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Ozonation of Hindered Vinyl Alcohols. Production of Free Radicals by Ozonation

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Abstract: Details concerning the formation of an oxy radical by ozonation of trimesitylvinyl alcohol are given. Evidence is presented for a mechanism by which the radical is produced, involving a π complex at one of the mesityl groups of trimesitylvinyl alcohol. Ozonation of 2,2-dimesitylvinyl alcohol at -150° also produces an oxy radical in good yield. The radical is isolated in the form of its dimer. Ozonation of 2,2-dimesitylvinyl alcohol at -78° affords no appreciable amount of the dimer. In contrast to these results, ozonation of 2-mesityl-2-phenylvinyl alcohol gave no sign of a radical or its dimer even at -150° .

In earlier communications, the first production of a stable radical *via* ozonation was reported.^{1,2} The radical was characterized as the oxy radical (VII) of trimesitylvinyl alcohol (I). In this paper, the experimental details of this work are reported, evidence is given for the probable mechanism by which the radical is produced, and the formation of the analogous, but less stable, radical from 2,2-dimesitylvinyl alcohol is described.

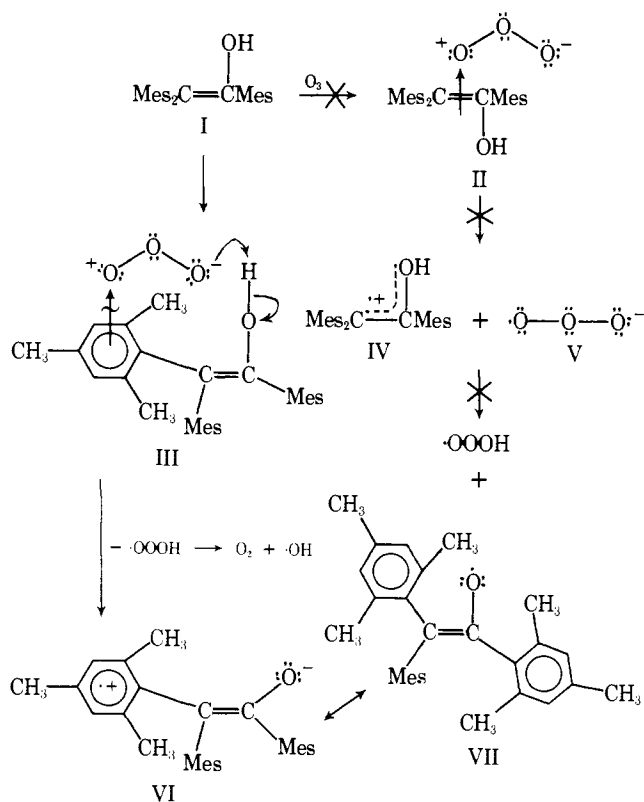
The discovery of the oxy radical VII and its formation *via* ozonation came from an extension of our studies of the competition between ozonolysis and epoxide formation during ozonation of hindered olefins.³ We had found that 1,1-dimesitylethylene gave at least 95% epoxide and wanted to study the effect of placing one or two more mesityl groups at the double bond.² Since trimesitylethylene was not known, we studied trimesitylvinyl alcohol, which had previously been synthesized by Fuson.⁴

Upon ozonation of a methylene chloride-methanol solution of trimesitylvinyl alcohol with an equivalent of ozone at

-78° , a black solution was produced which exhibited a strong epr signal, a broad singlet 7–8 G in width, with a g value of 2.004. When the reaction mixture was allowed to come to room temperature, it lost its color and epr signal after a short time. The recovery of trimesitylvinyl alcohol was 55–60%. When the above ozonation was repeated, after which an equivalent of hydroquinone was added to the cold reaction mixture, the color immediately disappeared. The recovery of the vinyl alcohol was 63%. In a third experiment, an equivalent of the efficient radical scavenger, galvinoxyl,⁵ was added to the cold reaction mixture containing the radical. At about -35° , the color and epr signals of both radicals disappeared, and a less than 10% recovery of I was obtained. It was shown that the radical could not be produced by oxygen alone, and that galvinoxyl did not react with the vinyl alcohol (I) at -35° . These data show that the radical was produced by ozone, it must have been present in the reaction mixture to the extent of more than 50%, and the most likely structure of the radical is VII, produced by

extraction of a hydrogen atom from I by ozone. In the presence of a hydrogen donor (hydroquinone or the solvent), the radical is converted back to the vinyl alcohol (I). Galvinoxyl, on the other hand, destroys it. The products of the galvinoxyl reaction were many and were not elucidated, other than a small amount of hydrogalvinoxyl.

