

Tetraphenylcyclobutadiene Derivatives. VI.^{1a} An Investigation of the Intermediacy of Tetraphenylcyclobutadiene

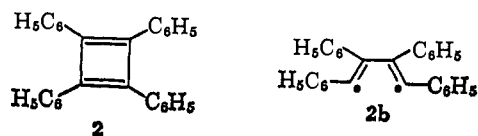
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Abstract: Tetraphenylcyclobutadiene has been postulated to be an intermediate in the pyrolysis reactions of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide (**1**). In the present work, a kinetic investigation confirmed the existence of an intermediate in these reactions, and a label-scrambling scheme established that the intermediate was a four-carbon cycle with two chemically equivalent adjacent ring bonds. While a tetraphenylcyclobutadiene structure meets these requirements, an epr study of the system revealed the presence of the 4-bromo-1,2,3,4-tetraphenylcyclobutenyl radical (**10**), another possible intermediate which fits the scrambling data. However, labeling experiments and the chemistry of the radical proved it is only a low-concentration by-product in the system. In the absence of other reasonable alternatives, tetraphenylcyclobutadiene is concluded to be the reactive intermediate in the pyrolysis of **1**. A brief investigation of the reaction of triphenylphosphine with the tetraphenylcyclobutadiene-palladium chloride complex (also reported to produce tetraphenylcyclobutadiene as a transient intermediate) indicated that the 4-chloro-1,2,3,4-tetraphenylcyclobutenyl radical could be responsible for the chemistry previously attributed by others to tetraphenylcyclobutadiene.

Cyclobutadiene and its substituted derivatives are among the relatively few simple organic molecules which have not yielded to synthesis. Cyclobutadiene chemistry, therefore, has been limited to the investigation of various systems in which cyclobutadienes appear to be generated as unstable reaction intermediates, their structure being inferred only from the products obtained.² Thus an investigation of the properties of a cyclobutadiene intermediate itself is timely. We now report a detailed investigation leading to the conclusion that the proposed intermediate from the pyrolysis of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide (**1**) has symmetry properties, as well as chemical properties, which support a tetraphenylcyclobutadiene structure.

Previous communications by one of us³⁻⁵ have established that the pyrolysis of **1** in the presence of various reagents leads to products which are consistent with the assumption that a tetraphenylcyclobutadiene-like species (**2** or **2b**) is an intermediate in the reaction. This chemistry is summarized in Figure 1. Our current investigation of this presumed intermediate embodies a



kinetic study of the pyrolysis reaction to establish the

(1) (a) Part V: H. H. Freedman and A. M. Frantz, Jr., *J. Am. Chem. Soc.*, **84**, 4165 (1962). (b) Author to whom inquiries may be addressed at the Michigan Technological University, Houghton, Mich. 49931.

(2) It is significant that even R. Criegee in his monumental study of the chemistry of tetramethylcyclobutadiene summarizes a review of his findings with the statement, "Moreover, all the reactions can be interpreted by assuming a mechanism involving products similar to cyclobutadiene, but not cyclobutadiene itself." (*Angew. Chem. Intern. Ed. Engl.*, **1**, 577 (1962)). In the light of this and similar conclusions by equally skilled investigators, it will be of interest to see if the most recent claim for the proof of existence of free cyclobutadiene (L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965)) will stand the test of time.

(3) H. H. Freedman, *ibid.*, **83**, 2194 (1961).

(4) (a) H. H. Freedman, *ibid.*, **83**, 2195 (1961); (b) G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *ibid.*, **86**, 4725 (1964); P. J. Wheatley, *J. Chem. Soc.*, 3136 (1965).

(5) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

existence of an intermediate, a label-scrambling scheme to probe its symmetry, and an epr and chemical examination of the radicals found to be present in the system.

Kinetics

In the absence of other reactants, the pyrolysis of **1** leads to a dimer of **2**, octaphenylcyclooctatetraene (**6**).⁴ The results of a kinetic study of this decomposition, in which the rates were followed by monitoring the methyl peak of **1** in the nmr spectrum, are shown in Table I.

Table I. Kinetic Data for the Pyrolysis Reactions of **1**

Reaction	Solvent	Temp, °C	Rate constant
			× 10 ⁴ sec ⁻¹
1 → 6	Benzonitrile	99.9	0.199
		122.4	1.13
		135.8	3.39
		146.4	7.50
1 → 6	Triglyme	129 ± 1	1.4
		143 ± 1	5.3
1 + 7.5 mol of DM ^a → 4	Bromobenzene	147.2	10.1
1 + 13 mol of DM ^a → 4	Bromobenzene	146.0	8.5

^a DM = dimethyl maleate.

An example of a typical first-order plot of the rate data and the Arrhenius activation energy curve are shown in Figures 2 and 3, respectively. The reaction displays first-order kinetics in spite of the fact that the product **6** is formed from 2 mol of **1**. To reconcile these two facts, one must postulate that an intermediate is formed in the rate-determining step, which in a subsequent fast step reacts either with itself or with **1** to produce **6**. Three additional bits of information about the reaction may be gleaned from the kinetic data. First, the activation energy (24 kcal/mol) is too low for the rate-determining process to be simply homolytic cleavage of the tin-carbon bond of **1**. Such a process would have an activation energy at least as large as the energy of the

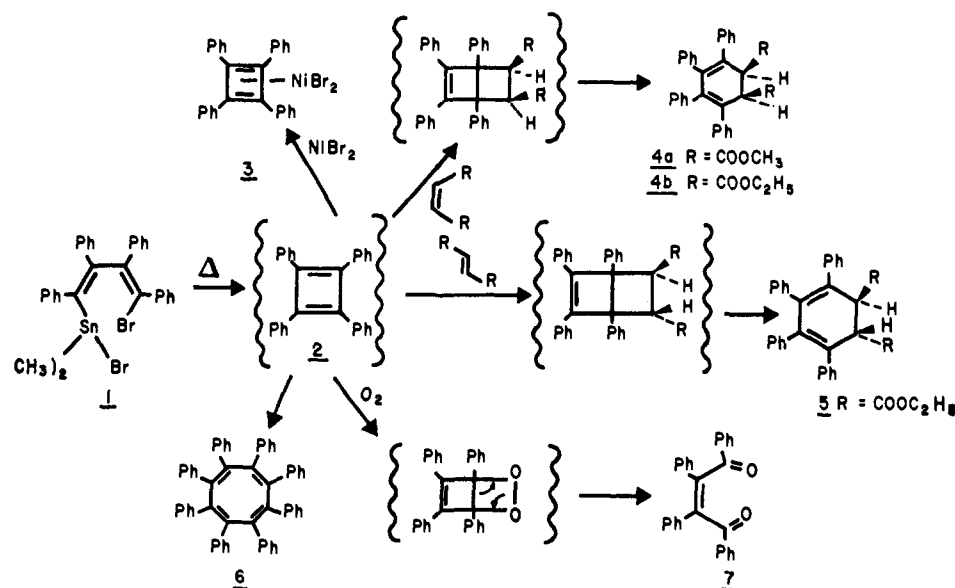


Figure 1. Chemistry of "tetraphenylcyclobutadiene."

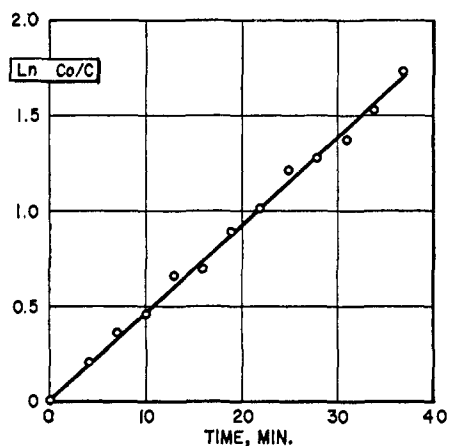


Figure 2. First-order plot of data from the pyrolysis of 1 at 146.4° in benzonitrile.

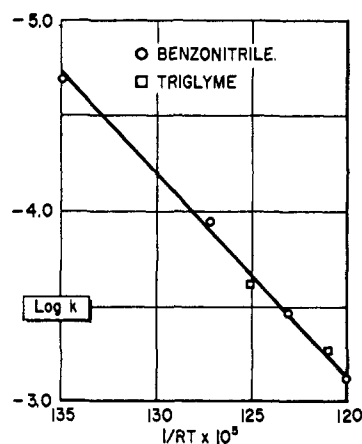


Figure 3. Arrhenius plot of first-order rate data from the pyrolysis of 1.

carbon-tin bond,⁶ about 50 kcal/mol. Second, the frequency factor ($3 \times 10^9 \text{ sec}^{-1}$) is considerably lower than that of most unimolecular reactions (10^{13} sec^{-1}), signifying a loss of entropy in going from 1 to the transition state,⁷ and suggesting that a cyclic transition state may be involved. Third, the insensitivity of the rate of the reaction to solvent polarity indicates that there is little charge separation in the transition state, and therefore the rate-determining step is not an ionic reaction.

