

195. Conventional and Laser Photolysis of a Bisdiaz Compound¹⁾

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Entirely different product distributions were observed when the bisdiaz compound **1** was irradiated by a conventional lamp (254 nm) on the one hand and by a pulsed excimer laser (248 nm) on the other. Continuous photolysis gave a complex reaction mixture (*Scheme 2*), of which eight products were identified. Pulsed laser photolysis gave (11*E*)-dibenzocyclooctatriene **20** as a new product in 49% yield (*Scheme 4*). We postulate that compound **20** is formed *via* the biscarbene intermediate **18** which results from the sequential absorption of two photons by a single molecule within a single laser pulse.

1. Introduction. – The high light intensities available from laser-light sources can give rise to results which are completely different from those obtained upon photolysis by conventional lamps or sunlight. These high-intensity processes have been investigated intensively by spectroscopic techniques [2]. In some cases, products involving more than one photon in their generation have been characterized and/or isolated [3]³⁾. Two-photon processes can be distinguished by the time span elapsing between the absorption of the two photons. Quasi-simultaneous two-photon absorption has become an important tool in molecular spectroscopy but is observed only under extremely high laser power and with sensitive detection methods [5]. More common are sequential two-photon processes in which the second photon is absorbed by molecules in an excited state [3a–f] or by reactive intermediates such as biradicals or radical ions [2e] [3g–l].

A related case is provided by bichromophoric molecules [6]. If both chromophoric moieties can be excited within sufficiently short time under high light-intensity conditions, bifunctional reactive intermediates may be formed which eventually can lead to new products. As an example of a bichromophoric molecule, we investigated the bisdiaz compound **1**. A comparison of the results of laser photolysis and conventional photochemistry are reported here¹⁾.

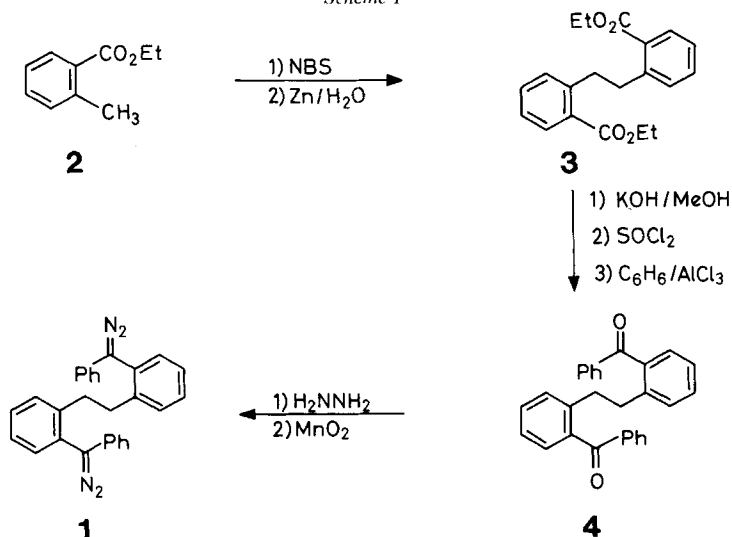
2. Synthesis. – Bisdiaz compound **1** was prepared by oxidation of the bishydrazone of the diketone **4** with MnO₂ [7] (*Scheme 1*). A large excess of hydrazine and long reaction times were necessary to achieve complete reaction of both C=O groups. Two different bishydrazone isomers could be isolated due to their solubility difference in CHCl₃.

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³⁾ In other cases, the monochromaticity of the laser light has been used to improve or alter the course of photochemical reactions [4].

Scheme 1

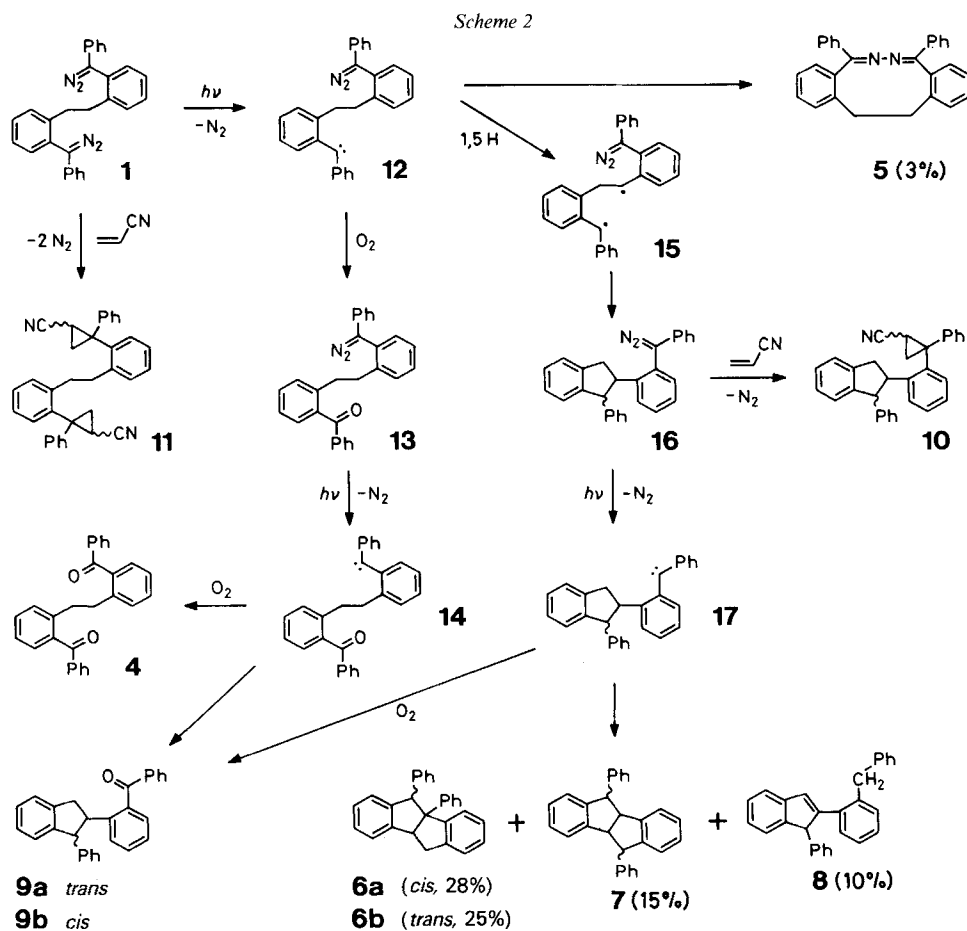


Since the reported synthesis of **4** [8] required the use of quite hazardous reagents, a more convenient synthesis was developed. The key step of the strategy was the coupling of two molecules of 2-(bromomethyl)benzoate, which was prepared by bromination of the ester **2**. Best yields of the diester **3** (40–50%) were obtained by using activated Zn [9] in H_2O . The major side products were the ester **2** and phthalate. The conversion of **3** to **4** was straightforward. All steps had yields exceeding 90%.

3. Conventional Photochemistry. – *Preparative Photolysis.* The photolyses of **1**, with either a high- or a low-pressure Hg lamp, gave essentially the same complex product mixture. The seven major products could be isolated by column chromatography, and their structure was assigned on the basis of spectral data.

The most polar compound, which was isolated in 3% yield, was identified as 5,6-dihydrodibenzo[*d,h*][1,2]diazecine **5** (Scheme 2). In the mass spectrum, the M^+ peak at m/z 386 indicated the loss of only 1 mol of N_2 from **1**. The ^1H -NMR spectrum shows a typical $AA'XX'$ spin system for the CH_2CH_2 bridge in the diazecine ring. The ^{13}C -NMR reveals a symmetrical structure; the signal at 157.4 ppm is characteristic for the $\text{C}=\text{N}$ bond. Note that **5** was not formed by the reaction of **4** with hydrazine or by refluxing the monohydrazone of **4**.

The two major products, accounting for *ca.* two thirds of the material balance, were identified as the 5,5a-diphenylindenoindenes **6a** and **6b**. The ^1H -NMR spectra of both compounds exhibit an ABX spin system for 2 H–C(10) and H–C(10a) and a *singlet* for H–C(5). The off-resonance ^{13}C -NMR spectra show the expected multiplicities. The configuration of the two isomers could be assigned on the basis of the unusually high resonance of one aromatic proton at 5.75 in **6b**. Decoupling experiments demonstrated unambiguously that this signal belongs to the aromatic spin system. The remarkable upfield shift of more than 1 ppm is rationalized as a shielding effect of the Ph group at



C(5), which is positioned just below the aromatic H–C(6) in **6b**, where the Ph groups at C(5) and C(5a) are *trans* to each other (Fig. 1). The *cis*-isomer **6a** does not show this effect.

