were transferred to the glovebox and NMR samples were prepared as described below. ¹H NMR spectra of the authentic ions were run in molten SbCl₃, SbCl₃-10% AlCl₃, and AlCl₃-NaCl-KCl (60:26:14 mol %). The spectra for each ion in the various solvents were identical² and were the same as those of the arenium ions formed in the hydride-abstraction reactions.

¹H NMR. Reactions were studied in situ in 5-mm o.d. NMR tubes (1-mm wall) filled with 0.8-1.0 g of SbCl₃, 0.050-0.075 g of AlCl₃, and 0.020 to 0.030 g of the hydroarene. A few runs were made in 10-mm o.d. NMR tubes (1-mm wall) with 4 g of SbCl₃, 0.25 g of AlCl₃, and 0.100 g of hydroarene. The tubes were filled in the glovebox and subsequently sealed under argon on a vacuum line. The ¹H NMR experiments were done at temperatures from 100-130 °C on either a Varian XL-100 spectrometer with a ¹⁹F external lock or a Varian FT-80 spectrometer with a ²H external lock. The chemical shifts were referenced internally to $(CH_3)_4N^4$ (δ 3.12) which was itself referenced to (CH₃)₄Si.

Separation and Identification. Products were identified from larger scale reactions (up to 0.25 g of the hydroarene in up to 9 g of SbCl₃-AlCl₃) performed in Schlenk glassware under argon. In a number of cases the reaction products were also separated from the in situ NMR experiments and found to be the same as those identified from the Schlenk-ware reactions.

The reaction mixture was hydrolyzed in 6 M HCl and the organics were dissolved in CH₂Cl₂ under argon. The mixture was filtered and the remaining solid was thoroughly washed with 6 M HCl (to remove AlCl₃ and unreacted SbCl₃) and CH₂Cl₂. The solid residue was oxidized with a 3:1 HCl-HNO₃ (v/v) mixture, and the resulting solution analyzed for antimony with an Instrumentation Laboratory atomic absorption spectrometer. The CH_2Cl_2 layer was separated from a CH_2Cl_2/HCl workup, and the solvent removed on a rotary evaporator.

The organic products were analyzed with a Bendix gas chromatograph with a flame-ionization detector and a column containing Dexsil 400 on 80/100-mesh Chromosorb G-HP. GC-MS were obtained with a Hewlett-Packard 5985 GC-mass spectrometer using a 30 m \times 0.25 mm i.d. glass capillary column coated with polyimide liquid phase. Only under these high-resolution conditions was the previously discussed mixture of isomers of THA and of OHA resolved. A Waters liquid chromatograph with a Whatman Partisil M9-ODS-1 reverse-phase column and CH₃OH-H₂O and CH₃OH-CH₂Cl₂ solvent system was used principally to confirm the absence of appreciable amounts of condensed products.

Determination of Product Yield. DHA Reaction. The amount of arenium ion formed was calculated from integration of the ¹H NMR spectrum. For example, the spectrum of a sample starting with 0.0201 g (0.112 mmol) of DHA and 0.0047 g (0.043 mmol) of the internal standard, (CH₃)₄NCl, dissolved in 1.075 g of SbCl₃-10 mol % AlCl₃ was integrated after 30 min at 100 °C. An integral ratio of 3.1 was obtained for the 12 equivalent protons of $(CH_3)_4NCl$ relative to the 2 equivalent protons on the sp³hybridized carbon at δ 4.9 for 1. The yield of 1 is then 0.083 mmol or 74% (estimated error $\pm 5\%$) based on the original arene. Results of three additional repetitive runs fell within the range of 75-77% yield.

A larger scale DHA reaction was performed at 100 °C for 30 min with 0.250 g (1.39 mmol) of DHA dissolved in 7.90 g of SbCl₃-10% AlCl₃. After quench and separation procedures, the organic products were quantitatively analyzed by GC using 9,10-dimethylanthracene as an internal standard. The yield of anthracene formed from the hydrolysis of the anthracenium ion, 1, was found to be 0.185 g (1.04 mmol) or 75% (estimated error $\pm 4\%$). This value is consistent with the yields of 1 obtained from in situ ¹H NMR (vide supra). The yield of hydroanthracenes, primarily THA and OHA, was also determined and found to be 0.050-0.062 g or 20-25%, thus giving approximate mass balance on the organics within experimental error. Analysis for Sb by AAS gave 0.041 ± 0.001 g (0.34 ± 0.01 mmol) of Sb which is in agreement with the stoichiometric value (0.35 \pm 0.02 mmol of Sb) calculated on the basis of the yield of 1 (74 \pm 5%) from ¹H NMR (i.e., 1/3 mol of Sb for every 1 mol of arenium ion).

