tively. The rest of the NMR spectroscopic data, including the pendant epoxide group at C-6′ and C-7′, which show the diagnostic doublet of doublets and doublet of quartets around δ 3.0, match very closely those of trichodermadiene.[2,8] These data are consistent with structure **2** assigned for deoxytrichodermadiene. Table I lists the ^{13}C and ^{1}H NMR chemical shifts of the two new compounds.

Experimental Section

General Methods. Ultraviolet spectra were determined on a Hitachi 100-80A spectrophotometer. Nuclear magnetic resonance spectra were determined in deuteriochloroform, unless otherwise noted, on a Varian XL-200, Varian XL-100, EM-390, or FT-80A spectrometer with tetramethylsilane as an internal standard. The ^{13}C NMR signals were assigned by using ^{1}H single-frequency off-resonance decoupling techniques, by using chemical shift relations, and by comparison with literature data. Mass spectra were determined by Harvey Chemical Laboratories, Charlottesville, VA, on a VG Micromass 70/70 HS instrument. Thin-layer chromatography was carried out on prepared silica gel plates (E. Merck), and visualization was effected with short-wavelength UV light or sulfuric acid/ethanol/vanillin (20/3/1) spray. Flash chromatography was carried out on silica gel 60 (230–400 mesh, E. Merck). Medium-pressure liquid chromatography (MPLC) was carried out on Licroprep 60 (E. Merck) silica gel. High-performance liquid chromatography (HPLC) was performed with an Altex Model 332 gradient liquid chromatograph. Separations were carried out on a Whatman Magnum 9 (10/15) semipreparative Partisil column.

Isolation of Verrol (1). The details of the fermentation and initial chromatographic separations leading to a fraction containing 1, i.e., fraction III, are described elsewhere.[2] The crude fraction (29 g) was subjected to flash chromatography (SiO_2, 0–8% methanol in methylene chloride) to yield three major fractions rich in roridin A (1.2 g), verrol (461 mg), and trichoverrins (195 mg), respectively. The verrol-containing fraction was subjected to flash chromatography again under the conditions described above to yield 230 mg of a fraction which was mostly verrol and trichoverrols. This was further purified by column chromatography on silica (10–25% 2-propanol in hexane) to yield 120 mg of verrol[9] as an oil ($R_f \approx 0.2$ in both 5% MeOH/CH_2Cl_2 and 25% 2-propanol in hexane): mass spectrum (chemical ionization, methane gas reagent), m/e 379.2112 ($M^+ + H$ calcd 379.2120).

Acetylation of Verrol. A mixture of 10 mg of verrol in 25 μL each of acetic anhydride and pyridine was allowed to stand overnight. Removal of solvents in vacuo followed by preparative TLC on silica gel (50% EtOAc in hexane) provided verrol diacetate whose NMR spectral data are presented in Table I.

Isolation of Deoxytrichodermadiene. The workup of mycelium leading to the fraction containing this compound is described elsewhere.[2] Fraction I (6 g) was passed through a silica gel flash column and eluted with dichloromethane to yield several fractions. The first fraction (0.50 g) was subjected to preparative TLC (20% hexane in CH_2Cl_2) on 2-mm silica gel plates to yield 25 mg of an oil. Further purification was done on a Magnum-9 column (Whatman, Inc., 9 mm i.d., SiO_2) under gradient conditions: 90–100% methylene chloride in hexane, 30 min. The procedure gave 12 mg of **2**: oil; $[\alpha]^{25}_D - 5.6°$ (c 0.95, $CHCl_3$); UV max (MeOH) 265 nm (log ε 3.42); mass spectrum (chemical ionization, methane gas reagent), m/e 371.2216 ($M^+ + H$ calcd 371.2222). See Table I for NMR data.

Acknowledgment. This investigation was supported by Grant No. CA-25967 awarded by the National Cancer Institute, DHHS.

Registry No. 1, 84412-91-9; 1 diacetate, 85994-28-1; 2, 85957-00-2.

(8) Jarvis, B. B.; Midiwo, J. O.; Stahly, G. P.; Pavanasasivam, G.; Mazzola, E. P. *Tetrahedron Lett.* **1980**, 787.

(9) From another strain of *M. verrucaria* we found that reverse-phase chromatography on a C-18 column employing 40–60% methanol in water as the solvent can be used to separate and isolate verrol from trichoverrols and trichoverrins, the order of elution being trichoverrol B, trichoverrol A, verrol, trichoverrin B, and trichoverrin A.

Photocyclization of 2,6-Dichlorocinnamic Acid Derivatives to 5-Chlorocoumarin

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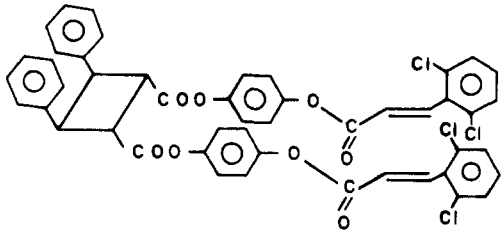
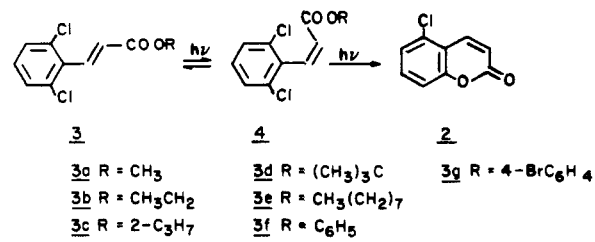
On UV irradation, 2,6-dichlorocinnamic acid and its esters undergo photocyclization with elimination of the elements of HCl or RCl (R = alkyl or aryl) to yield 5-chlorocoumarin (**2**); amide derivatives yield the corresponding imino analogues. Low-temperature irradiation monitored by infrared and optical spectrophotometry allowed the identification of o-quinomethyl ketene as one of the intermediates of this reaction and suggested a mechanism for the photocycloelimination.