The pyrolysis of 1 in the presence of dimethyl maleate to give dimethyl *cis*-1,2-dihydro-3,4,5,6-tetraphenylphthalate (4a) was also examined kinetically (see Table I). This reaction was found to be zero order in maleate and first order in 1. The near identity of the rate constant with that for the pyrolysis of 1 leaves little doubt that these two reactions have a common rate-determining step, the formation of a reactive intermediate.

(6) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co. (Publishers), Ltd., London, 1965, p 248.

(7) B. G. Gowenlock, *Quart. Rev.* (London), 14, 133 (1960).

Symmetry of the Intermediate

Having substantiated the presence of a reactive intermediate (or intermediates), we now turn to an investigation designed to probe its symmetry properties. Since the products from the several reactions noted in Figure 1 can plausibly arise from either a cyclic (2) or open-chain (2b) intermediate, a label-scrambling scheme which would distinguish between these alternatives was carried out.

The necessary labeling was accomplished by lithium codimerization of an equimolar mixture of diphenylacetylene and *p,p'*-dideuteriodiphenylacetylene,⁸ followed by reaction of the resulting dianion with dimethyltin dichloride to yield 1,1-dimethyl-2,3,4,5-tetraphenylstannole⁹ (0) having a statistical distribution of *p*-deuteriophenyl groups as shown in Figure 4. Treatment of 0 with 1 mol of bromine yielded labeled 1a, which upon heating in the presence of oxygen afforded

(8) W. Schlenk and E. Bergmann, *Ann.*, 463, 71 (1928); L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 63, 1184 (1941).

(9) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, 82, 5099 (1960).

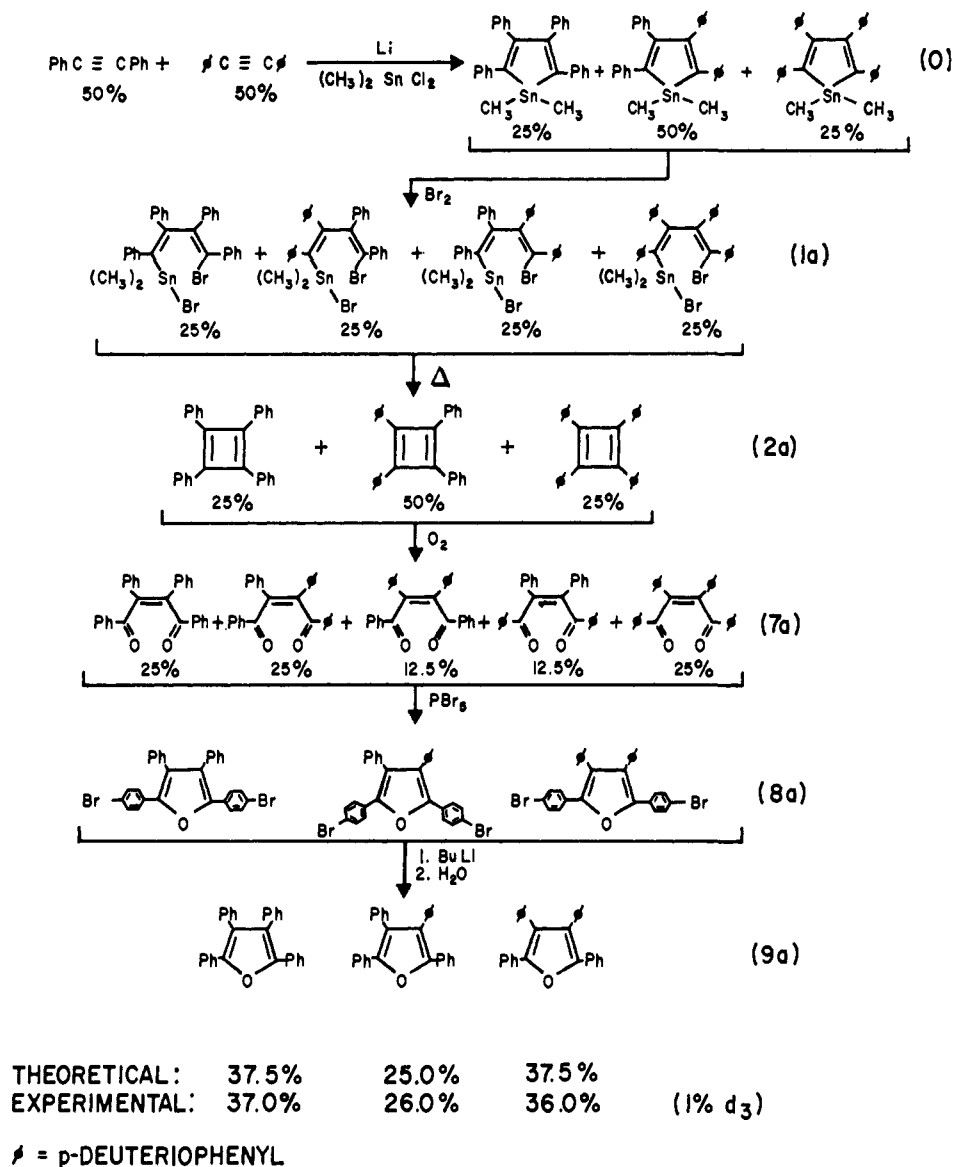


Figure 4. Scheme for investigation of the symmetry of the "tetraphenylcyclobutadiene intermediate."

cis-dibenzoylstilbene (**7a**). At this point the label distribution depends upon the structure of the intermediate: if the intermediate is a four-carbon cycle which reacts with oxygen in such a manner that any two adjacent ring bonds rupture with exactly equal facility to give products,¹⁰ as would be the case with intermediate **2a**, then the product, **7a**, should consist of the five different label distributions shown in Figure 4. Identification of the labeled positions was accomplished by treating **7a** with phosphorus pentabromide to affect concurrent reduction and bromination to 2,5-di(*p*-bromophenyl)-3,4-diphenylfuran (**8a**),¹¹ thus removing deuterium from the 2- and 5-phenyl groups. Treatment of **8a** with excess butyllithium followed by hydrolysis with water replaced the bromines with hydrogen, yielding tetraphenylfuran (**9a**) in which the proportions of

(10) Because the labeled phenyl groups in the dilabeled fraction of **1a** are equally divided between the 1,2 and 3,4 positions, any four-membered ring intermediate in which two adjacent ring bonds become chemically equivalent will give the same label scrambling results as that of an intermediate in which all four ring bonds are equivalent.

(11) C. F. Wilcox and M. P. Stevens, *J. Am. Chem. Soc.*, **84**, 1258 (1962).

non- (d_0), mono- (d_1), and dideuterated (d_2) material are predetermined by the symmetry properties of the intermediate. A cyclic intermediate such as **2a** requires 37.5% d_0 , 25% d_1 , and 37.5% d_2 while an open-chain intermediate would lead to a deuterium distribution of 25% d_0 , 50% d_1 , and 25% d_2 . Mass spectrometric analysis of **9a** yielded $37 \pm 4\%$ d_0 , $26 \pm 4\%$ d_1 , $36 \pm 4\%$ d_2 , and $1 \pm 4\%$ d_3 ,¹² in complete agreement with a cyclic intermediate.

The scheme presented thus far does not identify the step in which the cyclic intermediate occurs. Though most of the reactions other than the pyrolysis of **1a** are straightforward and would not be expected to lead to scrambling of the label, the dimerization of diphenylacetylene with lithium⁸ leads to a dilithio compound

(12) The spectra were run on a Modified Bendix Model 12 time-of-flight mass spectrometer. We are indebted to Roland S. Gohlke for assistance in obtaining the mass spectra. The error limits in the analysis are an estimate of the possible inaccuracy, due to incomplete resolution of the 372–375 mass peaks. Precision was much better, the average deviation from five traces being $\pm 1\%$. The small amount of d_3 reported may not be real since its determination involves the difference between two relatively large numbers. The d_3 compound could arise, however, from incomplete bromination of **7a**.