Scheme I



The radical appeared to be produced in much lower yields in solvents such as pentane, carbon tetrachloride, and the Freons or carbon disulfide but was much more stable in all of these solvents (except carbon disulfide) since hydrogen was either not present or was less readily extractable than in the methylene chloride-methanol solvent. A carbon tetrachloride solution of the radical was stable for several days.

Evaporation of a cold pentane solution of the radical gave a mixture of clear and purple crystals which, when redissolved, gave the same epr signal as already described. The carbon disulfide solution gave a signal with the same g value as the original singlet, but which was now resolved into a heptet. This is further evidence for the assigned structure. The heptet is thought to arise *via* through-space interactions of the oxy radical with the ortho methyl groups of one of the mesityl groups, most likely the one *cis* to the oxy radical. La Pine molecular models show the ortho methyl groups of either the *cis* mesityl group or of the mesityl group on the same carbon as the oxy group to be in close proximity to the oxy group.

Further evidence for the structure (VII) assigned to the radical was that it was also produced by hypochlorite oxidation of the vinyl alcohol (I), as evidenced by an epr signal with the same g value. Electrochemical oxidation of I also appeared to produce the same radical. By analogy, hypochlorite oxidation of 2,2-dimesitylvinyl alcohol gave the same type radical, isolated as its dimer, as will be described shortly.

As an extension to our theories concerning ozonations of hindered olefins which give epoxides or rearrangement products thereof,^{2,3} we suggested, in our original communi-

cation,¹ that an ozone π complex (II) is first produced at the double bond of trimesitylvinyl alcohol. Due, however, to the bulky mesityl groups, both 1,3-dipolar cycloaddition (to yield ozonolysis products) and collapse to an epoxide are hindered, and the only recourse left to the π complex is to dissociate to cation radical IV and the ozonate anion radical V. The ozonate anion radical then extracts a proton from IV to give the observed radical VII. Additional work, however, has made this mechanism untenable. No signal for the ozonate anion radical V was ever detected, although it is readily observed during ozonations of certain amines.⁶ Ozonations of the methyl ether and acetate of trimesitylvinyl alcohol gave a π complex but no cation radical; the latter would be expected from the proposed reaction scheme. The complex is thought to be centered at one of the mesityl groups.⁷ Molecular models show that the double bonds of the vinyl alcohol, its ether, and its acetate are so hidden by the adjacent mesityl groups that complexation with them would be impossible.

A visible spectrum of an ozonated isopentane solution of trimesitylvinyl alcohol (I), cooled to -195° , showed two main absorptions, one at about 530–560 nm, which persisted when the reaction mixture was allowed to warm to room temperature, and one at 480 nm, which disappeared as the reaction mixture temperature increased. The 530-nm peak was probably due to the radical and that at 480 nm due to the presence of the π complex at the low temperature. Based on the above evidence, we propose that upon ozonation of trimesitylvinyl alcohol (I), a π complex (III) is first produced at one of the mesityl groups, probably the one *cis* to the hydroxyl group, as also found with the methyl ether of I. The negative end of the ozone molecule then abstracts the proton of the hydroxyl group as the complex dissociates homolytically, to give VI which is a canonical form of the radical VII. Alternatively, the ozone molecule could abstract a hydrogen atom from I to give VII directly, but this does not seem likely since ozone does not have radical character.⁸

From the 1 mol equiv ozonation of I in methylene chloride-methanol at -78° , only one pure product could be isolated, besides regenerated vinyl alcohol, after the radical had been allowed to destroy itself at room temperature. This crystalline material, which was isolated in only 2–3% yield, was tentatively characterized as 2,3-dimesityl-4,6,7-trimethylbenzofuran (IX), based on the elemental analysis and mass, ir, and nmr spectra of the compound (Table I).