A *trans* ring fusion can be excluded for **6b**, since in none of the possible isomers with *trans* ring fusion the aromatic rings are in sufficient proximity to explain the 1-ppm shift

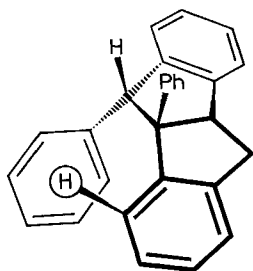


Fig. 1. Perspective drawing of **6a**, showing the overlap of H–C(6) (circled) with Ph–C(5)

observed in the ^1H -NMR spectrum of **6b**. Also for **6a**, a *cis* ring fusion is assumed, since, first, a *trans* ring fusion of two five-membered rings is very unlikely due to the large strain and, second, the *ABX*-spin system in ^1H -NMR spectra in **6a** and **6b** shows almost the same coupling constants, so that the same type of ring fusion is very reasonable. One isomer of **6** was already described by Salisbury [10], but the configuration of the compound had not been assigned. Physical and spectral data of **6b** are in accord with the described compound, so that a *trans*-configuration of the Ph groups can be assigned to Salisbury's compound.

Another fraction of the photolysis products contained three isomers in approximately equal amounts of 5% each. They have been identified as 5,10-diphenylindenoindenes **7**. Compounds **7a** and **7b** could be obtained in > 90% isomeric purity. It was not possible to separate **7c** from the other isomers, but its ^1H -NMR spectrum could be partially assigned. The configuration of the three isomers could be established on the basis of their ^1H -NMR spectra, particularly from the coupling constants of the aliphatic protons and the shielded aromatic protons at *ca.* 5.8 ppm in two of the isomers (Table 1). A *trans* ring fusion of the five-membered rings can be excluded for the same reasons as described for **6** (*vide supra*). Some isomers of **7** have been described previously [10] [11], but no configurations have been assigned.

Table 1. Dihedral Angles and NMR Coupling Constants of **7a**, **7b**, and **7c**

	Estimated dihedral angles/°			Coupling constants <i>J</i> /Hz			Lowest aromatic signal δ /ppm
	< H–C(5), H–C(5a)	< H–C(5a) H–C(10a)	< H–C(10), H–C(10a)	<i>J</i> (5,5a)	<i>J</i> (5a,10a)	<i>J</i> (10,10a)	
7a	0	0	120	9.2	7.7	2.8	5.97
7b	120	0	120	3.5	7.5	3.5	7.03
7c	0	0	0	9.5	7.8	9.5	5.79

An additional photoproduct, which was isolated in 10% yield, was identified as the indene derivative **8**. Its spectral data are in agreement with those reported for a related indene obtained by the photolysis of the diketone **4** [5c].

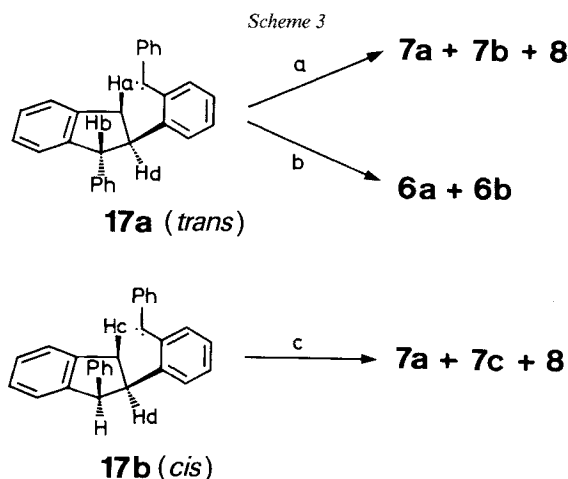
Trapping Experiments. Photolysis under O_2 yielded, besides the hydrocarbons **6–8** (10% total), the isomeric *ortho*-indanylbzophenones **9a** (3%) and **9b** (5%), and the diketone **4** (9%) as the major products. The other compounds present were a complex mixture of the photoproducts of **4** [5c]. The configuration of the ketones **9** was assigned based on the fact that the ^1H -NMR coupling constant *J*(1,2) for indane has a larger value for the *cis*-isomer than for the *trans*-isomer. Therefore, a *trans*-configuration at C(1) and C(2) was assigned to **9a** and a *cis*-configuration to **9b**.

When the mixture produced by photolysis of **1** to *ca.* 60% conversion was treated with acrylonitrile, the intermediate diazo compound **16** could be trapped. The trapping product **10** was isolated in 10% yield. Unconverted **1** was trapped by acrylonitrile to yield the bis(cyclopropanecarbonitrile) **11**. Both **10** and **11** were mixtures of stereoisomers, which could not be separated further. Fortunately, in the case of **10**, one of several isomers was obtained by crystallization from EtOH. *cis*-Configuration could be assigned to the indanyl moiety because of the large ^1H -NMR coupling constant *J*(1,2) = 10.2 Hz. However, the configuration at the cyclopropane ring could not be determined.

Thermal Decomposition. Thermolysis of **1** in refluxing benzene gave the same product ratios as observed after photolysis.

Reaction Scheme for the Conventional Photolysis. The mechanism proposed for the photoreaction of **1** is outlined in *Scheme 2*. All observed products can be rationalized by the loss of N₂ and the formation of the intermediate **12** in the first step. Formation of the cyclic azine **5** is easily explained by an intramolecular attack of the carbene to the diazo group in **12**. Azine formation is the major reaction step in the decomposition of many diazo compounds [12].

The other major products **6** to **8** can all be explained *via* a common intermediate **16**, which is formed by 1,5-H abstraction followed by ring closure of the 1,5-diradical **15**. Besides the observed 1,5-H abstraction in **12**, there also exists the possibility of a 1,4-H abstraction leading to an *ortho*-quinodimethane derivative, as has been observed in some cases [13]. In the photolysis of **1**, no products were found which might be derived by 1,4-H abstraction. Since not all products of the complex mixture have been identified, they cannot be excluded completely, but if there were any, they must be present in less than 3% yield. The 1,5-diradical **15** is formed *via* a six-membered transition state which is, in general, energetically favored over the five-membered transition state of a 1,4-H abstraction. A similar behavior was found by *Gutsche* and coworkers [14] who studied intramolecular carbene abstractions.



Ring closure of the diradical **15** can lead to two stereoisomeric forms of **16** in which the aryl groups at the indane ring are *trans* (**16a**) or *cis* (**16b**) to each other. N₂ extrusion from **16** leads to the carbenes **17a** and **17b** (*Scheme 3*). The *trans*-isomer **17a** possesses two H-atoms which are accessible for 1,5-H abstraction. Abstraction of H_a leads to the products **7a** (Ph groups are *trans*-configured) and **7b** (both Ph groups are in *exo*-position), while abstraction of H_b gives **6a** and **6b**. In the case of the *cis*-isomer **17b**, only one H-atom can be abstracted to form **7a** and **7c** (both Ph groups are *endo*-configured). All 1,5-diradicals derived from **17** close to the less strained indenoindenes **6** and **7** with *cis* ring fusion (*vide supra*).

It can be concluded from the observed product ratios that ring closure of **15** to the *trans*-isomer **16a** is preferred over the *cis*-form **16b**, since **6a** and **6b** are the major photolysis products (*Path b*, Scheme 3) and **7c** (*Path c*) is present only in *ca.* 5%. This can be rationalized in terms of steric congestion in the *cis*-form, *i.e.* that the ring closure of **15** gives preferentially the less crowded *trans*-isomer. The fact that *Path b* is preferred over *Path a* can be easily understood, since abstraction of H_b leads to a more stabilized radical than abstraction of H_a .

The indene **8** is most likely formed by disproportionation of diradicals which were formed from **17** via *Path a* or *c* (Scheme 3). This kind of biradical disproportionation has been observed previously [5c] [14] [15]. It is interesting to note that **8** becomes the major product, when **1** is decomposed in the GC injector. The preferred formation of **8** at high temperatures may be explained by an easier 1,4-H abstraction (*e.g.* H_a , Scheme 3) at higher temperature as found in other cases [13].

It is well known that carbenes react very efficiently with O_2 to yield carbonyl compounds [12]. Photolysis in the presence of O_2 was undertaken in order to trap the carbenes **12** and **17**. The indanylbenzophenones **9** and the diketone **4** were obtained as trapping products. Whereas the presence of **12** is, thus, demonstrated without doubt, **9a** and **9b** can be formed by two pathways: $12 \rightarrow 13 \rightarrow 14 \rightarrow 9$ and $12 \rightarrow 15 \rightarrow 16 \rightarrow 17 \rightarrow 9$ (Scheme 2). Most likely, both pathways are operating.

Further support of the proposed mechanism came from the trapping of the intermediate diazo compound **16** by acrylonitrile. 1,3-Dipolar cycloadditions of diazo-methanes with electron deficient olefins like acrylonitrile and subsequent spontaneous denitrogenation to form cyclopropanes are well established reactions [16]. The isolation of the trapping product **10** provides strong evidence for the presence of **16** as reaction intermediate.

The progress of the photolysis was also monitored by GLC. The starting material **1** and the intermediate **16** were quantified by their acrylonitrile trapping products **10** and **11**. The time dependence of the product concentrations (Fig. 2) shows again that **16** is an intermediate of the photolysis, since its concentration increased during the early stage of the photolysis, and then decreased as the photolysis progressed.

