

for the observed spectra. The new Avl and FeMo-co data essentially reproduce this earlier work, but under solvated rather than lyophilized conditions. Thus, it appears that the molybdenum site is very similar if not identical in all three systems. Further spectroscopic studies of nitrogenase and model compounds at liquid nitrogen temperatures should help reduce some of the current ambiguity about scatterer numbers, while solution studies of the steady-state nitrogenase system in the presence of substrates and inhibitors promise to yield information about the role of molybdenum in the catalytic mechanism.

**Acknowledgments.** We wish to thank Sebastian Doniach for numerous helpful discussions about the x-ray absorption spectroscopy analysis and for his continued encouragement. We thank Thomas Eccles for the computer programming of both data collection and data analysis packages and Deloria Jacobs for assistance with the AVI preparation. K.O.H. is a fellow of the Alfred P. Sloan Foundation and S.P.C. was an IBM Doctoral Fellow for 1976–1977. This work was supported by the National Science Foundation through Grant PCM-75-17105 and 76-24271 and by NIH Grant GM 22130. Synchrotron radiation time was provided through the Stanford Synchrotron Radiation Laboratory supported by NSF Grant DMR-07692-A02 in cooperation with the Stanford Linear Accelerator Center and the Department of Energy.

## References and Notes

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## The Photochemistry of 2-Vinylstilbenes. 2.<sup>1</sup> Photoreactions of 2-Vinyl- and 2-Propenylstilbene and of Ortho-Substitution Products

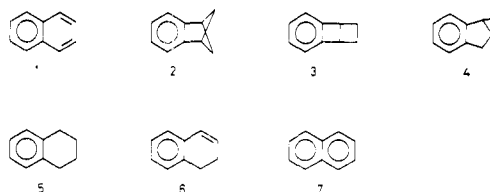
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**Abstract:** Irradiation of 2-vinylstilbene **19** results in the formation of *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (*exo*-**21**) as the main product (70%). As contrasted with the results with *o*-divinylbenzene no benzobicyclo[3.1.0]hex-2-ene derivative (**23**) is formed. Irradiation of 2-propenylstilbene (**20**) gives rise to both types of products, viz., 30% *endo*-5-methyl-*exo*-6-phenylbenzobicyclo[2.1.1]hex-2-ene (**27**) and 10% *exo*-4-methyl-*endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (**28**). Irradiation of 2-vinylstilbenes substituted at one ortho position of the  $\beta$  ring gives a qualitatively similar result as the parent compound; the main product is an *exo*-6-phenylbicyclo[2.1.1]hex-2-ene derivative. On introduction of an ortho substituent in the  $\alpha$  ring a similar product is obtained, but an *endo*-6-phenylbicyclo[3.1.0]hex-2-ene derivative is isolated as a second product. 2-Vinylstilbenes having two ortho substituents in the  $\beta$  ring give neither of these photoproducts. The different behavior has been explained by the supposition that the photoproducts mainly arise from the *cis* isomer of the starting compounds, and that distinct products originate from different conformations of the *cis* isomers. The supposition has been supported by stereochemical considerations, calculation of Mulliken overlap populations, and NMR data. Most probably the photoreactions occur from the  $S_1$  states. The bicyclo[2.1.1]hexene derivatives are formed by a radical reaction whereas the bicyclo[3.1.0]hexenes may arise from a concerted process. Only when the former reaction is not much faster than the latter are both types of products found.

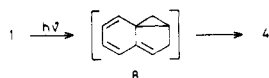
## Introduction

Some years ago Pomerantz<sup>2</sup> and Meinwald and Mazzocchi<sup>3</sup> reported for the first time the photochemical behavior of *o*-divinylbenzene (**1**), a hexatriene with one double bond of reduced bond order because of its inclusion in an aromatic ring. They envisaged that the replacement of the central double bond by a benzene ring should cause head-to-tail cycloaddition between the vinyl groups to give benzobicyclo[2.1.1]hexane (**2**), as observed with 1,5-hexadienes.<sup>4</sup> However, the irradiation of a dilute solution of **1** in ether or pentane yielded neither **2** nor the head-to-head cycloaddition product **3**, but rather benzo-



bicyclo[3.1.0]hexene (**4**) in 30% yield, a product analogous to one of the photoproducts of 1,3,5-hexatriene.<sup>5</sup> Furthermore, traces of tetralin (**5**), 1,2-dihydronaphthalene (**6**), and naphthalene (**7**) have been found.<sup>6</sup> The formation of **4** requires the

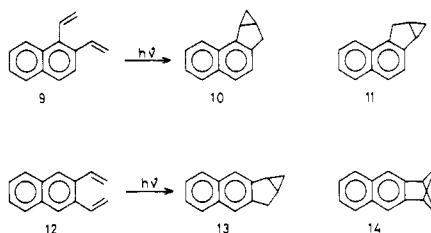
participation of  $\pi$  electrons of the benzene ring. Using the deuterated compound it was shown that no hydrogen atom migration took place. Therefore, a carbon skeleton rearrangement was suggested. In a possibly concerted  $[\pi 4_s + \pi 2_a]$  or  $[\pi 4_a + \pi 2_s]$  process **1** cyclizes to **8**; which undergoes a vin-



ylcyclopropane-cyclopentene rearrangement to give the bicyclo product **4**.

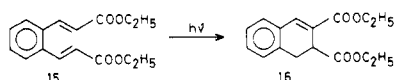
Further experiments with *o*-divinylbenzene derivatives, bearing alkyl substituents on the olefinic carbon atoms, indicated that similar isomerizations also occur in substituted *o*-divinylbenzenes.<sup>7-10</sup> Apparently, terminal alkyl substituents do not greatly influence the direction of photocyclization of divinylbenzenes.