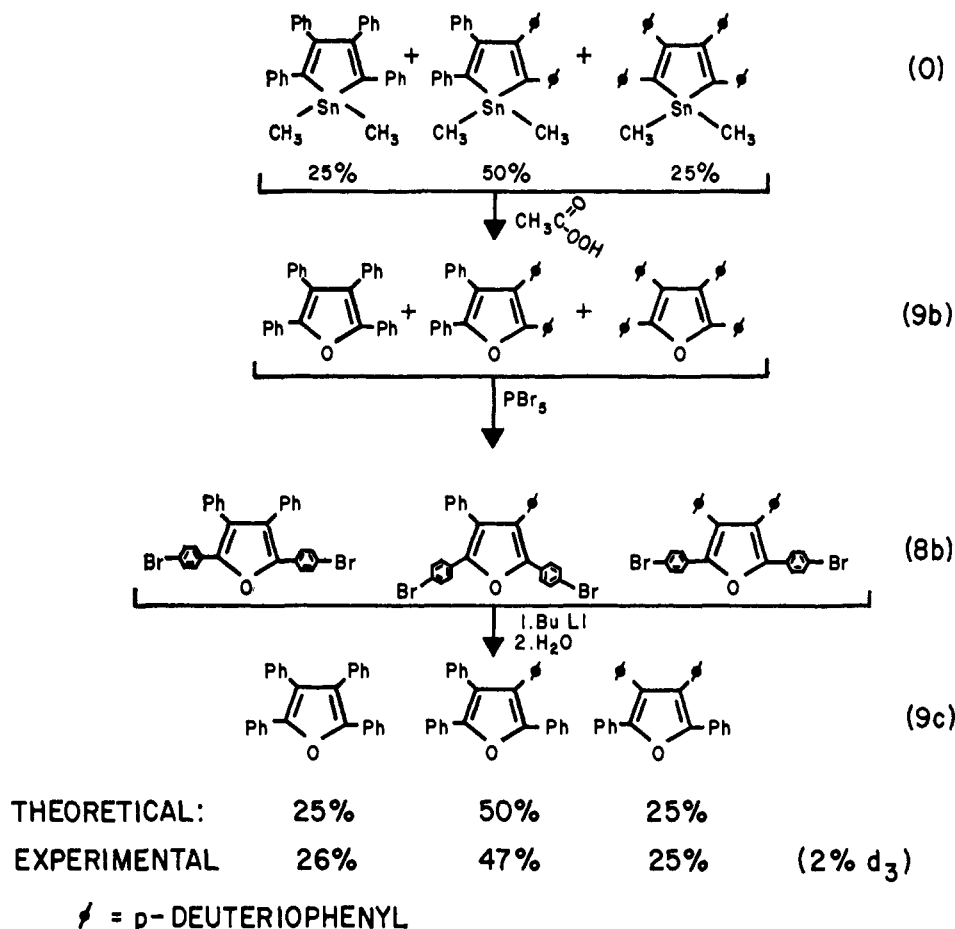


Figure 5. Scheme for identification of the label-scrambling reaction.

which is not well characterized,¹³ and perhaps label scrambling could occur in this step. To eliminate this possibility, part of the same sample of **0** used in the previous scheme was treated with peracetic acid in methylene chloride (see Figure 5) to give a small yield of **9b**, which was subsequently converted to **8b** by heating at 100° with phosphorus pentabromide in phosphorus oxychloride.¹⁴ Replacement of the bromines with hydrogen as before led to **9c** labeled in the ratio of 26 ± 4% d₀, 47 ± 4% d₁, 25 ± 4% d₂, and 2 ± 4% d₃, consistent with the theoretical values for the absence of phenyl scrambling. Thus the only logical reaction in which a cyclic intermediate could arise is the thermal decomposition of **1**.

Electron Paramagnetic Resonance Study

If the intermediate were tetraphenylcyclobutadiene, it might have a triplet ground state or a thermally populated triplet excited state. With this in mind, an epr study of the decomposition of **1** was undertaken. In a specially designed quartz sublimation apparatus capable of being fitted into an epr sample cavity, **1** was sublimed onto a liquid nitrogen cooled cold finger by heating the sample at 150° under a pressure of less than 10⁻³ torr. While the sublimate exhibited no epr signal with a spectroscopic splitting factor (*g* value) of 4¹⁵ and

thus gave no evidence for a triplet tetraphenylcyclobutadiene intermediate, it did show a low intensity, broad resonance line in the *g* = 2 region of the spectrum. When a sample of **1** was heated in tetrahydrofuran (THF) at 150° for 2 min and then cooled quickly in an ice bath, the spectrum shown in Figure 6a was obtained. The *g* of this radical was 2.0037, indicating spin density on a heteroatom.¹⁶ Upon further heating of the sample the epr spectrum broadened, then sharpened again to give the spectrum shown in Figure 6d,¹⁷ in which the *g* value of 2.0027 is in the range of most hydrocarbon radicals and radical ions.

The first radical (Figure 6a) was identified as the 4-bromo-1,2,3,4-tetraphenylcyclobutenyl radical (**10**)¹⁸ by the identity of its epr spectrum with that of an authentic sample of **10** prepared by treating 3,4-dibromo-1,2,3,4-tetraphenylcyclobutene¹⁹ (**11**) with mercury (eq 1 and Figure 6b). Apparently the unpaired electron is delocalized chiefly over the 1,3-phenyl rings inasmuch as the experimental spectrum can be closely matched by one calculated assuming interaction with six protons

(15) J. H. van der Waals and M. S. deGroot, *Mol. Phys.*, **2**, 333 (1959); **3**, 190 (1960).

(16) M. S. Blois, Jr., H. W. Brown, R. M. Lemmon, R. O. Lindblom, M. Weissbluth, Ed., "Free Radicals in Biological Systems," Academic Press Inc., New York, N. Y., 1961, p 117 ff.

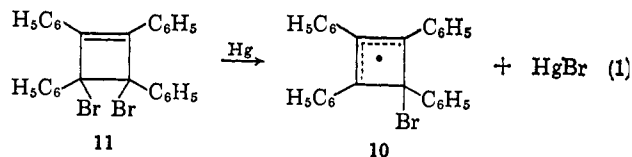
(17) This spectrum had been observed previously by D. Hollis at Varian Associates and B. Loy of The Dow Chemical Company.

(18) We thank B. Loy of the Physical Research Laboratories, The Dow Chemical Company, Midland, Mich., for suggesting that this radical might be formed in the pyrolysis of **1**.

(19) H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964).

(13) H. E. Zimmerman (private communication to V. R. S.) has speculated that this dianion could possibly be the Hückel aromatic tetraphenylcyclobutadiene dianion. If this were true, label scrambling would already have occurred in the synthesis of **1a**.

(14) For the analogous reaction with phosphorus pentachloride see R. E. Lutz and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **85**, 755 (1963).

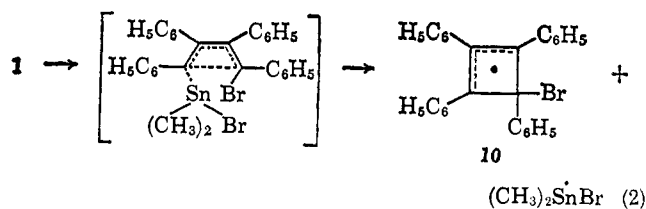


(the *ortho* and *para* protons of the 1,3-phenyls) with a hyperfine splitting constant of 2.94 G and four protons (*meta*) with splitting constant of 0.94 G (Figure 6c). This deep green²⁰ radical is surprisingly stable and its epr signal persists even after standing for more than 24 hr at room temperature in the absence of oxygen.

The radical observed upon longer heating of **1** has not been identified. Its epr spectrum can be interpreted as 13 lines of 1.7-G separation, further split into 9 lines of 0.85 G (Figure 6e). This interpretation assumes sets of 12 and 8 protons, respectively, interacting with the unpaired electron. Either the tetraphenylcyclobutadiene radical cation or anion could give such a spectrum if $a_{ortho} \approx a_{para} \approx 1.7$ G and $a_{meta} \approx 0.85$ G.²¹ In our system the radical cation would be more likely to be present since it could arise by ionization of **10**, a reaction which would be facilitated by the known ionizability of the halogen¹⁹ and the presence of a weak Lewis acid, dimethyltin dibromide.²²

Examination of the Role of the Radical 10

Since the radical **10** has been shown to be present in the pyrolysis of **1**, is it still logical to presume that tetraphenylcyclobutadiene is an intermediate in this reaction, or can the chemistry be explained solely by the presence of **10**? If **10** is formed in the rate-determining step, concerted Sn-C bond cleavage and ring formation (eq 2) must occur in order to account for the low activation energy (24 kcal/mol) observed for decomposition of **1**. Although there appears to be no precedent for anchimeric assistance in a radical-forming reaction,²³ such a process is not unreasonable. The cyclic transition state involved would also be consistent with the low fre-



quency factor. Thus the kinetic data are in accord with the assumption that **10** is the intermediate from the decomposition of **1**. Furthermore, two adjacent ring bonds of the allylic radical are equivalent in **10**, thus satisfying the label scrambling results. To shed further light on the question of the intermediacy of **10**, some of its chemistry was investigated.

Upon warming a triglyme solution of **11** with mercury in a nitrogen atmosphere, only a 1.5% yield of octaphenylcyclooctatetraene (**6**) was obtained. When **10**

(20) The transient green color in the pyrolytic decomposition of **1** was cited earlier^{4a} as evidence for the presence of a diradical species. This color, however, is undoubtedly due to the presence of **10**.

(21) This interpretation of the spectrum was suggested by L. C. Snyder of the Bell Telephone Laboratories (private communication).

(22) D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1610 (1961); G. Tagliavini and P. Zanella, *J. Organometal. Chem.* (Amsterdam), **5**, 299 (1966).

(23) C. G. Overberger and H. Gainer, *J. Am. Chem. Soc.*, **80**, 4561 (1958); J. A. Berson, C. J. Olsen, and J. S. Walia, *ibid.*, **84**, 3337 (1962).