DHN Reaction. The yield of arenium ion, 2, was also de-termined by ¹H NMR from a reaction run at 100 °C for 30 min with 0.0267 g (0.116 mmol) of DHN and 0.0024 g (0.022 mmol) of (CH₃)₄NCl in 0.89 g of SbCl₃-10% AlCl₃. An integral ratio of 1.6 was obtained for the 12 protons of $(CH_3)_4NCl$ relative to the 2 protons on the sp³-hybridized carbon at δ 4.9 for 2. Thus, the yield of 2 is 0.082 mmol or 71% (estimated error $\pm 5\%$) on the basis of the original DHN.

The other product yields were determined from a larger scale reaction performed in a 10-mm NMR tube at 100 °C for 30 min with 0.099 g (0.43 mmol) of DHN dissolved in 4.019 g of SbCl₃-10% AlCl₃. The yield of 2 based on integration of the ¹H NMR spectrum was $70 \pm 5\%$. After quench and separation procedures, analysis for Sb by AAS gave 11.5 ± 0.5 mg (0.094 \pm 0.004 mmol) of Sb. This value is consistent with the stoichiometric value $(0.100 \pm 0.007 \text{ mmol of Sb})$ calculated on the basis of the yield of 2 from ¹H NMR ($^{1}/_{3}$ mol of Sb for every 1 mol of arenium ion). The remaining $30 \oplus 5\%$ of the organics were not quantitatively analyzed, but GC-MS showed them to be primarily two tetrahydronaphthacenes (mol wt 232). As described in the text, the formation of all tetrahydroarene would stoichiometrically require a 67% yield of arenium ion and, thus, would be consistent with the amount of 2 (70 \pm 5%) found in this reaction.

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Registry No. 1, 46300-36-1; 2, 75716-22-2; DHA, 613-31-0; OHA, 1079-71-6; DHN, 959-02-4; THA, 2141-42-6; anthracene, 120-12-7.

Unprecedented Rearrangement Products from Ultraviolet Irradiation of a Model 2,5-Cyclohexadienone¹

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In the course of study of the photochemisty of cyclohexadienone 1b in acidic methanol, we have observed some new and unexpected photochemical rearrangements, which provide yet additional reaction pathways in a system well-known for its diversity of behavior on electronic excitation.² The original goal of this study was to generate products analogous to 2a, which is formed from the parent dienone 1a on excitation in acidic methanol.³ Such products preserve the stereochemistry of the zwitterion 3,



well established as an intermediate in the photochemistry of dienone 1.² While only one stereoisomer of 2a is gen-

⁽¹⁾ Photochemistry of Ketones in Solution. 61. Part 60: Schuster,

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(3) Schuster, D. I.; Abraitys, V. Y. Chem. Commun. 1969, 419.</sup>

Table I. UV, IR, ¹H NMR and Mass Spectral Data of Photoproducts A, B, and C and 3,4-Dimethylanisole^a