Meinwald et al.<sup>11,12</sup> found that irradiation of 1,2-divinylnaphthalene (**9**), which possesses a larger double bond character between the carbon atoms bearing the vinyl groups than *o*-divinylbenzene, gave only 1,2-naphthobicyclo[3.1.0]hex-2-ene (**10**). The preference to give **10** rather than **11** was as-



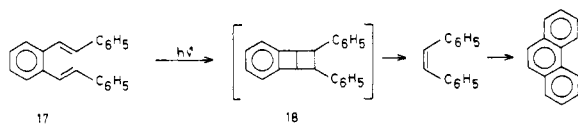
cribed to the preference of **9** for that conformation which leads to the observed product. 2,3-Divinylanthracene (**12**) reacts analogously, but also gives a small amount of naphthobicyclo[2.1.1]hexene (**14**). The formation of the latter product was explained by the fact that in the cycloaddition into **13** aromaticity of both rings is lost.

The photochemistry of *o*-phenylenediacylate (**15**) contrasts with that of the *o*-divinylbenzenes mentioned.<sup>13</sup> Upon irradiation of *trans,trans*-**15** the predominating process appeared



to be *trans*-*cis* isomerization; no intramolecular cyclization products related to benzobicyclo[3.1.0]hexene or indan were found. Only a small amount of the dihydronaphthalene derivative **16** was isolated.

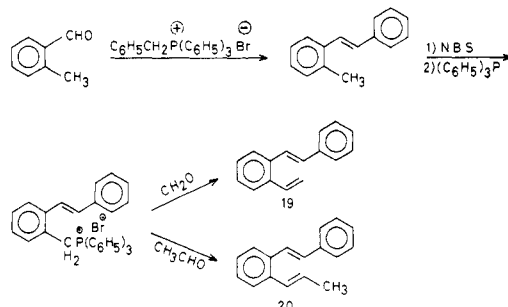
In all the reactions described above divinylbenzenes with aliphatic substituents were used. The photochemistry of *o*-divinylbenzenes substituted with two phenyl groups, viz., *o*-distyrylbenzene (**17**), has also been described.<sup>14</sup> In this case, the main reaction is a photodimerization, both under aerobic and anaerobic conditions. As minor products, *cis*- and *trans*-stilbene and phenanthrene are formed, probably via an intermediate like **18**, formed by a head-to-head cyclization.<sup>14b</sup>



This behavior of **17** is quite different from the usual photo-reactivity of stilbene derivatives. Other examples of similar reactions in stilbene-like compounds were found in the photochemistry of 1,8-divinyl- and 1,8-distyrylnaphthalene, where both head-to-head and head-to-tail cyclization products are formed,<sup>11,12</sup> and in the case of 2,2'-distyrylbiphenyl,<sup>15</sup> where only a head-to-head photocyclization occurs from the excited *trans,trans* isomer.<sup>16,17</sup>

In the light of these results, it could not be anticipated if divinylbenzene, substituted with only one phenyl group, viz., 2-vinylstilbene (**19**), should react as a stilbene or a divinylbenzene system. Formally, **19** might give rise to a series of photoproducts via several modes of intramolecular reactions: (1) an electrocyclic reaction forming a single  $\sigma$  bond between the ends of the conjugated  $\pi$ -electron system comparable to **5**, **6** and **7**; (2) a stilbene-like dehydrocyclization; (3) a cycloaddition in which two new single bonds are formed linking the ends of two  $\pi$ -electron systems (comparable to **2**, **3**, and **4**). Therefore, we have investigated the photoreactivity of 2-vinylstilbene and the homologous 2-propenylstilbene (**20**). In order to get insight into some mechanistic details of the photoreactions of these compounds, the photoreactivity of several ring-substituted derivatives of **19** has also been studied.

The compounds **19** and **20** were synthesized by a sequence of two Wittig reactions according to Scheme I. Benzyltri-



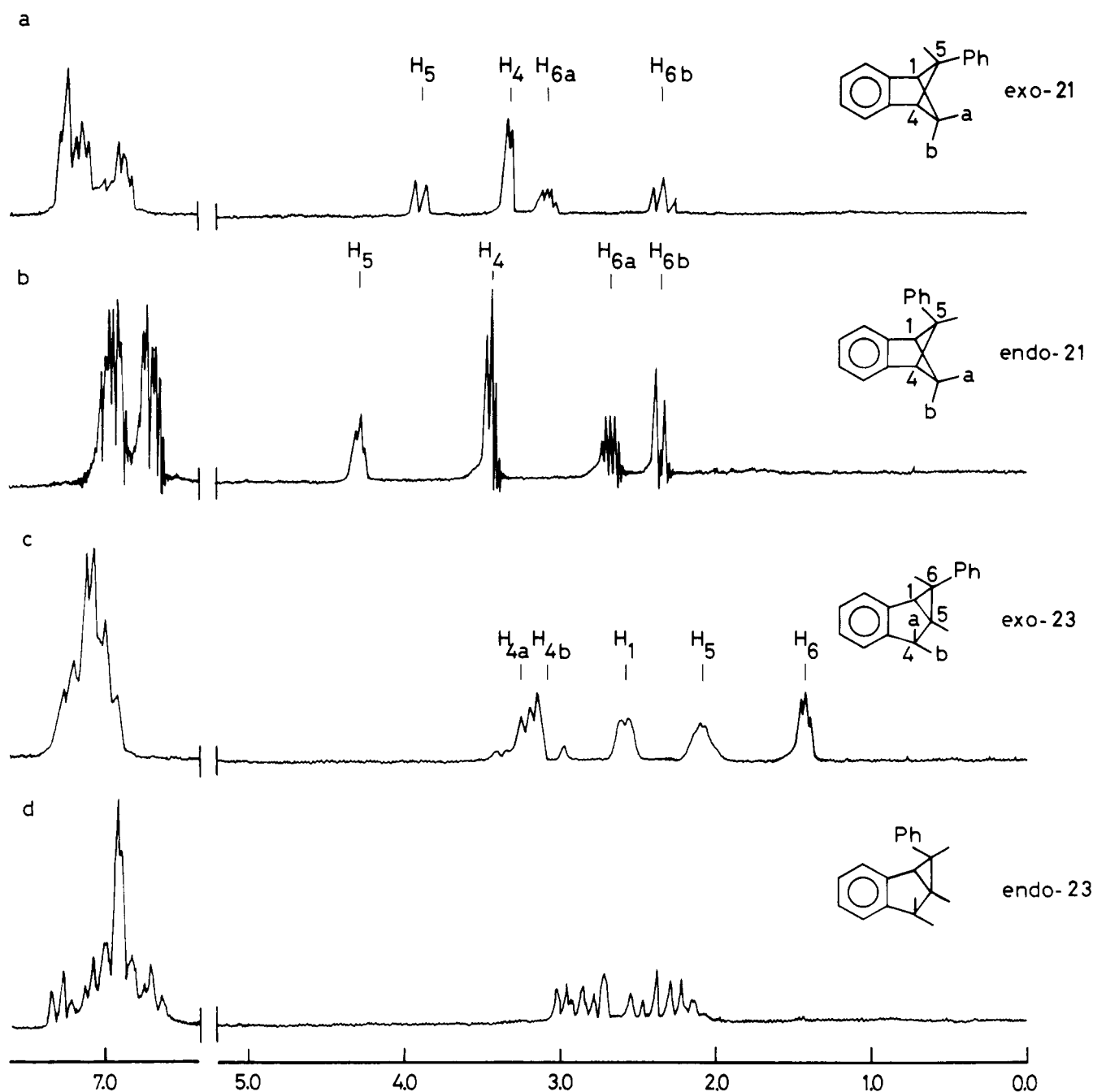
phenylphosphonium bromide reacted with *o*-methylbenzaldehyde to give 2-methylstilbene, which after monobromination and conversion into a triphenylphosphonium salt gave by reaction with formaldehyde or acetaldehyde the required products **19** and **20**.