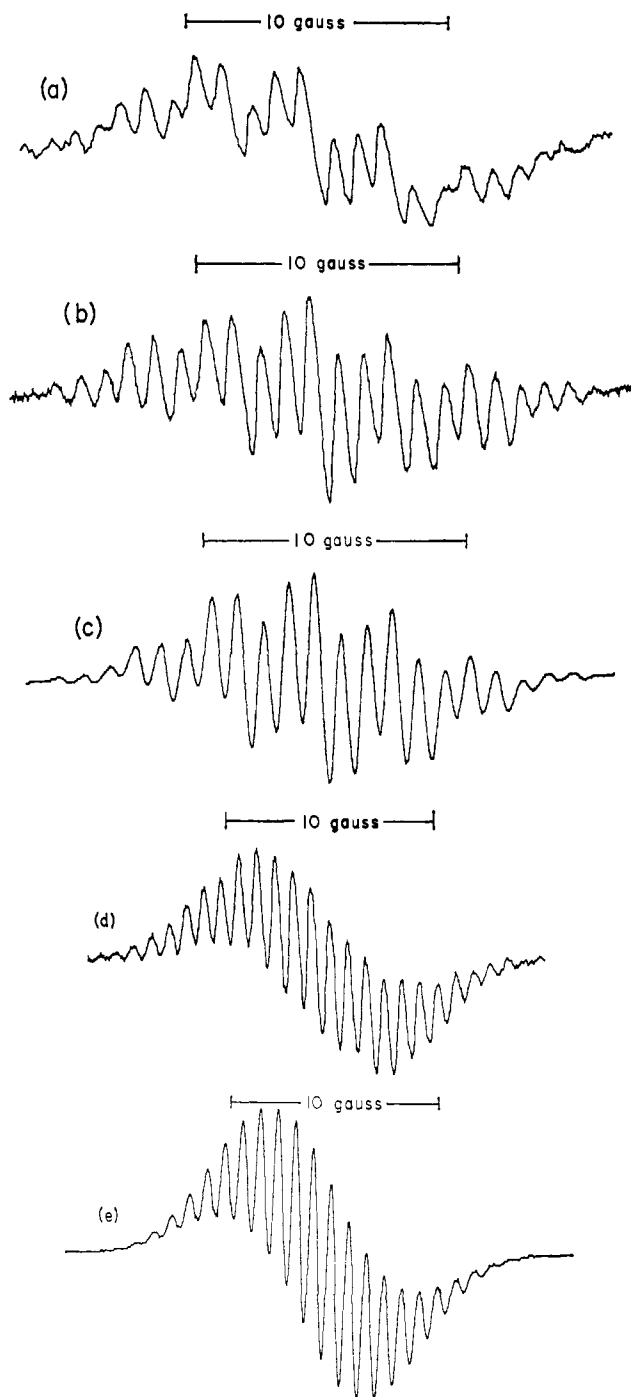


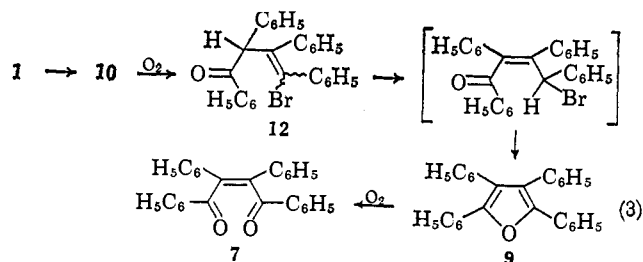
Figure 6. Epr spectra of radicals involved in the pyrolysis of **1**. (a) Radical found by heating **1** at 150° for 2 min. (b) Bromo radical **10** prepared by treating **11** with Hg. (c) Calculated spectrum using the following parameters: 6 H's, $a = 2.94$ G; 4 H's, $a = 0.94$ G; and derivative line width of 0.65 G. (d) Unidentified radical from prolonged heating of **1** at 150°. (e) Spectrum calculated by assuming 12 H's, $a = 1.7$ G; 8 H's, $a = 0.85$ G; and a line width of 0.65 G.

is formed in the pyrolysis of **1**, however, an equivalent amount of trivalent tin must also be produced, and this could influence the fate of **10**. In order to approximate this system a mixture of **11** and hexamethylditin in triglyme was treated with mercury, producing a 36% yield of **6**.

The intermediacy of **10** in this reaction was further investigated by a labeling technique. Tetradeuterated **10** was generated in about 1% conversion by allowing

a solution of 3,4-dibromo-1,2,3,4-tetra-(*p*-deuterio-phenyl)cyclobutene (**11-d₄**) to flow through a column of finely divided silver at a constant rate such that about 6×10^{-5} mmol of radical was produced per minute. The green effluent from the column was directed into a flask containing a solution of **1** at 142°. If **10** is an intermediate in the decomposition of **1**, **10-d₄** should be incorporated into the cyclooctatetraene **6**. Mass spectrometric analysis showed this product to contain $91.7 \pm 0.3\%$ *d*₀, $4.6 \pm 0.1\%$ *d*₄, and $3.5 \pm 0.1\%$ *d*₈. A blank run without Ag in the column yielded only **6-d₀**, eliminating the possibility that the deuterium incorporation resulted from the dibromocyclobutene, **11-d₄**. The quantity of **6-d₈** in the product was surprising and raises the possibility that tetraphenylcyclobutadiene-*d*₄ was also generated in the Ag column and is the source of **6-d₄**. If the cyclobutadiene has a half-life of approximately 1 min, slightly more than the time it took for the solution in contact with the Ag to flow into the reaction flask (~45 sec), the above data can be rationalized. However, in a similar deuteration experiment in which a long capillary was interposed between the Ag column and the reaction vessel to increase the time lag to about 15 min, the product **6** was essentially unchanged, being 89% *d*₀, 6.2% *d*₄, and 3.2% *d*₈. Thus it is apparent that the **6-d₈** is formed in the Ag column and the **6-d₄** arises from a relatively stable intermediate. It is logical at this point to accept that either the radical **10** is an intermediate in the formation of **6** from **1** or that it is in equilibrium with such an intermediate. However, the question as to whether **10** alone can satisfy all the chemistry attributed to tetraphenylcyclobutadiene remained unanswered and was explored further.

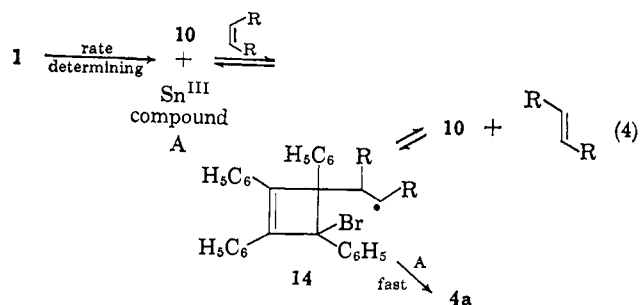
The reaction of **10** with oxygen at 100° yielded tetraphenylfuran (**9**, ~30%), 1-bromo-1,2,3-triphenyl-3-benzoylpropene (**12**, ~20%),¹ and *cis*-dibenzoylstilbene (**7**, ~10%). Pyrolysis of **1** at 150° in the presence of oxygen gives only one oxidation product, **7**.^{4a,24} Thus if **10** were the intermediate in both reactions, **9** and **12** must be converted to **7** in the pyrolytic oxidation of **1** as shown in eq 3. The presence of **9** in the reaction sequence was tested by heating an equimolar mixture of **9-d₂** and **1** at 150° in oxygen. The product was a mixture of **7-d₀** and **9-d₂** only, eliminating **9** as a possible intermediate in the pyrolytic oxidation of **1**. Since oxidation of the radical **10** gives **9**, **10** likewise cannot be an intermediate in this reaction.



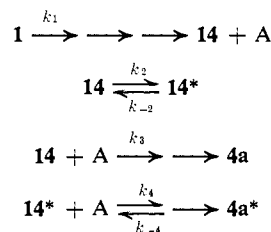
The reaction of **10** with dimethyl maleate to give dimethyl fumarate as the only isolable product is further evidence that this intermediate plays only an incidental role in the pyrolysis reactions of **1**. By contrast, the intermediate formed in the pyrolysis of **1** adds stereo-

(24) It was not expedient to study these two reactions at the same temperature because the radical precursor **11** undergoes electrocyclic ring opening at the higher temperature.

specifically to dimethyl maleate to give an almost quantitative yield of dimethyl *cis*-1,2-dihydro-3,4,5,6-tetraphenylphthalate^{4a} (**4a**). In less hindered systems such stereospecificity has been interpreted as indicating a single-step mechanism (cyclic transition state) in which spin inversion is not necessary.²⁵ Whereas a Diels-Alder addition of the dienophile to (singlet) tetraphenylcyclobutadiene would be expected to be stereospecific, radical additions to double bonds are usually nonstereospecific.²⁶ However, there is the possibility that steric crowding could produce rotational barriers in our system such that even a two-step radical addition to dienophile would be stereospecific. For example, consider the reactions shown in eq 4. If the



reaction of the Sn^{III} fragment A with the radical adduct **14** to form ring-closed products were fast compared to rotation about the bond adjacent to the radical site in **14**, stereospecific product would be obtained. In order to determine whether or not this process is reasonable, consider the following kinetic scheme which embodies only those steps necessary to obtain **4a** via the adduct **14**



where k_1 identifies the rate-determining step, A is a reducing agent necessary to remove the bromine, and $\mathbf{14} \rightleftharpoons \mathbf{14}^*$ signifies rotation about the bond adjacent to the radical site to give dimethyl *trans*-1,2-dihydro-3,4,5,6-tetraphenylphthalate (**4a***). The series of arrows signify more than one reaction may be involved. By assuming the reaction of **14** with A is diffusion controlled,²⁷ i.e., $k_3 \approx 10^9$ l. mol⁻¹ sec⁻¹, we may place a lower limit on the rotational barrier necessary to give stereospecific products.

