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AN EXAMPLE OF A 1,4-CARBENE ADDITION

presented by

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AN EXAMPLE OF A 1,4-CARBENE ADDITION

Ву

Jeffrey W. Raggon

A THESIS

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ABSTRACT

AN EXAMPLE OF A 1,4-CARBENE ADDITION

By

Jeffrey W. Raggon

In this thesis, a reinvestigation of the addition of dichlorocarbene to tetracyclones was performed. In the original work,³⁰ dichlorocarbene, prepared by the Makosza method,²⁹ was allowed to react with 2,3,4,5-tetraphenyl-cyclopentadien-1-one (38). The sole product reported for this reaction was the 1,2-dichlorocarbene adduct 39.

Upon reinvestigation, another product, 1,1-dichloro-2,3,4,5-tetraphenylcyclopentadiene 40 was isolated. It appears to arise from a 1,4-carbene addition. The possibility that 40 might be the result of a secondary rearrangement of the 1,2-dichlorocarbene adduct was examined. Solutions of 39, when subjected to acidic or basic conditions gave only recovered 39.

Heating solutions of 32 in mesitylene or o-dichlorobenzene, on the other hand, resulted in the formation of two products. The major product, a tetraphenylchlorophenol (48), was obtained in 40% yield. The minor product, obtained in 18% yield, was the cyclopentadiene 40. Since the temperature of the reaction for generating the dichlorocarbene by the Makosza method never exceeds 140°C (the temperature in which 40 is formed thermally), 40 appears to be a primary product.

The proposed mechanism for the formation of 40 involves the addition of dichlorocarbene in a 1,4-fashion to 38 followed by the elimination of carbon monoxide.

The addition of dibromocarbene to $\frac{38}{\sqrt{2}}$, under the Makosza conditions, was also investigated. In this case, however, the 1,4-addition was completely suppressed by the classic 1,2-addition.

Finally, the excited state chemistry of 39, or its dibromo-analog 47, was examined. The primary interest of this investigation was to see if the excited singlet states of 39 and/or 47 would undergo rearrangements similar to, or different from, those observed in the ground state thermolysis reactions. It was also of interest to us to see if the type of halogen on the cyclopropane ring would have any effect on these excited state rearrangements.

Irradiation of the $n\pi^*$ transition of 39 or 47 in chloroform, warm dioxane, or carbon tetrachloride for 3.75-4.5 h through a pyrex glass filter or 5-6 h through a uranium glass filter, with a 450-W high-pressure mercury-vapor Hanovia lamp, gave ca. 50% of the ring-expanded 3-chloro- or 3-bromo-2,4,5,6-tetraphenylphenol 48 or 50.

The proposed mechanism for the formation of 48 or 50 involves cleavage of the cyclopropane bond common to both rings followed by halogen migration, loss of halonium ion, aromatization and protonation of the resulting phenoxide anion.

The possibility of an ion pair as an intermediate in the formation of 48 or 50 is briefly discussed.

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INTRODUCTION

One characteristic reaction of carbenes is their addition to double bonds to yield cyclopropanes. This reaction, first reported by Doering and Hoffman in 1954,¹ has become an attractive method for synthesizing threemembered rings and has been further applied to other unsaturated substrates, such as allenes,² acetylenes,³ and aromatic compounds.⁴

A reasonable orbital depiction of the lowest energy singlet state of a carbene is an sp^2 hybrid with an empty p-orbital (Figure 1a).



Figure 1. Orbital depiction of the singlet and triplet state of a carbene.

The triplet state of a carbene is envisioned as a linear sp hybrid, with two half-filled p-orbitals (Figure 1b).⁵ Triplet carbenes may also be viewed as biradicals,⁶ though the two unpaired electrons are located on the same carbon.

Carbenes are electron-deficient species which in the singlet state appear to have an orbital structure similar to carbonium ions. On the other hand, they also possess a carbanion-like non-bonding pair of electrons. As a result, the electrophilic or nucleophilic character of singlet carbene depends strongly on the ability of substituents on the electron-deficient carbon to withdraw electrons from, or supply electrons to, the divalent center.⁶

Generally, singlet dihalocarbenes add in a 1,2-fashion across a double bond. There are, however, a few isolated examples where 1,4-attack occurs and has been observed to unequivocally arise from a one-step process. Unambiguous one-step mechanisms seem to be of five types: intramolecular 1,4-addition yielding benzvalene,⁷ homo-1,4addition of various halocarbenes to norbornadiene,⁸⁻¹⁴ addition of triplet dicyanocarbene to cyclooctatetraene (COT),¹⁵ addition of the nucleophilic carbene cycloheptatrienylidene to tetracyclones,^{16,17} and recently, the onestep intermolecular 1,4-addition of dichlorocarbene to 1,2-bismethylene cycloheptane.¹⁸

The first of these examples was observed by Burger, Gandillon and Mareda.⁷ They found that base-induced



c b CH₃a

Scheme I

a-elimination of hydrogen chloride from 5-chloromethyl-5methylcyclopenta-1,3-diene (1) produces 1-methyltricyclo-[3.1.0.0^{2,6}]hexene-3-(1-methylbenzvalene) (3), together with toluene and spiro[4.2]hepta-2,4-diene (5). A common intermediate 5-methylcyclopenta-1,3-dien-5-yl-carbene (2) was presumably responsible for the 1,4-carbene addition, 1,2carbon shift and CH-insertion, respectively (Scheme I).