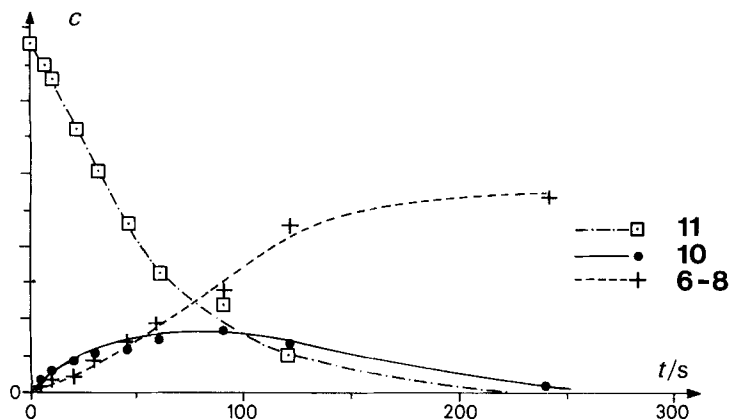


Fig. 2. Time dependence of the photolysis of **1**. Concentration unit: GLC area of compound vs. internal standard.

The final products **6–8** are present in appreciable amounts already at a very early stage of the photolysis. This leads to the suggestion that some amount of the products might be formed by spontaneous thermal N₂ extrusion from **15** or **16** without the involvement of a second photon. The energy for the spontaneous N₂ loss could come from the gain of binding energy of the ring closure **15**→**16**. Examples for the extrusion of 2 mol N₂ with only one photon are found in biscarbenes, which are conjugated *via* aromatic rings [17]^a).

Table 2. *Quantum Yields of N₂ Loss of 1 and Related Diazomethanes*

Compound	Φ_{-N_2} at 313 nm
Diphenyldiazomethane	0.71 ^a)
(2-Methylphenyl)phenyldiazomethane	0.81
1	0.43 ^b)

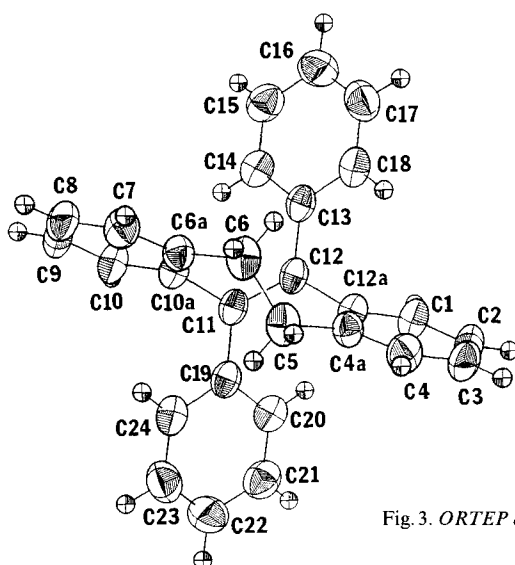
^a) [18]. ^b) Overall quantum yield for loss of 2 mol N₂.

To evaluate this possibility, a quantum-yield study was undertaken, and the results are summarized in Table 2. Diphenyldiazomethane was used as an actinometer [18], and *ortho*-methyldiphenyldiazomethane was also compared as a model compound. For **1**, only the overall quantum yield for the loss of two molecules of N₂ could be determined by spectrophotometric monitoring of the reaction. With the reasonable assumptions that the extinction coefficient of **1** is *ca.* twice as large as that of **16** and that the quantum yield for the loss of one molecule N₂ does not differ substantially from that of **16**, the quantum yield for the loss of one molecule of N₂ from **1** can be estimated to be *ca.* 0.86. Since this quantum yield is in the same range as that for the other diazomethanes (Table 2), it can be concluded that the major portion of **1** needs two photons on the pathway to the products **6–8**. However, the possibility that *via* a minor reaction pathway some of the products are formed by only one photon cannot be excluded. A study of the temperature dependence of the ratio of **10** to **6–8** in the early stage of the photolysis might answer this question.

4. Laser Photolysis. – Results. Irradiation of **1** at 248 nm with a pulsed excimer laser gave rise to a broad new absorption, $\lambda_{\max} = 363$ nm. This absorption was clearly detectable after a single laser pulse. GLC analysis showed that a new product was formed in high yield. Preparative laser photolysis gave 49% isolated yield of a yellow compound. Spectral data revealed that the molecule was free of nitrogen, symmetrical, and that the CH₂CH₂ bridge (*AA'**BB'* spin system in the ¹H-NMR) was part of a ring system. Comparison with the spectra reported for diphenyldibenzocyclooctene **19** [19] showed that the laser product was not identical with this compound. Compound **19** was, however, formed as the major reaction product upon the thermal decomposition of **1** on silica gel. ¹H-NMR analysis of the crude hydrocarbon fraction of the photolysis mixture showed that **19** was present in *ca.* 7% yield in the reaction mixture. The major laser product was identified as (11*E*)-dibenzocyclooctatriene **20** by X-ray structure determination (Fig. 3).

Control experiments demonstrated that **20** is not formed by secondary photolysis of the conventional photoproducts **6–8**, and that laser photolysis of the *cis*-isomer **19** gave

⁴) Multiple elimination of N₂ is observed only in cryogenic matrices and is attributed to hot ground-state reactions in these media of poor heat conductivity (*I. Iwamura*, University of Tokyo, personal communication, Oct. 1988).

Fig. 3. ORTEP drawing of **20**

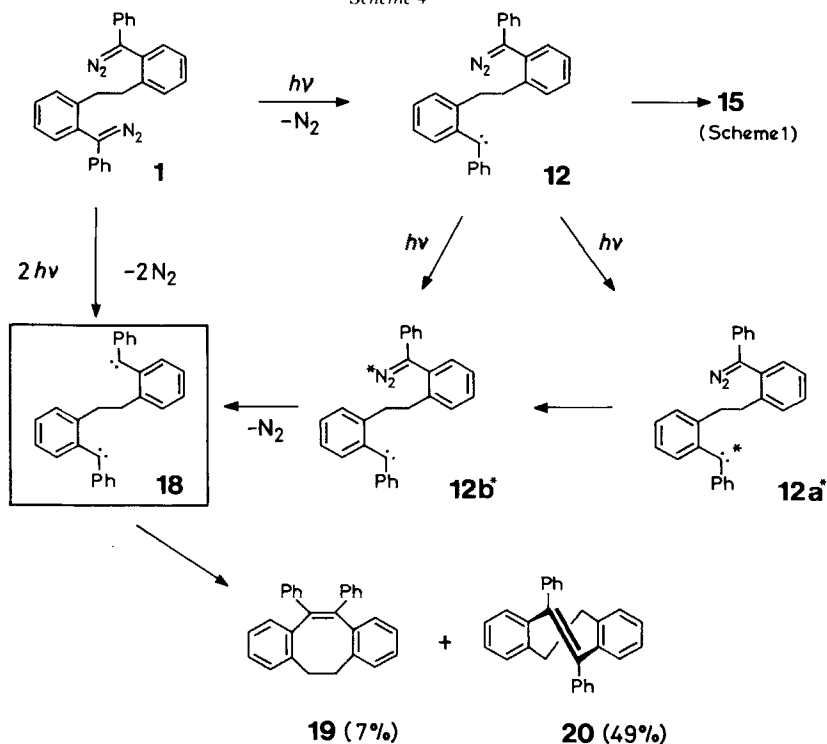
substantially less of **20** than photolysis of **1**. Little less of **20** (39%) was formed, when laser light of 308-nm wavelength was applied, but only traces of **19** and/or **20** were formed using the 530-nm light pulse of a frequency-doubled Nd-glass laser.

Discussion. As shown by control experiments, the new laser product **20** is not primarily a secondary photoproduct and is already formed with a single laser pulse. The amount of **20** is growing linearly with the number of pulses up to *ca.* 50% conversion. This indicates that the primary reaction step determining product distribution takes place within a single laser pulse of 20-ns duration.

The possible mechanisms for the formation of **20** are outlined in *Scheme 4*. As the most probable precursor, we propose the biscarbene **18**, since the dimerization of carbenes to olefins is a well established reaction [12]. The biscarbene **18** could be formed either directly from **1** or by a stepwise sequence *via* the diazocarbene **12**. It was determined by ps time-resolved laser spectroscopy of diphenyldiazomethane [20] that excited diphenyldiazomethane decays within 20 ps to the singlet carbene, and that intersystem crossing to the triplet carbene takes place within 300 ps. Since diphenyldiazomethane may be considered as a good model for the chromophores in **1**, it can be concluded that the direct formation of **20** from **1**, either by a simultaneous absorption of two photons or by re-excitation of excited diazomethane, is very unlikely. Our available laser power was not high enough to trigger this kind of fast two-photon processes.

