

DIBENZO[a,d]CYCLOHEPTENYLIDENE AND TRIBENZO[a,c,e]CYCLOHEPTENYLIDENE STEREOCHEMISTRY OF THE ADDITION REACTION

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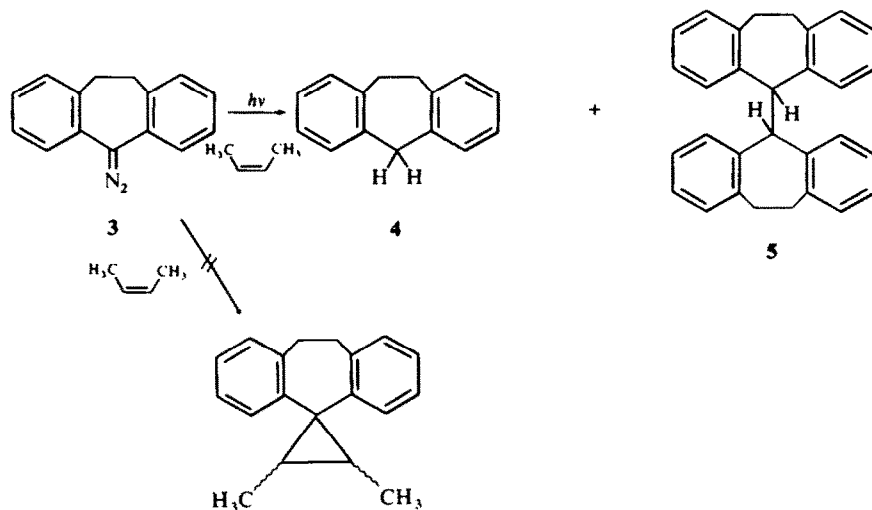
Abstract—Photolysis of 5-diazo[a,d]cycloheptene (**10**) and 9-diazotribenzo[a,c,e]cycloheptene (**23**) in *cis* and *trans*-2-butene led stereospecifically to the formation of cyclopropane derivatives. Nonstereospecific addition of dibenzo[a,d]cycloheptenylidene could not be detected by carrying out the photolysis in a large excess of cyclohexane, or by photosensitized decomposition of **10**. It is concluded that photolysis of **10** leads to a singlet (**6**) which converts to the triplet state and reacts stereospecifically with olefins to form cyclopropanes. These stereochemical results were reasonably explained by considering that a charge transfer complex plays an important role in the transition state of the addition reaction of **6** to olefins. The electronic structures of these carbenes are discussed in the light of results obtained from ESR and optical spectroscopy.

INTRODUCTION

IT IS KNOWN that carbenes substituted by aryl groups add to olefins in a nonstereospecific manner; this has been attributed to the triplet nature of the intermediate involved.¹⁻⁷ Thus Skell's hypothesis for the stereochemical course in addition reactions seems still to be valid in spite of the criticism.^{8,9} Fluorenylidene^{4,7} underwent nonstereospecific addition to *cis* and *trans* olefins, and showed strong abstraction of hydrogen^{4,10,11} or chlorine⁴ atoms. These reactivities would be attributed to the triplet state. According to Skell's hypothesis,² linear *sp* hybridization is an indispensable configuration for triplet diphenylmethylene, but fluorenylidene could not adopt such a linear configuration because of its central five membered ring. Therefore the results of fluorenylidene might stimulate us to reconsider Skell's hypothesis.

We have studied the chemistry of 10,11-dihydrodibenzo[a, d]cycloheptenylidene (**1**), since this carbene may have an electronic configuration similar to that of diphenylmethylene (**2**).⁵ Irradiation of 5-diazo-10,11-dihydrodibenzo[a, d]cycloheptene [**3**] in *cis*-2-butene gave 10,11-di-hydrodibenzo[a,d]cycloheptene (**4**, 6%) and 5,5'-bi(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl) (**5**, 81%). Formation of these compounds may be due to abstraction of the hydrogen atoms from olefins by carbene **1** (Scheme 1), and suggest that carbene **1** reacts in a triplet state.⁵

It is noteworthy that carbene **1** does not add to *cis*-2-butene, while diphenylmethylene adds to olefins nonstereospecifically. The results of ESR^{12,13} and electronic^{14,15,16} absorptions of carbene **1** and diphenylmethylene are summarized in Fig. 1. The fact that both carbenes showed similar spectral characteristics suggests that both carbenes have similar π -electronic configurations; carbene **1** absorbed at a longer wavelength than diphenylmethylene. This is consistent with the smaller *D* value of carbene **1** than that of diphenylmethylene. An important discrepancy between



SCHEME 1

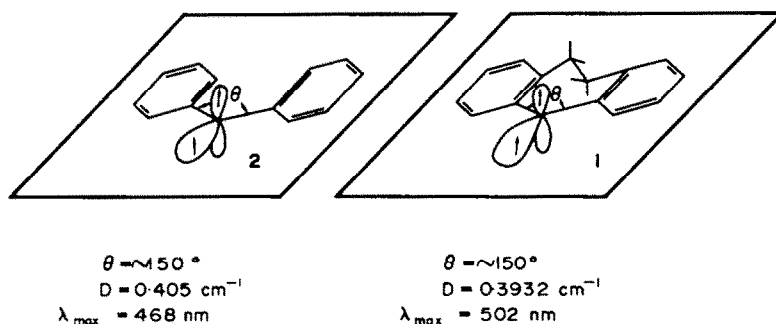


FIG 1. Comparison of the results of ESR and electronic absorption spectra of dihydro-5H-dibenzo[a,d]cycloheptenylium (1) and diphenylmethylene (2).

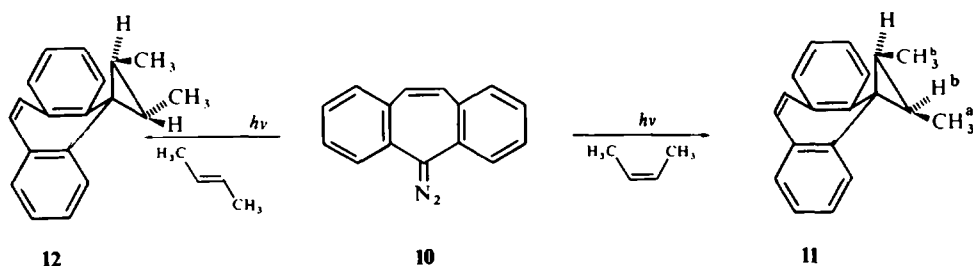
these two carbenes is the degree of delocalization of the π -electron system and one could imagine that this degree of delocalization affects essentially the reactivities of aryl carbenes. In this paper we wish to report that aryl substituted carbenes, dibenzo[a,d]cycloheptenylium (6) and tribenzo[a,c,e]cycloheptenylium (7), add to *cis* and *trans*-2-butenes stereospecifically, and to discuss the mechanism of the addition reactions.