For the reaction to be stereospecific, the ratio of rates of reduction to rotation must be greater than 10, and we may neglect k_{-2} .

$$\frac{k_3[\text{A}][\mathbf{14}]}{k_2[\mathbf{14}]} > 10 \quad k_2 < 10^8[\text{A}]$$

Because the reducing agent A is not detected by either nmr or epr, its concentration could not exceed 0.1[**1**]

(25) P. Scheiner, *J. Am. Chem. Soc.*, **88**, 4759 (1966); L. Watts, J. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).

(26) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 362; P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964).

(27) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 494-503.

or 0.01 *M*. The maximum value k_2 would have at 146° is 10^6 sec^{-1} , and from transition-state theory we may estimate the corresponding minimum rotational barrier.

$$k_2 < \frac{kT}{h} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right)$$

$$G^\ddagger_{146^\circ} > 2.3RT \log \frac{kT}{k_2 h} = 14 \text{ kcal/mol}$$

However, since each of the assumptions was biased so as to minimize the barrier, the actual barrier required to give stereospecificity is probably considerably higher than 14 kcal/mol.

In order to determine whether a 14-kcal rotational barrier is reasonable in the radical adduct **14**, a model was constructed with Stuart-Briegleb space filling models.²⁸ Rotation about the bond in question was possible in this model. For comparison, a model of *N*-methyl-2,4,6-trinitroaniline, in which the barrier to rotation about the phenyl-nitrogen bond was calculated from the data of Heidberg, *et al.*,²⁹ to be $\Delta G^\ddagger_{146^\circ} = 10 \text{ kcal/mol}$, was also constructed. Rotation was not possible in this model. We feel confident, then, that the adduct **14** could not have a rotational barrier in excess of 14 kcal/mol, and therefore that the radical **10** is not the reactive intermediate from the decomposition of **1** which adds to dienophiles. In the absence of other reasonable alternatives,³⁰ the conclusion that this intermediate is tetraphenylcyclobutadiene seems almost inescapable.

The question of whether tetraphenylcyclobutadiene is a singlet or triplet remains unanswered. Whereas it is tempting to cite the stereospecific addition to dienophiles as evidence for a singlet intermediate, we have no way of estimating the relative rates of spin inversion *vs.* rotation in a biradical adduct of a triplet intermediate and dienophile. Likewise, the rapid reaction of tetraphenylcyclobutadiene with oxygen interpreted earlier as indicating a triplet ground state^{4a} is not definitive. Even if the ground state were a singlet, the triplet state might be sufficiently populated thermally to account for the reactivity. There is also the remote possibility that singlet oxygen may be participating in this reaction.

Mechanism of the Formation of Tetraphenylcyclobutadiene

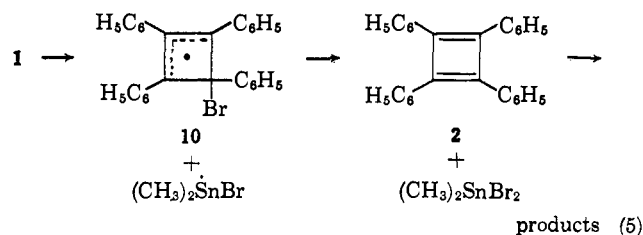
In proposing a mechanism for the pyrolysis reactions of **1**, we must explain the presence of the bromo radical

(28) An sp^2 carbon was used for the trivalent carbon.

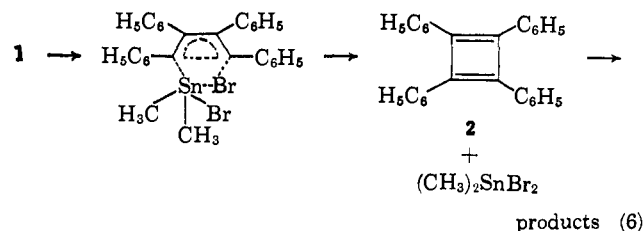
(29) J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

(30) A referee has pointed out that the 4-bromo-1,2,3,4-tetraphenylcyclobutenyl cation and anion have not been considered as possible intermediates, though they satisfy the symmetry requirements imposed by the label-scrambling scheme. The cation is easily eliminated in that it has been prepared as a stable species, and its chemical properties bear little resemblance to those expected of tetraphenylcyclobutadiene (see ref 1 and R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964)). Likewise, the chemistry in Figure 5 does not fit an anionic intermediate. Such an intermediate, for example, would be expected to add to the carbonyl of maleic and fumaric esters rather than the double bond. Stannole dibromide (**1**) also reacts smoothly with such anionoid reagents as methyl Grignard and butyllithium to yield 4-bromo-1,2,3,4-tetraphenylbutadienyltrimethyltin and 1,1-dimethyl-2,3,4,5-tetraphenylstannole, respectively (unpublished results of G. A. Dorakian, H. H. Freedman, and V. R. Sandel). The inability of organotin compounds to undergo addition reactions with carbonyl compounds indicates that heterolytic cleavage of the carbon-tin bond to give carbanions does not occur (R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960)).

10 and the incorporation of the organic portion of this radical into the products, as well as satisfy the kinetics and chemistry. The obvious mechanism in which the radical **10** is reduced to tetraphenylcyclobutadiene (eq 5) is not satisfactory. It is hardly conceivable that in



the reaction with oxygen either the radical **10** or the Sn^{III} fragment would survive long enough to react with each other. On the other hand, a concerted ring closure and elimination of dimethyltin dibromide (eq 6) has the merit of simplicity and does not suffer from the above deficiency. This process is reminiscent of the α elimination of organomercury halides³¹ and organosilicon³² and organotin³³ fluorides to form halocarbenes. A bimolecular elimination of trimethyltin



iodide has also been reported.³⁴ If the elimination of dimethyltin dibromide from **1** is a concerted process, then the bromo radical **10** must arise from a competing reaction or from a side reaction of the tetraphenylcyclobutadiene. In spite of the simplicity of this mechanism, we prefer the one presented below which more easily encompasses all of the observed phenomena.

Recent findings in this laboratory have suggested that sterically hindered or strained 1,3-dienes which are constrained to an approximately cisoid conformation may thermally equilibrate with their cyclobutene valence tautomers.³⁵ Spectroscopic and X-ray evidence indicates that **1** exists in such a cisoid conformation³⁶ and we thus propose that the rate-determining step in the pyrolysis of **1** is electrocyclic closure to form cyclobutene **17** (eq 7), followed by ionization of the bromine to form the resonance-stabilized cyclobutenium ion **17a**. Nucleophilic displacement on tin by the bromide ion completes the elimination of dimethyltin dibromide to form tetraphenylcyclobutadiene.³⁷ Thus we would explain

(31) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid.*, **87**, 4259 (1965).

(32) G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Commun.*, 382 (1965).

(33) H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960).

(34) D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organometal. Chem. (Amsterdam)*, **2**, 417 (1964).

(35) (a) H. H. Freedman and G. A. Doorakian, Abstracts of Papers, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, S122; (b) R. F. Bryan and H. H. Freedman, results to be published.

(36) F. P. Boer, J. Flynn, H. H. Freedman, S. V. McKinley, and V. R. Sandel, *J. Am. Chem. Soc.*, **89**, 5068 (1967).

(37) β eliminations, while common with silicon, apparently have not been observed in organotin chemistry. There is, however, ample precedent for the processes reported here. Halocyclobutenes ionize readily

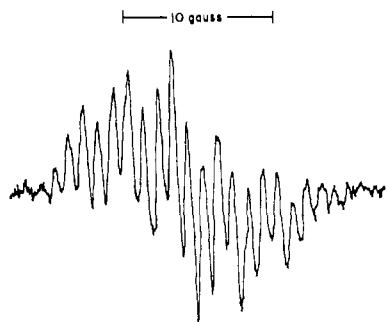
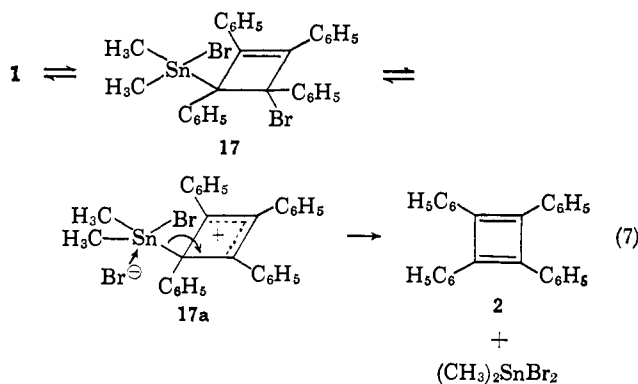
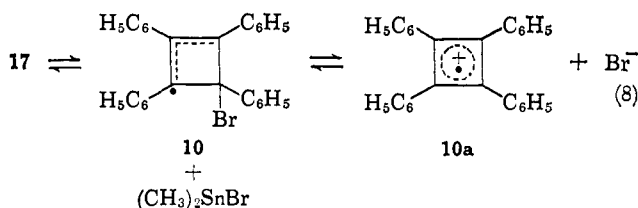


Figure 7. Epr spectrum of radical produced by treating the tetraphenylcyclobutadiene–palladium dichloride complex with triphenylphosphine.

all the pyrolysis reactions on the basis of a cyclobutadiene intermediate.