On the other hand, the triplet carbene (in our case **12**) is formed within 300 ps. The time elapsing between the excitation of **1** and the formation of **12** is, thus, expected to be short in comparison with the 20-ns pulse width. The formation of an excited triplet diphenylcarbene by the laser photolysis of diphenyldiazomethane has been demonstrated [3a] [21]. At low light intensities, the diazocarbene **12** is deactivated by 1,5-H abstraction to form the diradical **15**. H abstractions by diphenylcarbene are relatively slow, *e.g.* *ca.* 2 μ s for H abstraction from cyclohexane as solvent [22]. Intramolecular H abstraction in **12** is likely to be much faster, but the excitation of **12** by a second photon apparently

Scheme 4



competes efficiently with H abstraction. In other words, the lifetime of **12** is long enough that it can be excited under the given light intensities.

Bichromophoric molecules with independent chromophores can be excited at both sides. The probability, by which each chromophore is excited, depends on the extinction coefficient at the exciting wavelength. Unfortunately, the extinction coefficient of triplet diphenylcarbene at 248 nm is not known, but the fluorescence of the carbene was observed by excitation at this wavelength [3a]. Possibly, either moiety of **12** can be re-excited and either or both of **12a*** and **12b*** may be formed initially. Excited diphenylcarbene has an emission maximum at 505 nm [3a] which is close to the maximum of the $n\pi^*$ transition of the diazomethane chromophore at 515 nm. These are ideal conditions for an intramolecular *Förster*-type energy transfer, since the probability of this process increases with the overlap of the emission of the donor with the absorption of the acceptor chromophore. Therefore, **12a*** is expected to yield **12b*** rapidly by intramolecular energy transfer; **12b*** may then react under N_2 extrusion to the biscarbene **18**.

As a further possibility, the excited carbene might attack the diazo group directly, since excited intermediates can be more reactive than their ground state [23]. However, this process is not very likely, since it has to compete with intramolecular *Förster*-type energy transfer.

It is remarkable that the biscarbene **18** decays mainly to the (11*E*)-cyclooctatriene **20** and not to the more stable (11*Z*)-isomer **19**. Compound **20** is not (at least not predominantly) formed by photochemical *cis/trans*-isomerization of **19**, since the photolysis of **19**

by a single laser pulse gave less **20** than the photolysis of **1** under identical conditions. Whether the detected **19** is formed directly from **18** or by subsequent isomerization from **20** could not be determined. We have two possible explanations for the preferred formation of **20**. Both invoke the possible conformations along the reaction coordinate, and both might complement each other. First, **18** may be formed in a conformation which is already on the way to **20**, and for the formation of **19** a higher energy barrier has to be overcome. It is well documented from other photochemical reactions, that the conformation, in which a reaction intermediate is formed, can determine the further path of the reaction [24]. Second, spin statistics predicts that the dimerization of two triplet carbenes should mainly yield the olefin in the triplet state. Consideration of molecular models leads to the supposition that a hypothetical twisted triplet state has more similarity with the (11*E*)-olefin **20** than with the (11*Z*)-isomer **19**, and, hence, should predominantly decay to **20**.

5. Structure Data of 20. – The structure of **20** is shown in Fig. 3, selected bond lengths and angles are summarized in Table 3, and crystal data are reported in Table 4. The dihedral angles around the (*E*)-configured C=C bond are shown in Fig. 4.

The conformation of (*E*)-cyclooctene has been the subject of some controversy. The existence of two conformations has been postulated. *Manor et al.* [25] found a 'twist' (or 'crown') form in a Pt²⁺ complex by X-ray diffraction. The twist angle of the C=C bond was found to be 136.5° and the bond length 1.35(3) Å. Based on an electron-diffraction study of (*E*)-cyclooctene, *Gavin and Wang* [26] proposed a distorted chair structure with a C=C bond length of 1.363 Å. This experiment was repeated by *Traetteberg* [27]; she

Table 3. Selected Bond Lengths [Å], Bond Angles [°], and Dihedral Angles [°] of **20**^a. Standard deviations in parentheses.

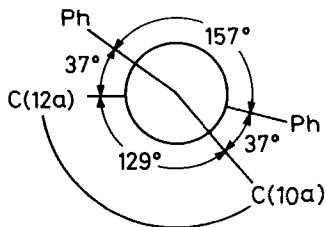
<i>Bond lengths</i>			
C(4a)–C(5)	1.530 (4)	C(12)–C(12a)	1.497 (3)
C(5)–C(6)	1.547 (6)	C(4a)–C(12a)	1.405 (3)
C(11)–C(12)	1.377 (5)	C(12)–C(13)	1.478 (4)
<i>Angles</i>			
C(4a)–C(5)–C(6)	119.2 (2)		
C(5)–C(4a)–C(12a)	123.0 (2)		
C(4a)–C(12a)–C(12)	115.4 (2)		
C(12a)–C(12)–C(13)	116.6 (2)		
C(12a)–C(12)–C(11)	119.1 (2)		
<i>Dihedral angles</i>			
C(12a)–C(12)–C(11)–C(19)	36.9 (3)		
C(12a)–C(12)–C(11)–C(10a)	128.9 (3)		
C(13)–C(12)–C(11)–C(19)	157.4 (3)		
C(13)–C(12)–C(11)–C(10a)	36.9 (3)		
C(11)–C(12)–C(13)–C(14)	31.5 (3)		
C(11)–C(12)–C(12a)–C(4a)	120.0 (3)		
H–C(5a)–C(5)–C(6)–H–C(6a)	9 (2)		
H–C(5a)–C(5)–C(6)–H–C(6b)	105 (2)		
H–C(5b)–C(5)–C(6)–H–C(6b)	141 (2)		

^a) Due to the fact that the molecule is symmetric (a C₂ axis passes through the C(11)=C(12) bond and the C(5)–C(6) bond), some atoms with different labels are crystallographically identical, e.g. C(5) = C(6), C(4a) = C(6a), C(12a) = C(10a), C(11) = C(12), etc.

Table 4. Crystal Data and Parameters of the Data Collection for **20**

Formula	C ₂₈ H ₂₂
Crystal system and space group	monoclinic, C ₂ /c (No. 15)
<i>a</i> [Å]	12.104 (2)
<i>b</i> [Å]	15.807 (3)
<i>c</i> [Å]	10.091 (4)
α [°]	90
β [°]	93.16 (2)
γ [°]	90
<i>V</i> [Å ³]	1927.8 (1.4)
<i>Z</i>	4
Crystal size [mm]	0.3 × 0.2 × 0.2
Temperature [K]	293
$\theta_{\max}$ [°]	27
Radiation	MoK α (λ = 0.71069 Å)
Scan type	$\Omega/2\theta$
Collected intensities	$\pm h, +k, +l$
μ [mm ⁻¹]	3.5
<i>F</i> (000)	760
No. of independent reflections	2178
No. of refl. used in refinements	1172 ($F > 2\sigma(F)$)
No. of variables	171
Observations per parameter	6.9
Largest δ/σ in refinement	0.01
Largest peak on a final ΔF -Fourier	0.19 e/Å ³
Final <i>R_w</i>	0.0519
Weighting system	1.58/($\sigma^2(F)$ + 4.70 · 10 ⁻⁴ <i>F</i> ²)

avored the crown conformation again with a C=C twist angle of 136.0°, a C=C bond length of 1.332 Å, and a C₂ axis through the molecule. That result is in good agreement with force-field calculations of *Ermer* [28] who further reported an X-ray and a neutron-diffraction study of (*E*)-2-cycloocten-1-yl 3,5-dinitrobenzoate [29] [30]. The crystal structure shows this compound to be in the crown conformation with a C=C bond twist of 137.7° (X-ray) and 138.1° (neutron diffraction). Our molecule **20** is also found to be in the crown conformation. The dinitrobenzoate derivative lacks the C₂ symmetry of **20**, but the distortions are marginal. We found a twist angle of C(10a)–C(11)=C(12)–C(12a) 128.9°. The nonplanar C=C bond deformation exhibits both twisting (36.9°; [30]: 19.6°) and out-of-plane bending (14.2; [30]: 22.3°). Thus, compound **20** is much more twisted along the C=C bond; the energetically favorable out-of-plane bending [30] seems to be enforced by the bulky Ph groups. All of these distortions are more pronounced than in parent (*E*)-cyclooctene, and the C=C bond is slightly elongated; we have found 1.377 Å as compared to *Ermer*'s values of 1.330° (X-ray) and 1.341 Å (neutron diffraction). These

Fig. 4. Newman projection of the double bond of **20** with dihedral angles

values should also be compared with the normal planar C=C bond in propene (1.334 Å [31]) and (*E*)-stilbene (1.33–1.34 Å [32]), the latter indicating that the elongation is not due to the repulsion of the Ph groups. The C(12)–C(13) bond length is the same as in (*E*)-stilbene (1.478; [32]: 1.474 Å).

6. Conclusion. – The course of the photochemical denitrogenation of the bisdiaz compound **1** is altered profoundly by high-intensity laser light. We postulate that **20**, the main product of the laser photolysis, is formed *via* the biscarbene **18** through a sequential absorption of two photons. Compound **20** is the first conjugated (*E*)-cyclooctatriene isolated, and it can be synthesized on a gram scale and in good yields by preparative laser photolysis of **1**.