				¹ H NMR (CDCl ₃ or CCl ₄),
compd	UV (hexane), λ_{\max} , nm (ϵ)	IR (CCl ₄), cm^{-1}	mass spectrum, <i>m/e</i>	δ
A (=4)	205 (18 000), 225 (6300), 282 (2000), 284 (1960), 291 (2000)	2990, 2940, 2925, 2895, 2820, 1612, 1580, 1500, 1465, 1420, 1325, 1305, 1290, 1260, 1255, 1195, 1165, 1050, 960, 870, 710	253, 252, 217, 182, 181, 147, 146, 145, 139, 137, 136, 135 (100%), 131, 121, 115, 105, 104, 103, 102, 92, 91, 77	$\begin{array}{c} 2.35 \ ({\rm s}, 3 \ {\rm H}, {\rm CH}_{3}), 3.74 \\ ({\rm s}, 3 \ {\rm H}, {\rm OCH}_{3}), 3.91 \ ({\rm s}, \\ 2 \ {\rm H}, {\rm CH}_{2}), 6.69 \ ({\rm dd}, 1 \\ {\rm H}, J = 2.5, 7.5 \ {\rm Hz}, {\rm H_{c}}), \\ 6.95 \ ({\rm br} \ {\rm s}, 1 \ {\rm H}, {\rm H_{a}}), \\ 7.05 \ ({\rm d}, 1 \ {\rm H}, J = 7.5, \\ {\rm H_{b}}) \end{array}$
CH ₃ CH ₃	218.5 (6810), 277 (1750), 283.5 (1590)	$\begin{array}{c} 3000,\ 2940,\ 2830,\ 1605,\\ 1575,\ 1500,\ 1460,\\ 1450,\ 1300,\ 1280,\\ 1255,\ 1205,\ 1135,\\ 1120,\ 1050,\ 860,\ 840,\\ 805,\ 795,\ 715,\ 710 \end{array}$		2.19 (s, 3 H, CH ₃), 2.22 (s, 3 H, CH ₃), 3.74 (s, 3 H, OCH ₃), 6.63 (dd, 1 H, $J = 2.5$, 7.5 Hz, H _c), 6.71 (br s, 1 H, H _a), 7.03 (d, 1 H, $J =$ 7.5, H _b)
B (=5(?))	208 (3908), 247 (3615), 302 (23), 308 (33), 321 (45), 335 (33), 351 (12)	2930, 2910, 1735, 1725, 1635, 1255, 1140, 1075, 1065, 910, 870, 705	$\begin{array}{c} 235,234\;(100\%),219,\\ 199,172,171,167,\\ 165,163,157,156,\\ 155,151,139,136,\\ 135,127,126,121,\\ 115,94,93,91 \end{array}$	1.37 (s, 3 H, α -CH ₃), 2.00 (s, 3 H, vinylic CH ₃), 2.51 (dd, 1 H, $J = 3, 18$ Hz, H $_{\alpha}$), 2.86 (dd, 1 H, $J = 3, 18$ Hz, H $_{\alpha}$), 3.76 (s, 3 H, OCH ₃), 6.23 (t, 1 H, $J = 3$, vinyl H)
C (=6)	267 (8), 277.5 (14), 286 (19), 295 (20), 306.5 (17), 317.5 (6), end absorption below 310	2960, 2920, 2860, 2820, 1750, 1455, 1400, 1370, 1345, 1265, 1250, 1200, 1175, 1150, 1120, 1110, 1080, 990, 980, 870, 835	236, 235, 231, 200, 199, 171, 157, 141, 139, 137, 115, 113, 99, 91, 79, 77, 76, 75 (100%), 67	1.21 (s, 3 H, α -CH ₃), 1.51 (s, 3 H, β -CH ₃), 1.80 (dd, 1 H, $J = 5$, 1.5 Hz, H ₄), 2.34 (d, 1 H, $J =$ 18, H ₄ endo), 2.72 (dd, 1 H, $J = 5$, 18 Hz, H ₄ exo), 3.37 (s, 3 H, OCH ₃), 3.52 (s, 3 H, OCH ₃), 3.87 (s, 1 H, H acetal)

^a Data for 3,4-dimethylanisole from Sadtler Standard Spectra, Sadtler Laboratories, Inc.

erated from 1a, the photochemical behavior of $1b^4$ suggested that both stereoisomers of 2b should be formed (i.e., with CCl_3 in the endo as well as exo orientation at C_6) in yields reflecting the ratio of the intermediate epimeric zwitterions, a ratio that is of considerable interest to us.⁵

The course of events on excitation of 1b in acidic methanol proved otherwise. No products of type 2 could be either detected spectroscopically or isolated by column chromatography. When the irradiation of 1b was carried out for 35 min at 40-50 °C, a major product A and a minor product B were isolated in yields of 63% and 3%, respectively. When the irradiation was carried out at -20°C, the major product was a new material C, formed in 56% yield. Additional minor products were formed according to GLC analysis and have not yet been isolated. The NMR spectrum of a sample of 1b in MeOH/HCl, identical in concentration with the solutions used in the above irradiations, was not altered after the solution had been heated at reflux in the dark for 24 h, indicating that formation of A, B, and C does indeed reflect photochemical rather than thermal transformations of 1b in this medium (vide infra). The identification of A, B, and C proved to be a considerable challenge, in part due to the fact that these products arise by rearrangement pathways not encountered previously in cyclohexadienone photochemistry. The interested reader is invited to attempt to work out the product structures from the data to be presented, as well as reaction mechanisms for these novel transformations. Our own tentative mechanistic suggestions are presented at the conclusion of the paper.