The UV spectrum of *trans*-2-vinylstilbene **19** possesses large absorptions at 298 nm ( $\epsilon$  24 000), 250 (20 400), and 220 (19 700). Comparison with unsubstituted *trans*-stilbene [308 nm ( $\epsilon$  28 500), 296 (29 000), 229 (16 400), 203 (24 000)] reveals that notwithstanding the larger conjugated system of **19** the extinction is decreased; moreover, the fine structure has disappeared. This is due to steric interaction of the 2 substituent with the stilbene moiety.<sup>18</sup> Comparison with *trans*-2-methylstilbene [307 nm ( $\epsilon$  28 000), 295 (29 500), 229 (16 800)] shows that the steric interaction of the vinyl group is larger than that of a methyl group. The UV spectrum of *cis*-2-vinylstilbene **19** [ $\lambda_{\max}$  248 nm ( $\epsilon$  18 000)] indicates as expected a great hypsochromic shift in comparison with *cis*-stilbene [ $\lambda_{\max}$  277 nm ( $\epsilon$  10 400)].

The UV spectra of *cis*- and *trans*-propenyl-*trans*-stilbene do not differ much from each other. The *trans,trans* isomer **20** possesses absorptions at 300 nm ( $\epsilon$  24 800), 254 (20 600), 240 (sh, 14 900), and 223 (15 400); the *cis,trans* isomer at 299 nm ( $\epsilon$  26 000), 245 (sh, 13 600), 232 (sh, 15 900), and 222 (17 400).

#### Irradiation of 2-Vinylstilbene under Anaerobic Conditions.

*o*-Vinylstilbene was irradiated at 300 and 350 nm in hexane, benzene, and methanol. The same photoproducts resulted from all these experiments, but the reaction rates differed largely. The quantum yields for the main product were estimated to be 0.024 in hexane, 0.01 in benzene, and 0.009 in methanol. For preparative purposes ca.  $10^{-3}$  M solutions of 2-vinylstilbene in hexane, previously degassed with nitrogen or argon, were irradiated at 300 nm for 6-8 h until no starting compound, whose separation from the photoproduct is difficult, remained. After the irradiation the mixture was eluted with hexane-benzene from a silica gel column to remove polymeric products and oxidation products. The resulting mixture was then chromatographed over alumina. The main photoproduct,



**Figure 1.** The NMR spectra of *exo*- and *endo*-5-phenylbenzobicyclo[2.1.1]hexene (**21**) and of *exo*- and *endo*-6-phenylbenzobicyclo[3.1.0]hexene (**23**).

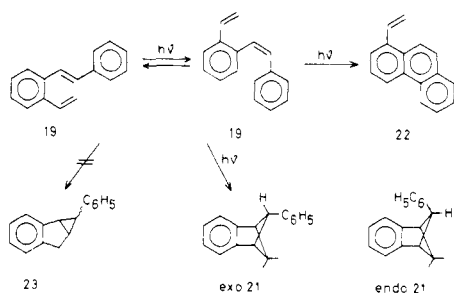
isolated from the first fractions by elution with hexane, was *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (*exo*-**21**, mp 32–33 °C), obtained in a 70% yield. The *endo* isomer (*endo*-**21**, yield 2%) was isolated from the fractions containing an *exo*-*endo* isomer mixture by repeated thin layer chromatography on alumina. 1-Vinylphenanthrene **22** was isolated from the column with hexane–benzene (20:1) as eluent in a 10–15% yield. Two other photoproducts were detected by NMR spectroscopy in fractions eluted with hexane but not isolated owing to their minute quantities.