The authors were also able to synthesize an authentic sample of 2-methylbenzvalene (6) by another method outlined in Scheme II. Contrasting the spectral characteristics of the authentic 2-methylbenzvalene (6) with the spectral characteristics of the three products formed via the presumed intermediate 2 (see Scheme I), allowed the authors to demonstrate that the intramolecular cyclopropanation was completely suppressed by the three alternative processes (i.e., intramolecular 1,4-addition, 1,2-carbon shift and CH-insertion).



Scheme II

A second example of a 1,4-carbene addition involves the addition of various halocarbenes to norbornadiene systems.^{8,9} Jefford and co-workers reasoned that the least electrophilic of the dihalocarbenes (i.e., difluorocarbene)⁶ should possess a greater likelihood of reacting with a suitable diene in 1,4-addition fashion. This notion was based on the assumption that the 1,2- and 1,4-addition modes are in formal competition. Since both theoretical and experimental studies attest to the electrophilic behavior of halocarbenes in the 1,2-addition mode, it was reasoned by Jefford that any feature in the carbene which would disfavor the 1,2-addition mode could alternatively, favor 1,4-addition. Thus, a carbene, less electrophilic with respect to 1,2-addition, (e.g., difluorocarbene) should exhibit a greater potential for 1,4-addition. They have been

9

10(55-62%)

11(4-11%)



12(34%)

Scheme III

successful in showing that singlet difluorocarbene does indeed add in a 1,4-fashion to norbornadiene 2, and that the product does not arise from a secondary thermal rearrangement of the 1,2-addition product (Scheme III).

Other 1,4-carbene additions to various norbornadienes have also been established for CF_2 ,^{8,10,11} CFC1,^{8,10,11} $CC1_2$,^{9,12,13} and CBr_2 .⁹

A third instance of a 1,4-carbene addition involves the addition of triplet dicyanocarbene, generated thermally $(\underline{ca.} 80^{\circ}C)$, to cyclooctatetraene (13) (Scheme IV).



Initially, the product of the reaction of singlet dicyanocarbene with COT (13) was thought to be the dihydroindene 15.¹⁹ However, in a reinvestigation carried out by the authors¹⁵ it was discovered that on conducting "variable dilution" experiments there was a significant parallel between the magnitude of the 14 to 16 ratio and the previously observed¹⁹ loss of stereochemistry in the reaction of dicyanocarbene with either cis- or trans- 2-butene. This loss of stereochemistry was shown to arise from the increase in the amount of triplet carbene with increasing dilution. Hence, the authors concluded that the pronounced dilution effect coupled with the knowledge that the two adducts (14 and 16) do not interconvert at the reaction temperature, (14 does not rearrange to 16 at the reaction temperature (80°C); it does so slowly; however, at 160°)¹⁵ requires that 14 and 16 are formed from singlet and triplet dicyanocarbene, respectively.

Another unambiguous one-step 1,4-carbene addition to a series of substituted cyclopentadienones has been reported. 16,17 In this particular example, the nucleophilic carbene cycloheptatrienylidene 17 was generated in the presence of tetracyclones (1:1.5 M) by pyrolysis (di-glyme; 100°C; 5 h) of the sodium salt of tropone toluene-p-sulfonylhydrazone. Work-up followed by chromatography on alumina gave a mixture of benzocycloheptatrienes 25 and 26 in a ratio of <u>ca</u>. 1:2 in a total yield of 30-40%.

The benzocycloheptatrienes 25 and 26 presumably arise from intermediates 22 and 23, believed to be equilibrating through the bis-norcaradiene 21 (Scheme V).

A final example of a conjugate 1,4-addition was recently discovered by Turkenburg, et al.¹⁸ They found that dichlorocarbene prepared by the Makosza method²⁹ reacted with 1,2-bismethylenecycloheptane 28 yielding, besides the 1,2-addition product 28, the 1,4-addition product 30 in a ratio of 99:1, respectively (Scheme VI).

It was determined that 22 rearranged to 30 only at elevated temperatures (285°C). Since the thermal rearrangement was not observed below 200°C, the 1,4-adduct 30 must be a primary product.

The authors also make reference to an analogous reaction described by Landheer²⁰ in his Ph.D. thesis. He proposed that the formation of 35 from the 1,2-bismethylenecyclopentane 34 occurred <u>via</u> the intermediate 36 (Scheme VII).

