the total of 2,2,3,3-tetramethylbutane was formed during the coupling reaction. By means of a control reaction it was established that a 16% increase in the amount of 2,2,3,3-tetramethylbutane resulted during the coupling reaction with allyl bromide.

Finally, it was possible to observe an esr signal that was shown conclusively to occur during the reaction of n-butylmagnesium chloride and allyl bromide and was not present in the reagents. The signal is transient and difficult to observe but it is reproducible.

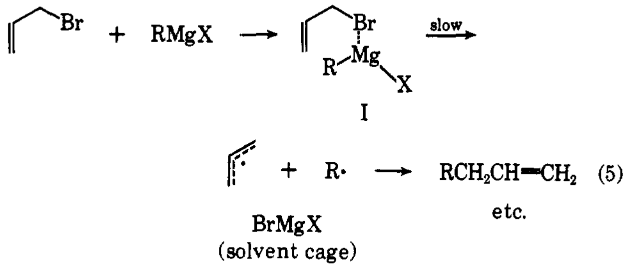
These three observations, plus the reactivity sequence, $t\text{-}C_4H_9 > sec\text{-}C_4H_9 > n\text{-}C_4H_9 > C_6H_5$, suggest a free-radical mechanism.

Assuming the validity of a free-radical process, a mechanism such as in eq 4 does not appear consistent

$$RMgX \longrightarrow R\cdot + \cdot MgX \xrightarrow{CH_2{=}CHCH_2Br} RCH_2CH{=}CH_2 + MgXBr \quad (4)$$

with the high yields of $RCH_2CH{=}CH_2$ (85–90%) observed here and in previous studies.[2c] It is known[8] that important reaction paths for alkyl radicals under these conditions are hydrogen abstraction from ether, dimerization, and disproportionation.

Alternatively, we suggest the mechanism in eq 5.



Typically, in free-radical reactions involving the production of a free radical from a neutral species, ρ is in the range of −0.5 to −1.0.[9] The larger value, in an absolute sense, of ρ in the Grignard coupling reaction is probably a reflection of the fact that in the proposed complex (I), the alkyl group R possesses appreciable anionic character.

For the scheme in eq 5, relative rates calculated from the relative amounts of $RCH_2CH{=}CH_2$ would be valid only if the fraction of the caged species that goes on to $RCH_2CH{=}CH_2$ is constant for each R group. This appears reasonable since the yield of $RCH_2CH{=}CH_2$ is 90% for n-butylmagnesium halide and 85% for t-butylmagnesium halide.[2b]

The proposed reaction course suggests the formation of RH and R–R as minor by-products. Limitations in experimental design precluded the detection of the gaseous hydrocarbons and an effort to detect n-octane from the reaction of n-butylmagnesium halide and allyl bromide was not successful.

Experimental Section

The butyl halides used for this study were free of isomeric halides, as established by gas chromatography under conditions shown to separate the isomeric butyl halides.

A. Typical Competition Reaction.—A 300-ml, three-necked, round-bottomed flask was fitted with a condenser, magnetic stirrer, and serum-type rubber stopper. Purified argon provided an inert atmosphere into which 0.050 mol of each of the competing, clear, water white, Grignard reagents was placed. The mixture was cooled to 0° and allyl bromide (0.025 mol) was added by means of a hypodermic syringe. After stirring at 0° for 30 min, the mixture was slowly poured into 200 cc of crushed ice. The mixture was acidified and the organic products were extracted with ether and dried over anhydrous magnesium sulfate. Concentration of the ethereal solution was achieved by distilling the ether through a 6-in. column packed with glass helices. The ratio of the products was determined by gas chromatography using a 6-ft column packed with 10% XE-60 on Gas Chrom R, 60–80 mesh. The column was calibrated using known quantities of independently prepared reference compounds having the structures of the expected products.