In order to account for the presence of the radical **10** in the system, we postulate that the cyclobutene **17** undergoes a slower homolytic cleavage of the carbon–tin bond. If this process were reversible, we could account for the incorporation of deuterium from the radical **10-d₄** into the pyrolysis products of **1**. Another more plausible way of explaining the deuterium incorporation, however, is to assume that the radical **10** is converted to the tetraphenylcyclobutadiene radical cation (**10a**) in the pyrolysis mixture as previously suggested. This then could undergo very rapid electron exchange with tetraphenylcyclobutadiene in the medium (eq 8).



Comments on Earlier Literature

Several other reactions have been reported to produce tetraphenylcyclobutadiene and products derived from it.^{38–41} Of these, the only one which gives good yields

and nucleophilic displacement on tin by halide ion is well known. A somewhat analogous δ elimination has been reported by F. M. Rabel and R. West (*J. Am. Chem. Soc.*, **84**, 4169 (1962)).

(38) (a) P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 330 (1962); (b) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); (c) P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965).

(39) E. H. Braye, W. Hubel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

(40) J. F. McOmie and B. K. Bullimore, *Chem. Commun.*, 63 (1965).

of products attributable to tetraphenylcyclobutadiene is the apparent displacement of this species from its palladium chloride complex by phosphines and phosphites, reported first by Maitlis and Stone,^{38a} and then by Cookson, *et al.*^{41a} Both authors report the presence of radicals in their systems and the latter authors also published an epr spectrum. Although both groups claim that the radical is related to tetraphenylcyclobutadiene, neither considers the possibility that it is the radical rather than the cyclobutadiene which gives rise to the observed products.

We have also generated this radical from the reaction of triphenylphosphine with the tetraphenylcyclobutadiene–palladium chloride complex and obtained the spectrum shown in Figure 7 with a *g* value of 2.0027. This spectrum differs from that published by Cookson and Jones^{41a} but is identical with that obtained by Maitlis and Stone.⁴² The unsymmetrical nature of Cookson's spectrum suggests that it is due to more than one radical.

An epr spectrum identical with that in Figure 7 was also obtained by warming 3,4-dichloro-1,2,3,4-tetraphenylcyclobutene with mercury. The method of preparation suggests that this is the 4-chloro-1,2,3,4-tetraphenylcyclobutenyl radical (**18**). The spectrum may be rationalized, and duplicated theoretically, by assuming small couplings from the cross-conjugated phenyl in addition to those in the corresponding bromo radical **10**. If the chemical properties of **18** were similar to those of the corresponding bromo radical **10**, the products resulting from the treatment of the tetraphenylcyclobutadiene–palladium chloride complex with phosphines could easily be explained on the basis of this radical being the reactive intermediate. In the presence of oxygen this reaction has been reported to yield tetraphenylfuran,^{38a,41a} the main product also obtained from the bromo radical **10** under similar conditions, whereas the pyrolysis of **1** in oxygen yields *cis*-dibenzoylstilbene. Although Cookson's assumption that this difference is due to reduction of a peroxide precursor of *cis*-dibenzoylstilbene by the phosphine may still be correct, it is superfluous.

Cookson and Jones^{41a} have also reported the addition of the elements of tetraphenylcyclobutadiene to cyclopentadiene and to methyl phenylacetylenecarboxylate to yield an adduct, C₃₃H₂₈, and methyl pentaphenylbenzoate, respectively. Admittedly these appear to be Diels–Alder reactions, but it is quite conceivable that the products could arise *via* the chloro radical **18** by a mechanism similar to that postulated earlier for the intermediacy of the bromo radical **10**. The arguments used previously in eliminating **10** as an intermediate in our Diels–Alder reactions are not applicable to the results of Cookson and Jones. The role of radicals in the decomposition of tetraphenylcyclobutadienyl–metal halide complexes will be discussed further in a later publication.

Beynon, Cookson, *et al.*,^{41b} have investigated the thermal decomposition of tetraphenylcyclobutadiene–palladium dichloride complex in the mass spectrom-

(41) (a) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965); *Proc. Chem. Soc.*, 115 (1963); (b) J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams, *J. Chem. Soc.*, 7052 (1965).

(42) We thank Professor Maitlis for providing a copy of this spectrum.

eter. They reported pertinent peaks at masses 426, $[C_4(C_6H_5)_4Cl_2]^+$; 391, $[C_4(C_6H_5)_4Cl]^+$; 356, $[C_4(C_6H_5)_4]^+$; and 178, $[C_2(C_6H_5)_2]^+$; and possibly $[C_4(C_6H_5)_4]^{2+}$.⁴³ In the presence of water vapor and oxygen, the peaks at 391 and 426 were replaced by peaks at 372 and 388, indicating reaction to form tetraphenylfuran and *cis*-dibenzoylstilbene. From these data they conclude that "monomeric tetraphenylcyclobutadiene has, therefore, been produced in the gas phase." If tetraphenylcyclobutadiene is the primary product of this reaction, it is not clear how the authors justify the mass peaks at 391 and 426. Blomquist and Maitlis^{38b} reported the pyrolysis of the same complex in a vacuum-sublimation apparatus to yield a greenish black sublimate from which a 26% yield of 1,4-dichloro-1,2,3,4-tetraphenylbutadiene was isolated. Their description of the reaction suggests that the primary products could be chloro radical **18** (the green color) and dichlorocyclobutene. The mass spectrum of Beynon and Cookson is in complete accord with this thesis. The origin of the halogen-containing 391 and 426 peaks is obvious and their replacement by 372 and 388 peaks in the presence of water vapor and oxygen is expected since the hydrolyses of the dihalocyclobutenes give rise to tetraphenylfuran and *cis*-dibenzoylstilbene.⁴⁴ The reaction of **18** with oxygen should also give tetraphenylfuran. The abundant 356 ion is probably a daughter ion from the 391 and 426 peaks since both *cis,cis*-1,4-dichloro-1,2,3,4-tetraphenylbutadiene and *cis,cis*-1,4-dibromo-1,2,3,4-tetraphenylbutadiene exhibit large 356 peaks in their mass spectra as well.⁴⁴ Thus the conclusion that tetraphenylcyclobutadiene is an intermediate in this pyrolysis is totally unwarranted.

Similarly, the reported pyrolysis of tetraphenylcyclopentadienone at 300° to give tetraphenylcyclobutadiene in the mass spectrometer⁴⁵ seems unlikely. McNelis⁴⁶ studied this pyrolysis on a preparative scale and found no evidence for a tetraphenylcyclobutadiene intermediate.

Conclusions

Until tetraphenylcyclobutadiene is isolated and characterized, one can never be certain that it exists. However, the balance of evidence favors its presence as an unstable intermediate in the pyrolysis of the stannole dibromide **1**. The case for its generation by displacement from its palladium chloride complex is clouded by the presence of a radical which could have chemical properties in this system similar to that of tetraphenylcyclobutadiene.

Experimental Section

Kinetic Experiments. The kinetics of the decomposition of **1** were followed by observing the decrease in integrated intensity of the methyl peak in the nmr spectrum with time. Each sample contained a small amount of either ethylene dibromide or aceto-

(43) Beynon, Cookson, *et al.*, were not able to distinguish between the contribution of $[C_4H_10]^+$ and $[C_2H_2]^{2+}$ to the 178 mass peak (ref 41b). If $[C_2H_2]^{2+}$ contributes significantly, however, a 178.5 peak corresponding to the 357 doubly charged ion would have to be present. Since no 178.5 mass peak was reported, we assume it must have been less than 2%. This would limit the maximum contribution of $[C_4(C_6H_5)_4]^{2+}$ to the 178 peak to 6%.

(44) Unpublished data of H. H. Freedman, G. A. Doorakian, and V. R. Sandel.

(45) J. H. Beynon, R. F. Curtis, and A. E. Williams, *Chem. Commun.*, 237 (1966).

(46) E. McNelis, *J. Org. Chem.*, **30**, 4324 (1965).

nitrile as a nonreactive internal standard, and throughout each run the integrations were normalized to a constant value for the intensity of the standard. The benzonitrile and bromobenzene solvents used in the experiment were Eastman Kodak White Label grade and were used without further purification. The triglyme solvent was dried over calcium hydride and distilled before use. The reactions were carried out by placing sealed nmr tubes containing the reaction solution into a constant temperature bath for a specified period, plunging them directly from the constant temperature bath into ice water, and then carrying out the nmr measurements at 38.5°. The first-order rate constants and activation energy were calculated from the data by least-squares techniques.