#### Structure of the Photoproducts

***exo*-5-Phenylbenzobicyclo[2.1.1]hex-2-ene (*exo*-**21**).** The compound, obtained in a 70% yield, has in its mass spectrum a parent peak at *m/e* 206 and fragmentation peaks at *m/e* 128, 115, and 91 indicating the loss of benzene and benzyl fragments. The UV spectrum with absorptions at 274, 267, 260,

and 254 nm is characteristic for benzene derivatives without substituents extending conjugation. The NMR spectrum (see Figure 1a) consists of a nine-proton multiplet at  $\delta$  6.8–7.26, a doublet at 3.87 ppm (H<sub>5</sub>,  $J$  = 7.5 Hz), a doublet at 3.31 ppm (H<sub>1</sub>, H<sub>4</sub>,  $J$  = 2.5 Hz), a doublet at 3.07 ppm (H<sub>6a</sub>, H<sub>6b</sub>,  $J$  = 6.25, 2.5 Hz), and a doublet of doublets at 2.32 ppm (H<sub>6a</sub>, H<sub>6b</sub>,  $J$  = 7.5, 6.25 Hz). The NMR spectrum does not correspond with a benzobicyclo[3.1.0]hexene spectrum (Figures 1c,d) but is in accordance with *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (*exo*-**21**). It possesses a large long-range coupling between H<sub>endo-6</sub> and H<sub>endo-5</sub><sup>19–23</sup> ( $J$  = 7.5 Hz) but no coupling between H<sub>exo-6</sub> and H<sub>endo-5</sub>. According to molecular models the dihedral angle between either bridgehead proton and *endo*-H<sub>6</sub> or *endo*-H<sub>5</sub> is very close to 90°, so that no coupling between them is observed. H<sub>exo-6</sub> is coupled, however, with H<sub>1</sub> and H<sub>4</sub> ( $J$  = 2.5 Hz). The long-range coupling between H<sub>1</sub> and H<sub>4</sub> cannot be seen because of the symmetry of the molecule.

Scheme II



Chemical support for the supposed structure was obtained by catalytic reduction. The product of the treatment with hydrogen and Pd/C could be identified as 1-benzylindan by its spectroscopic properties and comparison with an authentic sample. From this result a structure like phenylbicyclo[2.2.0]hexene is excluded. Moreover, the photoproduct cannot be 5-phenylbicyclo[3.1.0]hexene-2 (23), whose reduction product is 2-benzylindan.<sup>24</sup>

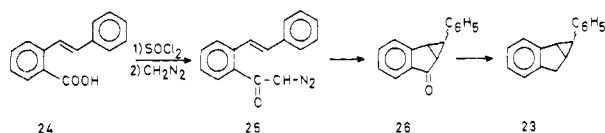
A final proof of the structure was given by thermolysis. Heating *exo*-21 at 200 °C gave rise to 2-vinylstilbene (19) as indicated by its UV spectrum and GLC analysis.

**endo-5-Phenylbicyclo[2.1.1]hex-2-ene (endo-21).** This structure was given to the small fraction present in the bulk of the *exo* isomer. It showed an almost identical mass and UV spectrum and a rather similar NMR spectrum (Figure 1b). The only differences in the NMR spectrum were the absence of the long-range coupling and the occurrence of the signal of H<sub>1</sub> and H<sub>4</sub> as a triplet because of coupling with both the *exo*-H<sub>5</sub> and *exo*-H<sub>6</sub> proton.

**1-Vinylphenanthrene (22).** The third product isolated was identified by its phenanthrene-like UV spectrum with absorptions at 239 nm ( $\epsilon$  23 600), 258 (39 000), and 300 (14 000), and the characteristic pattern of a vinyl group in the NMR spectrum at 5.40 and 5.67 ppm. The structure was confirmed by an independent synthesis (see Experimental Section).

To be sure of the absence of *endo*- or *exo*-6-phenylbicyclo[3.1.0]hex-2-enes (23) in the irradiation mixture of 19 these compounds were synthesized according to Scheme III.

Scheme III

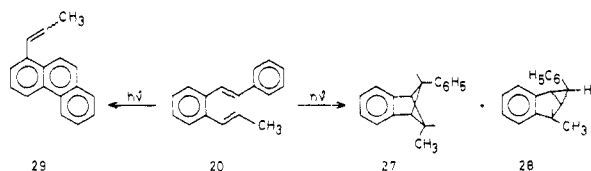


Comparison of the NMR spectra of *endo*- and *exo*-23 (Figures 1c and 1d) with those of the product fractions containing the remaining two unidentified products excluded that 23 had been formed from 19.

#### Irradiation of 2-Propenylstilbene (20)

A mixture of *cis*- and *trans*-2-propenyl-*trans*-stilbene (20) was irradiated under the same conditions as 2-vinylstilbene (19), at 300 nm in hexane as a solvent. In comparison with 2-vinylstilbene, the formation of products is slow. Even after irradiation for 25 h 20% of the starting compound 20 had only been converted into a mixture of four geometric isomers. The following new products were found: 30% *endo*-5-methyl-*exo*-6-phenylbicyclo[2.1.1]hex-2-ene (27), 10% *exo*-

Scheme IV



4-methyl-*endo*-6-phenylbicyclo[3.1.0]hex-2-ene (28), and 10% of a mixture of *cis*- and *trans*-1-propenylphenanthrene (29). Furthermore the reaction mixture contained 5% of a mixture of other photoproducts which could not be isolated due to their small quantity, and about 25% of polymeric and oxidation products.

#### Structure of the Photoproducts

The structures of the compounds obtained were determined on the basis of their spectra.

Both bicyclic products, 27 and 28, possess in their mass spectra the parent peak at the same mass as 2-propenylstilbene (20) ( $m/e$  220); the base peak of the bicyclic product (27) is at  $m/e$  205 and that of 28 at  $m/e$  129 indicating the loss of methyl and benzyl fragments, respectively.

The UV spectra with absorptions between 278 and 254 nm resemble those of the bicyclic products 21.

The NMR spectrum of *endo*-5-methyl-*exo*-6-phenylbicyclo[2.1.1]hex-2-ene (27) shows a great similarity with that of *exo*-21. At 3.82 ppm the benzylic proton H<sub>6</sub> appears as a singlet, indicating its *endo* position. A doublet centered at  $\delta$  3.28 can be attributed to the bridgehead protons coupled with H<sub>exo-5</sub> ( $J = 2.5$  Hz). The quartet of triplets can be assigned to *exo*-H<sub>5</sub> ( $J_{exo-5, Me} = 6.0$  Hz); the methyl protons appear as a doublet at  $\delta$  0.55.

