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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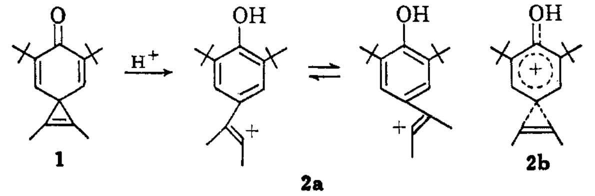
We should like to report the synthesis of 1,2-dimethyl-5,7-di-*t*-butylspiro[2.5]octa-1,4,7-trien-6-one (**1**), a compound containing both a cyclopropene[2] ring and a cyclohexadienone[2] moiety in a spiro configuration. This unusual system was expected to be highly reactive not only because of its 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.

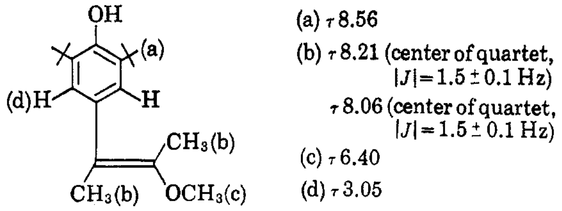


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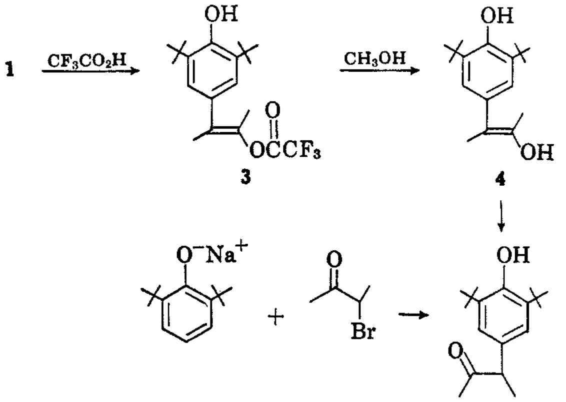
Figure 1.—Analysis of the nmr spectrum of the methanol adduct.

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**.

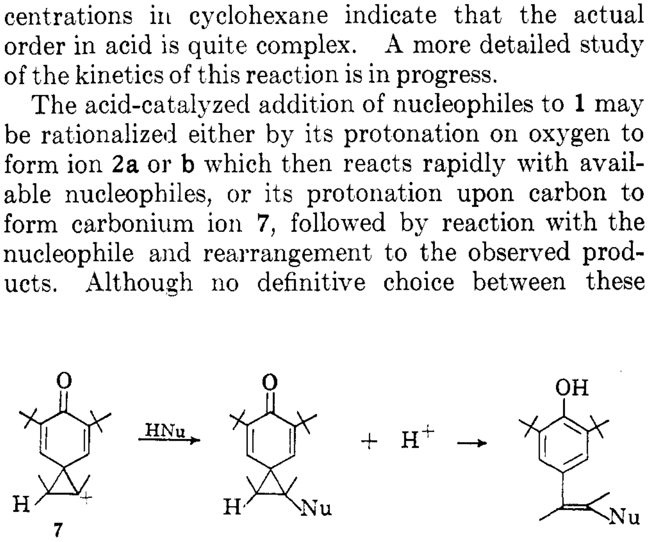
[5] On the basis of comparison of the magnitude of the long range coupling between the two vinyl methyls of adduct **6** (J_{obs} = 1.5 ± 0.1 Hz) and those of tiglic acid and methyl tiglate (J_{trans} = 1.5 Hz) and with those of angelic acid and methyl angelate (J_{cis} = 1.2 Hz) [see J. W. Emsley, J. 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.

secure. Additional support for structure **6** comes from the hydrolysis of the methanol adduct to ketone **5**.

The kinetics of the reaction of spirotrienone **1** with trifluoroacetic acid have been studied using the recently described stopped-flow apparatus in conjunction with a rapid scan ultraviolet spectrometer and auxiliary oscillograph equipment[7] to follow the reaction. After mixing, the time dependence of the trienone absorbance at 280 mμ has been followed oscillographically and rate data has been calculated from the photographically recorded oscilloscope traces. For cyclohexane solutions of spirotrienone 1 (0.73×10^{-4} *M*) and trifluoroacetic acid (2.95×10^{-4} *M*) at 25°, a second-order rate constant of 2.68×10^{3} l./(mol sec) has been calculated. Preliminary results at other acid concentrations in cyclohexane indicate that the actual order in acid is quite complex. A more detailed study of the kinetics of this reaction is in progress.

The acid-catalyzed addition of nucleophiles to **1** may be rationalized either by its protonation on oxygen to form ion **2a** or **b** which then reacts rapidly with available nucleophiles, or its protonation upon carbon to form carbonium ion **7**, followed by reaction with the nucleophile and rearrangement to the observed products. Although no definitive choice between these alternatives can yet be made, the great ease with which cyclohexadienones rearrange upon treatment with acids,[2] and the ready acid-catalyzed solvolysis of spiro[2.5]octa-4,7-dien-6-one,[8] may be considered as analogy for the first of these two alternatives.



7

Experimental Section

1,2-Dimethyl-5,7-di-*t*-butylspiro[2.5]octa-1,4,7-trien-6-one (1) was prepared by the photolysis of 3,5-di-*t*-butylbenzene-1,4-diazooxide in dimethylacetylene,[9] following the procedure recently described by Koser and Pirkle.[3] A nitrogen swept solution of 630 mg (2.54 mmol) of diazooxide in 80 ml of dimethylacetylene was irradiated for 3.5 hr through a filter solution,[3] with a 250-W sunlamp. Removal of solvent, followed by low temperature recrystallization from *n*-hexane, left 415 mg (1.61 mmol, 63%) of spirotrienone **1**. Colorless analytically pure trienone, mp 114–115°, was obtained after several low temperature recrystallizations from either pentane or hexane. The infrared spectrum of the trienone contains bands at 1590, 1605, 1620, and 1912 cm^{-1}. The nmr[10] spectrum in $CDCl_3$ consists of three singlets at τ 8.73, 7.85, and 3.70 of relative area 19:5.8:2.0. In cyclohexane, the trienone exhibits maximum absorption at 284 mμ (ϵ 18,100).

