pulse delay. Thirty blocks of 500 transients were collected. The methoxyl quartet appeared in this run, although it was missing in the normal run even though 4096 data points were utilized.

The spectra were all run in deuteriochloroform solution at the following concentrations (percent w/v): 1, 9.5; 2, ca. 6; 3, 5.5; 4, ca. 8; 5, 7.3; 6, 1.8; 7, 10.8; and 8, 9.2. In no case did either the ¹H or the ¹³C spectra indicate impurities. The chemical shifts were taken from the computer-generated print-out; the actual standard used was the center line of CDCl₃ but the data are reported vs. TMS, which was taken as 76.9 ppm from CDCl₃

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Oxidative Decarbonylation of 2,4,6-Tri-tert-butylresorcinol via a Probable *m*-Quinone Intermediate

W. H. Starnes, Jr.,*1 D. A. Plank, and J. C. Floyd

Plastics Technology Division, Exxon Chemical Company, Baytown, Texas 77520

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Oxidation of mixtures of 2,4,6-tri-tert-butylresorcinol (4) and its diketo tautomer (5) with alkaline ferricyanide at room temperature gives 2,3,5-tri-tert-butylcyclopentadienone (8) and carbon monoxide as major products. Control experiments show that these products are derived almost exclusively from 4 rather than 5. The oxidation is suggested to involve conversion of 4 into a singlet m-quinone (1b), which cyclizes into a cyclopropanone derivative (3b) capable of undergoing rapid decarbonylation. This mechanism is shown to be consistent with theoretical expectations and experimental data for related systems.

In connection with other studies in this laboratory on the chemistry of phenolic antioxidants, we became interested several years ago in the properties of m-quinone (1a), the hypothetical species which would result from homolytic abstraction of the hydroxyl hydrogens of resorcinol. Our interest in 1a was intensified, to some extent, by the results of a simple Hückel molecular orbital (HMO) calculation.² which predicted that 1a would contain five nondegenerate bonding orbitals with delocalization energies of 2.314, 1.802, 1.287, 0.590, and 0.445 β . Since *m*-quinone has eight π electrons, its ground-state electronic configuration was thus required to be a singlet;³ consideration of this result, together with the bond orders and electron densities calculated for m-quinone by our procedure, suggested that the substance could be represented, at least to a first approximation, by the dipolar structure 2. This species might be expected to collapse to the fully covalent structure 3a,



which should reveal its presence by undergoing characteristic cyclopropanone reactions⁴ such as nucleophilic addition or decarbonylation.

However, in view of the approximations involved in the simple HMO method, it was realized that these conclusions could not be accepted without reservation; and, in particular, it seemed that the prediction of a singlet ground state for 1a was likely to be in error. Since the two highest bonding orbitals had been found to differ in energy by only 0.145 β , it was clear that they might actually prefer to exist as a degenerate pair, owing to electron repulsions that had been neglected in the simple HMO treatment.⁵ Nevertheless, thermal population of a low-lying singlet state of la remained as a reasonable possibility, and we therefore decided to attempt the preparation of a suitable derivative of m-quinone in order to examine its chemical properties.⁶ Oxidative dehydrogenation of 2,4,6-tri-tert-butylresorcinol (4) seemed especially attractive in this regard, since the *tert*-butyl groups would be expected to perturb the π system of 1b to only a minor extent, while preventing undesirable reactions of an anticipated monophenoxy radical intermediate.⁷ However, attempts to prepare 4 by direct alkylation gave 4,6-di-tert-butylresorcinol instead,8 and after a brief exploration of other potential routes to 4, its synthesis was temporarily abandoned.



At a later date, our interest was revived by the reported isolation of diketone 5 as a minor product from the irradiation of cyclohexadienone $6.^9$ Realizing that oxidation of 5 under conditions conducive to tautomerization might give results equivalent to those anticipated for 4, we attempted to synthesize 5 by repeating its published preparation. Our observations were quite unexpected, and some of them have already been reported.¹⁰ In our hands, irradiation of 6 gave a considerable amount of the novel cyclobutenone, 7^{10a} which could be smoothly converted into mixtures of 4 and 5 by brief periods of heating^{10b} (Scheme I). With both 4 and 5 available, it was now possible to pursue our original objective, and the results of this investigation are described in the present paper.