Compound A is a white crystalline solid, mp 38-40 °C. Its mass spectrum shows a molecular ion at m/e 252

containing three chlorines, which corresponds to a molecular formula of $C_{10}H_{11}Cl_3O$, confirmed by elemental analysis. This composition corresponds to the addition of the elements of CH₂ to dienone 1b, presumably the result of the addition of CH_3OH and the loss of H_2O . The base peak in the mass spectrum at m/e 135 results from loss of a CCl₃ group. IR, UV, and mass spectra (Table I) all indicate that A is an aromatic compound containing no carbonyl group, while IR bands at 2820 and 1050 cm⁻¹ suggest the presence of a methoxy group. The ¹H NMR spectrum (Table I) shows singlets for aromatic methyl and methoxy groups and a strongly deshielded methylene group, in addition to a multiplet for three aromatic protons whose pattern is consistent with 1.2.4-substitution on a benzene ring. The aromatic proton resonances in A are strikingly similar to those in 3,4-dimethylanisole (Table I), suggesting that compound A has structure X or Y.



A decision between X and Y was reached as follows. Irradiation of the methylene resonance led to a sharpening of the resonances of H_c and H_a , while irradiation of the methyl resonance appeared to sharpen the H_b resonance. While not entirely unambiguous, these data favor structure X over Y. The completely decoupled ¹³C NMR spectrum shows ten resonances in positions consistent with X or Y and similar in many respects to the spectrum of 3,4-dimethylanisole (Table II). The spectrum with gated decoupling (Table II) was more informative. It is well es-

⁽⁴⁾ Schuster, D. I.; Prabhu, K. V. J. Am. Chem. Soc. 1974, 96, 3511.
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tablished that ¹³C⁻¹H coupling constants are larger for CCCH coupling than for CCH coupling in aromatic systems.⁶ Thus, the carbons at C₂ and C₆ are split ($J \simeq 6.5$ Hz) by the protons on C₆ and C₂, respectively, but C₂ also shows long range coupling ($J \simeq 6.5$ Hz) to the methylene group. Likewise, C₅ clearly shows long range coupling to the methyl group, while the ring carbon to which the methyl is directly attached is split by two ring protons which must be located meta to it. These data strongly support a structure 4 (=X) for product A, in which the methyl is at C₄ and the CH₂CCl₃ group is at C₃, over the alternative Y. Structure 4 for photoproduct A was unequivocally established by an independent synthesis outlined in Chart I, based on the thermal rearrangements of dienone 1b discovered some years ago by Newman and co-workers.⁷

The data for product B are incomplete because of the small quantities of pure compound, mp 56-58 °C, which could be isolated. Most important are a carbonyl band at 1735 cm⁻¹ suggestive of a nonconjugated cyclopentanone and UV absorption at 247 nm (ϵ 3600) suggestive of a conjugated diene. Other IR bands support the presence of olefinic and ether moieties. The molecular ion at m/e234 contains two chlorines, consistent with the composition $C_{10}H_{12}Cl_2O$, resulting from addition of CH_3OH to 1 and loss of the elements of HCl. The ¹H NMR spectrum (Table I) shows two methyls, one probably on a C=C bond, two geminally oriented protons, probably α to the carbonyl, and a single vinyl proton coupled to the geminal protons (J = 3 Hz). Exchange with D₂O most strongly reduced the signals for the geminal protons. These data allow a tentative assignment to product B of structure 5. This will be subject to confirmation when ¹³C data become available.



The greatest problems were experienced with the assignment of structure to product C, a white crystalline solid, mp 93–95 °C. Two independent elemental analyses were consistent with a molecular formula of $C_{11}H_{16}Cl_2O_3$,



⁽⁶⁾ Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 10, p 358.