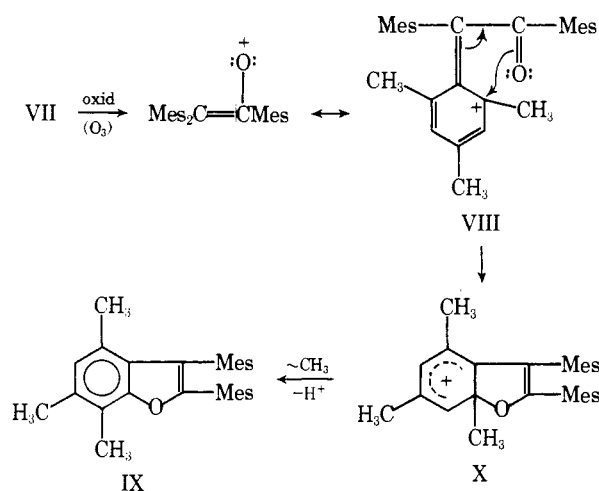
Table I. Spectral Data for Benzofuran IX

High resolution mass m/e (found)	Formula	Nmr ^a		
		δ^b	No. of protons	Probable assignment
396.2466	C ₂₉ H ₃₂ O	6.72	4	Mesityl ring H's
381.2228	C ₂₈ H ₂₉ O	6.64	1	Benzo ring H
365.1906	C ₂₇ H ₂₅ O	2.39	3	4 and 7 position
366.1972	C ₂₇ H ₂₆ O	2.32	3	Methyl H's
351.1754	C ₂₆ H ₂₃ O	2.23	6	Mesityl <i>o</i>
276.1516	C ₂₀ H ₂₀ O	2.03	6	Methyl H's
261.1279	C ₁₉ H ₁₇ O	1.97	6	Mesityl <i>p</i> -methyl H's
261.1639	C ₂₀ H ₂₁	1.90	3	6-Position methyl H's

^a 100-MHz nmr spectral peaks. ^b δ values in ppm, all singlets.

These data show that the substance has two less hydrogen atoms than the parent vinyl (I), only five aromatic hydrogens, and no hydroxyl or carbonyl group. This suggests a cyclic structure in which one of the mesityl groups of I is involved in the formation of a new ring. Most of the mass spectra peaks involve loss of methyl, methane, or mesityl-

Scheme II

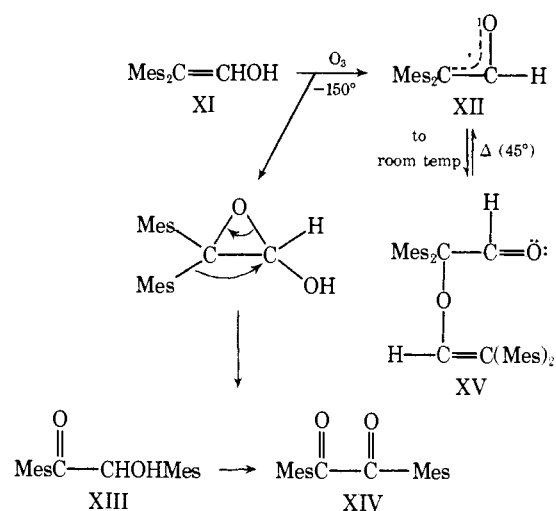


ene. A possible route to IX is shown in Scheme II. Upon continued ozonation of the vinyl alcohol (and its radical) in methylene chloride-methanol at -78° , a total of 3 mol of ozone per mole of I reacted, and the color of the radical disappeared. The only crystalline product isolated was a 1-2% yield of dimesityl ketone. All other products were intractable oils, both from the 1 mol and the 3 mol ozone reactions. An intractable mixture of products also was obtained from ozonation of the methyl ether of I.