There have been other claims of achieving 1,4-carbene additions which, however, are dubious. These examples either involve gas-phase reactions having a high probability of "hot" molecule isomerization, $^{21-23}$ catalysis with copper, 24,25 or conditions so harsh as to raise the possibility of thermal rearrangement of the initially formed product. 26

From a qualitative viewpoint, the key interaction in



Scheme V













1,4- and 1,2-addition is between the p-orbital (LUMO) of the carbene and the π_2 (HOMO) of the 1,3-diene (Figure 2a,b). The π_1 bonding orbital of the 1,3-diene is symmetry forbidden from reacting with the LUMO of the carbene. Consequently, much of the favorable $p-\pi_2$ interaction between the HOMO of the 1,3-diene and the LUMO of the carbene is offset by the repulsive interaction between the filled σ -orbital of the carbene and the π_1 -orbital of the diene (Figure 2c). On the other hand, no such difficulty is present in the 1,2-addition mode, since both π_1 and π_2 orbitals can donate electron density to the LUMO of the carbene²⁷ (Figure 2b,d).

These qualitative arguments outlined above have been recently confirmed by semi-empirical MO calculations.²⁸

In this thesis, a new, previously unobserved example of a 1,4-carbene addition to a diene is described.

The addition of dichlorocarbene to a substituted cyclopentadienone, tetracyclone, under phase transfer conditions was previously reported.³⁰ Narasimhan, Gurumurthy and Balasubaramanian obtained the 1,2-dichlorocarbene adduct of tetracyclone in 60% yield as a white crystalline solid. However, in a reinvestigation of that experiment we were able to uncover new results which will be discussed in detail in the Results and Discussion section of this thesis.



(a) 1,4-addition mode;
 p-orbital (LUMO) of
 carbene interacting
 with π₁ (HOMO) of diene.



(b) 1,2-addition mode; orbital interactions same as (a).



(c) 1,4-addition mode; symmetry-forbidden interaction of π_l of diene with p-orbital (LUMO) of carbene.



- (d) 1,2-addition mode; p-orbital of carbene interacting with π₁ of diene.
- Figure 2. Molecular Orbitals (MO's) for 1,2- and 1,4- additions.

RESULTS AND DISCUSSION

Addition of dichlorocarbene under phase transfer conditions²⁹ to tetracyclone 38 afforded two products in addition to some recovered starting material (Scheme VIII).





The expected dichlorocarbene adduct 32 was obtained by flash column chromatography of the crude reaction product on silica gel. After recrystallization from methylene chloride and hexane a 30% yield of 32 was obtained as a white crystalline solid. The 1,2-dichlorocarbene adduct's structure was confirmed by comparing its infrared, mass,

and ¹H NMR spectra to those reported in the literature.³⁰

An unexpected second product was also eluted from the same column. After recrystallization from methylene chloride and hexane, a 25% yield of 40 was obtained as bright yellow plate-like crystals. The product was identified as 1,1-dichloro-2,3,4,5-tetraphenylcyclopentadiene (40) by infrared, proton and carbon-13 NMR, and mass spectroscopy, as well as by chemical transformations.

The absence of a sharp carbonyl absorbance at 1720 cm⁻¹ in the infrared spectrum of 40 indicated that this functional group was no longer present in the molecule. Moreover, the failure to detect the loss of carbon monoxide (M^+-28) in the mass spectrum of 40 also confirmed this fact. In addition, the ¹³C NMR spectrum of 40 showed no more than eleven peaks in the aromatic region. This indicated a highly symmetrical molecule consistent with a structure such as 40. A single peak at 690.59 ppm also suggests the presence of an sp³ carbon which could reasonably be the carbon bearing the two chlorines in 40. Acid hydrolysis of 40 with sulfuric acid in refluxing benzene gave the tetracyclone 38. This seems to substantiate the ¹³C NMR result that C-1 of 40 bears two chlorines.

Finally, unequivocal evidence, which points to a highly symmetrical structure such as 40, was obtained by examining the ¹³C and ¹H NMR spectra of the cyclopentadiene

derivative 46^{31} prepared under Makosza conditions similar to those used to obtain 40 (See Scheme IX). If the structure of 40 is correct, then the two methyls of both the ptolyl groups of 46 should appear in the proton and carbon-13 NMR spectra as singlets. And indeed, this is what was observed. Therefore, we can conclude that the original structural assignment of 40 (<u>i.e.</u>, substituted cyclopentadiene where C-1 in quarternary center being two chlorines) is correct.

The generality of the 1,4-cycloaddition under Makosza conditions was also tested using other dihalocarbenes. Thus, the addition of dibromocarbene to tetracyclone 38using bromoform, 50% sodium hydroxide, and a catalytic amount of triethylbenzylammonium chloride (TEBA) gave 41% of the 1,2-dibromocarbene adduct of tetracyclone 47 (Scheme X). A pure product was obtained through recrystallization from methylene chloride and hexane.

Unfortunately the 1,4-addition product (<u>i.e.</u>, 1,1dibromo-2,3,4,5-tetraphenylcyclopentadiene) did not form. From a qualitative viewpoint, it appears as though the bulky bromine atoms lack the ability to increase the electrophilicity of the divalent carbon to the extent that permits it to add in a 1,4-fashion to an electron-deficient 1,3-diene, such as tetracyclone $\frac{38}{2}$.