While the solution photobehavior of the cyclobutane derivative **1**[1] was being studied (as a possible route to a tricyclic derivative containing two cyclobutane rings), it was found that instead of the anticipated product, a totally



1

Scheme I



3 **4** **2**

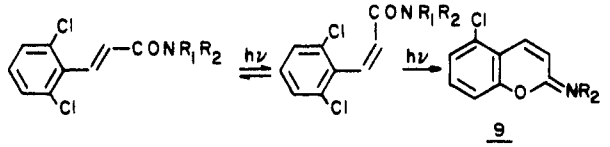
3a R = CH_3
3b R = CH_3CH_2
3c R = 2-C_3H_7
3d R = $(CH_3)_3C$
3e R = $CH_3(CH_2)_7$
3f R = C_6H_5
3g R = 4-BrC_6H_4

† Present address: Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel 76100.

(1) R. Arad-Yellin, Ph.D. Thesis, Weizmann Institute of Science, Rehovot, Israel, 1977.

0022-3263/83/1948-2578$01.50/0

Scheme II



6 $R_1 = R_2 = H$

7 $R_1 = H$ $R_2 = CH_3$

8 $R_1 = R_2 = CH_3$

different, unexpected reaction occurred, leading to a compound identified as 5-chlorocoumarin (2).[2]

Subsequent irradation of 2,6-dichloro-(*E*)-cinnamic acid and alkyl and aryl ester derivatives revealed, in each case, $E \rightarrow Z$ photoisomerization followed by a facile photocyclization involving the loss of the elements of RCl (R = H, alkyl, or aryl) to yield the observed product 2 (scheme I).

The photocycloelimination reaction was observed only with 2,6-disubstituted cinnamic acid derivatives. Irradiation of the related 2,4-dichloro analogues (e.g., methyl 2,4-dichlorocinnamate, (5) for much longer periods of time led solely to $E \rightarrow Z$ photoisomerization; no traces of coumarin, or additional products, were detected.

Although cis → trans photoisomerization of cinnamic acid derivatives is a commonly observed and well-studied reaction,[4] the photocyclization is novel and differs markedly from the known photoreactivity of cinnamates.[5] In addition, in spite of the fact that photocleavage of aromatic C–Cl bonds has been described in several systems,[6] photocycloelimination reactions with the loss of two non-hydrogen groups are unusual. For these reasons we have decided to examine this reaction in greater detail and attempted to elucidate its mechanism.

Results and Discussion

The photoreactivity of a series of 2,6-dichlorocinnamic acid derivatives was examined. In each case 5-chlorocoumarin (2) was obtained. This compound (mp 94-95 °C) was identified by its spectral properties (NMR, IR, MS) as well as elemental analysis. Irradiation of dilute solutions, $<10^{-3}$ M, with quartz-filtered light resulted in chemical yields approaching 100%, while in more concentrated solutions, and with longer wavelength light, subsequent photodimerization of 2 took place.[7] The photocycloelimination displayed no marked solvent dependence; it proceeded smoothyly in benzene, methanol, methylcyclohexane, and 2-methyltetrahydrofuran. The reaction proceeded equally well in the presence of oxygen or in its absence.

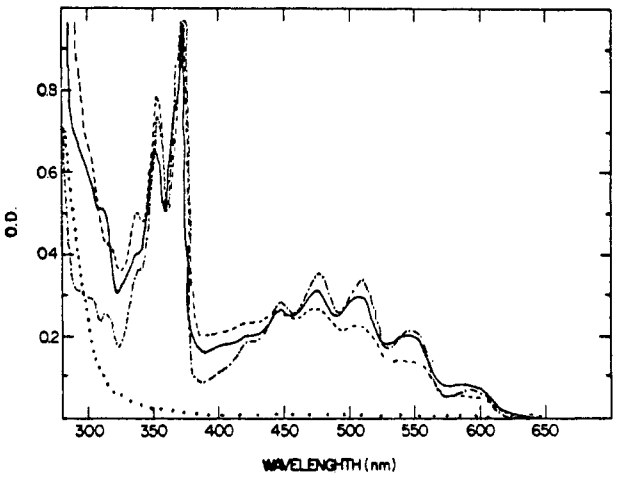


Figure 1. UV spectra of 2,6-dichloro-*cis*-cinnamic acid esters (10^{-4} M) in methylcyclohexane–isohexane (2:1) at 80 K: (···) methyl ester, before irradiation; (–) methyl ester, after irradiation; (- - -) phenyl ester, after irradiation; (-·-·-) ethyl ester, after irradiation.

2,6-Dichlorocinnamide (6) and its *N*-methyl (7) and *N,N*-dimethyl (8) derivatives also underwent photoreaction; a chlorine atom and the group attached to the nitrogen were eliminated to give the iminocoumrin 9. The latter was readily hydrolyzed to 2 in the presence of moisture (Scheme II).

2-Chloro-6-methoxycinnamic acid (10) (prepared from 2 by ring opening of the lactone with base and methylation with dimethyl sulfate) and its methyl ester (11) underwent smooth photocyclization to yield 5-methoxycoumarin (12); only a trace of 2 was formed. When 2,6-dimethoxycinnamic acid (13) (prepared from 12 by treatment with a base and methylation with dimethyl sulfate) or its methyl ester (14) were similarly irradiated, cis–trans photoisomerization took place, photocyclization was very sluggish, and only traces of 12 were detected. Irradiation of ethyl 2,4,6-trimethylcinnamate (15) displayed only cis–trans photoisomerization after long irradiation periods. We conclude therefore that in this photoreaction a chlorine atom is eliminated with a greater preference over a methoxy group while methyl groups are not eliminated at all.

In order to elucidate the mechanism of this novel photocycloelimination process, intermediates along the pathway to product were sought by irradiation and spectral monitoring at low temperatures. Irradiation at 83 K with light of wavelength between 260 and 340 nm (100-W Hg lamp filtered with $NiSO_4$–$CoSO_4$ solution) produced a new, red species having structured absorption extending to 640 nm; the same spectra were observed on irradiation of alkyl (**3a–e**) and aryl (**3f–g**) esters of 2,6-dichlorocinnamic acid (Figure 1). When the solutions containing the species were warmed to 125 K, the spectra changed to that of 2 (Figure 2).

A similar UV spectrum was described[8] for the photocolored species obtained on irradiation of chromenes. An *o*-quinonemethide structure was proposed[9] for these species.