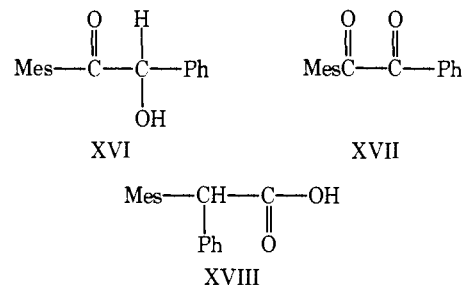
Next, 2,2-dimesitylvinyl alcohol (XI) was ozonized. At -78° , the results were essentially the same as reported earlier by Fuson and coworkers.⁹ Although a faint pink color appeared during the ozonation, essentially the only product was mesitoin (XIII). Ozonation at -150° produced a deeper pink to purple color which disappeared when the reaction mixture was allowed to come to room temperature. From work-up of the reaction mixture, three products were obtained: mesitoin (XIII), the dimer (XV) of radical XII, and a small amount of mesitol (XIV). Spectral analysis of the reaction mixture indicated yields of 45% mesitoin (XIII), 53% dimer (XV), and 2% mesitol (XIV). The dimer was shown to be identical with that obtained by Fuson, *et al.*,⁹ by sodium hypochlorite oxidation of dimesitylvinyl alcohol (XI). They, however, did not characterize it. The infrared and nmr spectra are consistent with the presently assigned structure (XV). The ir spectrum shows a strong carbonyl peak at 1720 cm^{-1} . The nmr spectrum shows an aldehydic proton at δ 9.76, an olefinic proton at δ 6.02, aromatic protons at δ 6.70 and 6.55, and methyl protons at δ 2.25-2.15 and 1.85. When a methanol solution of the dimer was heated to about 45° , the pink color of the radical appeared. Both this solution and the -150° pink ozonolysis mixture gave a strong esr signal for a radical, a singlet with a g value of 2.0034. When the 45° solution was cooled again to room temperature, the color disappeared. If the dimer was melted, the resulting liquid also was pink. These phenomena indicate that ozonation of XI at -150° goes through a π complex, as suggested for trimesitylvinyl alcohol, to give radical XII, which dimerizes as the temperature is allowed to rise. At temperatures above room temperature, however, the dimer XV reversibly dissociates again into the radical. These reactions are outlined in Scheme III.

In contrast to trimesitylvinyl (I) and dimesitylvinyl (XI) alcohols, 2-mesityl-2-phenylvinyl alcohol did not appear to give either a radical or a π complex⁷ at -150° ; no color appeared, and there was no evidence of a dimer after the temperature was allowed to rise. Essentially, the only product was the substituted benzoin (XVI). The other products, reported earlier from ozonations at higher temperatures,¹⁰ the

Scheme III



correspondent benzil (XVII) and phenylacetic acid (XVIII), were present only in trace amounts, if at all.



Attempts to produce radicals by ozonation of phenol and α - and β -naphthol at low temperatures failed. It appears that steric bulk in the vicinity of the hydroxyl group is a requirement, presumably both for the stability of the radical and as a deterrent to other reactions of ozone with the system. But steric bulk alone is not sufficient; the failure to obtain a cation radical from the methyl ether and acetate of trimesitylvinyl alcohol shows that a protic function, in conjugation with the π system, is necessary.

Experimental Section

Materials. Trimesitylvinyl alcohol,⁴ its acetate,⁴ and its methyl ether,² also 2,2-dimesitylvinyl alcohol⁹ and 2-mesityl-2-phenylvinyl alcohol,¹⁰ were prepared by previously published methods. The other substances, solvents, and reagents employed were high quality materials obtained commercially.

Ozonation and spectral equipment and procedures were as described in earlier papers.^{2,6,7,11,12}

Ozonation of Trimesitylvinyl Alcohol (I) in Methylene Chloride-Methanol. A. Production of Oxy Radical VII. In these experiments 2-20 mmol of trimesitylvinyl alcohol (I) in 50-250 ml of 3:1 methylene chloride-methanol was allowed to react with 1 mol equiv of ozone at -78° . The solution immediately took on a light violet color which progressed to opaque black as the ozonation continued. A small portion was used for an epr spectrum, giving a strong, broad (7-8 G) singlet with a g value of 2.004. When the reaction mixture was allowed to warm to room temperature, the color and signal soon disappeared. The reaction mixture was evaporated to dryness, and the residue was recrystallized from methanol. A 55-60% recovery of trimesitylvinyl alcohol (I, mp $160-161^\circ$) was obtained. When the ozonation was carried out with 1 equiv of ozone in a nitrogen stream, the yield of molecular oxygen evolved¹² was 51-59%.

B. Quantitative Determination of Radical. The above ozonation was repeated using 10 mmol of the vinyl alcohol (I) and 10 mmol of ozone in 150 ml of methylene chloride-methanol solvent. To the cold reaction mixture containing the radical was added a cold

(-78°) solution of 10 mmol of hydroquinone in 30 ml of methylene chloride. The black solution faded to a pale yellow within 2 min. Recovery of the vinyl alcohol, as described above, was 63% (mp $157-159^{\circ}$).