*exo*-4-Methyl-*endo*-6-phenylbicyclo[3.1.0]hex-2-ene (28) has a more complex NMR spectrum. The methyl protons occur at  $\delta$  1.27 ( $J_{Me, exo-4} = 6.25$  Hz). The doublet of doublets at  $\delta$  1.96 is attributed to the homobenzylic proton on C-5 ( $J_{5, endo-4} = 0.2$ ,  $J_{1,5} = 6$ ,  $J_{5, exo-6} = J_{1, exo-6} = 8.5$  Hz). The triplet at 2.43 ppm must then be the cyclopropyl proton *exo*-6, since  $J = 8.5$  Hz corresponds to the characteristic *cis*-cyclopropane coupling constants.<sup>25</sup> The multiplet at 2.88 ppm corresponds to H<sub>1</sub>- and the *endo*-H<sub>4</sub> proton. Spin decoupling techniques confirmed the above assignments.

The 1-propenylphenanthrenes (29), isolated by column chromatography with hexane-benzene (20:1) as eluent in 10% yield, were likewise identified from spectral data.

#### The Mechanism of the Cycloaddition

As already mentioned in the Introduction, there are several possibilities of photocyclization in 2-vinylstilbenes. Experimentally, however, [2 + 2] head-to-tail cycloaddition appears to be the main route. If concerted, this intramolecular reaction can be viewed either as a [ $\pi 2_s + \pi 2_s$ ] or a [ $\pi 2_a + \pi 2_a$ ] reaction, both of which are photochemically allowed according to the Woodward-Hoffmann rules.<sup>26</sup> It must then be characterized by stereospecificity and a lack of solvent polarity effects. However, irradiation of *cis*-19 as well as *trans*-19 gave rise to nearly the same ratio of *exo*- and *endo*-21; in both cases the sterically more favorable *exo* product (21) strongly predominated over the *endo* isomer. Unfortunately, it could not be established from which isomer of 19 the predominating product arose, since *trans* to *cis* isomerization is much more rapid than the cycloaddition ( $\phi_{t \rightarrow c} = 0.37$ ;  $\phi_{cycloaddition} = 0.024$ ). According to the Woodward-Hoffmann rules, *exo*-21 should arise only from *trans*-19.

In order to get more information about the multiplicity of the cycloaddition several experiments with a triplet sensitizer (benzophenone) and quenchers have been done.

Excitation of benzophenone in the presence of 19 did not lead to formation of 21, which excluded the occurrence of a triplet intermediate.

Irradiation of 19 in the presence or absence of *trans*-piperylene gave equal yields of 21. Probably *trans*-piperylene cannot act as a triplet quencher in this experiment because of its high triplet energy ( $E_t = 59.2$  kcal/mol) in comparison with 19. (For *cis*- and *trans*-stilbene  $E_t < 57$  kcal/mol). It is known, however, that *trans*-piperylene also quenches the first excited

singlet state of several aromatic compounds. This effect is not observed in the photoconversion of **19**, however; piperylene added in various concentrations equally did not quench the fluorescence of **19**.

With azulene ( $E_t = 40.6$  kcal/mol<sup>27</sup>) the yield of **21** was decreased on irradiation of **19** at 360 nm. This effect could be accounted for, however, by the competition in absorption between **19** and azulene.

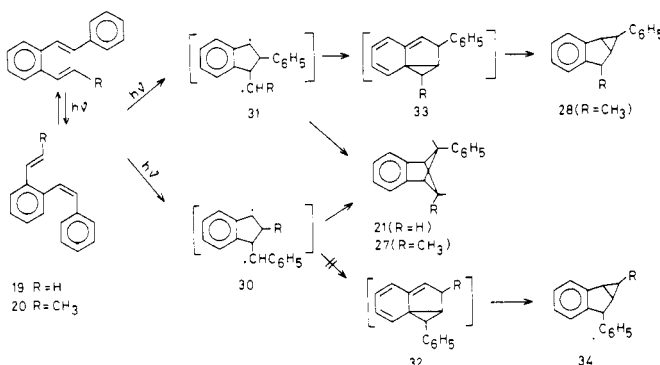
On irradiation of **19** in the presence of 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide<sup>28</sup> ("dinitroxide",  $E_t = 30.9$  kcal/mol) the yield of **21** was also reduced. It is known that the "dinitroxide" is also a radical scavenger. To check whether this effect was observed, another scavenger of transient free radicals,<sup>29</sup> viz., di-*tert*-butyl nitroxide (DTBN),<sup>30</sup> was used. Indeed, again a decrease in the formation of **21** was observed, whereas the amount of vinylphenanthrene **22** formed had increased. The latter result can easily be ascribed to hydrogen abstraction by DTBN from the 4a,4b-dihydrophenanthrene derivative which is intermediate in the photocyclodehydrogenation to **22** and is known to arise from the  $S_1$  state.<sup>31</sup>

It is interesting to mention that Caldwell<sup>32,33</sup> reported that DTBN quenches the triplet state of stilbene with high efficiency, whereas Singer<sup>34</sup> showed that DTBN might be a useful quencher of excited singlet states, long lived enough for bimolecular interaction with DTBN. Weiss<sup>35</sup> found that DTBN quenches both singlet and triplet states. In our case a significant quenching of the fluorescence of **19** by DTBN was observed.

Although the results gave no conclusive evidence, the most probable explanation is that the formation of **21** is a radical reaction starting from the excited singlet state of **19**, although with ESR no radical intermediates could be demonstrated.

A radical pathway to form **21** from **19** and **27** from **20** is given in Scheme V.

Scheme V



In the photoreaction of **19** in the presence of iodine only 1-benzylidene was isolated. This suggests that only the radical **30** arises from **19**, as the radical **31** should have led to 1-methyl-2-phenylindan. This conclusion is consistent with the higher stability of **30** because of the presence of two benzyl radical parts.

The formation of **28** from 2-propenylstilbene (**20**) may occur via two different mechanisms: by a radical reaction via **31** and **33** or by a concerted process leading directly to **33**. To establish by which way **28** is formed **20** was irradiated in the presence of dinitroxide as described above. When **33** should arise via a concerted process and **27** via a radical reaction it could be expected that the formation of **27** should be repressed whereas the amount of **28** should remain unaffected. The experiments gave no decisive answer, however, because the interaction with the scavenger led now mainly to phenanthrene derivatives and other, unidentified compounds.