On the basis of the above information and the infrared data presented below, the *o*-quinomethyl ketene structure

(2) A preliminary account of this work has appeared: R. Arad-Yellin, B. S. Green, and K. A. Muszkat, *J. Chem. Soc., Chem. Commun.*, 14 (1976). Compound 2 was therein identified as a new material, but we later learned that 2 had been synthesized previously.[3]

(3) K. A. Thakar adn D. D. Goswami, *Ind. J. Appl. Chem.*, **35**, 93 (1972).

(4) (a) B. K. Vaidya, *Proc. R. Soc. London, Ser. A*, **A129**, 299 (1930); (b) A.R. Olson and L. Hudson, *J. Am. Chem. Soc.*, **55**, 1410 (1933); (c) H. G. Curme, C. C. Natale, and D. J. Kelly, *J. Phys. Chem.*, 71, 767, (1967).

(5) Cis–trans photoisomerization:[4] photocycloaddition (e.g., T. Ishigani, T. Murata, and T. Endo, *Bull. Chem. Soc. Jpn.*, **49**, 3678 (1976)); photoreduction (E. F. Ullman, E. Babad, and M. T. Sung, *J. Am. Chem. Soc.*; **91**, 5792 (1969)); photooxidation (J. Kagan, *ibid.*, **88**, 2617 (1966)). The last reaction is exemplified by oxidative photocyclization of 3,4-dihydroxycinnamic acid to 6,7-dihydroxycoumarin; the mechanism has not yet been reported.

(6) W. A. Henderson, Jr., R. Lopresti, and A. Zweig, *J. Am. Chem. Soc.*, **91**, 6049 (1969); (b) J. Bratt and H. Suschitzky, *J. Chem. Soc., Chem. Commun.*, 949 (1972); (c) N. Kharash and Z. S. Ariyan, *Chem. Ind. (London)*, 302 (1965); (d) J. Grimshaw and A. P. de Silva, *J. Chem. Soc., Chem. Commun.* 302 (1980), (e) J. Grimshaw and A. P. de Silva, *Acc. Chem. Res.*, 181 (1982) and references therein.

(7) R. Arad-Yellin and B. S. Green, unpublished work.

(8) L. Edwards, J. Kolc, and R. S. Becker, *Photochem. Photobiol.*, **13**, 423 (1971).

(9) R. S. Becker and J. Michl, *J. Am. Chem. Soc.*, 88, 5931 (1966).

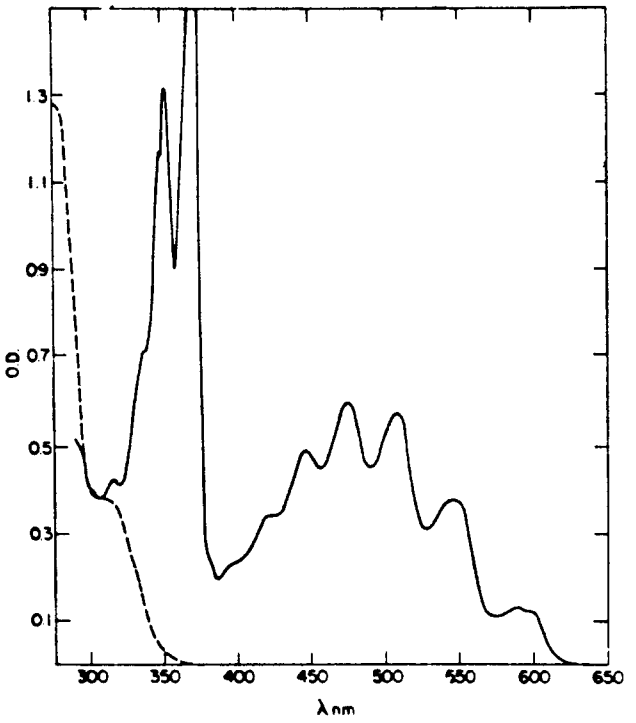
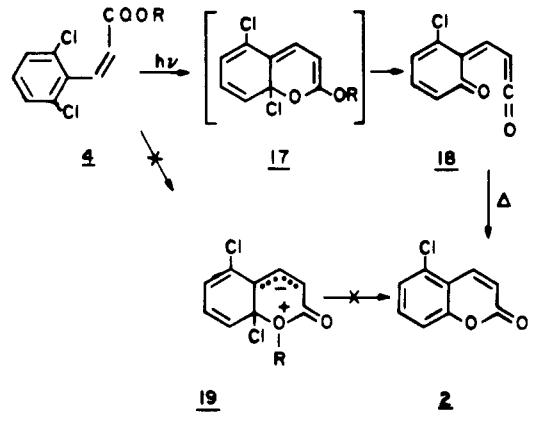


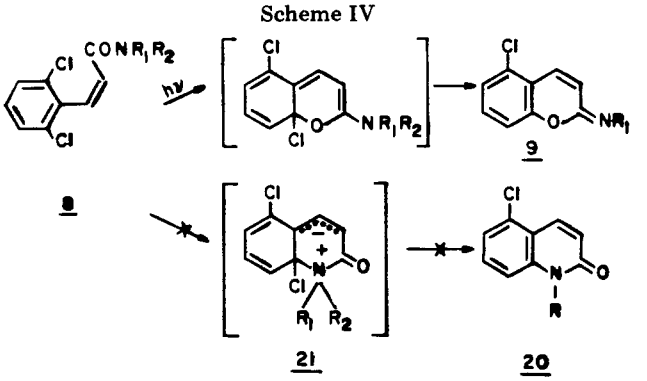
Figure 2. UV spectra of ethyl 2,6-dichlorocinnamate (10^{-4} M) in MCH–IH 2:1: (–) irradiated for 240 min at 83 K; (- - -) after irradiation and warming to 130 K.

Scheme III



18 is assigned to the red species observed during low-temperature irradiation (Scheme III). Electrocyclic ring closure of 18 then directly yields the isolated product 2. The *o*-quinomethyl ketene structure 18 demands a pathway involving other intermediates as it requires the transfer of the carbonyl oxygen in the starting material (4) to the phenyl ring in 2. Attempts to adduce spectral evidence for intermediates between 4 and 18 were not successful. Even at 4.2 K, irradiation of 4 gave the red intermediate 18. Despite the absence of experimental support for 17, this intermediate satisfies the required chemical demands, and although alternate formulations are possible for the conversion of 4 to 18, 17 represents the most economical in terms of number of intermediates. Species 17 rationalizes the appreciable chemical reorganization that occurs with so little thermal activation. It is a highly labile species: the leaving chlorine atom is attached to a tertiary carbon, is adjacent to an oxygen (α-chloro ethers are highly reactive), and is at the end of highly conjugated allylic system. Elimination of this chlorine and electronic reorganization with the loss of the ester alkyl or aryl group affords 18. When the potential leaving group

Scheme IV



at the ortho position is H, CH_3, or OCH_3 instead of Cl, the analogous intermediate to 17 is not formed or, if formed, it rapidly reverts back to the cis-cinnamate instead of reacting further.