B. Determination of the Amount of 2,2,3,3-Tetramethylbutane Formed during the Allylic Coupling Reaction.—Two identical aliquots, A and B, were taken from the same solution of t-butylmagnesium chloride. To each aliquot was added an equal amount of biphenyl to serve as an internal, quantitative gas chromatography standard. Allyl bromide was added to one aliquot (A) and both aliquots were subjected to identical reaction conditions and work-up procedures. By quantitative gas chromatographic analysis it was established that sample A contained 1.16 ± 0.02 times as much 2,2,3,3,-tetramethylbutane as sample B.

C. A Typical Esr Experiment.—To a serum-capped, nitrogen-filled, esr tube, an ethereal solution of allyl bromide was added by hypodermic syringe. This was frozen in liquid nitrogen and a solution of n-butylmagnesium chloride was added and frozen. By keeping the reagents frozen, mixing and reaction were prevented. The tube was placed in the spectrometer and the solids were allowed to melt. No signal was observed from the completely melted solutions at −40°. However, when the tube was removed from the spectrometer, inverted several times to cause mixing of the layers, and replaced in the spectrometer at −40°, a signal was observed. The signal was transient and disappeared before a well-characterized spectrum could be obtained. However, it was reproducible.

Registry No.—C_6H_5MgBr, 100-58-3; $n\text{-}C_4H_9MgCl$, 693-04-9; $sec\text{-}C_4H_9MgCl$, 15366-08-2; $t\text{-}C_4H_9MgCl$, 677-22-5; allyl bromide, 106-95-6.

Acknowledgments.—Appreciation is expressed to the American Petroleum Institute for partial support of this research and to the National Science Foundation for funds which aided in the purchase of the esr spectrometer.

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[8] M. S. Kharasch, F. Engelmann, and W. H. Urry, *J. Amer. Chem. Soc.*, **66**, 365 (1944).

[9] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 180.

The Ozonation of Pyrene. A Monomeric Monoozonide formed in Polar Solvents

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Received September 21, 1967

Since it was first reported by Vollman[1] in 1937, the reaction of ozone with pyrene to give 4-formyl-5-phenanthrenecarboxylic acid has been investigated repeatedly[2–6] but the mechanism has not heretofore been

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[1] H. Vollman, H. Becker, M. Correll, and H. Streeck, *Ann.*, **531**, 1 (1937).

[2] L. F. Feiser and F. C. Novello, *J. Amer. Chem. Soc.*, **62**, 1855 (1940).

[3] M. S. Newman and H. S. Whitehouse, *ibid.*, **71**, 3664 (1949).

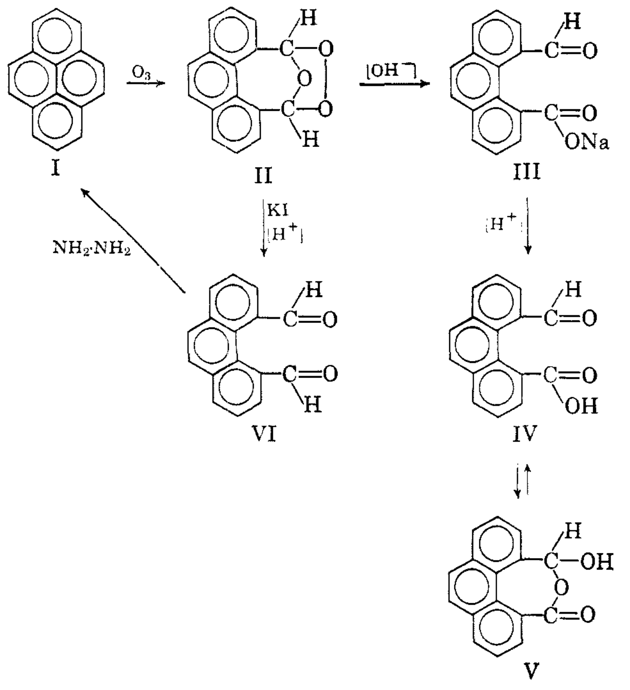
[4] G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 2326 (1950).