In a second experiment, an equivalent of the stable radical (and radical scavenger) galvinoxyl [2,6-di-*tert*-butyl- α -(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyl] in a cold (-78°) methylene chloride solution was added, instead of hydroquinone, to the cold ozonation mixture which had been degassed of ozone by a nitrogen stream. When the reaction mixture temperature was allowed to rise to -30° , the color changed to tan, showing that the radicals had destroyed each other. In preliminary experiments, it had proven difficult to recover the vinyl alcohol (I) from hydrogalvinoxyl and other products of the galvinoxyl reaction. Therefore, the yield of recovered vinyl alcohol was estimated by nmr (the vinyl alcohol proton peak at δ 5.0, which was distinct from peaks of the reaction products). *sym*-Tetrachloroethane, which was not affected by any of the products, was used as an internal standard (δ 5.9, s). The reaction mixture was evaporated, the residue was taken up in carbon tetrachloride, the internal standard was added, and the nmr peaks were integrated. Within the accuracy of the determination, it was shown that the maximum yield of unreacted vinyl alcohol was 10%. Compared with the 63% vinyl alcohol recovered in the hydroquinone experiment, this suggests a 50-60% yield of the radical. Prior to the above reaction with galvinoxyl, it had been shown that galvinoxyl was stable in the solvent for a period of many hours, and that both the vinyl alcohol and galvinoxyl were stable in the presence of each other over a period of several hours.

C. Products of Trimesitylvinyl Alcohol Ozonation. The ozonation in methylene chloride-methanol was repeated at -78° with 10 mmol of the vinyl alcohol (I) and 10 mmol of ozone. After recovery of the vinyl alcohol as described earlier, the methanolic filtrate was evaporated, and the residue was dissolved in pentane and chromatographed over neutral alumina. The column was eluted, successively, with petroleum ether (bp $60-80^{\circ}$) and petroleum ether with increasing amounts of benzene, benzene-ethyl acetate, and benzene-methanol. From the petroleum ether fractions were obtained colorless crystals melting at $158-159^{\circ}$ (25° depression in mixture with the vinyl alcohol). The ir spectrum showed no absorption in the hydroxyl or carbonyl regions but showed a strong ether band at 1100 cm^{-1} . The nmr and mass spectral data are shown in Table I. On the basis of the structural assignment as 2,3-dimesityl-4,6,7-trimethylbenzofuran (IX), the yield was 2-3%.

Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{O}$ (396): C, 87.87; H, 8.08. Found: C, 87.41; H, 8.45; mol wt (vapor pressure in acetone), 375.

From the other chromatography fractions, only intractable oils and solids containing many components could be obtained. Mass spectra showed peaks as high as m/e 516. A very prominent peak was at m/e 412.

In another experiment, 20 mmol of the vinyl alcohol was ozonized with 60 mmol of ozone in methylene chloride-methanol at -78° . The color of the radical appeared as before but was destroyed when the ozone absorption neared 3 mol equiv. The reaction mixture was reduced with iodide, and the iodine was removed with thiosulfate. Extraction with 5% sodium hydroxide solution afforded less than 1% of acidic material. The organic layer was evaporated, and the residue was chromatographed as in the preceding experiment. None of the benzofuran (IX) was found in the petroleum ether fractions. A low yield (1-2%) of dimesityl ketone (mp $137-139^{\circ}$) was isolated from the petroleum ether-benzene fractions (identified by a mixture melting point with an authentic sample). The only other significant fractions obtained were a yellow oil (0.2 g) from the benzene-ethyl acetate fraction and a red-brown solid (3.0 g, mp $50-60^{\circ}$) from the benzene-methanol fraction. These materials resisted separation or purification by chromatography, recrystallization, or sublimation. The ir spectra showed carbonyl groups. Mass spectra showed peaks as high as m/e 476 for the yellow oil and 450 for the red solid. Additional peaks varied by 16 mass units. Oxidation of the red solid with hydrogen peroxide gave a yellow solid (mp $92-102^{\circ}$) with properties similar to those of the yellow oil.

Ozonation of Trimesitylvinyl Alcohol in Other Solvents. The ozonations were carried out using 0.3-1.0 mmol of the vinyl alcohol (I) in 15-25 ml of spectrograde pentane, methylene chloride, carbon tetrachloride, or Freon 11 and 5-15 ml of spectrograde carbon

disulfide, usually at -78° . The colors of the radical were violet in pentane, methylene chloride, carbon tetrachloride, and Freon 11 but light to dark yellow in carbon disulfide. The radical was stable in pentane, carbon tetrachloride, and Freon 11 at room temperature, but not in carbon disulfide. ESR experiments in all solvents except carbon disulfide at -78° showed a radical with the same g value and width as obtained in methylene chloride-methanol. In carbon disulfide, the spectrum was a broad heptet. The pentane solution of the radical was evaporated at -78° under reduced pressure, giving a mixture of light purple and colorless crystals. When the solid was redissolved in pentane, the resulting solution gave the same epr signal as before. A carbon tetrachloride solution of the solid gave ir and nmr spectra identical with those of the vinyl alcohol (I) itself.