RESULTS

Photolysis of 5-diazodibenzo[a,d]cycloheptene (10)

p-Toluenesulfonylhydrazone (**9**) was obtained from the corresponding ketone (**8**) in 71% yield. Treatment of this hydrazone with NaOMe in dry pyridine afforded the diazo compound **10** in 25% yield. Irradiation of a solution of **10** in *cis*-2-butene afforded *cis*-2,3-dimethylspiro[cyclopropane-1,5'-(dibenzo[a,d]cycloheptene)] (**11**, 11%) stereospecifically (Scheme 2). Stereospecific addition of **6** was confirmed on the following basis. *trans*-2,3-Dimethylspiro[cyclopropane-1,5-dibenzo[a,d]cycloheptene] (**12**) was not detected during the photolysis of **10** in *cis*-2-butene. The hydrocarbon fraction obtained was subjected to alumina chromatography and divided into *ca.* 50 fractions, checked by IR spectroscopy. No sign of the *trans* isomer was detected. Furthermore, the crude hydrocarbon fraction was analyzed by VPC and no peak corresponding to the *trans* isomer (**12**) was detected.



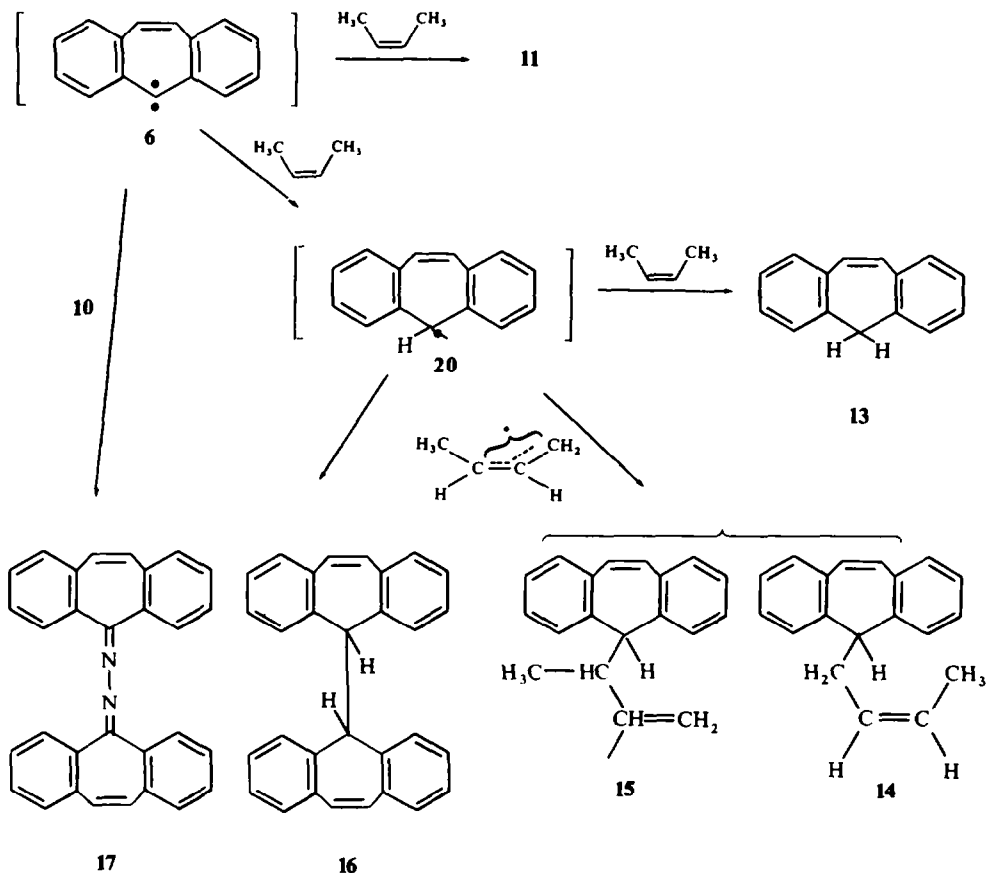
SCHEME 2

Compounds **11** and **12** are shown to be isomeric by mass spectroscopy (m/e 246, common to both). Compound **11** shows maxima (EtOH) at 214 nm ($\log \epsilon$ 4.5) and 285 nm (4.1). The NMR spectrum consists of doublets at δ 0.47 and 1.30 ($J = 7$ cps, Me protons) and multiplets at δ 1.7–2.0 and 0.5–0.8 (cyclopropyl protons). This result shows that inversion of the nonplanar ring in compound **11** is difficult,¹⁷ although inversion of tropyliene is very fast.¹⁸ This can be interpreted in terms of steric repulsion between the hydrogen atoms of the benzene rings and the Me groups in a planar transition state. Thus, the Me protons H^a and cyclopropyl proton H^b are deshielded by the anisotropy of both benzene rings.

Photolysis of **10** in *cis*-2-butene gave the following compounds in addition to cyclopropane derivative **11**; hydrogen abstraction products, 5H-dibenzo[a,d]cycloheptene (**13**, 2%), *cis*-4-(5H-dibenzo[a,d]cyclohepten-5-yl)-2-butene (**14**, 2%), 3-(dibenzo[a,d]cyclohepten-5-yl)-1-butene (**15**, 2%), and 5,5'-bi(5H-dibenzo[a,d]cycloheptenyl) (**16**, 23%), ketazine (**17**, 9%), 5H-dibenzo[a,d]cyclohepten-5-ol (**18**, 8%) and di(5H-dibenzo[a,d]cycloheptenyl)ether (**19**, 2%).

Irradiation of a solution of **10** in *trans*-2-butene gave the *trans*-2,3-dimethylcyclopropane derivative (**12**) in 2% yield. The mass spectrum (m/e 296) and UV spectrum (E_{max}^{EtOH}) 214 nm ($\log \epsilon$ 4.2) and 285 nm (3.8) showed the predicted values. The NMR spectrum consists of broad singlets at δ 0.60 and 1.42 (Me protons) and multiplets at δ 1.35–1.5 and 0.5–0.65 (cyclopropyl protons). Other products were **13** (4%), **15** (2%), **16** (20%), **17** (18%), **18** (15%) and **19** (6%).

The compounds, **13**, **14**, **15** and **16** would be formed through a 5H-dibenzo[a,d]-cycloheptyl radical (**20**) formed by hydrogen abstraction of carbene **6** as shown in Scheme 3; dimerization of **20** gave **16**, further hydrogen abstraction gave **13** and coupling with an allyl radical gave **14** and **15** (Scheme 3). Alcohol **18** and ether **19** may be formed through reductive photochemical processes¹⁹ involving the ketone, formed from reaction of **6** with oxygen.