Anal. Calcd for $C_{18}H_{26}O$: C, 83.66; H, 10.14; mol wt, 258. Found: C, 83.34; H, 10.48; mass spectrometrically determined molecular weight, 258.

1-Trifluoroacetoxy-1,2-dimethyl-2-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)ethylene (3).—Trifluoroacetic acid (17 μl, 0.23 mmol), was added to a solution of 60 mg (0.23 mmol) of spirotrienone **1** in 3 ml of chloroform. After about 45 min, the solvent was evaporated, leaving a brown oil which was chromatographed on silica gel using methylene chloride as eluant. The oily trifluoroacetate (45 mg, 0.12 mmol, 53%) thus obtained was molecularly distilled and the distillate was caused to crystallize by cooling to *ca.* −5°. The trifluoroacetate **3**, mp 52–56°, has infrared absorption bands at 1790 cm^{-1} (ester carbonyl) and 3600 cm^{-1} (non-hydrogen-bonded hydroxyl). The pmr spectrum (in trifluoroacetic acid) eshibits singlets at τ 8.51, 8.01, and 2.82 of relative area 0.84:2.9:9.0. In chloroform-*d*, the resonances occur at τ 8.52, 8.05 (multiplet), and 2.96. The fluorine resonance spectrum exhibits a singlet 0.75 ppm downfield from trifluoroacetic acid.

Anal. Calcd for $C_{20}H_{27}O_3F_3$: C, 64.50; H, 7.30; mol wt, 372. Found: C, 64.63; H, 7.59; mol wt, 372 (mass spectrometry).

3-(3′,5′-Di-*t*-butyl-4′-hydroxyphenyl)butanone-2 (5). A. From 1-Trifluoroacetoxy-1,2-dimethyl-2-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)ethylene (3).—A solution of **3** (prepared by dissolving 104 mg (0.40 mmol) of **1** in 1 ml of trifluoroacetic acid) was poured into methanol. After 3 hr, the solvent was evaporated and the crude product was chromatographed (silica gel, ether) to yield 55 mg (0.20 mmol, 50%, based on **1**) of crystalline 3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)butanone-2. Sublimation gave analytically pure ketone: mp 105.5–106°; ir, 1705 and 3625 cm^{-1}; nmr (in chloroform-*d*), τ 8.69, 8.56, 7.95, 6.32 (center of a quartet), 4.83, and 2.99 (relative areas 3.0:20:3.3:1:1:2).

Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.22; H, 10.20; mol wt, 276. Found: C, 78.04; H, 10.48; mol wt, 276 (mass spectrometry).

B. From 2,6-Di-*t*-butylphenol.—To a suspension of 201 mg of sodium hydride (60% dispersion in mineral oil) in *ca.* 1 ml of dry dimethylformamide was added a solution of 1.0 g (4.85 mmol) of 2,6-di-*t*-butylphenol in 6 ml of dimethylformamide. The solution was stirred for 45 min, after which time 1 ml of 3-bromobutanone-2 was added. After being stirred at room temperature overnight, the reaction mixture was poured into water. The precipitated product was collected and chromatographed on silica gel to give 707 mg (2.56 mmol, 53%) of ketone **5**, mp 105.5–106.5°. Spectral data are identical with those described in procedure A.

Anal. Found: C, 78.01; H, 10.20.

C. From 1,2-Dimethyl-1-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)-2-methoxyethylene (6).—A 10% solution of spirotrienone **1** in 1:1 methanol–chloroform-*d* exhibits an nmr spectrum which changes from that of **1** to that of **6** in about 1 hr at 30°. Treatment of this solution with water causes hydrolysis of the enol ether to ketone **5**. Evaporation of the solvent leaves a light tan solid, which, after sublimation, has mp 104–105.5°, and displays spectral characteristics identical with those described in procedure A.

Kinetics.—Spirotrienone **1** was purified by recrystallization from *n*-hexane. Trifluoroacetic acid was purified by distillation. Reagent grade cyclohexane was successively washed with concentrated sulfuric acid, water, 5% potassium carbonate, and water, dried over anhydrous calcium sulfate, and finally distilled. The flow system and ultraviolet spectrometer used for the measurements have been described.[5]

The transmittance at 280 mμ of mixed solutions of trifluoroacetic acid and **1** was recorded by photographing an oscilloscope display of the spectrometry output. Second-order rate constants were obtained from the slope of a second-order rate plot[11] calculated from the observed per cent transmittance data. The rate constants calculated from four runs were $10^{-3}k_2$[l./(mol sec)] = 2.71, 2.66, 2.64, and 2.72.

Registry No.—**1**, 15982-70-4; **3**, 16033-83-3; **5**, 15982-71-5; **6**, 15982-72-6.

Acknowledgment.—The authors wish to thank Dr. S. G. Smith and Mr. J. Billet for extensive assistance and discussion and for the use of their stopped-flow spectrometer system.

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[7] S. G. Smith and J. Billet, *J. Amer. Chem. Soc.*, **90**, 0000 (1968).

[8] R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963).

[9] Columbia Organic Chemicals, Columbia, S. C.

[10] Nmr spectra were determined on a Varian A56/60 A spectrometer. TMS was used as an internal standard.

[11] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, p 17.