Uv spectra of the vinyl alcohol and of the ozonized vinyl alcohol in isopentane (taken at -195°) were identical, showing peaks in the range 190-350 nm. The visible spectrum of the radical (at -195°) showed peaks at about 480 and 530-560 nm. The latter persisted, but the former disappeared when the reaction mixture was allowed to warm.

The percentage yield of radical produced by 1 mol equiv of ozone in pentane at -78° was estimated by "titration" with galvinoxyl. Upon addition of 0.1 equiv of galvinoxyl, part but not all of the vinyl alcohol radical was destroyed, and no galvinoxyl remained, as determined by epr. Addition of 0.2 equiv of galvinoxyl destroyed all of the vinyl alcohol radical, but galvinoxyl remained. Therefore, the yield of radical was 10-20%. No meaningful estimates were made with the other solvents, but judging from the colors of the solutions, the yields were low.

Oxidation of Trimesitylvinyl Alcohol with Sodium Hypochlorite. A methylene chloride solution of 0.5 g of trimesitylvinyl alcohol was stirred vigorously with 50 ml of a 5% sodium hypochlorite solution for 2 hr. An epr spectrum of the solution showed a broad singlet with a g value of 2.004, just as in the ozonation experiments. The only isolable material was starting material.

Electrochemical Oxidation of Trimesitylvinyl Alcohol. A 0.01 M solution of the vinyl alcohol in methylene chloride containing *tert*-butylammonium iodide as an electrolyte was oxidized in a special cell¹³ at -78° while in the cavity of the epr spectrometer. The voltage was varied from 5 to 100 V. A radical was produced as the potential neared 100 V. The spectrum was very weak but continued to increase as current was applied until it became very intense; the solution also became burgundy red. As more current was passed, the signal decreased in intensity until it was only 10% of its original strength. Tlc chromatograms on silica gel were made of the solutions when the signal was at its highest strength, and when it had decreased greatly. These chromatograms showed many of the same spots as chromatograms of the ozonized trimesitylvinyl alcohol. Notably missing, however, was the benzofuran (IX) spot.

Ozonations of 1,2,2-Trimesityl-1-methoxyethylene and 1-Acetoxy-1,2,2-trimesitylethylene. Ozonations of the methyl ether and acetate of trimesitylvinyl alcohol (I) in various solvents at temperatures ranging from -78 to -150° gave no evidence for production of a radical. At very low temperatures a π complex was observed.⁷ The reaction between ozone and the ether was slow even at -50° . At 20° , in carbon tetrachloride, some vinyl alcohol remained even after 3 equiv of ozone had reacted. Tlc indicated at least 15-20 products. Efforts to affect separations failed.

Ozonation of 2,2-Dimesitylvinyl Alcohol. Two millimoles of 2,2-dimesitylvinyl alcohol in 50 ml of an approximately 95% Freon 12-5% methanol solution, prepared by condensing Freon 12 into the ozonation vessel containing the other materials, was ozonized with 2 mmol of ozone in a nitrogen stream¹² at -150° . The solution became pink to purple in color. The reaction mixture was allowed to stand for 3 hr, after which the Freon 12 was evaporated as the reaction mixture came to room temperature. The residue partially crystallized, yielding a colorless material which melted at $177-179^{\circ}$ (pink) after recrystallization from methanol. Evaporation of the filtrates under reduced pressure and crystallization of the residue from ethyl acetate-methanol gave fine yellow crystals melting at $110-112^{\circ}$. The ir spectrum showed a strong carbonyl band at 1690 cm^{-1} , but no hydroxyl band. It was identified as mesitol (XIV).⁹ Evaporation of the filtrate and recrystallization of the residue from petroleum ether (bp $60-70^{\circ}$) gave mesitoin (XIII),⁹ mp $122-123^{\circ}$; ir hydroxyl band at 3500 cm^{-1} and carbonyl band at 1690 cm^{-1} . The isolated yields of the pure products