[5] R. E. Dessy and M. S. Newman, *Org. Syn.*, **38**, 32 (1958).

[6] P. G. Copeland, R. E. Dean, and D. McNeil, *Chem. Ind.* (London), 98 (1960).

demonstrated. In 1963, it was postulated[7] that the route in anhydrous methyl alcohol lay through a dimethoxy peroxide intermediate in a manner analogous to that followed by phenanthrene to 2′-formyl-2-biphenylcarboxylic acid (or diphenic acid after treatment with alkaline hydrogen peroxide), all in strict accordance with the Criegee zwitterion mechanism.[8] The intermediate dimethoxy peroxide, however, was not isolated. The yield of 4,5-phenanthrenedicarboxylic acid was 30% which contrasts markedly with the 85–90% yields of biphenyl derivatives easily obtained from phenanthrene.

The authors have isolated an intermediate product which can be rearranged readily into 4-formyl-5-phenanthrenecarboxylic acid. It has been characterized as a monomeric monoozonide of pyrene. This is the first of such species to be identified in the arene series. Yields suggest that it is the lone source of the aldehyde-acid.



The intermediate (II) was first detected as a golden yellow impure solid deposited when the ozonation reaction was conducted in aqueous *t*-butyl alcohol solutions. These solvents had been found to be particularly well suited to the ozonation of phenanthrene[9] and of mixtures of anthracene and phenanthrene recovered from creosote oil.[10] The yellow solids contained active oxygen and yielded pyrene and the sodium salt of 4-formyl-5-phenanthrenecarboxylic acid on treatment with sodium hydroxide. Extraction with benzene served to separate the pyrene and the free acid was obtained upon acidification of the extracted aqueous phase.

A series of cryoscopic molecular weight determinations in benzene was made on the initial ozonation products of a number of runs. Acceptable agreement was found between the composition of the binary mixture calculated from active oxygen determinations expressed as pyrene ozonide and that calculated in the same manner from molecular weight determinations. In no instance was there any indication of the presence of compounds of molecular weight higher than that of the monoozonide.

Examination by infrared spectroscopy of the precipitates obtained in a series of some 20 runs in which pyrene was treated with ozone in aqueous *t*-butyl alcohol of different concentrations showed the absence of any band in the 5–6-μ (carbonyl) region and the presence of strong bands at 9.2, 9.4, 9.6, 10.2, 10.5, 12.9, 13.8, and 14.8 μ together with all the bands of the pyrene reference curve.[11,12] In this connection it may be noted that the relative intensities of the band at 13.8 μ and the adjacent pyrene band at 14.05 μ served as useful indications of the composition of the mixtures in hand. When the two bands were of about equal height, the crude product was found to contain about 50% pyrene and 50% ozonide calculated from active oxygen determinations. The relative intensities of the two bands in other compositions were in proportion. When the pure ozonide was finally prepared the pyrene band at 14.05 μ was very small and barely discernible or absent.

Additional evidence that the authors were indeed dealing with an ozonide of pyrene was found in the superimpossibility of infrared absorption curves of products of similar active oxygen contents prepared in inert solvents such as alcohol-free chloroform or carbon tetrachloride, on curves of products prepared in anhydrous *t*-butyl alcohol or methyl alcohol, or mixtures of these latter with water. The formation of ozonide intermediates would be expected only in the inert solvents according to the Criegee mechanism.[8]

Preparation of the monomeric monoozonide in relatively pure form was attended by considerable difficulty. The compound is sensitive to heat and decomposes and/or rearranges slowly at room temperatures. Samples stored at freezer temperatures acquire a steadily deepening orange or orange-red color in a period of several weeks. The change is more pronounced as the purity is increased to the extent that with mixtures of pyrene containing more than 60% ozonide it is advisable to run infrared spectra as Nujol mulls rather than as potassium bromide disks. The ozonide breaks down under the pressures used to prepare the disks. A whole series of absorbants was tried without success in column chromatography. Separation of the pyrene with trace amounts of other colored materials was effected readily but the active oxygen of the colorless fraction was invariably improved only marginally or actually decreased as a result of rearrangement to 4-formyl-5-phenanthrenecarboxylic acid. The purest product was prepared by treating pyrene with 2.5 molar equiv of ozone using as solvent a mixture of *t*-butyl alcohol, water, and 30% hydrogen peroxide.