Ketene intermediates are often traped by nucleophiles, and yet irradiation at room temperature shows no difference in rate of formation of 2 in benzene or methanol, the latter being expected to react with 18. However, at 77 K there is a significant difference in the rate of reaction in methylcyclohexane–isohexane (2:1) and in 2-propanol–propanol (2:3), the latter being only ca. one-fourth as fast as the former. We conclude that at low temperatures nucleophilic trapping of 18 competes with cyclization 18 → 2 but at room temperature the cyclization is too rapid to allow trapping of 18.

A 6π-electron pericyclic reaction 4 → 17 involving the carbonyl oxygen is favored over an alternative possibility involving the ether oxygen attack to yield a charged species (19). The latter would be expected to show marked solvent polarity dependence, but as noted, 4 → 2 proceeds equally well in polar as well as nonpolar solvents. In addition, the results observed during irradiation of amide analogues preclude such an intermediate. Irradiation of 8 led to formation of the iminocoumarin 10 and not the carbostyril 20 expected if an intermediate 21 analogous to 19 was formed in the reaction (Scheme IV).

The proposed intermediate 18 incorporates a ketene function and as such should show strong infrared absorption at about 2100 cm^{-1}. As this intermediate is stable only at low temperatures, the infrared spectrum should be recorded at these low temperatures. This technique was initially used in photochemical studies in 1968[10] and has found wide application since that time. A sample of neat methyl 2,6-dichloro-(*Z*)-cinnamate (4) was irradiated at 83 K until a red color, indicating the presence of the intermediates (18), developed. The IR spectrum that was recorded revealed a new band at 2300 cm^{-1}. This absorption, which disappeared on warming to 123 K (Figure 3), is attributed to the ketene function (the small bathochromic shift that is observed may be due to the conjugation of the ketene group to the tetraene system). The same results were obtained when the ester 4 was irradiated in solution (Figure 4).

The simultaneous appearance of the red coloration (and characteristic UV spectrum) together with the IR absorption of a ketenic group on low-temperature irradiation and the disappearance of both on warming strongly support structure 18 for this labile species.

Unsaturated lactones such as α-pyrone and related compounds were reported to undergo a ring opening on

(10) (a) O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.* **90**, 2333 (1968); (b) O. L. Chapman and J. D. Lassila, *ibid.* **90**, 2449 (1968); (c) J. Griffith and H. Hart *ibid.*, **90**, 5296 (1968); (d) G. Quinkert, *Photochem. Photobiol.*, **7**, 783 (1968).

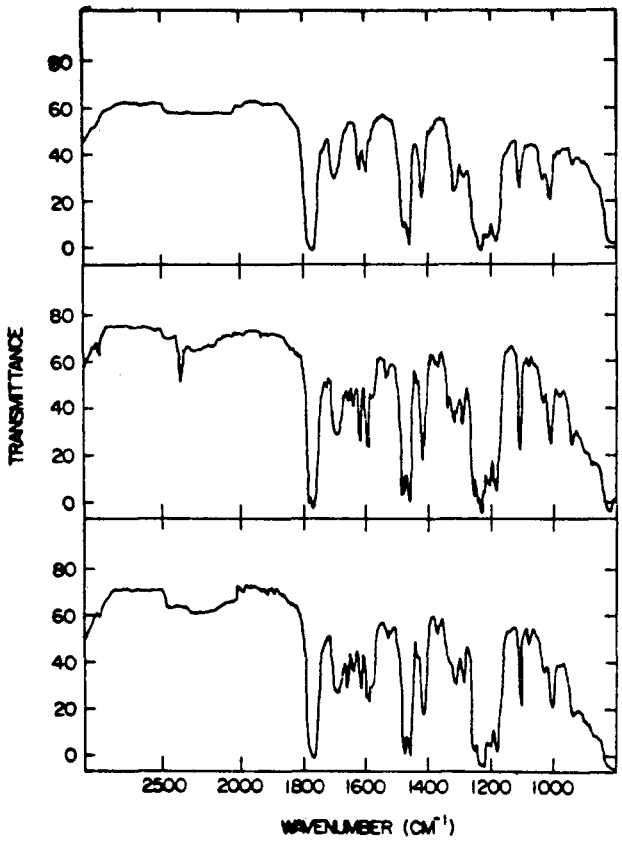


Figure 3. IR spectra of a sample of neat methyl 2,6-dichloro-*cis*-cinnamate on NaCl plates: (upper spectrum) before irradiation; (middle spectrum) after irradiation at 77 K for 60 min; (lower spectrum) after irradiation at 77 K and warming to 120 K.

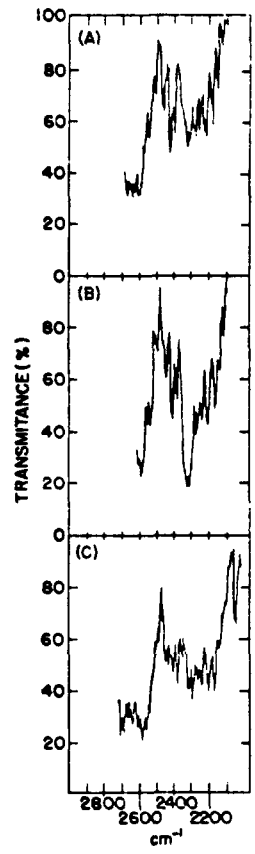


Figure 4. IR spectra of methyl 2,6-dichlorocinnamate in MCH–MCP (1:1): (upper part) before irradiation; (middle part) after irradiation for 60 min at 77 K; (lower part) after irradiation and warming to 120 K.