Preparation of *p,p'*-Dideuteriodiphenylacetylene. Bibenzyl was brominated by the method of Bance, *et al.*,⁴⁷ to give 1,2-dibromo-1,2-di(*p*-bromophenyl)ethane. This was converted to *p,p'*-dibromodiphenylacetylene by the method of Fieser.⁴⁸ To a slurry of 38 g (0.113 mol) of *p,p'*-dibromodiphenylacetylene in 225 ml of anhydrous ether at 0° was added 225 ml (0.417 mol) of 1.85 *N* *n*-butyllithium in hexane over a period of 20 min. The mixture was warmed to 27° and stirred at that temperature for 1.5 hr. Then with rapid stirring, 18 ml of deuterium oxide was slowly added. The organic layer was decanted, washed with water, and evaporated. The resulting brown-yellow solid was recrystallized from ethanol and sublimed to yield 13.1 g (64%) of *p,p'*-dideuteriodiphenylacetylene, mp 59–60.5°.

Preparation of Labeled 1,1-Dimethyl-2,3,4,5-tetraphenylstannole (0). Following the published⁹ procedure, 5.54 g (0.0308 mol) of *p,p'*-dideuteriodiphenylacetylene and 5.48 g (0.0308 mol) of diphenylacetylene were dimerized with lithium metal and treated with dimethyltin dichloride to yield 8.08 g (52%) of stannole **0**, mp 189.5–191.5° (lit.⁹ mp 192–193°).

Labeled (4-Bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin Bromide (1a). Stannole **0** was brominated to yield the title compound, mp 141.5–142° (lit.⁹ mp 141–143°).

Pyrolytic Oxidation of Labeled Stannole Dibromide 1a.^{4a} Oxygen was bubbled through a solution of 1.50 g of **1a** in 12 ml of triglyme for 15 min at room temperature. While the introduction of oxygen continued, the mixture was heated to 150° and maintained at that temperature for 1 hr. Upon cooling, the reaction mixture was poured into water to yield a semisolid organic phase. After decanting the water, the organic material was taken up in methylene chloride, ethanol was added, and the solution was concentrated. Attempts to crystallize the product from this solution failed. The solution was then poured into water, and the organic material was extracted into methylene chloride. After washing the methylene chloride solution with water, it was dried and evaporated. The residue was chromatographed on a 2 × 15 cm column of silica gel. Elution with 4% methylene chloride in pentane yielded crude *cis*-dibenzoylstilbene (**7a**). Recrystallization of the product from ethanol gave 0.329 g (39%), mp 216.5–218.5° (lit.¹¹ mp 215–216°).

Reductive Bromination of Labeled *cis*-Dibenzoylstilbene (7a). The procedure was a modification of that used by Wilcox and Stevens.¹¹ A sealed ampoule containing 0.100 g of **7a**, 0.3 g of phosphorus pentabromide, and 0.7 ml of phosphorus oxychloride was heated for 7 min on a steam bath. Upon cooling, the mixture was poured onto ice. When the ice had melted, the remaining solid was filtered off and washed successively with water and with 2 ml of ethanol. After three recrystallizations from ethanol, 0.115 g of 2,5-di(*p*-bromophenyl)-3,4-diphenylfuran (**8a**), mp 197–198° (lit.¹¹ mp 192°), was obtained.

Removal of Bromine from Labeled 2,5-Di(*p*-bromophenyl)-3,4-diphenylfuran (8a). To a stirred suspension of 0.115 g of **8a** in 8 ml of ether was added 0.4 ml of 1.61 *N* *n*-butyllithium in hexane. After stirring for 1 hr at room temperature, the mixture was hydrolyzed with water. The ether layer was separated, dried, and evaporated. The residue was chromatographed using a 2 × 11 cm column of silica gel slurry packed with 2% methylene chloride in hexane. The column was eluted with varying concentrations of methylene chloride in hexane. The **8a** came off the column with 10% methylene chloride in hexane and was recrystallized three times from ethanol to give a melting point of 173–174° (lit.⁴⁹ mp 171°).

(47) S. Bance, H. J. Barber, and A. M. Woolman, *J. Chem. Soc.*, 1 (1943).

(48) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 182.

(49) R. E. Lutz, C. R. Bouer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

Oxidation of Labeled Stannole 0. A solution of 1.0 g of **0** and 1.0 ml of 40% peracetic acid in 15 ml of methylene chloride was heated at reflux for 8 min. The solution was extracted with two 20-ml portions of water. Ethanol (10 ml) was added to the methylene chloride solution, and it was concentrated to a volume of 8 ml. On cooling, a white precipitate formed, which was filtered off and extracted with 10 ml of a 50% benzene solution in hexane. The undissolved material was taken up in methylene chloride, about 5 ml of ethanol was added, and the solution was concentrated to a volume of about 4 ml. Cooling yielded 0.112 g of tetraphenylfuran (**9b**), mp 173–174°.

Bromination of Labeled Tetraphenylfuran¹⁴ (9b**).** An ampoule containing 0.100 g of **9b**, 0.30 g of phosphorus pentabromide, and 0.65 ml of phosphorus oxychloride was heated on a steam bath for 7 min. Upon cooling, the mixture was poured onto ice. When the ice had melted, the remaining solid was filtered off and washed with a few milliliters of ethanol. It was then dissolved in methylene chloride; ethanol was added, and the solution was concentrated until the vapors of methylene chloride could no longer be detected. Upon cooling, 0.129 g of labeled 2,5-di(*p*-bromophenyl)-3,4-diphenylfuran (**8b**), mp 197–198.5° (lit.¹¹ mp 192°), was obtained.

Electron Paramagnetic Resonance (epr) Spectra. Samples were prepared by standard vacuum line techniques and epr spectra were run at room temperature on a Varian V-4502-15 spectrometer. The *g* values were determined by the dual-cavity technique using peroxyaminodisulfonate as a standard.⁵⁰ The theoretical spectra were calculated using a JEOL RA-1 spectrum accumulator.

Thermal Decomposition of the 4-Bromo-1,2,3,4-tetraphenylcyclobutenyl Radical (10**).** A mixture of 0.200 g of 3,4-dibromo-1,2,3,4-tetraphenylcyclobutene (**11**), 4.2 g of mercury, and 5.0 ml of dry, degassed triglyme was rapidly stirred for 0.5 hr at 100° under nitrogen. Initially a green color appeared, intensified, then faded to a gold color. The cloudy organic solution was decanted from the mercury with the aid of approximately 10 ml of methylene chloride. Filtration yielded 2 mg of octaphenylcyclooctatetraene (**6**). The filtrate was extracted three times with 100-ml portions of water, dried over sodium sulfate, and concentrated. Ethanol was added, and the solution was concentrated until the odor of methylene chloride could not be detected. Upon cooling the solution 0.017 g of tetraphenylfuran was obtained (identified by ir). Further concentration of the mother liquor yielded 0.048 g of 1-bromo-1,2,3-triphenyl-3-benzoylpropene (**12**), mp 140–142° (lit.¹ mp 143–145°).

Reaction of Bromo Radical **10 with Hexamethylditin.** To a degassed solution of 0.516 g of dibromocyclobutene **11** in 10 ml of dry triglyme under nitrogen was added 1.2 ml (about 1.6 g) of hexamethylditin. The mixture, now beginning to turn green, was frozen in liquid nitrogen, and the system was sealed off after thorough evacuation. A pea-sized drop of mercury was maneuvered from a side arm onto the frozen organics, and the mixture was allowed to thaw. It was then heated on a steam bath with rapid stirring for 10 min. During the heating the mixture became dark green, then yellow brown, and a precipitate formed. The organic material was decanted from the mercury and filtered to yield 0.127 g of **6** as identified by ir. Attempts to obtain a crystalline material from the filtrate failed.

Preparation of 3,4-Dibromo-1,2,3,4-tetra-(*p*-deuteriophenyl)cyclobutene (11-d₂**).**⁵¹ The title compound was prepared by previously reported reactions from *p,p'*-dideuteriodiphenylacetylene.^{3,5,19}

Addition of Tetradeuterated Bromo Radical **10-d₂ to Decomposing Stannole Dibromide **1**.** A solution of 0.10 g of **11-d₂** in 10 ml of triglyme under nitrogen was added to a 0.6 × 5.5 cm column of freshly prepared silver powder packed in purified triglyme. The column exit was arranged so that the effluent could be directed either into a reaction flask containing 0.40 g of stannole dibromide **1** in 5 ml of triglyme or into an empty flask. The column flow was regulated by a Teflon needle valve, and the whole system was maintained under a nitrogen atmosphere. The column flow was started and was regulated at 0.25 ml/min while the effluent ran into the empty flask. When the column effluent became green (about 45 sec after the flow was started), it was directed into the rapidly stirring solution of **1**, while simultaneously raising an oil bath at 142° to heat the reaction flask. When the liquid level in the column reached the top of the silver packing, the flow was stopped, and the oil bath was removed. The solid formed during the reaction was

collected, and washed with methylene chloride and then acetone to yield 0.060 g of **6**. Mass spectrometric analysis of the product using an Atlas CH₄ spectrometer showed the product to be 91.7 ± 0.3% *d₀*, 4.6 ± 0.3% *d₄*, and 3.5 ± 0.1% *d₈* with no *d₁*, *d₂*, *d₃*, *d₅*, *d₆*, and *d₇*.