Since the 1,4-addition mode was not observed when dibromocarbene was allowed to react with 38, attention was





+



44 Ar²=p-tolyl Ar¹=phenyl



45

43





Scheme X

again turned to the formation of 40. It was originally thought that might result from a secondary rearrangement of the 1,2-dichlorocarbene adduct . To test this hypothesis, was subjected to acid and base. Reacting with the two-phase system of 50% sodium hydroxide and chloroform in the presence of a catalytic amount of TEBA resulted in the quantitative recovery of . This result proved that was not derived from 39 under the basic conditions characteristic of the Makosza method. Similar results were obtained when was allowed to react under

acidic conditions with glacial acetic acid-acetic anhydride with a catalytic amount of 70% perchloric acid or p-toluenesulfonic acid (PTS) in refluxing benzene or trifluoroacetic acid in chloroform. In each case 39 was recovered unchanged. Thus, it appears that 40 in a primary product and not the result of an acid- or base-catalyzed rearrangement of the initially formed dichlorocarbene adduct 32. These results do not, however, rule out the possibility that $\mathcal{A}\mathcal{Q}$ results from a secondary thermal rearrangement of 39. To test this possibility, solutions of 39 in various aromatic solvents were heated. Refluxing solutions of 32 in benzene and toluene gave only recovered 32. On the other hand refluxing solutions of 32 in mesitylene or o-dichlorobenzene, induced a facile rearrangement of 39 at 150°C within reasonable reaction times (3-5 h). Heating 32 under these conditions afforded 33% of recovered starting material and two products (48 and 40), all isolated by preparative thin layer chromatography (Scheme XI).

The least polar thermolysis product was obtained at an optimum yield of 18%. Identification of this product as 40 was ascertained in two ways. First, by comparing its spectral data to that of an authentic sample of 40 prepared previously under the Makosza conditions, and secondly, by hydrolyzing the product in the presence of acid to tetracyclone 38. Recalling that 40 was obtained previously at reaction temperatures below 60°C, it does



not appear that 40 is formed under Makosza conditions as a result of a secondary thermal rearrangement of 32 following the initial 1,2-addition of dichlorocarbene to 38. Since 40 was not formed from 39 in appreciable amounts below temperatures of 140°C, one can safely assume that cyclopentadiene 40 is a bonafide 1,4-carbene adduct of tetracyclone 38.

As to the mechanism, it seems that the 1,4-carbene addition to 38 is followed by the elimination of carbon monoxide yielding cyclopentadiene 40.

The major thermolysis product of 32 (<u>i.e.</u>, 48) was obtained in 40% yield. When the thermolysis of 32 was followed by infrared spectroscopy, a band began to appear at 1680 cm⁻¹ after <u>ca</u>. 0.5 h. This absorbance, which decreased as the reaction continued, may have been due to an intermediate unsaturated dienone resulting from the initial cleavage of the carbon-carbon bond common to both rings in 32 (see Scheme XI). Exposure of this unsaturated dienone to silica gel during work-up causes a facile rearrangement with aromatization to the 3-chloro-2,4,5,6-tetraphenyl-phenol 48. The structure of 48 was determined by examining the infrared, ¹H and ¹³C NMR, and mass spectra.

The infrared spectrum of 48 revealed that the sharp carbonyl band at 1720 cm⁻¹, characteristic of enone 32, had disappeared. A new absorbance at 3540 cm⁻¹ in the infrared spectrum and a singlet at $\delta 5.08$ ppm in the ¹H NMR spectrum of 48 indicated the presence of a hydroxyl group. Moreover, the electron-impact mass spectrum of 48 showed that it had only one chlorine.

With these facts in mind, the mechanism in Scheme XI can be proposed. Thermally induced opening of the cyclopropane bond common to both rings in 39 yields the intermediate dienone. This intermediate dienone eliminates Cl^+ on silica gel from C-6 followed by aromatization of the sixmembered ring dienone and subsequent protonation of the resulting phenoxide anion yielding 48.

Even though the spectral data and analysis showed that the product 48 is a tetraphenyl chlorophenol, the exact location of substituents had to be determined. It was reasoned that removal of the chlorine from $48 \over \sqrt{3}$ followed by quenching with a protic solvent would yield a tetraphenylphenol. The latter could then be utilized by comparing its spectral and physical characteristics (i.e., melting point) to those of authentic tetraphenylphenols previously prepared by Yates and Hyre.³² Since the 2,3,4,5and 2,3,4,6-tetraphenylphenols melt at 183-184°C and 244-245°C, respectively, 32 one could pinpoint the exact location of the substituents in 48. It should be noted that the 4-chloro-2,3,5,6-tetraphenylphenol was not considered to be a candidate for structure 48 as neither the ¹H nor ¹³C NMR spectra were consistent with such a symmetric structure.