Results and Discussions

Use of alkaline ferricyanide as an oxidant seemed particularly attractive for our purposes, since this reagent was known to give excellent yields of phenoxy radicals from many hindered phenols.¹¹ Moreover, basic conditions were expected to cause tautomerization of 5 and also prevent a potential acid-catalyzed loss of *tert*-butyl from the sterically crowded 2 position.⁹ In actuality, oxidation of mixtures of 4 and 5 with alkaline ferricyanide occurred rapidly at room temperature to give good yields (based on 4) of 2,3,5tri-*tert*-butylcyclopentadienone (8) and carbon monoxide, in approximately equal amounts (Scheme I). Unlike most



alkyl-substituted cyclopentadienones,¹² compound 8 is stable toward dimerization for periods of several days; its structure was established by spectral methods and by conversion to dimethyl 3,4,6-tri-*tert*-butylphthalate upon treatment with dimethyl acetylenedicarboxylate.¹³ That carbon monoxide and 8 were derived almost exclusively from 4 rather than 5 was shown by the recovery of considerable amounts of 5 from the oxidates, and by the failure of 5 to give appreciable amounts of carbon monoxide and 8 (or, indeed, any identifiable products) when attempts were made to oxidize it alone under comparable conditions.

Although conversion of 5 into 4 had been previously shown to be difficult,^{9,10b} it was thought that our failure to accomplish a clean oxidation of 5 might have been due to its lack of solubility in the aqueous oxidizing medium. We therefore attempted to oxidize mixtures of 4 and 5 in a homogeneous system using pyridine as the solvent and 2,3dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as oxidizing agent. However, dealkylation occurred despite the presence of the nitrogen base, giving 4,6-di-*tert*-butylresorcinol as the major product; little, if any, oxidation occurred under these conditions.

In the interim following our early attempts to prepare 4, Güsten et al.¹⁴ had reported the formation of arylated cyclopentadienones and carbon monoxide from reactions of tetraphenylresorcinol, 2,4,6-triphenylresorcinol, and 2,4diphenyl-1,3-naphthalenediol with various one-electron oxidants.¹⁵ The oxidative decarbonylation of resorcinols thus appears to have some generality; and, indeed, our demonstration of its occurrence with a substrate containing only alkyl substituents suggests that it may, in fact, be characteristic of the *m*-quinone π system, per se. However, bulky groups have been present in all examples reported to date; thus the role of steric factors needs clarification.

The sequence $4 \rightarrow \mathbf{lb}$ (singlet) $\rightarrow 3\mathbf{b} \rightarrow \mathbf{8} + \mathbf{CO}$ constitutes an attractive rationale for our results and is analogous to the scheme proposed by Güsten et al.^{14b} for oxidative decarbonylation of arylresorcinols. In hopes of trapping an intermediate cyclopropanone (or zwitterion), we carried out a ferricyanide oxidation of 4 and 5 using furan¹⁶ as the organic solvent. Entrapment was not observed, but this result was hardly surprising in view of the rapidity of the decarbonylation process. In any event, the suggested path seems to be consistent with theoretical principles and experimental observations on related systems. Thus, the disrotatory cyclization of 1b to form 3b is in keeping with the stereochemical consequences of orbital theory,^{5,17} if 1b can be regarded as a derivative of the cyclopropanone isomer, "oxyallyl" (9, cf. 2). Theory also predicts a strong thermodynamic driving force for cyclopropanone formation in the case of 9 itself,^{17,18} and this prediction is consistent with