Characterization of the compound containing the active oxygen as a monomeric monozonide of pyrene was based essentially on elemental analyses, molecular weight determinations, and on infrared spectroscopy.

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[7] C. Danheux, L. Hanoteau, R. H. Martin, and G. Van Binst, *Bull. Soc. Chim. Belg.*, **72**, 289 (1963).

[8] P. S. Bailey, *Chem. Rev.*, **58**, (1958), contains a discussion of the Criegee mechanism.

[9] M. G. Sturrock, E. L. Cline, and K. R. Robinson, *J. Org. Chem.*, **28**, 2340 (1963).

[10] M. G. Sturrock, E. L. Cline, and K. R. Robinson, U. S. Patent 2,898,350 (August 4, 1959).

[11] R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955).

[12] D. Garvin and C. Schubert, *J. Phys. Chem.*, **60**, 807 (1956).

As corroborative evidence, the presence of the expected 4,5-phenanthrenedicarboxaldehyde in the products of reduction of the ozonide was established. Yields of the dialdehyde were low and elemental analyses corresponded more closely to the monohydrate although melting points were close to that reported by Criegee[13] for the free dialdehyde. Criegee prepared 4-5-phenanthrenedicarboxaldehyde by oxidation of *trans*-pyrenediol with lead tetracetate. Criegee's findings that the dialdehyde cannot be recrystallized were confirmed. Indeed in our hands the compound was found to be so unstable that it could not be preserved for any length of time. Melting points could not be reproduced and on exposure to air the white crystals turned red. Its identity, however, was established by conversion back to pyrene by treatment with hydrazine hydrate.[14] Attempts to isolate the dialdehyde in high yield were finally abandoned and the entire reduction product was quickly treated with hydrazine. Pyrene was recovered in good yield. In passing it is interesting to note that Fieser's attempts[2] to isolate the dialdehyde by the catalytic hydrogenation of a pyrene ozonide prepared in ethyl acetate yielded only the aldehyde–acid.

A definite melting point cannot be reported for the monoozonide because it decomposes on heating and the rate of decomposition is a function of the rate of heating. Observed in a differential scanning calorimeter the decomposition was manifest by an extremely large exotherm which completely obscured the relatively small heat of fusion.

The ozonide is stable to moderate shock and in this respect it is quite safe to handle. It should be noted, however, that it can be extremely irritating to the face, particularly to the nose and lips. It is bulky and light when dry and continued exposure to its dust should be avoided.

The unlimited applicability of the Criegee zwitterion mechanism to sterically hindered alkenes has been questioned recently.[15-17] No direct evidence has been adduced here to show that similar limitations exist in the sterically hindered arene series such as, for example, that the product could not have originated in the zwitterion. On the other hand, the usual direct evidence that the zwitterion is an intermediate in the reaction is similarly absent. If the zwitterion were formed and for steric reasons could not react with the alcohol, it would be expected to follow the Criegee predictions and react with itself to form, at least, a dimeric ozonide. Further, it has been demonstrated[9] that water acts as a participating solvent when phenanthrene is ozonized in mixtures of aliphatic alcohols and water. If the zwitterion were formed, it might have been expected to react with water to form a dihydroxy peroxide in a manner analogous to the phenanthrene reaction. None of these speculations is supported by experimental evidence. It is certain, however, that insofar as the Criegee zwitterion mechanism is concerned, the reaction of ozone with pyrene to form 4-formyl-5-phenanthrenecarboxylic acid must be regarded as anomalous in that an ozonide has been identified as an intermediate product in solvents which behave and are recognized as "participating" solvents in similar reactions with homologically related arenes.