Regrettably, all attempts to dehalogenate 48 or its methyl ether 49 were unsuccessful. Thus, the o-methyl-3-chloro-2,4,5,6-tetraphenylphenol 49 failed to give a dehalogenated product on treatment with magnesium dust in refluxing tetrahydrofuran^{33,34} or sodium formate in dimethylformamide at 100°C in the presence of a catalytic amount of palladium [0].³⁵ Moreover, 48 was similarly reluctant to undergo dehalogenation when treated with a variety of reagents, such as titanium tetrachloridelithium aluminum hydride,³⁶ molecular hydrogen on 10% palladium/charcoal in tetrahydrofuran,³⁷ two equivalents of n-butyllithium,³⁸ and two equivalents of methyllithium³⁸ both followed by quenching with methanol.

Thus, the structural determination of 48 rests on the interpretation of the obtained spectral data and a close examination of the most reasonable mechanistic pathways available to 38 (<u>i.e.</u>, loss of Cl⁺ from C-6 and subsequent aromatization rather than loss of Cl⁺ from C-5, see Scheme XI).

Knowing that 32 undergoes reaction thermally yielding the ring-expanded phenol 48 and the cyclopentadiene 40, it was of interest to us to examine the excited state chemistry of 32 and its dibromocarbene analog 47. We were particularly interested in whether the singlet excited state of 32 would undergo rearrangements similar to that observed in the thermolysis of 32. Of secondary interest,

was whether substituting two bromine atoms on the cyclopropane ring would have any effect on these previously observed rearrangements.

Irradiation of the $n\pi^*$ transition ($\lambda_{max} = 310$ nm) of 32 or 47 in chloroform, warm dioxane, or carbon tetrachloride for 3.75-4.5 h through a pyrex glass filter or 5-6 h through a uranium glass filter, with a 450-W highpressure mercury-vapor Hanovia lamp gave <u>ca</u>. 50% of the ring-expanded 3-chloro- or 3-bromo-2,4,5,6-tetraphenylphenol 48 or 50, respectively (see Scheme XII).



Scheme XII

Filtration through silica gel followed by two recrystallizations from benzene and high boiling petroleum ether yielded products with sharp melting points. Positive identification of both photolysis products from the two separate irradiations was obtained by comparing the spectral data, either directly (in the case of irradiating 32) or through analogy (in the case of irradiating 42), to that of previously accumulated spectral data on 48 as obtained from the thermolysis of 32.

As to the mechanism for the photolysis of 32 and 47, it seems that the irradiation of the $n\pi^*$ chromophore of the enone results in the cleavage of the cyclopropane bond common to both rings, followed by the migration of one of the halogen atoms (chlorine or bromine) to the carbon bearing the positive charge of intermediate 51 or 52.³⁹ Workup of the ring expanded dienone 53 or 54 resulted in





Scheme XIII

loss of halonium ion, subsequent aromatization, and protonation of the resulting phenoxide anion yielding 48 or 50Scheme XIII).

26

The possibility also exists that an ion pair could be an intermediate in this process (Scheme XIV). 40



Scheme XIV

Molecular-Orbital Discussion

The formation of the 1,1-dichloro-2,3,4,5-tetraphenylcyclopentadiene 40 from tetracyclone 38 and the foregoing discussions led to the assertion that a 1,4-carbene addition has occurred.

Theory²⁸ suggests that a concerted linear cheletropic 1,4-addition of singlet carbene to a cisoid 1,3-diene is a symmetry allowed process. Nevertheless, examples of intermolecular 1,4-carbene additions are rare.

One factor that accounts for the rarity of the 1,4addition is of an entropic nature. This shortcoming can best be alleviated by choosing a diene possessing rigidity and/or planarity. This was first demonstrated by Jefford and coworkers in a series of papaer dealing with the homo-1,4-addition of various halocarbenes to norbornadiene.⁹⁻¹⁵ Tetracyclone 38 provides another example of a rigid cisoid diene that possesses a high probability of observing a 1,4-addition. In addition to this entropic factor, the ideal symmetry of the frontier orbitals demands that both pairs of interacting orbitals (<u>i.e.</u>, LUMO_{carbene}-HOMO_{diene} and LUMO_{diene}-HOMO_{carbene}) have the correct symmetry for 1,4-ring closure (Figure 3).

Once we admit that these two factors (<u>i.e.</u>, planarity and/or rigidity of diene and correct symmetry of the frontier orbitals are present in the intermolecular addition of dichlorocarbene to 38, then the formation of 40 can best be explained by a legitimate 1,4-carbene addition.

.27





Figure 3. Symmetry of frontier orbitals. Left: diene, right: carbene in top view.

EXPERIMENTAL

General Methods

Melting points were determined on a Thomas Hoover Unimelt apparatus and are uncorrected. ¹H NMR spectra were recorded on a Varian T-60 or on a Bruker WM-250 spectrometer with chemical shifts reported in &-units relative to tetramethylsilane. ¹³C NMR spectra were recorded on a Varian CFT-20 spectrometer or on a Bruker WM-250 spectrometer. IR spectra were obtained on a Perkin-Elmer 167 Grating Spectrophotometer. Low-resolution mass spectra were determined by a Finnigan Model 4000 spectrometer.