the results of experimental structural studies.¹⁹ However, cyclopropanone 3b is inordinately strained; thus it may represent an atypical situation. Cyclopropanones bearing cis tert-butyls have not been previously described in the literature; and, indeed, the failure of attempts to prepare tri-tert-butylcyclopropanone²⁰ from the E and Z forms of 10 suggests that cis-tert-butylcyclopropanones may be less stable than their allene oxide isomers in certain cases. Nevertheless, the thermodynamic stability of 3b is not necessarily less than that of 11 and 12, since these allene oxides would be destabilized, themselves, by the presence of a bridgehead olefinic linkage.²¹ Furthermore, 3b is not required to be present in high concentration if its decarbonylation is sufficiently fast. Prediction of the effects of steric factors on decarbonylation rate is difficult in this case, as no good model systems are available for comparison.²² However, there are good reasons for believing that the rate may be greatly influenced by electronic factors, as well. In this connection, we note that the concerted decarbonylation of cyclopropanone is a disrotatory cheletropic reaction which is required by orbital symmetry rules to proceed by a nonlinear path.²³ Extended Hückel calculations^{23b} indicate that the transition state for decarbonylation can be approximated by a structure, 13 (the complete charge distribution^{23b} is not shown), which will be strongly stabilized by groups that can delocalize the negative charge on carbon. Decarbonylation of 3b (and related compounds)¹⁴ should thus be much faster than that of cyclopropanones which lack effective delocalizing substituents, and this conclusion could also apply to a nonconcerted decarbonylation process

involving complete heterolysis of one C-C $bond^{23b,24}$ (cf. 13) as the initial step. The facile decarbonylation reported



for another negatively substituted cyclopropanone,²⁴ 14, offers experimental support for this hypothesis,²⁵ and the recent literature contains several other examples of reactions which appear to involve thermal decarbonylation of cyclopropanones bearing α -carbonyl substituents.²⁶

Finally, we wish to comment on the possible relevance of our results to oxidations of other resorcinol-type compounds. Resorcinol itself gives carbon monoxide upon autoxidation in aqueous alkali,²⁷ but the yield is miniscule and is lower, in fact, than the yields of carbon monoxide obtained from the other isomeric dihydroxybenzenes in an identical experimental situation.²⁷ Thus there is no need to invoke the "*m*-quinone mechanism" for resorcinol oxidation under these conditions. Alkaline autoxidation of 4,6di-*tert*-butylpyrogallol gives a product, 15,²⁸ which can be



envisaged to arise from further oxidation of an hydroxycyclopentadienone intermediate (16, or its diketo tautomer). However, other routes to 15 are clearly available; thus its formation provides no real evidence for oxidation via a mquinone. The same comment applies, and with equal force, to the reported formation of carbon monoxide in oxidations of pyrogallol itself.^{27,29}

Experimental Section

Melting points were determined with a Fisher-Johns apparatus and are uncorrected. NMR spectra were obtained with Varian Model HA-100 or A-60 instruments using dilute solutions containing Me₄Si as internal standard. Infrared measurements were made with a Perkin-Elmer spectrometer, Model 21; mass spectra were recorded with an AEI MS-9 instrument using c = 12 amu as the reference standard for exact measurements of m/e. Organic solutions were dried over Drierite; evaporations were carried out on rotary evaporators at room temperature under ca. 10 mm of pressure, unless noted otherwise. Petroleum ether had a nominal boiling point of 30-60°; all chemicals were of the highest purity available commercially. Purities were verified by spectral measurements and the determination of appropriate physical constants.

2,4,6-Tri-tert-butylresorcinol (4) and 2,4,6-Tri-tert-butyl-4-cyclohexene-1,3-dione (5). The preparation of 90:10 mixtures of 4:5 by thermolysis of 7 in tetrachlorothiophene was described in an earlier paper.^{10b} Unfortunately, the physical constants of tetrachlorothiophene made it an inconvenient solvent for preparative work, and efforts to convert 5 into 4 gave results that were unsatisfactory.9,10b We therefore attempted to develop a more practical synthesis of 4 by thermolyzing neat 7 under various conditions. A series of aliquots taken from a large sample of 7 all gave 30:70 mixtures of 4:5 (analysis by NMR in C_6D_6 solution) upon heating at various constant temperatures ranging from 120 to 180°. These results were rather disappointing, but we were encouraged to find that recrystallization of the large sample of 7 from aqueous methanol gave a material that yielded a higher ratio of 4:5 (60:40) after thermolysis at 160°. Nevertheless, the thermolysis results showed no further improvement after an additional recrystallization of 7, and other batches of 7 gave 4:5 ratios ranging from ca. 25:75 to 50:50 under various thermolysis conditions. These experiments were discontinued when it was found that 4 could be oxidized readily in the presence of 5 (see below). However, after the present work was completed, good methods were developed for preparing either 4 or 5 from the corresponding monoketo tautomer. 30