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Experimental Part

1. General. All commercial compounds and solvents used for synthesis were of reagent grade and were used without further purification. *Uvasol* spectroscopic-grade solvents (*Merck*) were used for photolysis. Org. extracts were dried over MgSO₄. Degassing was performed by three freeze-pump-thaw cycles. Conventional photolyses were done with an *Osram HBO* 200-W high-pressure lamp or a *Grätzel* Hg low-pressure lamp (254 nm; 50 W); laser photolyses with a *Lambda Physik EMG 101 MSC* excimer laser-operated on KrF (248 nm, *ca.* 200 mJ/pulse, 20 ns pulse width). GLC: *Perkin-Elmer 8500 Gas Chromatograph* with *Perkin-Elmer LCI* Integrator; 12-m cross-linked dimethylsilicone-fused silica column; temp. program 180° (5 min), with 7°/min up to 290° (15 min). UV: $\lambda_{\max}$ [nm] (log ϵ), hexane as solvent. IR: KBr pellets; $\tilde{\nu}$ [cm⁻¹]. ¹H-NMR: at 400 MHz. ¹³C-NMR: at 101 MHz; CDCl₃ as solvent; δ [ppm] relative to internal TMS and *J* [Hz]. MS and GC/MS: 70 eV; *m/z* (rel. %).

2. Synthesis. *Ethyl 2-(Bromomethyl)benzoate*. A mixture of 10.0 g (60.9 mmol) of *ethyl 2-methylbenzoate* (**2**), 11.0 g (61.5 mmol) of *N*-bromosuccinimide and 5 mg of benzoyl peroxide in 250 ml of CCl₄ was refluxed for 1.5 h. The soln. was filtered over silica gel, and the silica gel was washed with 200 ml of CCl₄. Evaporation of the combined filtrates gave 13.0 g (88%) of a pale-yellow liquid. The bromo-ester was used without further purification. IR (film): 1715, 1300, 1270, 1115, 1080, 770, 712. ¹H-NMR: 1.38 (*t*, *J* = 8, CH₃); 4.35 (*q*, *J* = 8, CH₂O); 4.92 (*s*, CH₂Br); 7.25–7.6 (*m*, 3 arom. H); 7.8–8.15 (*m*, 1 arom. H).

Diethyl 2,2'-Ethylenedibenzoate (**3**). *Ethyl 2-(bromomethyl)benzoate* (15.8 g, 65 mmol) was added to a suspension of 16.0 g (245 mmol) of activated Zn [9] and heated for 4 h at 80–90°. Et₂O (50 ml) was added, and the suspension was filtered. The residue was washed several times with Et₂O, and the combined Et₂O layers were dried and evaporated, yielding 8.15 mg of crude product. Crystallization from MeOH gave 4.6 g (43%) of **3** as colorless needles. M.p. 67–68°. IR: 1705, 1475, 1440, 1390, 1360, 1290, 1265, 1240, 1160, 1120, 1105, 1070, 1040, 1020, 760, 710, 665, 535. ¹H-NMR: 1.37 (*t*, *J* = 7, 2 CH₃); 3.27 (*s*, CH₂CH₂); 4.36 (*q*, *J* = 7, CH₂O); 7.1–7.4 (*m*, 6 arom. H); 7.8–8.0 (*m*, 2 arom. H).

2,2'-Ethylenedibenzoic Acid. A soln. of 3.64 g (65 mol) of KOH in 5 ml of H₂O was added to 4.45 g (13.7 mmol) of **3** in 100 ml of MeOH, and the mixture was refluxed for 20 h. The solvent was evaporated, the residue was dissolved in H₂O and extracted once with 50 ml of toluene. The aq. layer was acidified with conc. HCl, the white precipitate was collected by filtration, washed with H₂O, and dried *i.v.* over P₂O₅, yielding 3.40 g (92%) *2,2'*-ethylenedibenzoic acid. M.p. 237–239° (CHCl₃/acetone; [33]; 226–228°). IR: 3150–2400 (br.), 1670, 1590, 1565, 1480, 1450, 1390, 1295, 1265, 1250, 920, 755, 700. ¹H-NMR (CDCl₃/(D₆)DMSO): 3.26 (*s*, CH₂CH₂); 5.8–6.6 (br. *s*, 2 OH); 7.13–7.48 (*m*, 6 arom. H); 7.80–7.96 (*m*, 2 arom. H).

2,2'-Ethylenedibenzoyl Chloride. *2,2'*-Ethylenedibenzoic acid (6.16 g, 22.8 mmol) in 70 ml of freshly distilled SOCl₂ was refluxed for 17 h. The excess SOCl₂ was removed by distillation, and the residue (7.0 g), which was dried *i.v.*, was used without further purification for the next step. IR: 1750 (br.), 1600, 1570, 1480, 1465, 1455, 1315, 1210, 1190, 1100, 880, 790, 775, 755, 675, 655, 540. ¹H-NMR: 3.16 (*s*, CH₂CH₂); 7.3–7.7 (*m*, 6 arom. H); 8.1–8.4 (*m*, 2 arom. H).

2-[2-(2-Benzoylphenyl)ethyl]benzophenone (**4**). To an ice-cooled suspension of 9.60 g (72 mmol) of AlCl_3 in 100 ml of dry benzene, a soln. of 7.0 g (22.8 mmol) of 2,2'-ethylenedibenzoyl chloride in 100 ml of dry benzene was added dropwise. After the addition was complete, the mixture was stirred for 2 h at r.t. and poured into 300 ml of ice water, containing 50 ml of conc. HCl . The benzene layer was separated, and the aq. phase was extracted with benzene. The combined org. layers were washed with a NaHCO_3 soln. and H_2O . Drying, filtration over silica gel, and evaporation yielded 9.17 g (90%) of crude **4** which was further purified by crystallization from MeOH with charcoal giving 5.80 g (57%) light-yellow crystals. M.p. 124–125°. UV (MeCN): 250 (4.42), 279 (3.63), 290 (3.47), 332 (2.34). IR: 3050, 2940, 2860, 1655, 1600, 1580, 1490, 1445, 1310, 1285, 1270, 1255, 1140, 925, 760, 705, 697, 640. $^1\text{H-NMR}$: 2.93 (s, CH_2CH_2); 7.16–7.28 (m, 6 arom. H); 7.33 (d, $J = 7.5$, 2 arom. H); 7.42 (t, $J = 7.5$, 4 arom. H); 7.56 (t, $J = 7.5$, 2 arom. H); 7.75 (d, $J = 7.5$, 4 arom. H). $^{13}\text{C-NMR}$: 35.45 (t); 125.17 (d); 128.14 (d); 128.40 (d); 129.94 (d); 130.11 (d); 130.27 (d); 132.84 (d); 137.73 (s); 138.13 (s); 140.46 (s); 198.03 (s). MS: 390 (19, M^+), 372 (56), 209 (19), 196 (31), 195 (100), 194 (29), 178 (20), 165 (40), 152 (19), 105 (28), 77 (58).

2-{2-[2-(Hydrazonophenylmethyl)phenyl]ethyl}benzophenone Hydrazone. Diketone **4** (5.50 g, 14.1 mmol) and 50 ml (1 mol) of hydrazine hydrate in 150 ml of abs. EtOH were refluxed for 72 h. Hydrazine hydrate (5 ml) were added and refluxed for an additional 24 h. The precipitated white solid was collected by hot filtration. The residue was treated with CHCl_3 , isomer **b** and the monohydrazone were dissolved and isomer **a** was obtained by filtration. Crystallization from dioxane gave 2.35 g (40%) of isomer **a**. The CHCl_3 extract was evaporated and chromatographed on silica gel using $\text{CH}_2\text{Cl}_2/10\%$ AcOEt as eluent, 160 mg (3%) of monohydrazone and 570 mg (10%) of isomer **b** could be obtained. Isomer **a**: IR: 1625, 1585, 1495, 1445, 1165, 1070, 950, 770, 750, 700, 675, 660. $^1\text{H-NMR}$: 2.4–3.6 (m, CH_2CH_2); 6.0 (m, 2 NH_2); 6.9–7.5 (m, 18 arom. H). MS: 418 (1, M^+), 402 (17), 388 (33), 387 (100), 386 (21), 385 (62), 371 (23), 370 (57), 209 (17), 193 (42), 192 (25), 178 (18), 165 (26), 77 (34). Isomer **b**: IR: 1620, 1585, 1495, 1450, 1340, 1175, 1165, 1070, 955, 770, 730, 700, 675, 660. $^1\text{H-NMR}$: 2.65–2.95 (m, CH_2CH_2); 5.4 (m, 2 NH_2); 7.0–7.6 (m, 18 arom. H).