Experimental Section

The equipment and procedures used were similar to those previously described[9] except that a Welsbach T-408 ozone generator replaced the T-23 model. The pyrene was Aldrich "puriss" grade (mp 147–154°)[18] ground to acceptance by a 100 mesh sieve. It was shown that purification through picrate formation (giving pyrene mp 153–154°) offered no advantage. A similar observation had been made in the preparation of 4-formyl-5-phenanthrenecarboxylic acid in dimethylformamide.[5] All other chemicals employed were reagent grade.

The Monomeric Monoozonide of Pyrene (II).—A 10-g sample of pyrene (I) was suspended in a solution composed of 140 ml of *t*-butyl alcohol, 37 ml of water, and 33 ml of hydrogen peroxide (30%) and treated with a stream of ozonized oxygen containing 1.73 g of ozone/ft^3 at a rate of 0.006 ft^3/min. Under these conditions 98% of the ozone being introduced was absorbed by the reaction mixture. After treatment for 7 hr in this way, the ozone absorption decreased sharply to 90% and finally to 80% during the final hour. A total of 5.4 g of ozone was introduced of which 5.1 g were absorbed. The solid product was separated by suction filtration and washed on the filter with 70 ml of 50% (by volume) aqueous *t*-butyl alcohol. The yield was 2.9 g of off-white, finely divided powder after air drying overnight. Lead tetraacetate test for hydroperoxide[19] was negative.

Anal.[20] Calcd for $C_{16}H_{10}O_3$: C, 76.80; H, 4.02; O, 19.18; active oxygen, 6.07; mol wt, 250.24. Found:[21] C, 76.88; H, 4.15; O, 18.54; active oxygen, 5.50; mol wt, 252.0 (270).

4-Formyl-5-phenanthrenecarboxylic Acid (V).—Compound II (1 g) was dissolved in 25 ml of hot sodium hydroxide solution, cooled, and acidified with dilute hydrochloric acid. The white precipitate was removed by filtration, washed, and dried under vacuum at 90°. There was recovered 0.8 g[22] of minute white crystals, mp 277–278°. The literature gives the following melting points for compound V: 276°;[1] 279–280°;[2] 272–276°;[5] with sample prepared as in ref 5, mmp 275–276°.

4-5-Phenanthrenedicarboxaldehyde (VI).—Compound II (1 g) was added to a mixture of 5 ml of glacial acetic acid, 5 g of potassium iodide, and 75 ml of absolute methyl alcohol previously cooled to −20°. A small piece of Dry Ice was added, the flask was loosely stopped, and the contents were agitated by a magnetic stirrer for 45 min at room temperature. The white suspension turned yellow and then deep amber. The liberated iodine was titrated with 0.1 *N* sodium thiosulfate using starch as an outside indicator; 70 ml were required. The solution was then diluted to 500 ml. The attractive appearance of the white precipitate so formed was misleading. It proved to be a sticky substance, extremely difficult to manipulate tending to congeal into an amber glass. No solvent was found from which the material could be recrystallized satisfactorily.[13] Selected white needles separated by means of a spatula melted at 169–171° (Criegee[13] reported 170–171°) when freshly prepared but the melting point could not be duplicated after several hours standing. On exposure to the air at room temperature for several days the sample turned to a deep magenta color. The elemental analysis conformed more closely to the monohydrate than to the free aldehyde.

Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.0; H, 4.3; O, 13.7. Calcd for $C_{16}H_{10}O_2 \cdot H_2O$: C, 76.2; H, 4.8; O, 19.0. Found: C, 75.1; H, 5.3; O, 19.6.

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[13] R. Criegee, E. Hoger, G. Huber, P. Kruck, F. Marktscheffel, and H. Shellenberger, *Ann.*, **599**, 81 (1956).

[14] R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1375 (1958).

[15] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966).

[16] P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966).