Oxidations of Mixtures of 4 and 5 with Alkaline Ferricyanide. In a typical experiment, 2.00 g (7.18 mmol) of 7 was converted into a 4:5 mixture (ca. 40:60) by heating in a round-bottom flask for 265 sec at 160°. The mixture was dissolved in benzene (20 ml), and a magnetic stirring bar was introduced; then the flask was attached to a short condenser connected to a demountable gas trap and a gas buret containing mercury. After careful degassing by the freeze--thaw method, the apparatus was filled with nitrogen and allowed to warm to room temperature, while a separate solution of potassium ferricyanide (10.0 g, 30.4 mmol) and potassium hydroxide (1.4 g, 25 mmol) in water (50 ml) was being degassed by nitrogen ebullition. The ferricyanide solution was introduced into the reaction vessel through a rubber septum by means of a hypodermic syringe, and the reaction was then allowed to proceed for 1.0 hr at 26-28° with rapid stirring. Gas evolution was essentially complete after 0.45 hr; ca. 85% of the gas evolved during the initial 0.2 hr of reaction. VPC analysis using a standard procedure developed by the Analytical Division of these laboratories showed that the gas was essentially pure carbon monoxide (2.14 mmol, 75% yield based on 4). The liquid layers were separated, and the aqueous phase was back-extracted several times with ether. The combined organic layers were washed repeatedly with water until a neutral aqueous moiety was obtained, then dried and evaporated to give 1.64 g of material which was dissolved in a minimum amount of petroleum ether and subjected to column chromatography on Alcoa F-20 alumina (94 g) using petroleum ether as eluent. Continued elution caused separation of an orange band which crystallized into slender orange needles of cyclopentadienone 8: 0.47 g (66% yield based on 4); mp $52.5-53.5^{\circ}$ (lit.^{13,31} mp $55-55.5^{\circ}$); ir (CCl₄) 1710 cm⁻¹ (strong, C=O), no OH [lit. ir (CCl₄)³¹ 1690 cm⁻¹, ir (KBr)¹³ 1715 cm⁻¹]; NMR (100 MHz, CCl₄) singlets at δ 1.11 (9, t-Bu), 1.28 (9, t-Bu), 1.30 (9, t-Bu), and 6.56 ppm (1, vinyl H) (cf. NMR in ref 31).

A similar experiment was performed using furan in place of benzene. The yield of carbon monoxide was not reduced, and NMR analysis of the crude product mixture showed that 8 was a major constituent. The high resolution mass spectrum of the mixture gave no evidence for the presence of an adduct derived from 3b (or 1b) and furan.

In another experiment, 7.42 g (26.7 mmol) of 7 was pyrolyzed for 300 sec at 160°. The pyrolysate was dissolved in benzene (75 ml) and oxidized in the usual manner (room temperature, 1.0 hr) with potassium ferricyanide (40.0 g, 122 mmol) and potassium hydroxide (5.0 g, 89 mmol) in water (200 ml). Work-up in the usual way gave 6.73 g of crude product which afforded 2.51 g (34% yield based on 7) of crude 5 as pale yellow granules, mp 95–112° (mostly at 103–112°), upon crystallization from methanol at 0°. Pure 5 melted at 117–119° (lit.⁹ mp 114–115.5°) after recrystallization from petroleum ether; its NMR spectrum (60 MHz) was identical with the spectrum previously described.⁹ The material remaining in the mother liquor gave 1.40 g (21% yield based on 7) of 8, mp 52.5–53.5°, after column chromatography in the manner described above.