Delayed Addition of Bromo Radical **10 to Decomposing Stannole Dibromide **1**.** The previous experiment was repeated except that a 0.2 × 122 cm capillary was interposed between the column and the flask containing stannole dibromide. This introduced a 15-min delay between formation of the radical and the time it dripped into the reaction flask. A 0.075-g yield of **6** was obtained which contained 89% *d₀*, 6.2% *d₄*, and 3.2% *d₈*.

Estimation of the Radical Concentration in the Above Two Experiments. Bromo radical **10** was generated in a column under the same conditions as in the previous two experiments. The effluent was run through an epr tube designed to maintain liquid in that section which is in the epr cavity. The rate of flow was maintained at 0.25 ml/min throughout the experiment. A dual cavity was used, the bromo radical being run at 100-kHz modulation of sufficient amplitude to broaden the spectrum to a single line, while the Varian pitch sample was run at 400 Hz simultaneously. After an initial 5-min sweep, the spectrum was swept continuously every minute for the duration of the experiment. There was no significant change in spectrum amplitude with time.

Using the same apparatus and spectrometer settings, the spectrum of 1.0 × 10⁻³ *M* solution of freshly recrystallized diphenylpicrylhydrazyl in triglyme was compared in amplitude to the Varian pitch sample. The spectra of both the bromo radical **10** and diphenylpicrylhydrazyl were integrated graphically to get the absorption curves, and then were again integrated with a planimeter. After normalization of the two double integrals to constant pitch sample amplitude, comparison indicated the concentration of bromo radical **10** to be 2.3 × 10⁻⁴ *M*.

Reaction of Bromo Radical **10 with Oxygen.** Oxygen was bubbled through a rapidly stirred mixture of 0.50 g of dibromocyclobutene **11** in 7 ml of dry triglyme. While the bubbling continued, 10 g of mercury was added, and the mixture was heated on a steam bath for 0.5 hr. The organic material was decanted from the mercury into water. A gray semisolid formed and was removed with a stirring rod. Crystallization of this material from ethanol yielded 0.086 g of tetraphenylfuran. The milky mixture remaining after removing the gray semisolid was allowed to stand overnight, whereupon an orange-yellow solid precipitated. This was dissolved in methylene chloride; ethanol was added, and the solution was concentrated to yield 0.083 g of a mixture of 1-bromo-1,2,3-triphenyl-3-benzoylpropene (**12**) and *cis*-dibenzoylstilbene (**7**), estimated by infrared analysis to be in the ratio of 60:40. Concentration of the mother liquor yielded 0.040 g of almost pure bromo ketone **12**. Further concentration yielded 0.017 g of tetraphenylfuran. Estimated yields of the three products were 30% tetraphenylfuran (**9**), 20% bromo ketone **12**, and 10% *cis*-dibenzoylstilbene (**7**).

Oxidative Pyrolysis of Stannole Dibromide **1.** A solution of 0.360 g of stannole dibromide **1** in 25 ml of dry benzene in a Parr hydrogenation bottle was pressurized to 10 psig with oxygen. The apparatus was then lowered into a 150° oil bath, and the solution was stirred for 1 hr. The pressure in the bottle rose to 75 psig. Upon cooling and releasing the oxygen pressure, the product solution was evaporated. Trituration of the residue with ethanol yielded 0.202 g (100%) of *cis*-dibenzoylstilbene, mp 209–213.5°.

Preparation of Tetraphenylfuran-*d₂*. The bromines of 2,5-di(*p*-bromophenyl)-3,4-diphenylfuran (**8a**) were replaced by deuterium by the same procedure used previously to replace them with hydrogen. Chromatography followed by recrystallization of the product gave tetraphenylfuran-*d₂*, mp 170–172°.

Oxidative Pyrolysis of Stannole Dibromide **1 in the Presence of Tetraphenylfuran-*d₂*.** A solution of 0.360 g of stannole dibromide **1** and 0.201 g of tetraphenylfuran-*d₂* in 25 ml of dry benzene was pressurized to 10 psig, and heated in a 150° oil bath for 1 hr. After cooling and releasing the pressure in the system, the solution was evaporated. The residue was extracted with 10 ml of ether and filtered. The undissolved solid, 0.135 g, was *cis*-dibenzoylstilbene, mp 213–215°. The ether solution was evaporated and heated under vacuum on a steam bath to sublime out dimethyltin dibromide. The residue was dissolved in a mixture of methylene chloride and ethanol, and the solution was concentrated. Upon cooling the solution, 0.150 g of tetraphenylfuran, mp 169–173°, was obtained. No further separation of the products was attempted. Mass spectrometric analysis of the products indicated them to be *cis*-dibenzoylstilbene-*d₀* and tetraphenylfuran-*d₂* only.

(50) W. Low, "Paramagnetic Resonance," Academic Press Inc., New York, N. Y., 1963, p 705. See also Varian Associates' "EPR at Work," Series No. 28.

(51) We thank Dr. A. E. Young for carrying out this synthesis.

Reaction of Bromo Radical 10 with Dimethyl Maleate. A mixture of 0.200 g of dibromocyclobutene **11** and 0.100 g of dimethyl maleate was degassed by several freeze-thaw cycles, and 3.0 ml of degassed, dry triglyme was distilled into the mixture. After freezing the mixture in liquid nitrogen, 10 g of mercury was poured onto the frozen organics from a side arm. The mixture was allowed to thaw, and then was heated with rapid stirring on a steam bath for 15 min. During the heating the solution turned deep green, then faded to a golden yellow. After cooling, the vacuum was released, and the solution was decanted from the mercury into water. After standing overnight, a solid precipitated and was filtered off. The solid was extracted with methylene chloride and filtered. The undissolved solid was soluble in ammonium hydroxide (presumably HgBr). The filtrate was diluted with ethanol and then concentrated until

the odor of methylene chloride could no longer be detected in the vapors. Cooling the solution yielded 0.054 g (54%) of dimethyl fumarate (identified by ir). Further concentration of the mother liquor gave 0.108 g of yellow solid. Thin layer chromatography indicated this solid contained at least five components with no one predominating.

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The Influence of Substituents on the Direction of Episulfonium Ion Ring Opening

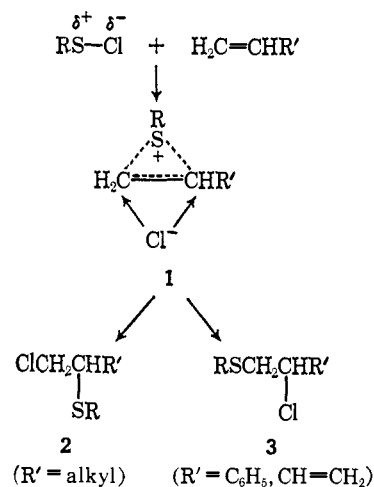
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Abstract: The reactions of methanesulfonyl chloride with α,β -unsaturated carbonyl, nitrile, and sulfone systems have been investigated, and the relative distribution of isomeric adducts determined. It was also demonstrated that under the conditions used for reaction and analysis the isomer ratios were truly representative of the kinetically controlled reaction and not the result of a subsequent rearrangement to the thermodynamically preferred isomer. On this basis it was possible to obtain data concerning the influence of functional group substituents on the direction of the ring-opening attack by chloride ion on each of the episulfonium ion intermediates. The data indicate that steric factors are quite important, preferential attack occurring at the least substituted carbon unless the functional group provides strong activation for attack on the adjacent carbon. The relative ability of the functional groups to activate the α position to attack by chloride ion parallels the well-known activation of α -halocarbonyl and related compounds toward nucleophilic displacements. The extent of episulfonium ion ring opening by attack at the α carbon decreases with decreasing ability of the functional group to accommodate a nucleophile (acid chloride > ester > amide > nitrile > sulfone). The striking resemblance between α activation in nucleophilic displacement on α -halocarbonyl compounds, and activation of the α position toward chloride ion attack in the ring opening of similarly substituted episulfonium ions, suggests that similar transition-state structures in which the nucleophile is partially bonded to both the α -carbon and the functional group are important and serve to lower the energy for attack at the α position.

Kharasch and Buess² postulated a mechanism involving a cyclic episulfonium ion intermediate to explain the *trans* addition of 2,4-dinitrophenylsulfenyl chloride to olefins. Episulfonium ion intermediates have also been proposed to account for the unusual anti-Markovnikov orientation and *trans* stereochemistry of products from the addition of alkyl- and arylsulfenyl chlorides to olefins.³ Both observations are consistent with a cyclic intermediate which is opened by chloride attack from a direction *trans* to the sulfur bridge.

When R' is an alkyl substituent, the predominant ring-opening reaction occurs by attack at the terminal carbon giving the kinetically controlled anti-Markovnikov product **2**. The bonding of the chloride to the terminal position is inconsistent with an open carbonium ion and is explained more satisfactorily by invoking a cyclic intermediate **1**. The product structure would then be determined by factors influencing the



direction of the ring opening. Steric factors appear to be quite important with nonconjugated olefins since chloride ion preferentially attacks the least hindered terminal carbon giving the primary chloride.³

In contrast, the addition of sulfenyl chlorides to conjugated olefins⁴ (R' = C₆H₅, vinyl) gives the Mar-

(1) To whom inquiries should be directed.
 (2) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).
 (3) W. H. Mueller and P. E. Butler, *ibid.*, **88**, 2866 (1966).