[17] F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

[18] All melting points determined with a Nalge precise melting point apparatus with standardized thermometer.

[19] R. Criegee, *Fortschr. Chem. Fortsch.*, **1**, 536 (1950).

[20] The analyses for the elements and the molecular weight determinations shown in parentheses were performed by a commercial testing laboratory. The other molecular weight was determined in the Texas Woman's University laboratory by freezing point depression in benzene. It is believed that the sample sent away deteriorated in transit under summer temperatures.

[21] Active oxygen determinations were by the method recommended by G. Lohaus [*Ann.*, **583**, 6 (1953)] and endorsed by S. Fliszar, D. Gravel, and E. Cavalieri, *Can. J. Chem.*, **44**, 67 (1966).

[22] The aldehyde–acid is significantly soluble in water and losses sustained in washing it free from chloride ion are unavoidable.

Conversion of VI into I.—Compound II (1 g) was reduced with KI and acetic acid as discussed above and after dilution and separation of the reduced product, the latter was dissolved in 60 ml of glacial acetic acid followed by 10 ml of hydrazine hydrate added dropwise. The solution was boiled for 30 min, cooled, and diluted to 500 ml with water. The light yellow precipitate weighed 0.8 g and melted at 150–150.5°. Mixture melting point with authentic pyrene 150–151°. This reaction identifies VI as crude 4-5-phenanthrenedicarboxaldehyde.

Differential Thermal Analysis of II.—A thermograph of II was obtained in a Perkin Elmer Model DSC 1-B differential scanning calorimeter. The rate of heating was 20°/min. The curve showed increasing evolution of heat from 390 to 415°K at which point it rose rapidly with an extremely large exotherm manifest at 450°K and which completely obscured the heat of fusion. No further change of state was evident up to 525°K.

Registry No.—I, 129-00-0; II, 16203-57-9; VI, 16162-34-8.

Acknowledgment.—The authors are grateful to the Robert A. Welch Foundation (Grant M-216) for financial assistance in the prosecution of this work and to the National Science Foundation Research Participation for College Teachers Program (Grant G-Z-613) which provided for Miss Duncan's support during the summer of 1967.

1,2-Dimethyl-5,7-di-*t*-butylspiro[2.5]octa-1,4,7-trien-6-one. Synthesis and Chemistry

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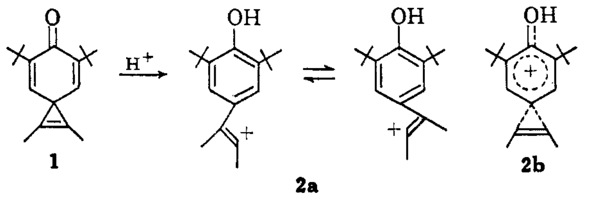
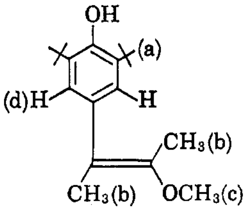
We should like to report the synthesis of 1,2-dimethyl-5,7-di-*t*-butylspiro[2.5]octa-1,4,7-trien-6-one (**1**), a compound containing both a cyclopropene[2] ring and a cyclohexadienone[2] moiety in a spiro configuration. This unusual system was expected to be highly reactive not only because of its high degree of strain, but also because of the possibility that aromatization of the cyclohexadienone portion of the molecule might supply strong driving force for reaction. The system is intriguing, also, in that protonation of the oxygen might lead to a vinyl carbonium ion (**2a**) which could conceivably be bridged, as shown in **2b**.