⁽⁷⁾ Newman, M. S.; Bayerlein, F. J. Org. Chem. 1963, 28, 2804. See also: Newman, M. S.; Wood, L. L., Jr. J. Am. Chem. Soc. 1959, 81, 6450; Newman, M. S.; Bajzer, W. X. J. Org. Chem. 1972, 35, 270.



Figure 1. ORTEP plot of X-ray crystallographic structure for photoproduct C (6).

which would be the result of the addition of two molecules of CH_3OH and the loss of HCl. The mass spectrum (Table I) showed no peak for the molecular ion on electron impact and only a faint peak with chemical ionization. Dimeric structures were eliminated by crude molecular-weight determinations. Peaks are seen at m/e 235, 231, 206, and 200 which correspond to the loss from the putative molecular ion (266) of the elements of OCH_3 , Cl, Cl₂, and $OCH_3 + Cl$, respectively. The base peak at m/e 75 corresponds to $C_3H_7O_2$ (based on the M + 1 intensity and the absence of Cl). The carbonyl band in the IR at 1750 cm^{-1} indicates a saturated ketone in a five-membered or similarly strained ring, and the UV spectrum indicates no conjugation in the molecule. The ¹H NMR spectrum (Table I) shows the presence of two methyls, two methoxy groups, two protons at δ 2.30 and 2.72 which are apparently geminally related (J = 18 Hz) and both coupled to a third proton at δ 1.82, and a proton downfield at δ 3.88. The completely decoupled and SFORD ¹³C spectra of C (Table II) accounted for only 10 carbons, which was a source of confusion for some time, since only a single upfield methyl resonance could be seen at 15.0 ppm. This was subsequently resolved (barely) into two methyl resonances in the spectrum with gated decoupling and more effectively in the presence of the lanthanide shift reagent $Eu(fod)_3$. These ¹³C spectra indicated the presence of a carbonyl carbon, two methoxy groups, two methyl groups, three upfield methine groups (which were completely resolved only in gated spectra), and a downfield methine at 112.0 ppm.

Various structures for compound C could be generated from these data and from considerations of likely reaction mechanisms, but none were consistent with all the data. In particular, the nature of the strongly deshielded proton at δ 3.88, the methine carbon at 112 ppm, and the two quaternary carbons (as well as the carbon attached to the two chlorines) eluded interpretation. The presence of diasterotopic methoxy groups seemed likely, but in all test structures these were placed on a bicyclic ring system by analogy with previous work. Attempts to assign the structure using the McConnnell–Robertson relation⁸ based upon lanthanide-induced shifts in ¹H and ¹³C NMR spectra also failed.

A single crystal of photoproduct C was prepared by rapid crystallization from hexane and submitted for X-ray crystallographic study. The crystals were monoclinic, space



group $P2_1/n$, and were exposed to Ni-filtered Cu K α radiation. Significant decomposition of the crystal was observed during preliminary study, which could be inhibited when crystals were mounted in thin-walled capillaries. The structure was solved by using the direct phasing program MULTAN,⁹ which gave a final *R* factor of 10.8%. An ORTEP figure is displayed in Figure 1, corresponding to structure 6 for photoproduct C. It is obvious that a profound structural reorganization has occurred in formation of 6, in which the formerly exocyclic CCl₃ group has been incorporated into the ring system, while (presumably) the carbon with the acetal functionality is originally C₂ of the cyclohexadienone ring.



A tentative mechanism for formation of photoproduct A (4) is shown in Scheme I. Although control experiments demonstrated that this rearrangement requires photochemical initiation since no reaction of 1b occurred upon extended heating at reflux in MeOH/HCl, the transformation of 1b to 4 is strikingly similar to the rearrangements of 1a, 1b, and analogous dienones observed⁷ on reaction with PCl₅ or acetic anhydride containing small amounts of a strong acid, examples of which are shown below. There are many similarities between the mechanism in Scheme I and the mechanism proposed many years ago by Newman et al.⁷ for these thermal rearrangements. The photochemical rearrangement is most likely initiated upon protonation of the intermediate zwitterion 3b to give cation 7a which is converted under the reaction conditions to the methoxyallyl cation 7b (conversion to the enol ether functionality could conceivably occur at a later stage of the reaction). Rather than being captured nucleophilically by methanol as is $3a^2$, 7b undergoes endocyclic ring opening to give cation 8 (stabilized by the methyl at C_3)

⁽⁸⁾ McConnell, H. M.; Robertson, R. E. J. Chem. Phys. 1958, 29, 1361. Willcott, M. R., III; Lenkinski, R. E.; Davis, R. E. J. Am. Chem. Soc. 1972, 94, 1742 and references cited therin.