Addition of Dichlorocarbene to 2,3,4,5-Tetraphenylcyclopentadien-1-one (38)

A solution of tetracyclone (100 g, 26 mmol) in chloroform (400 mL) was stirred at room temperature with 50% sodium hydroxide (100 mL) and benzyltriethylammonium chloride (1.0 g) until the reaction was complete (color changes from deep purple to yellowish-orange and sodium chloride precipitates). An equal volume of water was added and the aqueous phase was extracted three times with chloroform. The combined organic layers were washed with 10% aqueous hydrochloric acid, dried over magnesium sulfate ' and concentrated under reduced pressure to yield 14.7 g of crude reaction product. Purification by column chromatography on 400 g of silica gel starting with 1:10 methylenechloride to hexane and increasing the polarity of successive elutions by 10% in methylene chloride until 100% methylene chloride is reached afforded 3.7 g (30.5%) of the dichlorocarbene adduct of tetracyclone 39, 2.9 g (25.5%) of 1,1-dichloro-2,3,4,5-tetraphenylcyclopentadiene 40 and 1.4 g (13.8%) of the starting material.

39: mp 184-186°C; IR (KBr) 3100-3000, 1715, 1450, 1350, 730, 695 cm⁻¹; ¹H NMR (CDCl₃) δ 7.0-7.4 (m); mass spectrum,

m/e (relative intensity) 469 (13), 467 (58, M⁺), 466 (61), 439 (89), 438 (100), 432 (71), 431 (68), 403 (30), 396 (44), 367 (68), 289 (89), 189 (32), 77 (52).

4Q: mp 171-172°C; IR (KBr) 3100-3000, 1950, 1885, 1810, 1765, 1490, 1465, 1450, 1030, 920 810, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.5-6.6 (m); ¹³C NMR (CD₂Cl₂) δ 143.69, 141.29, 133.50, 132.94, 131.05, 130.15, 128.37, 128.22, 128.05, 90.59; mass spectrum, m/e (relative intensities) 442 (8), 440 (70), 438 (83, M⁺), 403 (22), 367 (39), 325 (26), 289 (100), 189 (28), 182 (36), 176 (42), 145 (60), 125 (41), 91 (33), 78 (71), 77 (64), 51 (51), 36 (43). Anal. Calcd. for C₂₉H₂₀Cl₂: C, 79.27; H, 4.59; Cl, 16.14. Found: C, 78.80; H, 4.55; Cl, 16.14.

Addition of Dibromocarbene to 2,3,4,5-Tetraphenylcyclopentadien-l-one (38)

A solution of tetracyclone (5.0 g, 13 mmol) in bromoform (100 mL) was stirred at 5-7°C while 50 mL of 50% sodium hydroxide and 100 mg of benzyltriethylammonium chloride were added. The ice bath was removed and the two phases were allowed to stir vigorously for 3.5 h. An equal volume of water was added and the aqueous phase was extracted twice with chloroform. The combined organic layers were washed with 10% aqueous hydrochloric acid and dried over magnesium sulfate. Removal of the bromoform and chloroform under reduced pressure gave 10.0 g of a dark

brown tarry substance. Purification by column chromatography on 300 g of silica gel, eluting with methylene chloride/hexane (1/1) gave 3.0 g (41%) of the 1,2-dibromocarbene adduct of tetracyclone (47) as light brown needlelike crystals with a melting point of 168-170°C. Recrystallization of (47) gave a nearly quantitative yield of pale yellow crystals with a melting point of 169-170°C; IR (KBr) 3100-3000, 1720, 1640, 1620, 1500, 1455, 1355, 1170, 750, 740, 700 cm⁻¹; ¹³C NMR (CDCl₃) δ 169.58, 132.96, 132.78, 131.94, 131.72, 130.65, 130.33, 129.93, 128.95, 128.56, 128.03, 127.53, 54.56; mass spectrum, m/e (relative intensities) 555 (0, M⁺), 478 (66), 476 (100), 396 (53), 318 (5), 289 (49), 189 (52), 181 (45), 159 (63), 144 (41), 79 (37), 77 (31), 44 (34); Anal. Calcd. for C_{30}^{-} H₂₀OBr₂: C, 64.77; H, 3.62; Br, 28.72. Found: C, 64.87; H, 3.59; Br, 28.81.

Thermolysis of the 1,2-Dichlorocarbene Adduct of Tetracyclone (39)

Into a 25-mL pear-shaped flask was placed 300 mg (0.64 mmol) of 39 and 10 mL of freshly distilled 1,3,5trimethylbenzene. The solution was stirred at 150°C for 5 h. Two compounds in addition to starting material were separated from the reaction mixture using preparative thin layer chromatography. One compound, closest to the solvent and obtained in 18% yield as a yellow oil, was identified as 1,1-dichloro-2,3,4,5-tetraphenylcyclopentadiene 40: IR (thin film) 3100-3000, 2950, 2900, 2840, 1260, 750, 725, 680 cm⁻¹; mass spectrum, m/e (relative intensities) 442 (10), 440 (60), 438 (100, M⁺), 403 (11), 367 (43), 289 (75), 182 (32), 176 (50), 149 (39), 133 (95), 105 (40), 73 (58), 57 (82), 43 (56). Unequivocal structural determination of 40 was obtained by hydrolyzing it to tetracyclone 38 with a few drops of concentrated sulfuric acid in refluxing benzene (60%).