UV irradiation,[11-13] yielding a ketene derivative. The red species might, therefore, have been thought to rise by photochemical ring opening of 5-chlorocoumarin. As the photochemical ring opening of coumarin itself has apparently not been discussed in the literature, we irradiated solutions of coumarin and of its 5-chloro derivative at low temperature. In neither system was there any evidence, by IR or UV spectroscopy, for ring opening on prolonged irradiation. This observation is in agreement with that of Miller and co-workers[12] who claimed that ketenes are readily formed if no disruption of aromatic ring is necessary on ring opening; they are not formed if net loss of aromatic sextet is necessary. We conclude, therefore, that intermediate **18** arises solely through the reaction scheme proposed above (Scheme III).

Fate of the Leaving Groups. In the outline of the mechanism the pathway for the loss of the ortho chloro and the ester (or amide) alkyl or aryl groups was not considered explicitly. Several experiments were performed in order to determine the fate of these groups.

A benzene solution of **3a** was irradiated, and besides 5-chlorocoumarin (and its dimer), we found in the reaction mixture HCl, biphenyl, and traces of chloromethane.

When 4-bromophenyl ester was irradiated (chosen in order to lower the volatility of the byproduct derived from the ester group), 4-bromobiphenyl was isolated and identified.

(11) (a) P. DeMayo, *Adv. Org. Chem.*, **2**, 394 (1960), (b) J. P. Guthrie, C. L. McIntosh, and P. DeMayo, *Can. J. Chem.*, **48**, 237 (1970); (c) W. H. Pirkle and L. H. McKendry, *J. Am. Chem. Soc.*, **91**, 1179 (1969); (d) C. L. McIntosh and O. L. Chapman, *ibid.*, **95**, 247 (1973); (e) O. L. Chapman and C. L. McIntosh, *ibid.*, **91**, 4309 (1969).

(12) B. Miller and A. K. Bhattacharya, *Tetrahedron Lett.*, **22**, 3757 (1981).

(13) O. L. Chapman and C. L. McIntosh, *J. Chem. Soc.* D, 383 (1971).

Summary

The results presented above are consistent with a radical mechanism involving an homolytic cleavage of the *O*-alkyl or *O*-aryl group in the intermediate **17** and loss of the chloro group as Cl·. This mechanism is supported by the following additional observations: (1) The reaction proceeds at approximately the same rate in polar and nonpolar solvents. (2) The rate of conversion of the esters **3** to **2** correlates with the stability of the radicals derived from the ester residue. Thus, under similar conditions, the *tert*-butyl, phenyl, and *p*-bromophenyl esters reacted more readily than the methyl, ethyl, and *n*-octyl esters. This is in agreement with higher stability of *tert*-butyl, phenyl, and *p*-bromophenyl radicals compared to the methyl, ethyl, and *n*-octyl radicals. (3) On irradation of the 2,6-dichloro cinnamic acid anion, $Z \rightleftarrows E$ photoisomerization was observed but no 5-chlorocoumarin was obtained.

Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Unless otherwise noted, infrared spectra were detd. on a Perkin-Elmer Model 237b spectrophotometer using potassium bromide pellets, and ultraviolet spectra were determined on a Cary 14 spectrophotometer. NMR spectra were recored on Varian A60 and HFX-10 Burker 90-MHz spectrophotometers using tetramethylsilane as an internal standard. Unless otherwise mentioned irradiations were performed by using a Hanovia 450-W lamp (Pyrex filtered) inserted in an immersion well in the irradiation flask. TLC was performed on silica gell on aluminum foil (DC. Karten SIF), and column choromatography was done on Merck Silica gel (0.063–0.2 mm). VPC analysis was performed on a Varian Aerograph Series 1200 instrument, using 1 m × $^1/_8$ in. stainless steel column packed with 10% SE30 on Chromosorb W 30/60. The injector was maintained at 200 °C and the detector at 250 °C. The column temperature was pro-

grammed from 100 to 270 °C at a rate of 20°/min.

2,6-Dichlorocinnamic acid was prepared in 80% yield by established procedures:[14] mp 196 °C (lit.[14] mp 196 °C); ^{1}H NMR (CD_3OD) δ 7.18–7.63 (3 H, aromatic), 7.82 (1 H, d, J = 16 Hz, Hβ), 6.56 (1 H, d, J = 16 Hz, Hα).

Methyl 2,6-dichlorocinnamate (3a) was prepared in 95% yield by heating 2,6-dichlorocinnamic acid in refluxing methanol that contained several drops of thionyl chloride for 2 h. The product was recovered by evaporating the solvent and was purified by recrystallization from *n*-hexane: mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 7.13–7.49 (3 H, aromatic H), 7.86 (d, J = 16 Hz, 1 H, Hβ), 6.66 (d, J = 16 Hz, 1 H, Hα), 3.83 (s, 3 H, CH_3). Anal. Calcd for $C_{10}H_8Cl_2O_2$: C, 51.98; H, 3.49; Cl, 30.68. Found: C, 52.06, H, 3.52; Cl, 30.82.

Ethyl 2,6-dichlorocinnamate (3b) was prepared in 80% yield by refluxing the acid chloride (prepared by treating 2,6-dichlorocinnamic acid with boiling thionyl chloride and removing the excess in vacuum) in ethanol for 24 h. Evaporation of the solvent left a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.05–7.40 (m, 3 H, aromatic H), 6.57 (d, J = 16 Hz, 1 H, Hα), 7.82 (d, J = 16 Hz, 1 H, Hβ), 1.34 (t, J = 8 Hz, 3 H, CH_3), 4.31 (q, J = 8 Hz, 2 H, CH_2). Anal. Calcd for $C_{11}H_{10}Cl_2O_2$: C, 53.90; H, 4.11; Cl, 28.93. Found: C, 53.87; H, 4.37, Cl, 28.62.

Isopropyl 2,6-dichlorocinnamate (3c) was prepared in 84% yield by overnight refluxing of 2,6-dichlorocinnamoyl chloride (1 g, 4 mmol) and 2-propanol (3 mL) in dry benzene that contained several drops of pyridine. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL) and washed with 5% aqueous $NaHCO_3$ soluiton (2 × 15 mL), 5% HCl solution (2 × 15 mL), and water (2 × 15 mL). After the solution was dried over $MgSO_4$, the solvent was evaporated, and the product was obtained as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.06–7.40 (m, 3 H, aromatic H), 6.57 (d, J = 16 Hz, 1 H, Hα), 7.78 (d, J = 16 Hz, 1 H, Hβ), 1.33 (d, J = 7 Hz, 6 H, CH_3), 5.16 (septet, J = 6 Hz, 1 H, CH). Anal. Calcd for $C_{12}H_{12}Cl_2O$: C, 55.62; H, 4.67; Cl, 27.36. Found: C, 56.42; H, 5.16; Cl, 26.91.