2-[2-(Benzoylphenyl)ethyl]benzophenone Hydrazone. M.p. 114–116° (MeOH). IR: 1670, 1590, 1490, 1450, 1320, 1280, 1260, 1165, 1070, 935, 770, 720, 700, 670, 660, 645. $^1\text{H-NMR}$: 2.6–3.0 (m, CH_2CH_2); 5.2 (br. s, NH_2); 7.0–8.0 (m, 18 arom. H). MS: 404 (2, M^+), 388 (62), 374 (32), 373 (100), 370 (32), 295 (28), 209 (39), 195 (29), 194 (50), 193 (89), 192 (61), 178 (29), 165 (50), 105 (46), 77 (62).

Diazo-2-{2-[2-(diazophenylmethyl)phenyl]ethyl}phenyl}phenylmethane (**1**). A mixture of 1.00 g (2.39 mmol) of bishydrazone (isomer **a** or **b**), 10.0 g of Na_2SO_4 , and 10.0 g (115 mmol) of activated MnO_2 (Merck) in 300 ml of CHCl_3 was stirred in the dark at r.t. for 15 h. After filtration, the filtrate was evaporated (20°) yielding 990 mg (99%) of a red oil, which crystallized slowly. Pure **1** could be obtained by crystallization from hexane. M.p. 117–119° (dec.). UV: 285 (4.56), 510 (2.20). IR: 3060, 2940, 2040, 1595, 1495, 1450, 1315, 760, 750, 695, 650. $^1\text{H-NMR}$: 2.81 (s, CH_2CH_2); 6.77–7.03 (m, 4 arom. H); 7.04–7.15 (m, 2 arom. H); 7.15–7.45 (m, 12 arom. H); $^{13}\text{C-NMR}$: 34.76 (t); 59.16 (s); 122.41 (d); 123.97 (d); 127.06 (s, d); 128.98 (d); 129.11 (d); 130.31 (d); 131.84 (s, d); 142.30 (s). MS: 386 (8, $M^+ - \text{N}_2$), 359 (31), 358 (100, $M^+ - 2 \text{N}_2$), 280 (29), 279 (29), 267 (45), 265 (22), 203 (17), 179 (31), 178 (22), 165 (20), 91 (12), 77 (13). CI-MS (NH_3): 415 (8, $M^+ + 1$), 387 (50), 376 (100), 359 (60).

3. Conventional Photolyses. Preparative Photolysis of **1**. A soln. of 415 mg (1.00 mmol) of **1** in 70 ml of dry benzene were degassed and irradiated until the red color had disappeared (1 h). The solvent was removed, and the residue was chromatographed on silica gel with hexane/15% toluene. The following fractions were obtained in order of elution: 80 mg of **6b** (25%, including the amount of the next fraction), 81 mg of a mixture containing ca. 15% **6b** and approximately equal amounts of the three stereoisomers of **7** (19%), 33 mg of **8** (10%), 95 mg (28%) of **6a** and increasing the toluene portion of the eluent to 50%, 11 mg of **5**. The fraction which contained **7** was dissolved in hot EtOH, and when the soln. had cooled slowly to r.t., different types of crystals had grown. The crystals were collected by filtration and were sorted out by hand, which gave fairly pure material of **7a** and **7b**. Isomer **7c** could not be separated from **7a** and **7b**, but its $^1\text{H-NMR}$ could be partially assigned.

5,5a,10,10a-Tetrahydro-*r*-5,10-*cis*-5a-diphenylindenof[2,1-*a*]indene (**6b**). Colorless needles. M.p. 137–142° (EtOH). UV: 274 (3.36), 267 (3.39), 260 (sh, 3.27). IR: 3058, 3028, 2920, 2848, 1600, 1580, 1490, 1478, 1452, 1262, 1076, 1032, 794, 782, 766, 752, 740, 728, 720, 702, 632. $^1\text{H-NMR}$: 3.22, 3.32 (AB of ABX, $J = -16$, 0, 8, 2 H–C(10)); 4.19 (d, X of ABX, $J = 8$, H–C(10a)); 5.43 (s, H–C(5)); 5.75 (d, $J = 7.7$, 1 arom. H); 6.77 (t, $J = 7$, 1 arom. H); 6.83 (br. d, $J = 7$, 1 arom. H); 7.02–7.08 (m, 2 arom. H); 7.14–7.30 (m, 12 arom. H); 7.36 (d, $J = 7.5$, 1 arom. H). $^{13}\text{C-NMR}$: 37.44 (t); 59.07 (d); 64.17 (d); 70.68 (s); 123.87 (d); 124.59 (d); 124.73 (d); 125.18 (d); 126.06 (d); 126.93 (d); 127.05 (d); 127.12 (d); 127.37 (d); 127.61 (2d); 128.13 (d); 129.93 (d); 130.32 (d); 140.22 (s); 142.31 (s); 143.84 (s); 144.25 (s); 146.16 (s); 146.89 (s). GC/MS: 358 (100, M^+), 280 (40), 279 (36), 267 (69), 265 (37), 252 (23), 203 (42), 202 (28), 179 (17), 178 (22), 165 (27).

5,5a,10,10a-Tetrahydro-*r*-5,10-*cis*-5a-diphenylindenof[2,1-*a*]indene (**6a**). Colorless needles. M.p. 164–165° (EtOH). UV: 274 (3.46), 267 (3.46), 260 (sh, 3.32). IR: 3070, 3030, 2930, 1500, 1485, 1458, 1450, 785, 770, 763, 755,

742, 730, 705, 634, 624. ¹H-NMR: 3.29, 3.50 (*AB* of *ABX*, *J* = −16, 0, 6, 2 H–C(10)); 4.61 (*d*, *X* of *ABX*, *J* = 6, H–C(10a)); 5.04 (*s*, H–C(5a)); 6.73–7.45 (*m*, 17 arom. H); 7.73 (*d*, *J* = 6, 1 arom. H). ¹³C-NMR: 37.56 (*t*); 54.35 (*d*); 62.80 (*d*); 69.65 (*s*); 123.91 (*d*); 124.81 (*d*); 125.18 (*d*); 125.50 (*d*); 125.57 (*d*); 125.86 (*d*); 126.48 (*d*); 127.29 (*d*); 127.42 (*3d*); 127.77 (*2d*); 129.27 (*d*); 141.35 (*s*); 142.46 (*s*); 143.43 (*s*); 145.64 (*s*); 146.00 (*s*); 149.51 (*s*). GC/MS: 358 (100, *M*⁺), 280 (39), 279 (33), 267 (66), 265 (36), 203 (43), 202 (30), 179 (17), 178 (23), 165 (31), 139 (15), 91 (11).

r-5,*c*-5a,*t*-10,*c*-10a-Tetrahydro-5,10-diphenylindeno[2,1-*a*]indene (**7a**). Colorless cubes. M.p. 167–171° (EtOH). UV: 275 (3.18), 268 (3.20), 262 (3.09). IR: 3062, 3021, 2903, 2891, 1598, 1493, 1473, 1456, 1450, 1030, 766, 754, 701. ¹H-NMR: 4.12 (*dd*, *J* = 2.8, 7.7, H–C(10a)); 4.61 (*dd*, *J* = 9.2, 7.7, H–C(5a)); 4.64 (*d*, *J* = 2.8, H–C(10)); 4.99 (*d*, *J* = 9.2, H–C(5)); 5.97 (*d*, *J* = 7.8, 1 arom. H); 6.78 (*t*, *J* = 7.5, 1 arom. H); 6.92 (*d*, *J* = 7.5, 1 arom. H); 6.99 (*t*, *J* = 7, 1 arom. H); 7.06 (*m*, 3 arom. H); 7.16–7.35 (*m*, 10 arom. H); 7.51 (*d*, *J* = 7.5, 1 arom. H). GC/MS: 358 (100, *M*⁺), 280 (38), 279 (30), 267 (56), 265 (30), 252 (20), 203 (37), 202 (29), 179 (20), 178 (28), 167 (24), 165 (30).

r-5,*t*-5a,*c*-10,*t*-10a-Tetrahydro-5,10-diphenylindeno[2,1-*a*]indene (**7b**). Colorless needles. M.p. 195–205° (EtOH). UV: 274 (3.34), 267 (3.37), 260 (3.25). IR: 3056, 3022, 2903, 1598, 1494, 1474, 1453, 1074, 1030, 761, 751, 700. ¹H-NMR: 4.21, 4.59 (*AA'XX'*, *J*_{AA'} = 7.5, *J*_{AX} = 3.5, H–C(5a,10a), H–C(5,10)); 7.03 (*d*, *J* = 7.3, 2 arom. H); 7.15–7.35 (*m*, 14 arom. H); 7.43 (*d*, *J* = 7.6, 2 arom. H). GC/MS: 358 (100, *M*⁺), 280 (40), 279 (33), 267 (65), 265 (35), 252 (22), 203 (38), 202 (26), 179 (20), 178 (25), 167 (24), 165 (29).

r-5,*c*-5a,*c*-10,*c*-10a-Tetrahydro-5,10-diphenylindeno[2,1-*a*]indene (**7c**). The compound could be obtained only in mixtures with the *'exo'*- and *trans*-isomer, but its ¹H-NMR could be partially assigned. ¹H-NMR: 4.46, 4.95 (*AA'XX'*, *J*_{AA'} = 7.8, *J*_{AX} = 9.5, H–C(5a,10a), H–C(5,10)); 5.79 (*d*, *J* = 8, 2 arom. H).