The other thermolysis product was obtained in 40% yield (110 mg). Its white needle-like crystals were identified as 3-chloro-2,4,5,6-tetraphenylphenol ($\frac{48}{20}$). mp 264-265°C; IR (KBr) 3520, 3100-3000, 1600, 1450, 1415, 1275, 1160, 950, 760, 740, 710 cm⁻¹; ¹H NMR (CDCl₃) 7.50 (m, 5H), 7.14 (m, 10H), 6.84 (m, 5H), 5.08 (s, 1H); ¹³C NMR (CDCl₃) δ 150.084, 142.321, 138.969, 135.264, 134.970, 133.147, 132.558, 130.912, 130.794, 130.382, 128.136, 128.206, 127.266, 126.913, 126.736, 126.383, 125.795; mass spectrum, m/e (relative intensities) 434 (30), 432 (100, M⁺), 396 (6), 379 (4), 367 (4), 289 (18), 189 (11), 182 (15), 145 (9), 44 (14).

A similar thermolysis reaction run in a dichlorobenzene at 150°C for 3 h gave the same 1,1-dichlorosubstituted cyclopentadiene 40 and ring-expanded phenol 48 in 11% and 36% yield, respectively, in addition to 120 mg (40%) of recovered starting material.

Addition of Dichlorocarbene to 2,5-Diphenyl-3,4-di-ptolylcyclopentadien-l-one (44)

The dichlorocarbene addition was performed according to Makosza conditions as follows: A solution of 44 (3.1 g, 7.52 mmol) in chloroform (80 mL) was stirred vigorously at room temperature with 50% sodium hydroxide (35 mL) and 100 mg of benzyltriethylammonium chloride (BTEA or TEBA) for 45 min. At the end of 20 min the deep purple solution had turned to a brownish-orange and a white precipitate had appeared (NaCl). An equal volume of water was added and the aqueous phase was extracted twice with chloroform. The combined chloroform layers were washed with 10% aqueous hydrochloric acid, dried over magnesium sulfate, and the solvent evaporated under reduced pressure affording 5.0 g of crude reaction product. Purification by column chromatography on 135 g of silica gel starting elutions with methylene chloride/hexane (1/10) and increasing the polarity of successive elutions by 10% in methylene chloride until 100% methylene chloride is reached afforded two products and recovered starting material. The least polar compound was 1,1-dichloro-2,5-dipheny1-3,4-di-ptolylcyclopentadiene 46 (1.6 g, 45%). Recrystallization from methylene chloride and hexane gave 1.1 g (31%) of a yellow crystalline material melting at 139-141°C; IR (KBr) 3100-2860, 1495, 1450, 1030, 830, 800, 780, 700 cm⁻¹; ¹H NMR (CD_2Cl_2) $\delta7.6-7.0$ (complex), 6.8 (complex s),

2.2 (s); 13 C NMR (CD₂Cl₂) δ 148.02, 145.26, 139.43, 138.37, 137.84, 133.32, 132.38, 130.32, 129.85, 129.61, 128.43, 128.14, 126.44, 80.15, 21.17; mass spectrum, m/e (relative intensities) 468 (76), 466 (100, M⁺), 431 (21), 395 (21), 339 (9), 303 (14), 182 (20). Anal. Calcd. for C₃₁H₂₄Cl₂: C, 79.65; H, 5.18; Cl, 15.17. Found: C, 79.48; H, 5.15; Cl, 15.27.

The other compound eluted from the column was the 1,2dichlorocarbene adduct of 44_{VV} (45, 2.0 g, 54%). Recrystallization from methylene chloride and hexane gave 1.6 g (43%) of an off-white crystalline material melting at 159-161°C; IR (KBr) 3100-2860, 1710, 1615, 1500, 1450, 1350, 1165, 750, 730, 695 cm⁻¹; mass spectrum, m/e (relative intensities) 498 (7), 496 (55), 494 (64, M⁺), 468 (57), 466 (73), 460 (59), 459 (100), 431 (33), 424 (87), 395 (64), 303 (28), 189 (23), 182 (44).

Anal. Calcd. for C₃₂H₂₄OCl₂: C, 77.57; H, 4.88; Cl, 14.31. Found: C, 77.40; H, 4.82; Cl, 14.25.

Preparation of 4,4'-Dimethylbenzoin (42)⁴¹

In a 500-mL round-bottomed flask fitted with a reflux condenser were placed 66 mL of 95% ethanol, 53 mL of water, 50 mL (0.424 mol) of freshly distilled p-tolualdehyde 41 and 5.1 g (0.078 mol) of potassium cyanide. The mixture was heated with vigorous stirring for 5.5 h. At the end of this period the solution was cooled, filtered through a Buchner funnel, and washed with a little water. The yield of crude 4,4'-dimethylbenzoin $\frac{42}{\sqrt{2}}$ was 36.6 g (72%). This crude product was used without further purification in the next step; mp 70-74°C (lit.⁴² mp. 88-89°C); IR (Nujol) 3480, 3080-3000, 1680, 1610, 1100, 780 cm⁻¹.