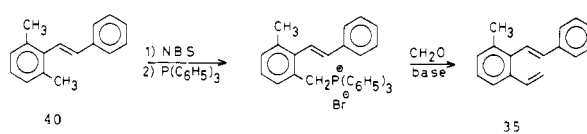
Although no experimental evidence could be obtained, we think that the formation of **33** via a concerted reaction is more probable than via a radical intermediate **31**. The thermody-

namically less favored endo isomer of the final product **28** must be formed from an isomer of **33** in which the cyclopropyl and phenyl group are at the same side of the cyclopentene ring. Formation of this configuration from a radical intermediate is improbable. The lower selectivity in the photoreactivity of **20** in comparison with **19** may be ascribed to the low reaction rate of the formation of **27** from **20**, which becomes comparable to that of the formation of **28**. The conversion of **19** into **21** is much faster, so that formation of **28** (R = H) is not observed.

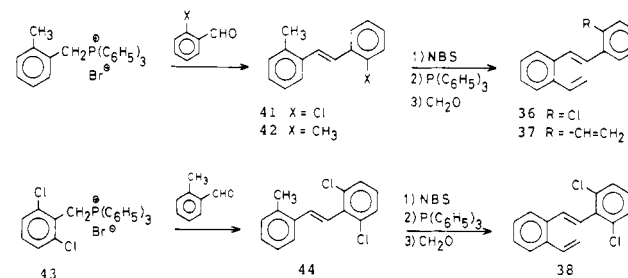
The investigations with the compounds **19** and **20** could not be used to answer the question whether the main product **21** and **27** arise from the *cis* or *trans* isomer (or both) of the parent compounds. Moreover, the large difference in the reaction rates of **19** and **20** remained unexplained. Therefore, we investigated the influence of possible steric factors on the product formation by the introduction of substituents in the parent compound (**19**). This was done in three ways: (1) with a substituent at C<sub>6</sub> in the vinyl substituted ring, 6-methyl-2-vinylstilbene (**35**); (2) with an ortho substituent at C<sub>2</sub>, in the unsubstituted ring, 2'-chloro-2-vinylstilbene (**36**) and 2,2'-divinylstilbene (**37**); (3) with two ortho substituents at C<sub>2'</sub> and C<sub>6'</sub> in the unsubstituted ring, 2',6'-dichloro-2-vinylstilbene (**38**) and 2',4',6'-trimethyl-2-vinylstilbene (**39**).

Compound **35** was obtained from 2,6-dimethylstilbene (**40**) by monobromination, conversion of the monobromide into a triphenylphosphonium salt, and a Wittig reaction of the salt with formaldehyde (Scheme VI). A similar procedure was used

Scheme VI

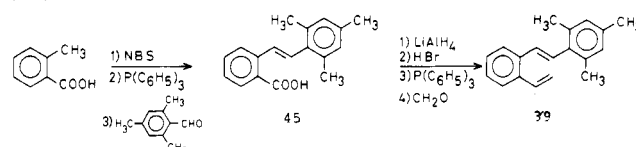


in the preparation of **36**, **37**, and **38**. The necessary 2-methylstilbenes containing the desired substituents (**41**, **42**, and **44**) were obtained as described in Scheme VII. In the synthesis of Scheme VII



**39** *o*-methylbenzoic acid was used as the starting compound. After monobromination and conversion into the corresponding triphenylphosphonium salt, it was subjected to a Wittig reaction with mesitaldehyde. In the resulting stilbene derivative (**45**) the carboxyl residue was transformed into a vinyl group by known methods (Scheme VIII). The UV spectra of the *trans*

Scheme VIII



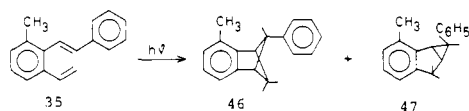
isomers thus obtained (Table I) show that the introduction of only one ortho substituent in the  $\beta$  ring of **19** causes only a slight decrease of the extinction coefficient of the longest wavelength bond; the introduction of two ortho substituents in the  $\beta$  ring or a second ortho substituent in the  $\alpha$  ring leads to a further reduction of  $\epsilon$ , and in addition to a hypsochromic shift.

**Table I.** UV Spectra of Substituted *trans*-2-Vinylstilbenes

Compd	Substituents	$\lambda_{\max}$ ( $\epsilon$ )
<b>19</b>		298 (24 000), 250 (20 400), 220 (19 700)
<b>35</b>	6-Methyl	286 (17 600), 252 (24 600)
<b>36</b>	2'-Chloro	298 (23 100), 250 (18 500)
<b>37</b>	2'-Vinyl	243 (18 000), 234 (17 300)
<b>38</b>	2',6'-Dichloro	300 (21 900), 245 (26 900), 218 (18 000)
<b>39</b>	2',4',6'-Trimethyl	285 (18 400), 241 (21 000), 225 (24 100)
		284 (18 000), 252 (18 500), 224 (21 500)

### Irradiation Experiments

**6-Methyl-2-vinylstilbene (35).** The irradiation was performed under anaerobic conditions at 300 nm in hexane as the solvent. After 24 h the irradiation mixture consisted of 51% of 7-methyl-*exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (**46**) and 17% of 7-methyl-*endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (**47**); 10% of the starting compound had remained; moreover,



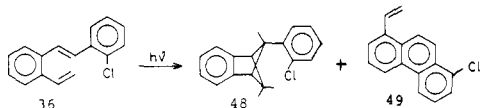
about 10% of unidentified products and 10% of polymeric products were present. The photoreaction is slower than with 2-vinylstilbene (**19**); the quantum yield of **46** appeared to be 0.007 (for **19** 0.024 was found). The products could be identified by comparison of their spectral data with those of the photoproducts **21**, **27**, and **28** from **19** and **20** described above. Especially the UV spectra of **21**, **27**, and **46** and of **28** and **47** were very similar.