⁽⁹⁾ Germain, G.; Main, P; Woolfson, M. M. Acta Crystallogr., Sect. A 1971, 27, 368.



which gives triene 9 upon loss of a proton. The final product 4 results from a [1,3] signatropic shift of the CCl_3 group. Formation of trienes analogous to 9 and subsequent shifts of CCl₃ and CHCl₃ groups was proposed by Newman et al.⁷ in the case of the thermal acid-catalyzed dienone rearrangements. By analogy, we suggest that the [1,3] shift of the CCl₃ group leading to 4 is probably a thermal process, although a photoinitiated [1,3] sigmatropic rearrangement is theoretically possible.¹⁰

Our proposed mechanism for formation of photoproduct B is shown in Scheme II, involving ring opening of an initial adduct 10 (the enol tautomer of the originally sought ketone 2b), followed by a 1,5 methyl shift which has ample precedent.9,11

We have been hard put to come up with a totally convincing mechanism for formation of photoproduct C (6). Our best present suggestion is outlined in Scheme III. We proposed that the initial adduct 11 (of unassigned stereochemistry) of methanol to zwitterion 3b undergoes a thermal or photochemical vinylcyclopropane rearrangement to give 12, in which the CCl₃ substituent ends up exo relative to the new cyclopropane ring. It is known that degenerate thermal rearrangements of deuterium-labeled bicyclo[3.1.0]hex-2-enes are not stereospecific,^{12,13} consistent with the fact that thermal orbital symmetry-allowed concerted pathways $({}_{\pi}2_{s} + {}_{\sigma}2_{a} \text{ or } {}_{\pi}2_{a} + {}_{\sigma}2_{s})$ are stereo-chemically impossible in this system, although photochemical symmetry-allowed pathways are structurally feasible. Thus, 12 could a priori be derived from intermediate 11 which possesses either an exo or endo CCl₃ substituent. Furthermore, as yet unisolated stereoisomers of product C may also be formed in the photochemical reaction. In any event, ring opening of 12 concomitant with nucleophilic displacement of Cl from the exo CCl₃ group (a most unusual and, to our knowledge, unprecedented reaction) leads to 13, which gives 6 after capture by a second molecule of methanol.

These mechanisms are without experimental verification at the present time and must be considered highly speculative, although they all start with zwitterion intermediates which have been strongly implicated in the photochemistry of these dienones and (except where noted) have resonable mechanistic analogy. At present, they are mechanistic curiosities which may have little general significance in dienone photochemistry. Indeed, their prin-





cipal utility may be as challenging problems to students of physical organic chemistry. Nonetheless, studies are in progress to better define the mechanisms of these photorearrangements and to probe their generality.

Experimental Section

Ultraviolet spectra were recorded on a Perkin-Elmer Coleman Model 124D double-beam spectrophotometer with digital data display. The samples in 1-cm Duracil cuvettes were dissolved in spectrophotometric-grade cyclohexane. Infrared spectra were recorded on a Perkin-Elmer Model 735 spectrophotometer, with calibration against the 1601-cm⁻¹ band on polystyrene film. Most samples were analyzed as dilute solutions in spectral-grade CCl₄ and some as neat liquids on sodium chloride plates. Mass spectra were recorded by Mr. Charles Strom on a Du Pont Model 21-492 double-focussing spectrometer with a CI/EI source. Proton NMR spectra were recorded at 60 MHz on a Hitachi Perkin-Elmer Model R-24 or R-20B spectrometer and at 100 MHz on a Varian Model XL-100 spectrometer equipped with a Nicolet Fourier transform accessory. Tetramethylsilane was used as the reference in 60-MHz spectra and CDCl_3 in 100-MHz spectra. $^{13}\mathrm{C}$ NMR spectra were taken by Mr. Charles Strom on the XL-100 spectrometer. Wide-band proton decoupling was usually employed, but some spectra were recorded by using single-frequency off-

⁽¹⁰⁾ Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: GmbH, Weinheim/Bergstr., 1970; Chapter