2-(2-Benzylphenyl)-1-phenylindene (**8**). Light yellow oil, which crystallized only partially. UV: 281 (4.11). IR: 3058, 3023, 2964, 2917, 1599, 1494, 1451, 1262, 1096, 1074, 1029, 801, 761, 732, 698. ¹H-NMR: 4.05, 4.07 (*AB*, *J* = −16, PhCH₂); 4.86 (*s*, H–C(3)); 6.78 (*s*, H–C(1)); 6.88–7.37 (*m*, 18 arom. H). ¹³C-NMR: 39.28 (*d*); 59.42 (*t*); 120.97 (*d*); 123.98 (*d*); 125.27 (*d*); 125.82 (*d*); 125.84 (*d*); 126.62 (*d*); 126.97 (*d*); 127.18 (*d*); 128.27 (*d*); 128.35 (*d*); 128.45 (*d*); 128.94 (*d*); 129.76 (*d*); 130.69 (*d*); 130.71 (*d*); 136.31 (*s*); 138.70 (*s*); 138.87 (*s*); 141.52 (*s*); 143.94 (*s*); 148.37 (*s*); 150.94 (*s*). GC/MS: 358 (100, *M*⁺), 280 (42), 279 (36), 267 (68), 265 (36), 252 (21), 203 (41), 202 (28), 179 (20), 178 (26), 167 (23), 165 (28).

5,6-Dihydro-11,14-diphenylidibenzof[d,h][1,2]diazecine (**5**). Pale yellow needles. M.p. 189–191° (EtOH). UV: 308 (3.98, sh), 272 (4.45). IR: 3060, 2944, 2866, 1565, 1485, 1445, 1323, 772, 760, 694. ¹H-NMR: 2.10, 3.06 (*AA'XX'*, *J* = 13, −14, 3, 6, CH₂CH₂); 7.14–7.36 (18 arom. H). ¹³C-NMR: 33.99 (*d*); 126.12 (*d*); 126.31 (*d*); 127.25 (*d*); 128.08 (*d*); 128.84 (*d*); 129.23 (*d*); 129.56 (*d*); 135.62 (*s*); 136.81 (*s*); 141.56 (*s*); 157.40 (*s*). GC/MS: 386 (1, *M*⁺), 195 (20), 194 (88), 193 (100), 192 (34), 178 (22), 165 (16), 115 (37).

Photolysis in Presence of O₂. A soln. of 450 mg (1.09 mmol) of **1** in 100 ml of benzene was saturated with O₂ and irradiated, until the red color had disappeared (2 h). Removal of the solvent and CC (silica gel, CH₂Cl₂/hexane 1:1) yielded the following fractions: 38 mg (10%) of **6–8**, 10 mg (3%) of *trans*-ketone **9a**, 20 mg (5%) of *cis*-ketone **9b**, and 40 mg (9%) of **4**. Control experiments indicated that the other fractions contained mainly photolytic decomposition products of **4**.

2-(*trans*-1-Phenylindan-2-yl)benzophenone (**9a**). UV: 330 (sh, 2.35), 273 (sh, 3.59), 247 (4.05). IR: 3061, 3025, 2924, 2853, 1743, 1662, 1597, 1491, 1449, 1264, 930, 786, 762, 701, 640. ¹H-NMR: 3.13 (*dd*, *J* = 15.7, 7.7, 1 H); 3.41 (*dd*, *J* = 15.7, 10, 1 H); 4.20 (*ddd*, *J* = 10, 8.3, 7.7, 1 H); 4.66 (*d*, *J* = 8.3, 1 H); 6.63 (*dd*, *J* = 7.8, 1.5, 2 arom. H); 6.71 (*d*, *J* = 7.7, 1 arom. H); 6.96–7.36 (*m*, 10 arom. H); 7.43 (*t*, *J* = 7.7, 2 arom. H); 7.57 (*t*, *J* = 7.4, 1 arom. H); 7.74 (*dd*, *J* = 7.8, 1.2, 2 arom. H). ¹³C-NMR: 37.23 (*t*); 47.88 (*d*); 56.41 (*d*); 124.20 (*d*); 125.33 (*d*); 125.58 (*d*); 126.04 (*d*); 126.94 (*d*); 126.97 (*d*); 127.53 (*d*); 127.68 (*d*); 128.31 (*d*); 128.40 (*d*); 128.96 (*d*); 129.11 (*d*); 130.32 (*d*); 133.31 (*d*); 137.55 (*s*); 139.53 (*s*); 139.79 (*s*); 141.22 (*s*); 143.39 (*s*); 145.45 (*s*); 198.83 (*s*). GC/MS: 374 (7, *M*⁺), 357 (30), 356 (100), 279 (50), 278 (25), 195 (20), 194 (49), 179 (47), 178 (75), 165 (54), 105 (20), 77 (39).

2-(*cis*-1-Phenylindan-2-yl)benzophenone (**9b**). M.p. 103–106°. UV: 330 (sh, 2.37), 273 (3.39), 248 (3.89). IR: 3061, 3025, 2924, 2851, 1737, 1664, 1597, 1449, 1266, 1232, 929, 746, 699. ¹H-NMR: 3.17 (*dd*, *J* = 15.6, 10.2, 1 H); 3.41 (*dd*, *J* = 15.6, 7.9, 1 H); 3.80 (*dd*, *J* = 10.2, 9.9, 7.9, 1 H); 4.53 (*d*, *J* = 9.9, 1 H); 6.82 (*d*, *J* = 7.7, 1 arom. H); 6.89 (*m*, 2 arom. H); 7.02–7.50 (*m*, 14 arom. H); 7.73 (*d*, *J* = 7.7, 1 arom. H). ¹³C-NMR: 41.42 (*t*); 52.90 (*d*); 59.44 (*d*); 124.13 (*d*); 124.68 (*d*); 125.65 (*d*); 126.58 (*d*); 126.70 (*d*); 127.04 (*d*); 127.64 (*d*); 128.17 (*d*); 128.25 (*d*); 128.30 (*d*); 129.90 (*d*); 130.00 (*d*); 132.85 (*d*); 137.41 (*s*); 140.26 (*s*); 141.58 (*s*); 142.40 (*s*); 142.53 (*s*); 145.68 (*s*); 198.72 (*s*). GC/MS: 374 (8, *M*⁺), 357 (28), 356 (100), 279 (48), 278 (22), 195 (17), 194 (40), 179 (49), 178 (73), 165 (54), 105 (20), 91 (19), 77 (40).

Trapping Experiments with Acrylonitrile. A soln. of 600 mg (1.45 mmol) of **1** in 50 ml of benzene was degassed and irradiated, until the absorbance at 600 nm had decreased from 0.94 to 0.4. The solvent was evaporated. The residue was dissolved in 20 ml acrylonitrile, and the soln. was kept at 30–40° for 1.5 h, until the red color had

disappeared completely. The acrylonitrile was removed *i.v.* and column chromatography ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 2:1) yielded 290 mg (56%) of **6–8**, 15 mg (3%) of **5**, 61 mg (10%) of **10**, and 120 mg (18%) of **11**.

2-Phenyl-2-[2-(1-cis-phenylindan-2-yl)phenyl]cyclopropanecarbonitrile (10a). The *cis*-isomer **10a** was isolated from the isomeric mixture by crystallization from EtOH: colorless crystals. M.p. 230–240° (dec.). IR: 3060, 3026, 2924, 2850, 2236, 1599, 1495, 1451, 1025, 773, 752, 700. $^1\text{H-NMR}$: -0.01 (*dd*, $J = 9.5, 5.8$, 1 cyclopropyl-H); 1.69 (*t*, $J = 5.7$, 1 cyclopropyl-H); 2.08 (*dd*, $J = 9.5, 5.6$, 1 cyclopropyl-H); 2.39 (*dd*, $J = 15.8, 8.4$, 1 H); 2.68 (*dd*, $J = 15.8, 10.3$, 1 H); 3.98 (*dt*, $J = 10.2, 8.4$, 1 H); 4.55 (*d*, $J = 10.2$, 1 H); 6.97 (*br. d*, $J = 6.2$, 1 arom. H); 7.04–7.40 (*m*, 16 arom. H); 7.61 (*d*, $J = 7.7$, 1 arom. H). GC/MS: 411 (55, M^+), 358 (37), 280 (36), 279 (50), 267 (58), 218 (38), 215 (34), 203 (50), 202 (38), 193 (62), 192 (47), 191 (47), 179 (95), 178 (100), 115 (55), 91 (72). The *trans*-isomer could not be obtained in a pure form.