Attempted Oxidation of Mixtures of 4 and 5 with 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ). Compound 7 (180 mg, 0.647 mmol) was converted into a mixture of 4 and 5 by thermolysis in the usual way. A solution of this mixture and DDQ (147 mg, 0.647 mmol) in pyridine (5.0 ml) was kept under nitrogen for 1.5 hr at 25-26°, then for 18.4 hr at 100°. After cooling, the mixture was poured into water (100 ml) and extracted with four 50-ml portions of ether. The combined ether layers were extracted with two 50-ml portions of 5% hydrochloric acid, then washed repeatedly with 30-ml quantities of aqueous sodium bicarbonate until a neutral aqueous layer was obtained. Evaporation of the dried ether solution gave 0.20 g of material whose NMR spectrum provided no evidence for the presence of 4, 5, or 8. Peaks attributable to 4,6di-tert-butylresorcinol comprised 75% of the total area, and the presence of this substance was confirmed by rerunning the spectrum after adding an authentic specimen: NMR (60 MHz, CDCl₃) singlets at $\delta 1.39(18, t-Bu's)$, 4.72 (broad, 2, OH's), 6.06 (1, 2-H), and 7.13 ppm (1, 5-H).

Efforts were also made to oxidize mixtures of 4 and 5 with DDQ in methanol under several sets of conditions. These experiments gave product mixtures that were shown by NMR analysis to be extremely complex; isolations were not attempted.

Dimethyl 3,4,6-Tri-*tert***-butylphthalate from 8.** A solution of 8 (100 mg, 0.403 mmol) in dimethyl acetylenedicarboxylate (1.00 ml, 1.56 g, 11.0 mmol) was stirred under nitrogen for 0.2 hr at

199-201°, then evaporated with gentle warming at ca. 1 mm pressure in order to remove most of the excess of starting ester. Examination of the residue by NMR suggested that essentially all of 8 had been converted into the anticipated phthalate product: no extraneous peaks appeared in the tert-butyl or aromatic regions of . the spectrum. Crystallization of the residue from absolute ethanol gave an oil which solidified into a mixture of amorphous material and colorless plates after 2 days of standing at room temperature. The plates were separated manually and identified as dimethyl 3,4,6-tri-tert-butylphthalate by the following observations: mp 118-119° (lit.¹³ mp 122-123°); ir (CS₂) 1736 cm⁻¹ (strong, ester C=O); NMR (100 MHz, CCl₄) singlets at δ 1.33 (9, t-Bu), 1.43 (9, t-Bu), 1.51 (9, t-Bu), 3.67 (6, MeO's), and 7.52 ppm (1, 5-H); mass spectrum (70 eV) m/e 362.2446 (parent ion; calcd for C₂₂H₃₄O₄, 362.2457).

Oxidation of 5 with Alkaline Ferricyanide. A solution of 5 (150 mg, 0.539 mmol) in benzene (5.0 ml) was combined with a solution of potassium ferricyanide (3.00 g, 9.11 mmol) and potassium hydroxide (0.50 g, 8.9 mmol) in water (15 ml) after rigorous degassing and blanketing with nitrogen in the manner described above for other ferricyanide oxidations. The mixture was stirred at room temperature for 16.2 hr and then at 70° for an additional 23.8 hr. No gas evolution could be detected volumetrically within the limits of experimental error, although VPC analysis of the vapor phase showed that ca. 0.025 mmol (yield ca. 5%) of CO had, in fact, been produced. The organic layer was separated, diluted with additional benzene to a volume of approximately 100 ml, and worked up according to the procedure employed for similar oxidation experiments (see above). Analysis of the total crude product (0.12 g) by ir and 100-MHz NMR showed that it was a complex mixture containing no 5 and little, if any, of 8.

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Registry No.-4. 24851-96-5; 5, 20784-81-0; 7, 54036-86-1; 8, 36319-95-6; DDQ, 84-58-2; dimethyl 3,4,6-tri-tert-butylphthalate, 54036-87-2

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 (25) Although **14** was not actually isolated,²⁴ its intermediacy seems highly
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