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(12) Cooke, R. S.; Andrews, U. H. J. Am. Chem. Soc. 1974, 96, 2974.
(13) Gajewski, J. J. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 4, pp 1 - 53.

resonance decoupling (SFORD) and others with the proton decoupler gated off during data acquisition. The position of each signal was measured relative to the middle peak of CDCl₃ triplet at δ 77.2 relative to Me₄Si. Gas-liquid partition chromatography (GLC) analyses were carried out on Hewlett-Packard Model 5710A and F & M Scientific Hewlett-Packard Model 5750 gas chromatographs. A Varian Aerograph Model 920 instrument was used for preparative-scale separations, with samples collected in U-tubes suspended in a dry ice-acetone bath. Melting points were taken in capillary tubes on a Thomas-Hoover apparatus and are uncorrected.

Photoproducts A and B. A solution of 1.2 g of dienone 1b⁴ (5 mmol) and 2.2 g of anhydrous HCl (60 mmol) in 120 mL of spectral-grade methanol was irradiated for 35 min in a large Pyrex test tube outside a water-cooled 450-W Hanovia lamp, both contained in a large water-filled beaker. The solution was continuously purged with nitrogen. The temperature of the solution went up as high as 50 °C. Analysis of the photolysate by GLC $(16 \times 1/8)$ in. column of 20% XE-60 on Chromosorb W, column temperature 125 °C) showed one major product ($t_{\rm R}$ 7.8 min) and three minor products (t_R 0.5, 2.5, and 19.5 min) in addition to recovered dienone ($t_{\rm R}$ 12.9 min). Column chromatography of 350 mg of the mixture on 30 g of magnesium silicate (Grade M-1, 50-100 mesh, Bio-Rad) using 2.85% ether in hexane as eluent, monitoring by GLC analysis, gave 269 mg of the major component (product Å) in $\sim 80\%$ purity in the first fraction (0–250 mL) and 8.6 mg of product B ($t_{\rm R}$ 19.5 min) in the fourth fraction (750–1000 mL). Both fractions were recrystallized from hexane to give 145 mg of product A as fluffy white needles, mp 38-40 °C, and 4.4 mg of product B, mp 56-58 °C.

Anal. Calcd for $\dot{C}_{10}H_{11}Cl_{3}O$ (photoproduct A): C, 47.37; H, 4.37; Cl, 41.95. Found: C, 47.42; H, 4.39; Cl, 41.41.

Photoproduct C. Since the photolysis solution became rather hot in the above experiment, an irradiation was performed at a lower temperature to see if the results would be different. Accordingly, 1.2 g of dienone 1b (5 mmol) was irradiated in 175 mL of spectral-grade methanol containing 2.2 g (60 mmol) of anhydrous HCl in a reaction vessel containing a water-cooled 450-W Hanovia lamp in a Pyrex immersion well. The system was cooled externally at -20 °C during the 40-min irradiation period. Aliquots of the reaction mixture were removed prior to irradiation and kept in the dark at room temperature and at 50 °C as controls. After workup, which involved careful treatment with anhydrous CaCO₃ at or below room temperature to remove the HCl, the organic material (after removal of solvent) was subjected to GLC analysis as above. The controls showed recovered dienone plus a single product $(t_{\rm R} 2.7 \text{ min})$ in a yield of 1%. The photolysate showed a major photoproduct ($t_{\rm R}$ 13.6 min), recovered dienone ($t_{\rm R}$ 17.1 min), three minor photoproducts ($t_{\rm R}$ 0.5, 3.0, and 9.0 min) and nine trace products. Half of the photolysate was chromatographed on 30 g of magnesium silicate, using 2% ether in hexane as eluent, to give 169 mg of material containing a large quantitiy of the major product (product C) in the 50-250-mL fraction. This material was recrystallized from hexane to give 30.4 mg of white crystals, mp 93-95 °C. Subsequent GLC analysis of the crystalline material showed that it decomposed thermally above 120 °C to give another material which has been isolated from a larger scale thermolysis, but whose structure is not yet securely assigned.

Anal. Calcd for $C_{11}H_{16}Cl_2O_8$: C, 49.46; H, 6.04; Cl, 26.54. Found: C, 49.54; H, 6.04; Cl, 26.17 (T. Bella, Rockefeller University, New York, NY); C, 49.97; H, 5.71; Cl, 27.15 (Chemalytics, Tempe, AZ).