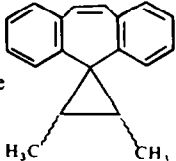
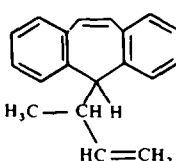
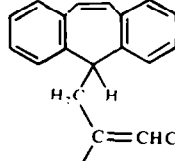
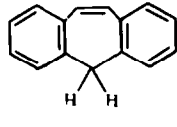
SCHEME 3

Carbene **6** adds to 2-butene in a stereospecific manner. Generally, carbenes with a π -benzene system adjacent to a divalent carbon add to olefins in a nonstereospecific fashion; furthermore, this nonstereospecific addition has been attributed to the triplet nature of carbenes. Accordingly, some experiments aimed at formation of the nonstereospecific component of the addition reaction were carried out.^{20, 21, 22}

Photolyses of diazo compound **10** in mixtures of cyclohexane and *cis*-2-butene were studied. It was hoped that the additive would function as an inert diluent, allowing the singlet to undergo enough fruitless collisions, such that an appreciable

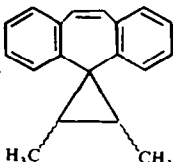
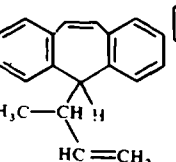
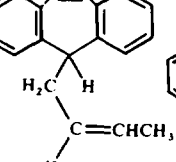
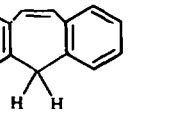
proportion would cross to the triplet state, leading to an enhancement of non-stereospecific addition. The data in Table 1 show that even under conditions where the cyclohexane:*cis*-2-butene was 100:1, stereospecific addition was observed. Hexafluorobenzene was examined but was observed to be not inert to **6**.²³

TABLE 1. THE DILUTION EFFECT OF 5H-DIBENZO[a,d]CYCLOHEPTENYLIDENE (**6**) BY CYCLOHEXANE

		The ratio of the product to the cyclopropane derivative			
The ratio of 2-butene to cyclohexane					
		11 (<i>cis</i>)	15	12	13
<i>cis</i>	100 (<i>cis</i>)	100 (<i>cis</i>)	20	18 (<i>cis</i>)	20
<i>cis</i> (1/20)	100 (<i>cis</i>)	100 (<i>cis</i>)	22	7 (<i>cis</i>)	35
<i>cis</i> (1/50)	100 (<i>cis</i>)	100 (<i>cis</i>)	20	14 (<i>cis</i>)	107
<i>trans</i>	100 (<i>trans</i>)	100 (<i>trans</i>)	110	235 (<i>trans</i>)	190
<i>trans</i> (5/1)	100 (<i>trans</i>)	100 (<i>trans</i>)	127	182 (<i>trans</i>)	69

Photosensitized decomposition of **10** was also carried out in attempts to increase the formation of the triplet carbene.^{22, 24} The data shown in Table 2, however, show that the stereospecificity of the addition reaction still remained.

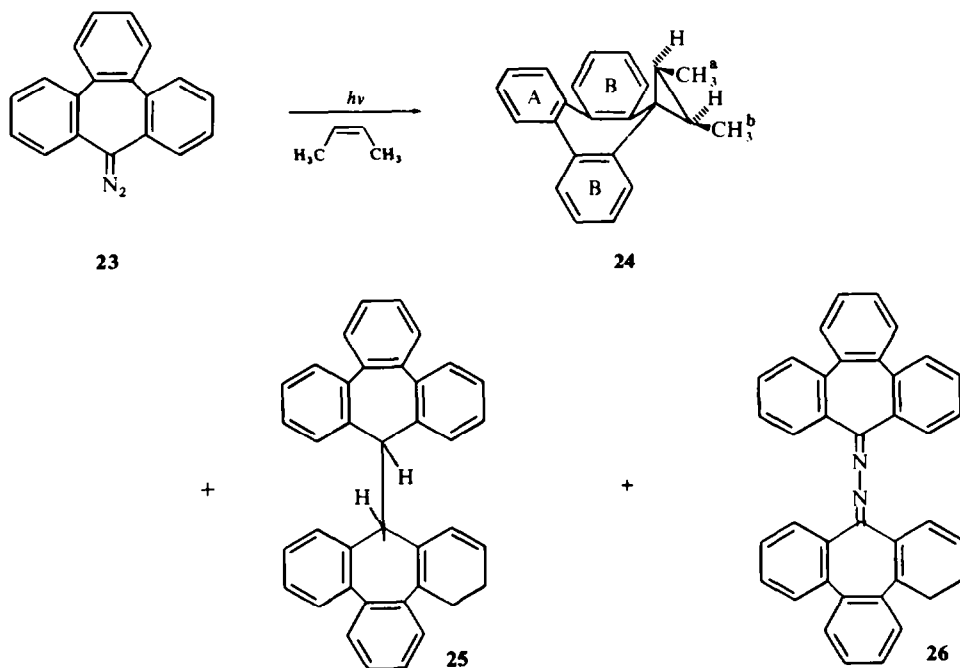
TABLE 2. PHOTOSENSITIZED DECOMPOSITION OF 5-DIAZO-5H-DIBENZO[a,d]CYCLOHEPTENE IN THE PRESENCE OF BENZOPHENONE

		The ratio of products to the cyclopropane derivative			
2-Butene	The ratio of 5-diazo[a, d]cycloheptene to benzophenone				
		11 (<i>cis</i>)	15	12	13
<i>cis</i>		100 (<i>cis</i>)	20	18 (<i>cis</i>)	20
<i>cis</i>	10/1	100 (<i>cis</i>)	28	31 (<i>cis</i>)	28
<i>cis</i>	1/100	100 (<i>cis</i>)	45	34 (<i>cis</i>)	229
<i>trans</i>		100 (<i>trans</i>)	110	235 (<i>trans</i>)	190
<i>trans</i>	1/10	100 (<i>trans</i>)	162	164 (<i>trans</i>)	88

Photolysis of 9-diazo-9H-tribenzo[a,c,e]cycloheptene (**23**)

Treatment of *p*-toluenesulfonylhydrazone (**22**), which was obtained from the corresponding ketone (**21**), with NaH afforded **23** in 4% yield. Irradiation of a solution

of **23** in *cis*-2-butene afforded *cis*-2,3-dimethylspiro[cyclopropane-1,9'-(9H'-tribenzo[a,c,e]cycloheptene)] (**24**, 70%), 9,9'-bi(9H-tribenzo[a,c,e]cycloheptenyl) (**25**, 2.3%), 9H-tribenzo[a,c,e]cyclohepten-9-one azine (**26**), and small amounts of 9H-tribenzo[a,c,e]cyclohepten-9-ol (**27**) and di(9H-tribenzo[a,c,e]cycloheptenyl)ether (**28**). The structure of the *cis*-2,3-dimethylcyclopropane derivative was assigned mainly by the NMR spectrum which consists of doublets at δ 0.20 and 1.23 ($J = 6.5$ cps, Me protons) and multiplets at δ 1.60–1.85 and 0.40–0.65 (cyclopropyl protons). The energy barrier of ring inversion of tribenzo[a,c,e]cycloheptene is so high²⁵ that the Me protons H^a of **24** (δ 0.20) are strongly shielded by the benzene ring A while H^b (δ 1.23) are deshielded by the benzene ring B (Scheme 4).