***tert*-Butyl 2,6-dichlorocinnamate (3d)** was prepared in 60% yield from the acid chloride (3.0 g, 0.012 mol), and *tert*-butyl alcohol (1 mL) in dry benzene by the same procedure as **3c**. The product was purified by sublimation (60 °C, 1 mmHg): mp 59–62 °C; ^{1}H NMR ($CDCl_3$) δ 7.05–7.41 (m, 3 H, aromatic H), 6.52 (d, J = 16 Hz, 1 H, Hα), 7.72 (d, J = 16 Hz, 1 H, Hβ), 1.55 (s, 9 H, CH_3); MS, m/e calcd for $C_{13}H_{14}Cl_2O_2$ 272.0371, measured 272.0376 (M^+).

***n*-Octyl 2,6-dichlorocinnamate (3e)** was prepared in 80% yield by the same procedure as **3c**. It was obtained as colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.16–7.54 (m, 3 H, aromatic H), 6.69 (d, J = 16 Hz, 1 H, Hα), 7.90 (d, J = 16 Hz, 1 H, Hβ), 0.67–1.38 (m, 15 H $(CH_2)_7CH_3$), 4.29 (t, J = 6 Hz, 2 H, OCH_2). Anal. Calcd for $C_{17}H_{22}Cl_2O_2$: C, 62.01; H 6.73; Cl, 21.53. Found: C, 62.05; H, 6.75; Cl 21.37.

Phenyl 2,6-dichlorocinnamate (3f) was prepared in 56% yield from 2,6-dichlorocinnamoyl chloride (1 g, 4 mmol) and phenol (3 mL) by the same procedure as **3c**. The product was crystallized from *n*-hexane: mp 62–65 °C; ^{1}H NMR ($CDCl_3$) δ 7.16–7.56 (m , 8 H, aromatic H). 6.81 (d, J = 16 Hz, 1 H, Hα), 8.01 (d, J = 16 Hz, 1 H, Hβ); MS, m/e 293.15 (M^+, calcd), 293.1279 (M^+, measured). Anal. Calc for $C_{15}H_{10}Cl_2O_2$: C, 61.46% H, 3.44; Cl, 24.19. Found: C, 61.83; H, 3.66; Cl, 23.58.

***p*-Bromophenyl 2,6-dichlorocinnamate (3g)** was prepared in 65% yield by the same procedure as **3c** by using the acid chloride and *p*-bromophenol. It was crystallized from cyclohexane: mp 107–109 °C; ^{1}H NMR ($CDCl_3$) δ 7.06–7.65 (m, 7 H, aromatic H), 6.81 (d, J = 16 Hz, 1 H, Hα), 8.03 (d, J = 16 Hz, 1 H, Hβ).

Irradiation of Methyl 2,6-Dichlorocinnamate. Methyl 2,6-dichloro-*trans*-cinnamate (18 g, 0.1 M) was dissolved in benzene (700 mL) and irradiated for 75 h. Concentration of the solution precipitated a white solid (1.7 g, mp 260–262 °C), identified as a dimer of 2.[7] The remaining reaction products were isolated by column chromatography (benzene); 250-mL fractions were collected. Fractions 1–4 contained methyl 2,6-dichloro-*cis*-cinnamate (13 g); fractions 5–7 contained methyl 2,6-dichloro-*trans*-cinnamate (1.15 g), and fraction 8–16 (2.1 g) contained a white compound identified as 5-chlorocoumarin (**2**).

Methyl 2,6-dichloro-*cis*-cinnamate: colorless oil; ^{1}H NMR ($CDCl_3$) δ 6.15 (1 H, d, J = 12 Hz, Hα), 6.81 (1 H, d, J = 12 Hz, Hβ), 7.1–7.38 (3 H, aromatic), 3.56 (3 H, s, OCH_3).

5-Chlorocoumarin (2): mp 94–95 °C (hexane) [lit[3] mp 93–94 °C]; ^{1}H NMR ($CDCl_3$) δ 6.50 (1 H, d, J = 10 Hz, Hα to C=O), 8.10 (1 H, d, J = 10 Hz, Hβ to C=O), 7.21–7.56 (3 H, aromatic); UV λ_{max} (MeOH) 283 nm (ϵ_{max} = 1.15 × 10^4), 315 (ϵ_{max} = 3.8 × 10^3); IR 1740 cm^{-1} (ν_{CO}), 735 ($\nu_{CH=CH\ cis}$); MS, m/e 180 (M^+), 152 (M^+ – CO, main peak).

2,6-Dichlorocinnamide (6). A solution of 2,6-dichlorocinnamoyl chloride (1.4 g) in dry benzene (20 mL) was added dropwise to an ice-cold solution of aqueous ammonium hydroxide (25%, 25 mL). The precipitate was filtered, dried, and recrystallized from water: mp 179–180 °C; 100% yield; ^{1}H NMR (CD_3OD) δ 7.18–7.48 (3 H, aromatic), 6.73 (1 H, d, J = 16 Hz, Hα) 7.70 (1 H, d, J. = 16 Hz, Hβ). Anal. Calcd for $C_9H_7Cl_2NO$: C, 50.03; H, 3.27; N, 6.48. Found: C, 50.18; H, 3.39; N, 6.39.

***N*-Methyl-2,6-dichlorocinnamide (7)** was prepared in 90% yield by the same procedure described for **6** by using a 25% aqueous methylamine solution. The product was crystallized from aqueous ethanol: mp. 180–182 °C; ^{1}H NMR ($CDCl_3$) δ 7.03–7.66 (3 H, aromatic), 6.5 (1 H, d, J = 16 Hz, Hα), 7.71 (1 H, d, J = 16 Hz, Hβ), 2.96 (3 H, d, J = 5 Hz, NCH_3), 5.23–5.76 (1 H, wide s, NH). Anal. Calcd for $C_{10}H_9Cl_2NO$: C, 52.20; H, 3.94; Cl, 30.82. Found: C, 52.38; H, 4.04, Cl, 30.60.