2-{2-[2-(2-Cyano-1-phenylcyclopropyl)phenyl]ethyl}-2-phenylcyclopropanecarbonitrile (11). This fraction contained a number of isomers. No attempts were made to separate this mixture. IR: 3060, 3026, 2974, 2922, 2868, 2238, 1602, 1496, 1448, 1028, 756, 700, 640, 558. $^1\text{H-NMR}$: 1.32–1.83 (*m*, 4 cyclopropyl-H); 2.12–2.30 (*m*, 2 cyclopropyl-H); 2.55–2.92 (*m*, CH_2CH_2); 6.85–7.52 (18 arom. H). GC/MS: 464 (13, M^+), 232 (100), 230 (54), 218 (61), 205 (70), 203 (39), 192 (39), 191 (66), 178 (45), 115 (32), 91 (48).

Monitoring of the Photolysis by Time. A stock soln. of 43.2 mg (0.104 mmol) of **1** in 15 ml benzene ($6.96 \cdot 10^{-3} \text{ M}$) was prepared. Aliquots (1 ml) of the stock soln. were degassed and irradiated for a certain time. After photolysis, 0.1 ml of a standard soln. ($7.74 \cdot 10^{-3} \text{ M}$ 1,1,2,2-tetraphenylethene in benzene) was added, the solvent was evaporated at 20°, and 0.25 ml of acrylonitrile was added. The mixture was kept for 1 h at 30–40°, until the red color had disappeared and was submitted to GLC analysis. The results are summarized in Fig. 1.

Quantum Yield Determination. A soln. of the diazomethane in hexane (*ca.* $5 \cdot 10^{-5} \text{ M}$) was photolysed in a UV cell with a Hanau St. 41 Hg arc equipped with a 313-nm line filter. The disappearance of the diazomethane was followed at 280 nm. The data were processed by the method of Gauglitz and Hubig [34], using diphenyldiazomethane ($\Phi_{\text{N}_2} = 0.71$ [18]) for calibration. The results are given in Table 2.

4. Thermolysis. A degassed soln. of **1** (1 ml, $7 \cdot 10^{-3} \text{ M}$) was heated for 15 h at 80°, until the red color had disappeared. The soln. was submitted to GLC analysis, and essentially the same product distribution as with the photolysis was obtained. Pyrolysis of **1** in the GC injector at 275° gave the following product composition: 52% of **8**, 13% of **6a**, 8% of **6b**, 6% of **7**, 4% of **5**, and 2% of **19** and/or **20**.

5. Laser Photolysis. Prep. Laser Photolysis of 1. A degassed soln. of 65 mg (0.16 mmol) of **1** in 50 ml of benzene was irradiated with the excimer laser at 248 nm (10 Hz, 200 mJ per pulse) for 12 min, until *ca.* 50% conversion was achieved. The solvent was removed and the residue was treated with 3 ml of acrylonitrile for 1.5 h at 30–40°, until the red color had disappeared. Mixtures of 4 runs were combined and chromatographed on silica gel (hexane + 15% toluene). The following fractions were collected: 10 mg (9%) of **6b**, 55 mg (49%) of **20**, 8 mg (7%) of **8**, 12 mg (11%) of **6a**, and 5 mg (4%) of **5**. By washing the column with MeOH, 140 mg of trapping products **10** and **11** (*ca.* 50%) were obtained. A $^1\text{H-NMR}$ spectrum of the combined hydrocarbon fractions showed that *ca.* 7% of the (11Z)-isomer **19** was present in the mixture.

(11E)-5,6-Dihydro-11,12-diphenyldibenzof[a,e]cyclooctene (20). Yellow crystals. M.p. 173–174° (EtOH). UV: 363 (4.16), 265 (4.25), 247 (4.20). IR: 3066, 3048, 3010, 2930, 2918, 2848, 1488, 1440, 1028, 774, 764, 748, 740, 694, 626, 558. $^1\text{H-NMR}$: 2.82, 2.91 (*AA'BB'*, $J = 9.8, -16.5, 0.6, 9.4$, CH_2CH_2); 6.91 (*d*, $J = 7.7$, 2 arom. H); 7.05 (*m*, 6 arom. H); 7.13 (*m*, 6 arom. H); 7.23 (*t*, $J = 7.3$, 2 arom. H); 7.44 (*d*, $J = 7.3$, 2 arom. H). $^{13}\text{C-NMR}$: 33.91 (*t*); 126.43 (*d*); 127.27 (*d*); 127.34 (*d*); 127.90 (*d*); 130.42 (*d*); 130.86 (*d*); 131.89 (*d*); 143.59 (*s*); 144.79 (*s*); 146.22 (*s*); 146.57 (*s*). MS: 358 (100, M^+), 280 (12), 279 (15), 267 (42), 265 (18), 203 (9), 179 (11), 178 (12), 165 (7).

UV Control of the Laser Photolysis at 248 nm. A degassed $2 \cdot 10^{-5} \text{ M}$ soln. of **1** in hexane was irradiated with the excimer laser at 248 nm with single pulses. After each pulse, the change in absorbance was monitored at 280 nm

Table 5. UV Control of the Laser Photolysis of **1** in Hexane at 248 nm

No. of pulses	<i>A</i> at 280 nm ^{a)}	<i>A</i> at 365 nm ^{b)}
0	0.773	0.048
1	0.618	0.102
2	0.529	0.126
3	0.442	0.148

^{a)} Disappearance of **1**. ^{b)} Appearance of **20**.

(disappearance of **1**) and at 365 nm (formation of **20**). The results are summarized in Table 5. With a more concentrated soln. of **1** in benzene ($8 \cdot 10^{-4}$ M), a linear increase of **20** was observed up to 100 pulses.

Laser Photolysis at 308 nm. A degassed soln. of 2 mg of **1** in 4 ml of benzene was irradiated with the excimer laser for 30 s at 308 nm (XeCl, 150 mJ/pulse) with 4-Hz repetition frequency. The reaction was monitored by UV and GLC. At 75% conversion, 30% of **20** and 62% of the conventional photoproducts **5** to **8** were formed.

Laser Photolysis at 530 nm. A degassed $1.5 \cdot 10^{-3}$ M soln. of **1** in 2 ml of benzene was irradiated with a frequency-doubled Nd-YAG laser (300 mJ/pulse, 0.25 Hz). The reaction was monitored by GLC and UV. After 330 pulses 15%, conversion was achieved but, if at all, only traces of **19** and/or **20** could be detected.

Control Experiments. a) In individual runs, solns. of 1 mg of **6a**, **6b**, **7**, and **8** in 3 ml of benzene were degassed and irradiated for 20 s at 248 nm (50 Hz repetition rate). The reactions were monitored by UV and GLC. In none of the runs, either **19** or **20** could be detected. b) 3 ml of a degassed $3.4 \cdot 10^{-5}$ M soln. of **19** was irradiated with the excimer laser at 248 nm by single pulses. After 3 pulses, the absorbance at 365 nm had increased by 0.038, compared to an increase of 0.100, when **1** was photolyzed under identical conditions.

(11Z)-5,6-Dihydro-11,12-diphenyldibenzof[a,c]cyclooctene (**19**). Silica gel (5 g) was added to a soln. of 107 mg (0.26 mmol) of **1** in 10 ml of CH_2Cl_2 , and the solvent was evaporated at 20° . After 2 h, the initial reddish silica gel was decolorized, and the products were washed out with CH_2Cl_2 . Evaporation of the solvent gave 50 mg (54%) of crude product which was crystallized from EtOH yielding 22 mg (24%) of colorless needles of **19**. M.p. $187\text{--}189^\circ$ (EtOH); [19]: $183\text{--}185^\circ$. UV: 288 (4.07), 230 (4.38). IR: 3054, 3014, 2924, 1490, 1452, 1440, 762, 734, 696, 638, 618. $^1\text{H-NMR}$: 2.95, 3.49 (AA'XX', $J = 11, -14, 5, 11, \text{CH}_2\text{CH}_2$); 6.93–7.25 (m, 18 arom. H). GC/MS: 358 (100, M^+), 280 (24), 279 (29), 267 (96), 265 (44), 252 (26), 203 (33), 202 (25), 179 (33), 178 (41), 165 (27).

6. **Crystal-Structure Analysis of 20.** A yellowish crystal of **20** was sealed in a glass capillary tube and measured on an Enraf Nonius CAD4 four-circle diffractometer with graphite-monochromatized MoK_α radiation. Details of crystal data and parameters of data collection are given in Table 3. Unit cell parameters were determined from accurate centering of 25 strong reflections by the least-squares method. Four standard reflections monitored every 3600 s showed no intensity loss. The raw data set was corrected for and polarization effects, but not for absorption ($\mu = 3.5 \text{ mm}^{-1}$). The structure was solved by the direct methods using program SHELXS-86 [35] and refined anisotropically by the full-matrix least-squares procedure. H-atoms were localized from a final difference Fourier map. The refinements were stopped when Δ/σ was less than 0.01 for all atoms. From the total of 2178 reflections, 1172 were considered to be observed ($F_o > 2\sigma(F_o)$) and used in the final refinement which gave an R_w factor of 0.052. Scattering factors are from Cromer et al. [36]. Fig. 3 shows an ORTEP plot of **20**. Selected bond lengths and angles are given in Table 4. Fractional coordinates are deposited in the Cambridge Crystallographic Data Base or are available from A. R.

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