SCHEME 4.

On the other hand, irradiation of a solution of **23** in *trans*-2-butene gave the *trans* isomer of **24** (**29**) (29%) and **25** (2%). The NMR spectrum of **29** showed broad singlets at δ 0.15 and 1.38 (Me protons), and multiplets at δ 0.15–0.3 and 1.2–1.45 (cyclopropyl protons).

It is clear that the addition of carbene **7** to 2-butene proceeds stereospecifically. This stereospecificity was confirmed by taking the NMR spectrum of the cyclopropane fraction of the reaction product.

ESR spectra

It has been shown that carbene **1** has a π -electronic configuration similar with that of diphenylmethylene. Larger delocalization should reduce the density of the π -

electrons on the divalent carbon atom, and also reduce the D value. The structure of **1** in the triplet state as shown in Fig. 1 is reasonable in order to rationalize the smaller D value of **1** compared to that of diphenylmethylene; the enlargement of the angle ($\sim 150^\circ$) of the axes of the hybrids at C-5 increases the s character of these carbon bonds and the planarity of the seven-membered ring which contributes to the delocalization of the electron of the C-5 atom to both benzene rings. Electron absorption spectra of **1** and diphenylmethylene have confirmed this electronic structure of **1**.

Notwithstanding these similar π -electronic configurations, discrepancies have been observed in the chemical reactivity between **1** and diphenylmethylene as mentioned above. Thus, it is of interest to know the electronic configurations of carbenes **6** and **7** which showed stereospecific addition to 2-butene.

Carbene **6** and **7** possess triplet ground states.¹² From the E/D ratio the angles for **6** and **7** were determined to be $\sim 150^\circ$; this value is larger than that of the internuclear angle of the seven-membered ring.²⁶ This suggests that the seven-membered ring is almost in a plane similar to that of tropylium ion.

Absorption spectra

Recent studies^{14, 15} by optical spectroscopy and ESR have revealed the molecular structure of carbenes to a considerable extent. As the matrix isolation technique is restricted to give information at low temp, the problem is whether or not one can discuss the chemical reactivity of carbenes produced at room temp in connection with the information obtained at 77°K.

A solution of **10** (ca. 10^{-4} – 10^{-3} mole) in a mixture of methylcyclohexane and isopentane was photolyzed at 77°K using a 250 w high pressure Hg lamp with a pyrex filter. After irradiation for a few min a transient absorption spectrum of **6** which has absorption maxima at 380, 395 and 486 nm was obtained. At 77°K this is stable but disappears at higher temp. The absorption spectrum at the delay time of 10 μ sec which was obtained from flash photolysis of a solution of **10** (5×10^{-5} mole) in deoxygenated liquid paraffin at room temp was consistent with the absorption spectrum obtained in the rigid glass at 77°K. Therefore, the electronic state of carbene **6** is the same either in the rigid glass at 77°K or in liquid paraffin at room temp. The spectrum of carbene **6** at room temp changed with delay time, and then disappeared within 500 μ sec. The life time of carbene **6** is estimated to be ca. 10 μ sec. Carbene **6** would abstract hydrogen from the solvent to form the 5-dibenzo[a,d]cycloheptenyl radical **20**.²⁷ From these results, one can reasonably conclude the chemical reactivity of carbenes produced at room temp in connection with the information obtained by physical methods at low temp (77°K).

Decay of the absorption spectrum of **6** was observed when a solution of **10** in pentan-2-ene or diethylmaleate was photolyzed at 77°K under the same conditions. This result indicates that carbene **6** would easily react with olefins in contrast to the result that diphenylmethylene was inert to olefins at 77°K.^{15c}

DISCUSSION

To our best knowledge, the stereospecific addition reaction of **6** and **7** to 2-butene is the first such example to involve aryl carbenes. Since stereospecific addition is usually interpreted in terms of a singlet state reaction, this stereospecific addition reaction

could be easily explained by assuming that all addition proceeds through the singlet state while hydrogen abstraction is a triplet state reaction.²⁸ This is in agreement with a triplet ground state as it is well known that methylene addition in solution is stereospecific although methylene also has a triplet ground state. The stereospecific addition of cyclopentadienylidene has recently been attributed to the singlet state, while its ground state is a triplet.²²

Another explanation might be advanced. In the reaction of carbene **6** with butene-2 were obtained considerable amounts of hydrogen-abstraction products (**13**–**16**) which were formed from the triplet state. Therefore, this triplet carbene (**6**) should add to olefins to give cyclopropane derivatives.^{1–7} If so, the observed stereospecific addition of **6** would have to be derived from the stereospecific addition of triplet **6** to butene-2.

In order to clarify this interesting point two methods might be considered; dilution by inert solvents and photosensitization. Jones showed that the dilution of a *cis* olefin in hexafluorobenzene lowers the ratio of *cis* to *trans* cyclopropane until the *trans* product predominates, presumably because collisions with the inert solvent can induce intersystem crossing in the initially formed singlet carbene and the triplet carbene so formed is not stereospecific in its addition. Similar conclusions as to the nonstereospecificity of triplet additions have been drawn.^{20, 27b, 27c}

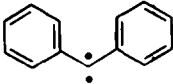
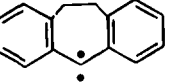
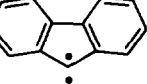
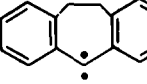
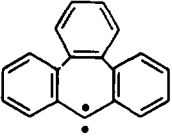
Diazo compound **10** was decomposed in a mixture of *cis*-2-butene and cyclohexane. The ratio of *cis*-2-butene to cyclohexane was changed from one twentieth to one hundredth. Careful analyses of the products revealed that there was no detectable amount of *trans* cyclopropane (**12**) formed in all cases (Table 1). Consequently, it seems reasonable that the spin state responsible for the addition reaction is a triplet. Although the yield of **13** increased in proportion with increase in the ratio of cyclohexane to *cis*-2-butene, the ratio of **11**/(**14** + **15**) scarcely changed. Thus, only one intermediate reacted with *cis*-2-butene; carbene **6** had already changed from an initially formed singlet state to a more stable triplet state, which then reacted with the olefin.