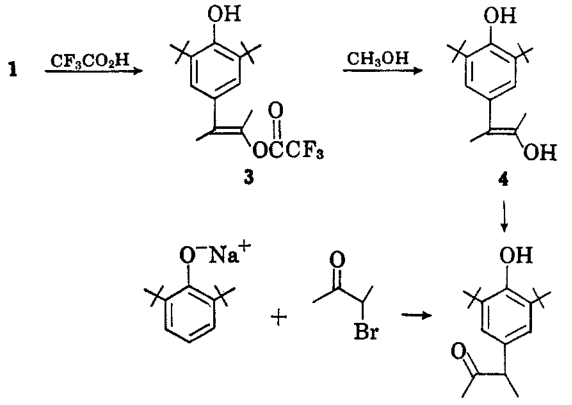
Trienone **1** was prepared by the photolysis of 3,5-di-*t*-butylbenzene 1,4-diazooxide[3] in dimethylacetylene, a synthetic approach similar to a recently reported spiro-[2.5]octa-4,7-dien-6-one preparation.[3] The nmr spectrum of the colorless crystalline spiro compound consists of three singlets at τ 8.73, 7.85, and 3.70 with relative areas 19:5.8:2.0. The infrared spectrum of trienone **1** shows strong bands at 1620, 1605, 1590, and 1912 cm^{-1}, the latter being assigned to the cyclopropene double bond.



(a) τ 8.56
(b) τ 8.21 (center of quartet, $|J| = 1.5 \pm 0.1$ Hz)
τ 8.06 (center of quartet, $|J| = 1.5 \pm 0.1$ Hz)
(c) τ 6.40
(d) τ 3.05

Figure 1.—Analysis of the nmr spectrum of the methanol adduct.

Incremental addition of trifluoroacetic acid to chloroform-*d* solutions of **1** causes immediate appearance of resonances at τ 8.52, 8.05, and 2.96. Peaks arising from remaining trienone are distinct and are observable until a molar equivalent of trifluoroacetic acid has been added, at which point, judging from the nmr spectrum, **1** is completely converted into a 1:1 adduct, 1-trifluoroacetoxy-1,2-dimethyl-2-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)ethylene (**3**).[4,5] After purification by chromatography upon silica gel, ester **3** has spectra and an elemental composition consistent with the assigned structure (see Experimental Section). Trifluoroacetate **3** undergoes methanolysis[6] to give a crystalline ketone **5**, identified as 3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)-butanone-2. Ketone **5** was synthesized independently by alkylation of sodium 2,6-di-*t*-butylphenoxide with 3-bromobutanone-2.



Trienone **1** reacts slowly with neutral methanol to yield 1,2-dimethyl-1-(3′,5′-di-*t*-butyl-4-hydroxyphenyl)-2-methoxyethylene (**6**).[5] This compound is formed much more rapidly if a trace of acid is present. Although **6** has not been isolated in sufficient purity to allow satisfactory elemental analysis, its identification, based on its nmr spectrum (see Figure 1), is believed to be

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[1] National Science Foundation Predoctoral Fellow, 1966–1968.

[2] For recent reviews of the chemistry of cyclopropenes and cyclohexadienones, see "Advances in Alicyclic Chemistry," H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, pp 53–256.

[3] G. F. Koser and W. H. Pirkle, *J. Org. Chem.*, **32**, 1992 (1967).

[4] Although the stereochemistry of this adduct is uncertain, it is thought, through analogy with the methanol adduct **6**,[5] that the two vinyl methyl groups are *trans* to one another as shown in **3**.

[5] On the basis of comparison of the magnitude of the long range coupling between the two vinyl methyls of adduct **6** ($J_{obs} = 1.5 \pm 0.1$ Hz) and those of tiglic acid and methyl tiglate ($J_{trans} = 1.5$ Hz) and with those of angelic acid and methyl angelate ($J_{cis} = 1.2$ Hz) [see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Inc., New York, N. Y., 1965, p 176], the vinyl methyls of **6** are believed to be *trans* to one another. However, this evidence is not compelling and the *trans* assignment should be considered tentative.

[6] The methanolysis of **3** presumably produces enol **4** which then rapidly tautomerizes to ketone **5**. Chromatography of **1** upon silica gel or alumina also causes its conversion into ketone **5**, presumably through hydration to enol **4** which subsequently tautomerizes.