Oxidation of 4,4'-Dimethylbenzoin (42)⁴³

In a 250-mL round-bottomed flask fitted with a reflux condenser were placed, 12 g (50 mmol) of the crude 4,4'dimethylbenzoin 42, 60 mL of glacial acetic acid, and 30 mL of concentrated nitric acid. The solution was heated at 90-95°C for 1.5 h. The addition of 200 mL of ice and water resulted in 10.8 g of the crude benzil. Extended cooling gave another 500 mg of product resulting in a total yield of 1.3 g (93%) of the crude 4,4'-dimethylbenzil 43. Recrystallization from methanol afforded pale yellow crystals with a melting point of 101-103°C (Lit.⁴⁴ mp. 104-105°C); IR (KBr) 3100-2840, 1660, 1600, 1575, 1225, 1175, 890, 830, 745 cm⁻¹.

Condensation of 4,4'-Dimethylbenzil (43) and Dibenzylketone^{45,46}

In a 250-mL round-bottomed flask fitted with a reflux condenser was added, 6.0 g (25.2 mmol) of 4,4'-dimethylbenzil 43, 5.3 g (25.2 mmol) of dibenzylketone, and 50 mL

of absolute ethanol. The temperature of the mixture was raised until refluxing began at which time 4.3 mL of 20% potassium hydroxide in ethanol was added slowly from an addition funnel. When the frothing subsided, the solution was refluxed for about 30 min and then cooled to 0°C. The solid was filtered with suction and washed with a little 95% ethanol affording 6.5 g (63%) of deep-purple crystals of 2,5-diphenyl-3,4-di-p-tolylcyclopentadien-1-one 44; mp. 189-191°C. Recrystallization from benzene and petroleum ether gave deep purple needle-like crystals with a melting point of 218-220°C. (Lit. 46 mp. 218-219); IR (KBr) 3100-2860, 1710, 1610, 1495, 1450, 1350, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.3-6.7 (m), 2.3 (s).

Irradiation of the 1,2-Dichlorocarbene Adduct of Tetracyclone (39)

A solution of 39 (467 mg, 1.0 mmol) in 130-mL of chloroform or carbon tetrachloride was irradiated through a pyrex glass filter with a 450-W high-pressure mercuryvapor Hanovia lamp for 3 h. Evaporation of the solvent under reduced pressure left a reddish-brown residue. Purification by column chromatography on 15 g of silica gel, eluting with methylene chloride/hexane (1/2), gave 220 mg (50%) of 48 as a white powdery solid. A purer product was obtained by recrystallization from benzene and petroleum ether. Mp 263-265°C; IR (KBr) 3520, 3100-3000, 1440, 1420, 1275, 1150, 750, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.506 (m, 5H), 7.128 (m, 10H), 6.828 (m, 5H), 5.08 (s, 1H); ¹³C NMR (CDCl₃) δ 142.5, 139.20, 135.20, 131.0, 130.9, 130.50, 129.0, 128.40, 127.50, 127.0, 126.70, 126.0; mass spectrum (m/e) 434 (14.61%), 432 (48.0%) 396, 289, 189, 182, 145, 77, 44, 40. Anal. Calcd. for $C_{30}H_{21}OC1$: C, 83.22; H, 4.89; Cl, 8.19. Found: C, 83.27; H, 4.94; Cl, 8.38.

Irradiation of the 1,2-Dibromocarbene Adduct of Tetracyclone (47)

A solution of 500 mg (0.900 mmol) of 47 in 130 mL of carbon tetrachloride was degassed for 0.5 h and irradiated for 3.75 h through a pyrex glass filter with a high-pressure mercury-vapor 450-W Hanovia lamp. Evaporation of the carbon tetrachloride under reduced pressure left a brown residue which was filtered through silica gel and washed with diethyl ether, freeing ca. 200 mg (47%) of the crude ring-opened phenol 50 from polymers. Recrystallization from benzene and petroleum ether gave pure 50 as a white crystalline solid melting at 263-264°C; IR (KBr) 3530, 3100-3000, 1450, 1400, 1270, 1150, 750, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.49 (m, 5H), 7.15 (m, 10H), 6.86 (m, 5H), 5.04 (br s, 1H); ¹³C NMR (CDCl₃) 131.1, 130.5, 128.8, 128.2, 127.4, 127.0, 126.6, 126.0; mass spectrum (m/e) 478 (86.2%), 476 (100%), 396, 319, 302, 289, 189, 182, 145, 78. Anal. Calcd. for C₃₀H₂₁OBr: C, 75.48; H, 4.45; Br, 16.74. Found: C, 75.38; H, 4.44; Br, 16.58.

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Addition of dichlorocarbene under phase transfer conditions²⁹ gave, after recrystallization, 31% 46 and 43% 45.

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