In order to substantiate the above results we investigated the photosensitized decomposition of **10**. It is expected that triplet carbene **6** will be formed by loss of N₂ from triplet diazo compound **10** formed in turn by energy transfer from triplet benzophenone. Jones observed a marked dependence of bis-carboethoxy carbene multiplicity on the method of generation.²¹ We have not observed any substantial discrepancy between direct and sensitized photolysis (Table 2). Consequently, the species involved must always be the triplet state. Then it may be safely concluded that triplet carbenes **6** (and **7**) undergo the stereospecific addition.

Recently, the 1-pyrazoline formed by the photochemical cycloaddition of 9-diazofluorene to norbornadiene and norbornene was isolated and submitted to thermal and photochemical decomposition.²⁹ These results add weight to the possibility of pyrazoline formation before its conversion to cyclopropane in many other analogous reactions between diazo alkanes and olefins which were widely interpreted as carbene additions to alkenes. In our case, the possibility of pyrazoline formation followed by decomposition to the cyclopropane derivatives was, however, eliminated by the fact that no pyrazoline was obtained from the reaction of diazo compounds **10** and **23** with 2-butene at 0°; furthermore, abstraction products, **13**, **16** and **25** were obtained.

As shown in Table 3 it is apparent that the highly conjugated carbenes show stereospecific addition to olefins. These carbenes have relatively large delocalization energies, which could play an important role in the addition reactions to olefins. There are only slight energy differences between a singlet state and a triplet state in highly conjugated carbenes. Thus, even if the triplet state of an aryl carbene is more stable than that of the singlet state it is possible that the singlet state reacts with olefins instead of the triplet state because of its higher reactivity. Stereospecific addition of cyclopentadienyliidene toward olefins could be interpreted as such a case.²² Cyclopropenyliidene³⁰ and cycloheptenyliidene³¹ have been studied, and it was hoped that the singlet carbene would derive important stabilization from the aromaticity. The demonstration that these carbenes have reacted only with olefins with electron-poor bonds is consistent with the important contributions of the charge delocalized forms, indicating the nucleophilic behavior of these carbenes toward olefins. Since no such special evidence is found for higher reactivities of the singlet state of carbenes 6 and 7, the stereospecific additions can not be attributed to their singlet states.

TABLE 3. THE RESULTS OF ADDITION REACTIONS AND THE DELOCALIZATION ENERGIES OF SOME ARYL CARBENE

					
Addition reactions	Nonstereospecific	—	Nonstereospecific	Stereospecific	Stereospecific
DE(β) (LCAO)	5-30	5-30	5-54	6-42	8-23
ESR (ground state)	Triplet	Triplet	Triplet	Triplet	Triplet

The electronic and ESR spectra (77°K) of carbene 1, 6, and 7 have revealed considerably the molecular structure of their triplet states.¹² It is doubtful, however, that one can discuss the reactivity of carbenes produced at room temp on the basis of the information obtained at 77°K. Flash photolysis techniques solved this problem.²⁷ There is no observable discrepancy between the electronic spectra at 77°K (rigid media) and that at 25°C (flash photolysis) for either carbene 1 or 6. Furthermore, in view of the fact that T-T' absorption spectra of carbenes 1 and 6 can be observed at room temp, it seems reasonable to assume that the singlet-triplet intersystem crossing can occur within 1-10 μ sec at room temp. Thus, the life time of the singlet state is too short to react with the olefin and the carbenes may react with the olefin in the triplet state. The absorption spectrum of carbene 1 decayed (life time, one to 50 μ sec) to that of the hydrogen abstraction product (a doublet free radical); the final product is the free-radical dimer. It is obvious that even at 77°K carbene 6 can react with olefins considerably rapidly since at 77°K the absorption spectrum of 6 could not be detected in excess olefin, and the absorption strength of the ESR spectra

of **6** in the presence of olefin was reduced. When less than an equivalent of olefin was used, the absorption strength of the ESR spectra of **6** decreased proportionately.

With these results, we would like to propose a new mechanism in which a charge transfer complex plays an important role in the transition state. A potential energy

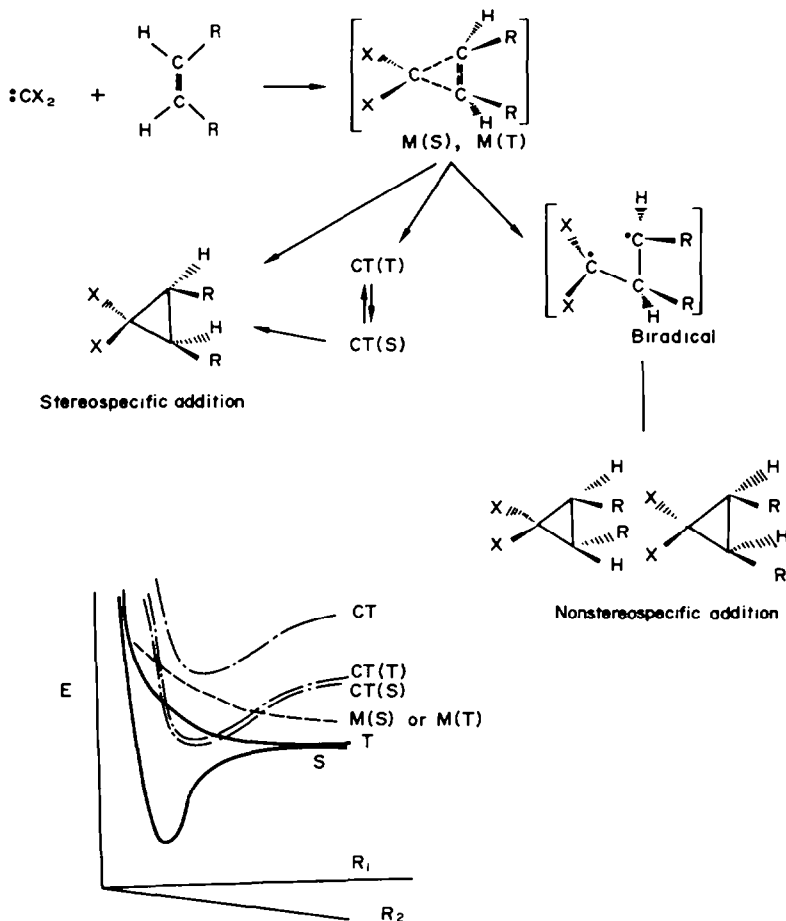


FIG 2. The energy diagram of the addition reaction of a carbene to olefin.