***N*,*N*-Dimethyl-2,6-dichlorocinnamide (8)** was prepared in 70% yield by the above method using a 25% aqueous dimethylamine solution. The product was crystallized from methylcyclohexane: mp 89.5–90.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.05–7.50 (3 H, aromatic), 7.04 (1 H, d, J = 16 Hz, Hα), 7.73 (1 H, d J = 16 Hz, Hβ), 3.13 (6 H, s, $N(CH_3)_2$). Anal. Calcd for $C_{11}H_{11}Cl_2NO$: C, 54.12; H, 4.54; Cl, 29.5. Found: C, 54.35; H, 4.69; Cl, 28.99.

Irradiation of 7: A solution of **7** (26 mmol) in acetonitrile was placed in a Rayonette reactor (equipped with RUL 3000 lamps having maxium emission around 3000 Å) and irradiated for 110 h at room temperature. TLC of the solution revealed three spots, which were separated by preparative chromatography (10% ethyl acetate in benzene). The upper spot was identified as **7** (28%). The second spot was *N*-methyl-2,6-dichloro-*cis*-cinnamide (56%), and the third was 5-chloro-2*H*-benzopyran-2-methylimine (**9**, 16%).

***N*-Methyl-2,6-dichloro-*cis*-cinnamide**: mp 159–160 °C (hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 7.04–7.38 (3 H, m), 6.15 (1 H, d, J = 12 Hz, Hα), 6.68 (1 H, d, J = 12 H, Hβ), 2.75 (3 H, d, J. = 4.5 Hz), 5.33 (1 H, q, J = 4.5 Hz, NH).

***N*-Methyl-5-chloro-2*H*-benzopyran-2-imine (9)**: ^{1}H NMR ($CDCl_3$) δ 3.16 (3 H, s, CH_3), 6.41 (1 H, d, J = 10 Hz, Hα to C=N), 7.96 (1 H, d, J = 10 Hz, Hβ), 6.98–7.68 (3 H, m, aromatic); IR 1670 cm^{-1} ($\nu_{C=N}$); MS, m/e 193 (M^+), 164 (M^+ – NCH_3), 134. The compound is very unstable and in all cases was accompanied by 5-chlorocoumarin (**2**).

Irradiation of 8. The amide was irradiated in benzene and in acetonitrile. The products of the reaction were cis and trans isomers and the hydrolysis product of **9**.

***N*,*N*-Dimethyl-2,6-dichloro-*cis*-cinnamide** was obtained from the reaction mixture by column chromatography (ethyl acetate–benzene–acetone 5:4:1) and crystallized from hexane–ethyl acetate (2:1): mp 96–97 °C; ^{1}H NMR ($CDCl_3$) δ 7.08–7.46 (3 H, aromatic), 6.51 (1 H, d, J = 10 Hz, Hα), 6.79 (1 H, d, J = 10 Hz, Hβ), 2.96 (6 H, d, J = 7.5 Hz, CH_3).

Irradiation of 6. The amide (0.5 g) was dissolved in benzene (700 mL) and was irradiated for 42 h. A precipitate (mp 260–262 °C) was formed. It was identified as the head-to-head anti dimer of 5-chlorocoumarin.[7] TLC of the filtrate (benzene–$CHCl_3$, 4:1) revealed 5-chlorocoumarin (**2**) and the cis and trans isomers of **6**. The cis isomer was isolated by preparative TLC as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.00–7.46 (3 H, aromatic), 6.73 (1 H, d, J = 12 Hz, Hβ), 6.19 (1 H, d, J = 12 Hz, Hα), 5.7–6.4 (2 H, wide s, amide H).

2-Chloro-6-methoxy-*cis*-cinnamic Acid (10). 5-Chlorocoumarin (1.17 g) was dissolved in 10% NaOH (10 mL) by heating the solution to 100 °C. After dropwise addition of dimethyl sulfate (1.5 g, 2 mL), the heating was stopped and stirring was continued overnight. The solution was acidified with a 10% HCl solution

(14) F. Bock, G. Lock, and K. Schmidt, *Monatsh. Chem.*, **64**, 401 (1934).

(10 mL), and the resulting precipitate was filtered, washed with water, and dried. The residue was dissolved in CH_2Cl_2 (20 mL), and the product was extracted with 5% $NaHCO_3$. The unreacted 5-chlorocoumarin (470 mg) was recovered from the CH_2Cl_2 solution; the product was precipitated from the bicarbonate solution by 10% HCl. It was filtered, dried, and recrystallized from hexane: mp 122–122.5 °C (525 mg, 64% yield); ^1H NMR ($CDCl_3$) δ 3.72 (s, 3 H, OCH_3), 6.14 (d, J = 12 Hz, 1 H, Hα), 6.95 (d, J = 12 Hz, 1 H, Hβ), 6.66–7.35 (m, 3 H, aromatic Hs), 9.85 (s, 1 H); UV λ_{max} (MeOH) 260 mn ($\epsilon = 3.8 \times 10^3$); IR 2500–3300 cm^{-1} (ν_{OH}), 1675 (ν_{CO}), 720 ($\nu_{CH=CH\ cis}$); MS, m/e 212 (M^+), 177 (M^+–Cl), 162, 152. Anal. Calcd for $C_{10}HgClO_3$: C, 56.48; H, 4.27; Cl, 16.68. Found: C, 56.67; H, 4.36; Cl, 16.48.

Methyl 2-chloro-6-methoxy-*cis*-cinnamate was obtained in 90% yield as colorless oil by refluxing the acid in methanol that contained several drops of thionyl chloride for 3 h: ^1H NMR ($CDCl_3$) δ 3.51 (3 H, s, CO_2CH_3), 3.70 (3 H, s, OCH_3), 6.02 (1 H, d, J = 12 Hz, Hα), 6.70 (1 H, d, J = 12 Hz, Hβ), 6.63–7.26 (3 H, aromatic H).

