styrene and a free-radical initiator leads to a peroxide-containing polymer whose rate of reaction and activation parameters ($k_1 = 1.98 \times 10^{-3}$ s^{-1} at 100.3 °C, $\Delta H^* = 27.2$ kcal/mol, $\Delta S^* = 1.7$ eu) indicate rate-determining two-bond scission of a polystyrene with pendent phenylperacetate groups.

The study of the reactivity of organic peroxides substituted in the molecule with centers that may promote scission of the peroxide function is of critical importance for the understanding of the chemistry of this family of materials. In previous work we have studied the reactivity of the bisperesters di-*tert*-butyl perphthalate (**1**)[1] and di-*tert*-butyl *p*-percarboxyphenylperacetate (**2**).[2] It was concluded[1,2] that cleavage of one of the peroxy functions in these molecules to generate a free-radical intermediate with a peroxidic group remaining in the molecule did not lead to radical induced decomposition of the second peroxide.



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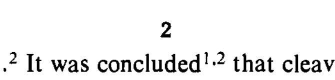
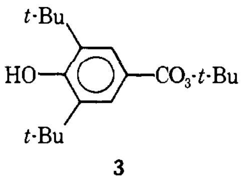
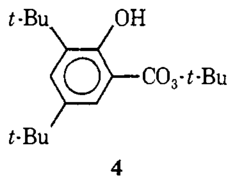


2

Related work has been reported recently from many laboratories. Examples include the phenolic peresters **3** and **4**. In the case of **3** radical or base removal of the hydroxy hydrogen leads to induced decomposition of the perester whereas the unimolecular reactivity of **3** is affected only by the normal substituent effect of the *p*-hydroxyl.[3] On the other hand, **4** is insensitive to base or radical induced decomposition, but undergoes rapid first-order reaction due to specific interactions with the *o*-hydroxyl.[4]



3



4

A variety of compounds have been studied which have two functional groups present which are potential sources of free radicals. These include bisperesters and bisdiacyl peroxides of the type **5**,[5] azo hydroperoxides and azo peresters of the type **6**,[6] diacyl peroxides of dicarboxylic acids of type **7** and **8**,[7a] and 2-substituted-1,3-perphthalates.[7b] Cyclic peroxides of diverse structural types have also been recently prepared and studied including compounds **9**,[8] **10**,[9] and **11**.[10]

Free-radical intramolecular induced decomposition routes