The NMR spectrum of the main product (**46**) consisted of a multiplet of eight aromatic protons at  $\delta$  6.70–7.44 ppm, a doublet at 3.88 ( $H_5$ ,  $J = 7$  Hz), two double doublets at 3.42 and 3.36 ( $H_1$  and  $H_4$ ,  $J = 2.5, 7$  Hz), a double triplet at 3.12 ( $H_{6-exo}$ ,  $J = 2.5, 5.75$  Hz), and a signal at 2.22–2.46 of  $H_{6-endo}$  which was partly overlapped by the signal of the methyl group at 2.30 ppm. As expected, the bridgehead protons  $H_1$  and  $H_4$  had slightly different chemical shifts, so that their long-range coupling ( $J = 7$  Hz), unlike that in **21**, could be observed. The spectrum is in full agreement with the structure of 7-methyl-*exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (**46**).

It appeared that **46** underwent thermolysis at considerably lower temperature than **21**. On heating on a boiling water bath two compounds containing vinyl groups were found as was shown by UV and NMR. One was identified as **35**; the other one seemed to be 3-methyl-2-vinylstilbene.

The NMR spectrum of the second product (**47**) differed from that of *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene in the aromatic region (8 protons,  $\delta$  6.42–7.12 ppm) and by the occurrence of a methyl signal at 2.30 ppm. The complex signal between 2.10 and 3.24 ppm (5 protons) was very similar, however, in both spectra. Together with the large similarity of the UV spectra these data proved that the product is 7-methyl-*endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (**47**).

**2'-Chloro-2-vinylstilbene (36).** A  $10^{-3}$  M solution of *trans*-**36** was irradiated under similar conditions as used in the irradiation of **35**. After 30 h the irradiation mixture contained 35% *exo*-5-(2-chlorophenyl)benzobicyclo[2.1.1]hex-2-ene (**48**), 5% of the corresponding *endo* isomer, 20% 1-chloro-8-vinylphenanthrene (**49**), and 40% of polymeric and oxidation

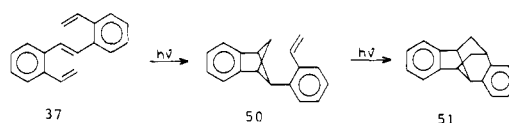


products. The main product, isolated by column chromatography on alumina, possessed a parent peak in its mass spectrum at  $m/e$  240; 242; a peak at  $m/e$  115 indicated the loss of a chlorobenzyl fragment. Its UV spectrum showed absorption maxima at 274, 266, 260, and 253 nm with low extinctions ( $\epsilon_{\max}$  ca. 1200) and was nearly identical with that of **21**. The wide similarity of its NMR spectrum with that of **21** proved the supposed structure **48**: the spectrum consists of a multiplet of eight aromatic protons at  $\delta$  6.84–7.60 ppm, a doublet at 3.92 of the  $H_{5-endo}$  proton ( $J = 7$  Hz), and a doublet at 3.46 of the bridgehead protons  $H_1$  and  $H_4$  ( $J = 2.5$  Hz);  $H_{6-exo}$  appears at 3.03 as a double triplet ( $J = 6, 2.5$  Hz),  $H_{6-endo}$  at 2.34 ppm as a double doublet ( $J = 6, 7$  Hz).

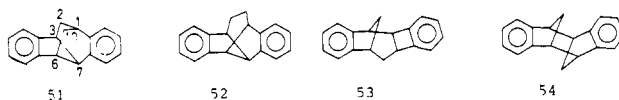
The *endo* isomer of **48** could not be isolated in a pure form. Its NMR spectrum, almost identical with that of *endo*-**21**, points, however, to a similar structure.

The structure of **49** was proven by the phenanthrene-like UV spectrum and the NMR spectrum with the characteristic vinyl pattern and the presence of the bay protons  $H_4$  and  $H_5$  at low field.

**2,2'-Divinylstilbene (37).** Short irradiation (ca. 1 h) of *trans*-**37** led to a reaction mixture in which according to NMR again an *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (**50**) was



present as the main photoproduct. On longer irradiation this compound disappeared, however, and after 24 h a photostable end product could be isolated in 70% yield. It possessed the same mass as **37** ( $m/e$  232). Its UV spectrum showed the absence of a vinyl residue in conjugation with a benzene ring; in the NMR spectrum no absorptions of vinyl protons were present. The ratio of aromatic and aliphatic protons in the NMR spectrum was 1, which was an indication that all three olefinic bonds of **37** had been involved in the formation of the product. The disappearance of the primary photoproduct (**50**) suggested that the end product had been formed by some light-induced interaction of the vinyl residue in **50** with the bicyclohexene moiety. Four such modes of reaction leading to the compounds **51–54**, respectively, seemed possible.



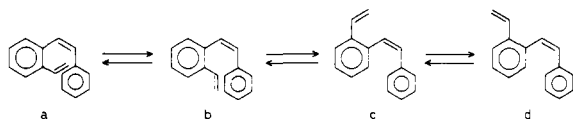
The NMR spectrum of the compound isolated possessed, besides the signal of eight aromatic protons at  $\delta$  6.98–7.35 ppm, a triplet at 3.72 (1 H), a quintet at 3.14 (1 H), a symmetrical multiplet at 2.82 (2 H), and a multiplet at 1.40–1.95 ppm (4 H). These data excluded the structures **52–54** because of their symmetry properties: **52** has four groups of equivalent aliphatic protons in the ratio 2:2:2:2; **54** has only three kinds in the ratio 4:2:2; in **53** all aliphatic protons are different. The remaining structure, dibenzotricyclo[4.3.1.0<sup>3,7</sup>]deca-4,8-diene (**51**), was, however, in full accord with the NMR data as was convincingly demonstrated by spin decoupling. The NMR signals were assigned as follows: the triplet at 3.72 ppm belongs to  $H_7$  ( $J_{6,7} = J_{3,7} = 4.5$  Hz); the quintet at 3.14 corresponds to  $H_1$  ( $J_{1,2} = J_{1,2'} = J_{1,10} = J_{1,10'} = 2.9$  Hz); the symmetrical multiplet at 2.82 arises from  $H_3$  and  $H_6$  ( $J_{6,7} = 4.5$ ,  $J_{6,10} = 9$ ,  $J_{6,10'} = 1.5$  Hz); finally, the multiplet at 1.40–1.95 ppm corresponds to the remaining protons  $H_2$ ,  $H_2'$ ,  $H_{10}$ , and  $H_{10'}$  ( $J_{2,2'} = J_{10,10'} = 12$  Hz). On spectrum simulation of the protons  $H_1$ ,  $H_2$ ,  $H_2'$ , and  $H_3$  by means of the LAOCOON3 program the part of the simulated spectrum containing the protons  $H_2$  and  $H_2'$  was identical with the experimental spectrum of  $H_2$ ,  $H_2'$ ,  $H_{10}$ , and