diagram of two atomic molecules can provide a simple picture for this mechanism (Fig 2). The distance between carbenes and olefins is presented by the horizontal line R_1 , the reaction coordinate for the formation of cyclopropanes by the second horizontal line R_2 , and the potential energy by the vertical line. A carbene approaches an olefin and forms a complex M (singlet, M_s , or triplet M_t) at the first stage of the reaction. When a carbene is in a singlet state, the reaction proceeds through a three centered mechanism to give a cyclopropane in stereospecific manner.³² When a carbene is in a triplet state, a similar complex M_t is formed. If a carbene has an extended conjugating system and hence has a large delocalization energy, it is expected to form

a rather stable charge transfer complex (CT),* whose energy level is low enough to cross with that of M(T). In such a case, the reaction will proceed from M(T) to CT(T). It has been reported that at the charge transfer stage, the intersystem crossing, CT(T) \rightarrow CT(S), can generally occur with much higher probability than for an ordinary singlet-triplet intersystem crossing.³³ Thus, it is reasonable to consider that the spin inversion of the triplet state to the singlet state will occur at this CT stage; therefore, the intermediate will not have enough life time to rotate about the single bonds resulting in the nonstereospecific addition.

On the other hand, when the delocalization energy of a carbene is not so large, the energy level of the CT state can not become low enough to cross the level M(T). The CT stage can not be involved in the reaction course and the process M(T) \rightarrow T \rightarrow S can occur to produce a cyclopropane. An intermediate diradical has an enough life time to rotate about the carbon-carbon single bond before final ring closure.

In brief, the triplet carbenes like **6** and **7** can undergo stereospecific additions because their delocalization energies are large enough to make the reactions go through the charge transfer complex.

EXPERIMENTAL

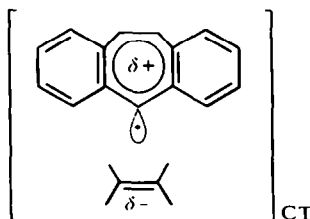
All m.ps are uncorrected. IR spectra were determined with a Hitachi-S2 spectrophotometer. NMR spectra were recorded with a JNM-4H-100 spectrometer. (internal TMS). UV spectra were measured on Hitachi EPS-2 or Cary 14 spectrometers. ESR spectra were obtained with a Japan Electron Optics Lab. JES-3BX with 100-kc field modulation. Petroleum ether refers to the fraction 40-70°.

5H-dibenzo[a,d]cyclohepten-5-one *p*-toluenesulfonylhydrazone (**8**). A soln containing **6**³⁴ (80 g, 0.39 mole), *p*-toluenesulfonylhydrazone (88 g, 0.47 mole) and conc. HCl (40 ml) in EtOH (300 ml) was heated at reflux

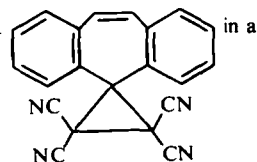
* Singlet carbenes are electrophilic,⁸ but such electrophilicities are not observed for triplet carbenes.

In a singlet carbene of which lowest vacant orbital receives an electron from an olefin, the electrophilicity of a carbene would increase relative to the degree of the delocalization.

In a triplet carbene, if it was electrophilic, the highest occupied orbital of the carbene would receive an electron, hence the electrophilicity of a carbene would decrease as the degree of the conjugation of the carbene increased. Thus, the triplet carbene of which π -electrons are highly delocalized would rather show a nucleophilic character because the ionization potential of a carbene is low. Therefore, the charge-transfer complex of the carbene(donor)-olefin (acceptor) would be stabilized. In carbene **6**, a *p*-orbital electron of the divalent carbon would transfer to an olefin to form the complex as shown below.



Irradiation of **10** in the presence of tetracyanoethylene gave rise to the adduct in a 60% yield.



for 9 hr. After cooling to room temp the crystalline material was filtered off and washed with alcohol. Recrystallization from acetone gave **8** (104 g, 71%), m.p. 204° (dec); IR (nujol) 3160 cm^{-1} (N-H). (Found: C, 70.50; H, 4.92. Calc. for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{S}$: C, 70.58; H, 5.85%).

5-Diazo-5H-dibenzo[a,d]cycloheptene (10). To a soln of **8** (104 g, 0.28 mole) in anhyd pyridine (750 ml) was added NaOMe (40 g). The soln was stirred at 56–58° for 2.5 hr, poured onto ice-water and ether extracted. The extract was washed with water, dried and concentrated at reduced pressure. Petroleum ether was added, and the precipitated crystalline material (15.1 g, 25%) filtered, m.p. 62° (dec); IR (nujol) 2025 cm^{-1} (N=N); UV max(methylcyclohexane) 222 nm (log ϵ , 4.49), 2.79 (4.5), 390^{sh}, 520^{sh}. NMR (CCl_4) δ 2.75–3.30 (m, 8H), 3.77 (s, 2H). (Found: C, 82.75; H, 9.69. Calc. for $\text{C}_{15}\text{H}_{10}\text{N}_2$: C, 82.50; H, 4.96%). This compound is unstable in EtOH. Thermal decomposition gave the corresponding ketazine. Acidification of the aqueous layer with HCl (pH 4) recovered tosylhydrazine **8** (50 g).

9H-Tribenzo[a.c.e]cyclohepten-9-one p-toluenesulfonylhydrazone (22). A mixture of **21**³⁵ (63 g, 0.24 mole), p-toluenesulfonylhydrazine (52 g, 0.28 mole), dioxane (500 ml) and conc. HCl (40 ml) was heated at reflux for 7 hr. The mixture was concentrated to one-third and petroleum ether slowly added. The resulting precipitate was filtered and washed with EtOH. Recrystallization from n-propanol gave **22** (87 g, 83%), m.p. 212–214 (dec); IR (nujol) 3250 cm^{-1} (N-H). (Found: C, 73.57; H, 4.61, S, 7.61. Calc. for $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2\text{S}$: C, 73.58; H, 4.72; S, 7.56%).

9-Diazo-9H-tribenzo[a.c.e]cycloheptene (23). To a soln of NaH (0.7 g) in dry pyridine (50 ml) was added **22** (9.4 g, 22 mmoles). After hydrogen evolution had ceased the mixture was stirred maintaining the temp at 56–59° for 1.5 hr. The mixture was poured onto ice-water and extracted with ether. The extract was washed and dried. Evaporation at reduced pressure gave 1 g of crude **23**, m.p. 60° (dec); IR (nujol mull) 2050 cm^{-1} (N=N); UV max(EtOH) 520 nm.

The content of pure diazo compound **23** (250 mg, 4%) in this crude mixture (mainly ketazine) was determined by titration with benzoic acid. The reaction of **23** with benzoic acid gave 9H-tribenzo[a.c.e]-cyclohepten-9-yl benzoate, m.p. 183.5–184° (EtOH); IR (nujol) 1715 cm^{-1} (C=O).