X-ray Structure Determination of Photoproduct C. The crystals of this material were monoclinic, A = 7.829 (2), B = 25.247 (5), C = 6.406 (1) Å; $\beta = 91.43$ (2)⁰, $D_c = 1.40$ g/cm, Z = 4, space group $P2_1/n$ (h0l, h + l = 2n + 1 absent; 0k0, k = 2n + 1 absent); Ni-filtered Cu K α radiation, $\lambda = 1.5418$ Å, μ (Cu K α) = 45.7 cm⁻¹. The intensities of 1241 independent reflections were measured

by using an Enraf-Nonius CAD4 diffractometer. The 785 reflections having $I_0 > 2\sigma(I_0)$, based on counting statistics, were considered as observed. The structure was solved by using the direct-phasing program MULTAN.⁹ The resulting E map revealed 14 of the 16 nonhydrogen atoms. A difference electron density map obtained from this phasing model showed the remaining two atoms. Full-matrix lease-squares refinement using isotropic and then anisotropic thermal parameters resulted in an R factor¹⁴ of 12.0%. The hydrogen atomic positions were then calculated from the known atomic positions and added to the model; their positional and thermal parameters were held constant during the subsequent refinement, which gave a final R factor of 10.8% and a weighted R (using unitary weights) of 13.8%. These rather high-reliability indices are the results of the crystal's decomposition. The X-ray '76 system modified for use on a PDP-10 computer was used for most calculations.

Thermal Control Runs. A solution was prepared of 0.31 g of dienone 1b in 35 mL of spectrograde methanol to which 0.58 g of gaseous HCl had been added. This solution was purged with nitrogen for 10 min, covered with aluminum foil, and heated at reflux for 24 h. Samples were withdrawn periodically for NMR spectra. No disappearance of 1b nor appearance of photoproduct A (4) was detectable in any of these spectra. Similar results were obtained with two aliquots of the low-temperature photolysis preparation, which were kept in the dark at room temperature and at 50 °C for 45 min, respectfully, and then analyzed by GLC. In addition to recovered dienone, only ~1% of a new product not formed in any of the photochemical reactions could be detected.

4-Methyl-3-(2,2,2-trichloroethyl)anisole. The acetate of 4-methyl-3-(2,2,2-trichloroethyl)phenol was prepared as described previously⁷ by heating 3,4-dimethyl-4-(trichloromethyl)-2,5cyclohexadienone (1b) in acetic anhydride containing a catalytic amount of concentrated H_2SO_4 at reflux for 5.5 h. The acetate was hydrolyzed to the corresponding phenol upon heating to reflux with a solution of aqueous methanol containing KOH for 10 min. ¹H NMR spectra of the acetate and the phenol were consistent with the structures assigned by Newman et al.⁷ The methyl ether of the phenol was obtained when 400 mg of the phenol was heated at reflux with 1 mL of 1 N NaOH and 0.26 g of methyl sulfate in 2 mL of methanol for 45 min. The oily product was recrystallized from hexane and had mp 37–38 °C. The ¹H NMR spectrum of the methylated phenol was indistinguishable from that of photoduct A.

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Registry No. 1b, 7499-12-9; 4, 75812-81-6; 5, 75812-82-7; 6, 75812-83-8; 4-methyl-3-(2,2,2-trichloroethyl)phenol, 42203-95-2; 3,4-dimethylanisole, 4685-47-6.

Supplementary Material Available: Complete X-ray data on compound 6 (photoproduct C) are available including tables of fractional atomic coordinates for nonhydrogen and for hydrogen atoms, thermal parameters, bond lengths, bond angles, observed vs. calculated structure factors, and torsion angles (21 pages). Ordering information is given on any current masthead page.

⁽¹⁴⁾ $R = \sum ||F_0| - |F_0|| / \sum F_0; R_w = \sum w ||F_0| - |F_0||^2 / \sum |F_0|^2 |^{1/2}$ (15) "The X-ray System-Version of 1976"; Steward, J. M.,

^{(15) &}quot;The X-ray System-Version of 1976"; Steward, J. M., Ed.; Technical Report TR-446 of the Computer Science Center, University of Maryland, College Park, MD, 1976.