Methyl 2-chloro-6-methoxy-*trans*-cinnamate (11) was obtained from the cis isomer by heating the latter in refluxing toluene that contained several crystals of iodine for 24 h. The mixture contained 65% trans and 35% cis isomers. The trans isomer was isolated by column chromatography (benzene eluent, 30-mL fractions) and was recovered from the residue of fractions 5 and 6. It was recrystallized from hexane, mp 73–74 °C; ^1H NMR (CCl_4) δ 3.82 (s, 3 H, CO_2CH_3), 3.66 (s, 3 H, OCH_3), 6.63 (d, J = 16 Hz 1 H, Hα), 7.83 (d, J = 16 Hz, 1 H, Hβ), 6.60–7.10 (m, 3 H, aromatic H); IR 1715 cm^{-1} (ν_{CO}), 970 ($\nu_{CH=CH\ trans}$). Anal. Calcd for $C_{11}H_{11}ClO_3$: C, 58.29, H, 4.89; Cl, 15.64. Found: C, 58.40; H, 4.91; Cl, 15.44.

Irradiation of Methyl 2-Chloro-6-methoxy-*cis*-cinnamate. Compound **1g** in dry benzene (700 mL) was irradiated for 46 h. The solvent was evaporated, and the residue was column chromatographed (benzene eluent, fractions of 50 mL were collected). Fractions 5 and 6 contained compound 11 (150 mg, mp 73–74 °C). Fractions 9 and 10 contained the cis isomer (750 mg). Fractions 11 and 12 contained the cis isomer and a trace amount of **2**. Fractions 16–25 contained **12** (100 mg, mp 84–85 °C).

5-Methoxycoumarin (12): mp 84–85 °C (hexane) [lit.[15] mp 85 °C]; ^1H NMR ($CDCl_3$) δ 3.90 (s, 3 H, OCH_3), 6.31 (d, J = 10 Hz, 1 H, Hα), 8.08 (d, J = 10 Hz, 1 H, Hβ), 6.62–7.66 (m, 3 H, aromatic H); UV λ_{max} (MeOH) 295 nm ($\epsilon_{max} = 1.03 \times 10^4$), 243 nm ($\epsilon_{max} = 4.95 \times 10^3$);[15] MS, m/e 176 (M^+), 148 ($M^+ - CO$), 133, 105.

2,6-Dimethoxy-*cis*-cinnamic acid (13) was prepared in 60% yield from **12** by the procedure used for **10**. The acid was isolated by column chromatography (acetone–hexane 1:1): mp 152–153 °C (methylcyclohexane) [lit.[16] mp 151–153 °C (ethanol–H_2O)]; ^1H NMR ($CDCl_3$ + CD_3OD) δ 3.79 (s, 3 H, OCH_3), 6.02 (d, J = 12 Hz, 1 H, Hα), 6.57 (d, J = 12 Hz, 1 H, Hβ), 6.54–7.38 (m, aromatic), 7.51 (s, 1 H, acidic H).

Methyl 2,6-dimethoxy-*cis*-cinnamate (14) was obtained in 90% yield as a colorless oil by stirring a methanolic solution of the acid that contained some drops of $SOCl_2$ for 48 h. The workup of the rection mixture was as described for methyl 2-chloro-6-methoxy-*cis*-cinnamate: ^1H NMR ($CDCl_3$) δ 3.61 (s, 3 H, CO_2CH_3, 3.76 (s, 6 H, OCH_3), 6.10 (d, J = 12 Hz, Hα), 6.70 (d, J = 12 Hz, Hβ), 6.47–7.33 (m, 3 H, aromatic H).

Ethyl 2,4,6-trimethyl-*trans*-cinnamate (15) was synthesized from 2,4,6-trimethylbenzaldehyde, sodium, and ethyl acetate:[17] ^1H NMR (CCl_4) δ 1.33 (t, J = 7 Hz, 3 H, CH_3 ester), 2.32, 2.27 (2 s, 9 H, CH_3 ring) 4.16 (q, J = 7 Hz, 2 H, OCH_2), 6.04 (d, J = 16 Hz, 1 H, Hα), 6.88 (s, 2 H, aromatic H, 7.84 (d, J = 16 Hz, 1 H, Hβ). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.25; H, 8.45.

Irradiation of 15. A solution of the ester in benzene was irradiated for 70 h. It was found (VPC) to contain two components: the cis isomer (>90%) and the trans isomer. The cis isomer was separated by column chromatography and was obtained as colorless oil: ^1H NMR (CCl_4) δ 1.05 (t, J = 7 Hz, 3 H, CH_3 ester), 2.1 (s, 6 H, CH_3), 2.25 (d, J = 5 Hz, 3 H, CH_3), 3.92 (q, J = 17 Hz, 2 H, OCH_2), 5.96 (d, J = 12 Hz, 1 H, Hα), 6.86 (d, J = 12 Hz, 1 H, Hβ), 6.70 (s, 2 H, aromatic H).

Low-Temperature UV Irradiation and Optical Spectrophotometry. These experiments were performed by using a 4-windowed quartz optical Dewar. The solutions were placed in quartz cells, 1-cm pathlength, inserted in a copper block cooled by drawing liquid nitrogen through it. A medium-pressure 10-W Mazda lamp was used as a light source. The optical filter was a $CoSO_4$–$NiSO_4$ solution. The absorption spectra were recorded on a Caryl 14 spectrophotometer.

Low-Temperature IR Spectrophotometry. Sodium chloride cavity cells (1-mm pathlength) or sapphire windows (for neat samples) were placed in a copper block cooled by a stream of liquid nitrogen. The copper block was surrounded by an insulated box provided with a pair of BaF_2 windows (for the IR measurement) and two quartz windows (for the UV irradiation). A slow flow of N_2 served to prevent moisture condensation. The irradiation was performed with a high-pressure HBO 200-W Osram mercury lamp using a $CoSO_4$–$NiSO_4$ solution filter. The spectra were recorded on a Perkin-Elmer Model A237 spectrophotometer.

Optical and Infrared Spectrophotometry at 4 K. The compounds, as 2% solutions in Oppanol B200 polyisobutyelene films, were spread on a sapphire disk (25-mm diameter). These films were obtained by evaporating $CHCl_3$ solutions of matrix material and solute. The sapphire disk was placed in the sample holder of a liquid helium cooled vacuum cryostat (Air Products Co., Allentown, PA). The temperature was measured with gold–chromel thermocouple.

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