Thermal decomposition of 9-diazo-9H-tribenzo[a.c.e]cycloheptene (23) in benzene. A soln of crude diazo compound **23** in C_6H_6 was heated at reflux for 10 min and the soln subjected to aluminum chromatography. Elution with C_6H_6 gave **26**, m.p. 294–295° (CH_2Cl_2 -petroleum ether); UV max(dioxane) 243 nm (log ϵ , 5.0); NMR (CDCl_3) δ 6.7–7.6. (Found: C, 89.35; H, 4.91; N, 5.42. Calc. for $\text{C}_{38}\text{H}_{24}\text{N}_2$: C, 89.75; H, 4.76; N, 5.42%).

Photolysis of 5-diazo-5H-dibenzo[a,d]cycloheptene (10) in the presence of cis-2-butene. A soln of **10** (10.3 g, 57 mmoles) in cis-2-butene (Matheson 99%, 400 ml) was placed in a 500 ml quartz 3-necked cylindrical flask equipped with a gas diffusion tube, solid CO_2 /acetone condenser and mechanical stirrer. The flask was cooled by immersing half way into ice-water. The mixture was photolyzed by high pressure mercury lamp (Halo 1000 w). During the photolysis solid was removed mechanically. After the violet-red color of diazo compound disappeared (8 hr), cis-2-butene was removed. The residual reaction products were dissolved in CH_2Cl_2 . Insoluble colorless compounds were filtered off. Recrystallization from C_6H_6 and dioxane gave **16** (13%), assigned by comparison with an authentic sample. UV max(dioxane) 222 nm (log ϵ , 4.95), 297 (4.61). (Found: C, 94.01; H, 5.78. Calc. for $\text{C}_{30}\text{H}_{22}$: C, 94.20; H, 5.80%). After evaporation of CH_2Cl_2 from the filtrate, the residue was dissolved in petroleum ether. An insoluble compound was filtered. Recrystallization from C_6H_6 gave 0.9 g of **17** (9%), also obtained, as mentioned above, from thermal decomposition of **10**. UV max(dioxane) 240 nm (log ϵ , 4.71), 290.5 (4.38). (Found: C, 87.96; H, 5.03; N, 6.48. Calc. for $\text{C}_{30}\text{H}_{20}\text{N}_2$: C, 88.21; H, 4.92; N, 6.81%). The petroleum ether soln was concentrated and subjected to an aluminum chromatography (100 g). Elution with petroleum ether (1100 ml) gave hydrocarbons. The eluents were collected in each 100 ml. The first three fractions (300 ml) were subjected to silica gel chromatography. Elution with petroleum ether gave colorless crystalline **11** (1.3 g, 11%), m.p. 60.5–61.5°; IR (nujol) 1175, 1155, 1120, 1106, 1070, 1040, 965, 940, 890, 870, 840, 830, 795, 785, 765, 755, 740, 715 cm^{-1} . UV and NMR spectra were mentioned above. Elution of the aluminum column with petroleum ether– C_6H_6 (10% C_6H_6 , 200 ml) gave 0.194 g of **19** (2%), consisted with the authentic sample; m.p. 207–209° (n-hexane– CCl_4 , 1:1); NMR (CCl_4) δ 4.86 (s, 2H), 6.83 (s, 4H). (Found: C, 90.19; H, 5.67. Calc. for $\text{C}_{30}\text{H}_{22}\text{O}$: C, 90.42; H, 5.57%). Elution with ether–EtOH (10% EtOH, 200 ml) afforded **18** (0.77 g, 8%), m.p. 122–123°.

Another experiment was repeated under the same conditions. The hydrocarbon fractions obtained from the aluminum chromatography was subjected to VPC (Apieson L, 2 m, column temp 240°). Four components were detected. The ratios of the other three products to **11** were one fifth; therefore, yields of the other three products were determined to be 2% respectively. Each peak was collected by VPC and its structure assigned. The compound corresponding to the first peak was assigned as **13**, m.p. 131° (lit³⁴ 131°); NMR (CCl_4) δ 7.0–

7.25 (m, 8H), 6.90 (s, 2H), 3.67 (s, 2H). The compound corresponding to the second peak was assigned as 15. IR (liquid film) 1643, 1492, 1454, 1436, 1414, 1370, 1282, 1160, 1112, 1082, 990, 908, 873, 827, 795, 762, 727 cm^{-1} ; UV (EtOH) max 227^{ab} nm (log ϵ , 4.93), 294 (4.57); NMR (CCl_4) δ 3.53 (d, 1H, $J = 10$ Hz), 0.63 (d, 3H, $J = 7$ Hz). (Found: C, 92.96; H, 7.28. Calc. for $\text{C}_{19}\text{H}_{18}$: C, 92.63; H, 7.37%). The third component was 11. The fact that the products from *cis*-2-butene were not contaminated with 12 was confirmed by VPC, and careful separation of the hydrocarbon fractions followed by checking with IR spectra. The compound corresponding to the last peak was 14. IR (liquid film) 1654, 1160, 1110, 1045, 990, 965, 940, 875, 835, 787, 762, 742, 725, 705, 690 cm^{-1} ; UV (EtOH) max 226^{ab} nm, 229; NMR (CCl_4) δ 5.0–6.4 (m, 2H), 1.34 (d, 3H, $J = 5$ Hz). (Found: C, 92.49; H, 7.39. Calc. for $\text{C}_{19}\text{H}_{18}$: C, 92.53; H, 7.51%). A trace amount of 8 was also detected. m.p. 89–90° (lit³⁴ m.p. 89°).

Photolysis of 5-diazo-5H-dibenzo[a,d]cycloheptene (10) in the presence of trans-2-butene. A soln of 10 (8.1 g) in *trans*-2-butene (360 ml) was photolyzed for 4 hr. and the products treated as above. The CH_2Cl_2 insoluble compound 16 (1.4 g, 20%) and the petroleum ether insoluble compound 17 (1.4 g, 18%) were obtained. The petroleum ether soluble compounds were subjected to aluminum chromatography. Elution with petroleum ether gave 0.17 g of 12 (2%), m.p. 59–60° (petroleum ether); IR (nujol) 1157, 1115, 1107, 1084, 1040, 1007, 964, 945, 895, 875, 844, 831, 800, 765, 757, 743, 720 cm^{-1} ; UV and NMR spectra reported above. (Found: C, 92.20; H, 7.29. Calc. for $\text{C}_{19}\text{H}_{18}$: C, 92.63; H, 7.37%). Further elution with benzene afforded 19 (0.44 g, 6%) and 18 (1.2 g, 15%). The hydrocarbon fraction were subjected to VPC. The first peak corresponded to 13 (4%), the second to 15 (2%), the third to 11, and the fourth to *trans*-4-(5H-dibenzo[a,d]cyclohepten-5-yl)-2-butene (4%). IR (liquid film) 1157, 1106, 1090, 1065, 1040, 965, 955, 940, 897, 876, 834, 795, 775, 757, 738, 721, 696 cm^{-1} ; NMR (CCl_4) δ 4.9–5.5 (m, 2H), 3.79 (t, 1H, $J = 7.5$ Hz), 2.25–2.45 (m, 2H) and 1.43 (d, 3H). A trace amount of 8 was also detected.