were low. Therefore, a quantitative analysis was made, on a fresh reaction mixture, making use of Beer's law as applied to certain distinct bands in the ir spectra of the mixture and pure samples of the products.¹⁴ The bands employed were 820 and 1690 cm^{-1} (mesitoin and mesitol) and 852 cm^{-1} (all three compounds). The percentage yields thereby obtained were 45, 2, and 53% for mesitoin, mesitol, and the other compound, respectively. The other compound was shown to be identical with the dimeric compound reported by Fuson from hypochlorite oxidation of 2,2-dimesitylvinyl alcohol.⁹ Its ir spectrum showed a carbonyl band at 1720 cm^{-1} , but no hydroxyl band. Its nmr spectrum and characterization as the dimer (XV) of radical XII were discussed earlier. When a solution of the dimer approached room temperature, it lost its color, but the color reappeared when the solution was warmed to 45° or higher.

Ozonation of 2,2-dimesitylvinyl alcohol at -78° gave a faint pink color, but no dimer was observed. The major product was mesitoin (XIII).

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Electron Paramagnetic Resonance Studies of Ion Pairs in Solutions of Cation Radicals

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Abstract: Effects due to the formation of ion pairs between the 1,2,4,5-tetramethoxybenzene (TMB) cation radical and halide anions in solution have been observed by esr spectroscopy. In particular the g shift ($g_{\text{free}} - g_{\text{ion pair}}$) is much greater in iodine oxidized systems than in bromine oxidized systems. The g shift also increases as the solvent becomes less polar. A consideration of the oxidation mechanism suggests that the counteranion is I_3^- for iodine oxidized systems and is a mixture of Br_3^- and Br^- for bromine oxidations. The effects of halogen concentration, addition of halide ions, and temperature are also indicative of the existence of equilibria, possibly of the contact ion pair \rightleftharpoons solvent separated ion pair variety.

The literature concerned with the study of anion radical-metal cation ion pairs (A^-M^+) by esr spectroscopy is considerable.¹ By contrast there is almost no work in the literature on cation radical-counteranion ion pair (C^+X^-) interactions. There has been one study in which direct effects on the esr spectrum of C^+X^- ion pairs have been postulated,² and there have been two studies in which ion pair formation has been suggested as effecting information derived from esr spectra.^{3,4} There is also a report of the interaction of halide ions with metalloporphyrin cation radicals in which hyperfine splitting from the halide ions has been detected, although the species present in these studies are thought to be complexes rather than ion pairs.⁵

Due to this obvious lack of information on C^+X^- ion pairs and because of the current growing interest in the chemistry of cation radicals,⁶ as well as their importance as intermediates in many oxidation processes (see for example ref 7-10), it seemed important to explore the possibility, given the right set of conditions, of observing effects in the esr spectrum of a cation radical due to ion pair formation. Our first consideration was how to optimise conditions so that effects due to ion pairing would be most likely to occur. In general, cation radicals have been prepared by oxidation

with compounds such as H_2SO_4 , AlCl_3 , SbCl_5 , BF_3 , etc., in solvents of high dielectric constant (CH_3NO_2 , CH_3CN , CF_3COOH). Under these conditions not only are the solvents likely to strongly solvate the ions but the counteranion is probably a complicated species. Obviously one needs to carry out the oxidations in solvents of lower dielectric constant with an oxidant which will produce a relatively simple anionic species, if one is to observe any effects due to ion-pair formation. The oxidants of choice are therefore molecular bromine or iodine, since they are known to act as one-electron oxidants toward some easily oxidized compounds and the counteranions should be relatively simple species. The compound to be oxidized, 1,2,4,5-tetramethoxybenzene (TMB), was selected for several reasons. The oxidation potential of TMB is 0.82 V¹¹ which indicates that oxidation by bromine, at least, should be successful. In addition the cation radical of TMB had been previously investigated by electrochemical oxidation¹¹ and by chemical oxidation in H_2SO_4 or $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ ¹² and had been shown to be a relatively stable species as compared to other cation radicals. The esr spectrum of $\text{TMB}^{\bullet+}$ is also relatively simple consisting of 13 groups of triplets ($a^{\text{H}_{\text{OCH}_3}} = 2.20$, $a^{\text{H}_{\text{CH}}} = 0.85$ G) and is easily recognizable (see Figure 1).