5H-Dibenzo[a,d]cyclohepten-5-ol (18). To a soln of 8 (5.1 g, 25 mmoles) in isopropyl alcohol (50 ml) was added 0.95 g of NaBH_4 and the mixture heated at reflux with stirring for 2 hr. After cooling to room temp the mixture was poured into water (800 ml) the precipitated crystalline material filtered. Recrystallization from petroleum ether– CH_2Cl_2 (1:1) gave 18 (96%), m.p. 122–123°; IR (nujol) 3400 cm^{-1} ; NMR (CDCl_3) δ 7.05–8.0 (m, 8H), 6.96 (s, 2H) and 5.00 (s, 1H). (Found: C, 86.17; H, 5.89. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}$: C, 86.16; H, 5.81%). Literature³⁴ reports the m.p. of the alcohol as 99–100°, but this compound should be 5-ethoxy-5H-dibenzo[a,d]cycloheptene. A mixture of 8 (20 g, 0.10 mole), NaOH (20 g), Zn (30 g) in EtOH (200 ml) was heated at reflux for 2 hr with stirring. After evaporation of EtOH the product was neutralized with HCl . The precipitated crystalline material was filtered and recrystallized from EtOH; 19 (22 g, 93%); m.p. 99–100°; IR (nujol) 1195, 1110, 1080 cm^{-1} (C—O); NMR (CDCl_3) δ 1.33 (t, 3H), 3.59 (q, 2H), 4.69 (s, 1H), 6.97 (s, 2H), 7.1–7.6 (m, 8H). (Found: C, 86.61; H, 6.89. Calc. for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.40; H, 6.83%).

Photolysis of 9-diazo-9H-tribenzo[a,c,e]cycloheptene (23) in the presence of cis-2-butene. A soln of 23 (4.2 g, crude diazo compound, pure diazo compound 840 mg) in ether (90 ml) and *cis*-2-butene (150 ml) was photolyzed for 2 hr as described above. After recovery of *cis*-2-butene, the product was dissolved in CH_2Cl_2 and insoluble 26 (15 mg, 2.3%) collected; m.p. 384° (toluene); UV (dioxane) max 224 nm (log ϵ , 4.73), 244 (4.78) and 264^{ab} (4.34). (Found: C, 94.17; H, 5.55. Calc. for $\text{C}_{38}\text{H}_{26}$: C, 94.57; H, 5.43%). The CH_2Cl_2 soln was condensed and subjected to aluminum chromatography (300 g). Elution with petroleum ether (350 ml) gave 660 mg of 24 (70%); m.p. 158–159.5° (MeOH); IR (nujol) 1243, 1222, 1174, 1153, 1118, 1087, 1072, 1046, 1000, 944, 880, 857, 840, 784, 760, 750, 735, 725 cm^{-1} ; UV and NMR spectra reported above. (Found: C, 93.40; H, 6.75. Calc. for $\text{C}_{23}\text{H}_{20}$: C, 93.20; H, 6.80%). Mass m/e 296, parent peak. Elution with CCl_4 gave azine 26. Further elution with EtOH gave a trace amount of 27 (m.p. 95–105°) and 28 (m.p. 240–245°).

Photolysis of 9-diazo-9H-tribenzo[a,c,e]cycloheptene (23) in the presence of trans-2-butene. A mixture of crude diazo compound 23 (5.5 g, 5.5 mmoles pure diazo compound), ether (130 ml) and *trans*-2-butene (155 ml) was photolyzed for 3 hr. After removal of 25 (48 mg, 23%) the mixture subjected to aluminum chromatography (100 g). Elution with petroleum ether gave hydrocarbons, again subjected to silica gel chromatography. Elution with petroleum ether gave 29 (480 mg, 29%); m.p. 112–112.5° (MeOH); IR (nujol) 1157, 1115, 1084, 1055, 1040, 1005, 970, 957, 937, 875, 860, 830, 810, 778, 760, 740, 725 cm^{-1} . UV and NMR spectra reported above. (Found: C, 93.06; H, 6.92. Calc. for $\text{C}_{23}\text{H}_{20}$: C, 93.20; H, 6.80%). Mass m/e 296, parent peak. Further elution of the aluminum column with CCl_4 gave 26 and elution with alcohol gave trace amounts of 27 and 28.

9,9'-Bi(9H-tribenzo[a,c,e]cyclohepteny)] (25). To a mixture of 27 (3.0 g) and CaCl_2 (4 g) in CH_2Cl_2 (50 ml) was bubbled dry HCl gas. After filtration of CaCl_2 , evaporation of CH_2Cl_2 gave 9-chloro-tribenzo[a,c,e]cycloheptene (1.7 g), m.p. 125–127° (petroleum ether). This chloride (1 g) was dissolved in dry C_6H_6

(50 ml) and added 0.8 g of Cu powder. The mixture was heated at reflux for 5 hr. After hot filtration, the colorless crystalline material (330 mg) was collected. m.p. 334° (toluene).

Dilution experiments. Diazo compound **10** was dissolved in a known mixture of cyclohexane and *cis*-2-butene, and photolysis was carried out. The product was distilled at reduced pressure with a short-path distillation flask, and the distillate subjected to VPC (Apiezon L, 2m. column temp 240°) (Table 1). 5-Cyclohexyl-5H-dibenzo[a, d]cycloheptene was also detected by VPC.

Benzophenone-photosensitized decomposition of 5-diazo-5H-dibenzo[a, d]cycloheptene. A mixture of **10** (2.6 g, 12 mmoles) and benzophenone (19 g, 106 mmoles) in *cis*-2-butene (300 ml) was photolyzed until the red color of **10** disappeared. After recovery of *cis*-2-butene the products were dissolved in CH₂Cl₂ and transferred to a small round-bottomed flask. Concentration of CH₂Cl₂ solution afforded crystals of benzophenone. Recrystallization from EtOH gave 16.7 g of pure benzophenone. The filtrate was evaporated, and the resulting residue distilled at reduced pressure. Addition of C₆H₆ to the distillate (0.52 g) gave crystalline dimer **16** (0.2 g). The filtrate was subjected to VPC as described above. (Table 2). The ratio of **8/11** was 13/100.

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