**Table II.** Irradiation Products from 2-Vinylstilbene Derivatives

Starting compd	Irradiation time, h	Products, %		
		Benzobicyclo[2.1.1]-hexene derivative	Benzobicyclo[3.1.0]-hexene derivative	Phenanthrene derivative
2-Vinylstilbene ( <b>19</b> )	6–8	70		10
2-Propenylstilbene ( <b>20</b> )	25	30	10 (endo)	10
6-Methyl-2-vinylstilbene ( <b>35</b> )	24	51	17 (endo)	
2'-Chloro-2-vinylstilbene ( <b>36</b> )	30	35		20
2,2'-Divinylstilbene ( <b>37</b> )	(24)	70 transiently formed		
2',6'-Dichloro-2-vinylstilbene ( <b>38</b> )	100			
2',4',6'-Trimethyl-2-vinylstilbene ( <b>39</b> )	100			Trace

**Table III.** NMR Data of Vinylic Protons in 2-Vinylstilbenes

Compd	Cis		Trans		$\Delta\delta H_1$	$\Delta\delta H_2$
	$\delta H_1$	$\delta H_2$	$\delta H_1$	$\delta H_2$		
2-Vinylstilbene ( <b>19</b> )	5.54	5.11	5.55	5.26	0.01	0.15
6-Methyl-2-vinylstilbene ( <b>35</b> )	5.50	5.08	5.57	5.17	0.07	0.09
2'-Chloro-2-vinylstilbene ( <b>36</b> )	5.56	5.22	5.56	5.31	0.0	0.09
2,2'-Divinylstilbene ( <b>37</b> )	5.56	5.22	5.59	5.30	0.03	0.08
2',6'-Dichloro-2-vinylstilbene ( <b>38</b> )	5.61	5.30	5.61	5.34	0.0	0.04
2',4',6'-Trimethyl-2-vinylstilbene ( <b>39</b> )	5.57	5.25	5.57	5.26	0.0	0.01

**Figure 2.**

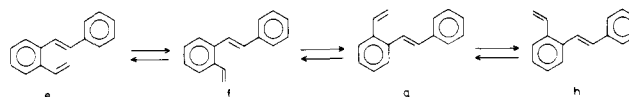
$H_{10}$ . The formation of **51** provides an additional argument for the exo configuration of **50**, and indirectly also of **21**.

**2',6'-Dichloro- and 2',4',6'-Trimethyl-2-vinylstilbene (38 and 39).** On irradiation of solutions of *trans*-**38** and *trans*-**39** under similar conditions as used in the preceding experiments no other photoreactions than *trans*-*cis* isomerization took place. Only after very prolonged irradiation of **39** (100 h) could formation of phenanthrene derivatives be detected by NMR.

## Discussion

The results of the photoreactions studied have been collected in Table II. Letting outside consideration the formation of the phenanthrene derivatives which can be ascribed to the photo-dehydrocyclization found with many stilbene-like compounds, it appears that the introduction of methyl or chloro substituents at the 6 position ( $\alpha$  ring, in **35**), the 2' position ( $\beta$  ring, in **36**) or the  $\beta'$  position (vinyl group, in **20**) slows down the photoreaction, which leads in **19** to intramolecular [2 + 2] cycloaddition. At the same time the yield of the normal photoproduct is lowered, and in two cases (**20** and **35**) a second product is formed via a [4 + 2] cycloaddition followed by a vinylcyclopropane-cyclopentene rearrangement.<sup>2,3</sup> The second product is not found on irradiation of **36** and **37** having one ortho substituent in the  $\beta$  ring. Compounds having two ortho substituents in the  $\beta$  ring (**38** and **39**) give neither [2 + 2] nor [4 + 2] cycloaddition products.

As the substituents used ( $CH_3$ , Cl) do not have strong electronic effects the differences found must originate from steric factors. It is known that the introduction of ortho substituents in *trans*-stilbene is of influence on the planarity of the molecule. This effect is rather small, however, as long as no more than one ortho substituent is present in one or both

**Figure 3.**

rings.<sup>18</sup> Thus, *trans*-**19** and *trans*-**36** will not show serious conformational differences, as appears from their very similar UV spectra (Table I).

Similar substitutions in *cis*-stilbene may have larger effects. It has been supposed for a long time that *cis*-stilbene has a propeller structure, as deduced from its UV spectrum<sup>36</sup> and from theoretical considerations.<sup>37</sup> Recently, this structure has been confirmed by nuclear magnetic relaxation measurements.<sup>38</sup> The aromatic rings in the molecule have been rotated by ca. 30° out of the plane of the olefinic bond, leading to a structure with  $C_2$  symmetry. In the case of *cis*-2-vinylstilbene four different conformations are possible (Figure 2), all of which are fairly free of steric hindrance according to molecular models in which the torsion angle of both phenyl rings is 30°. Strong preference for one of them seems therefore unlikely, although resonance effects may be of influence on the conformational equilibria.

Now it is clear that the introduction of further ortho substituents in general will have different effects in the distinct conformations and will change the equilibria, much more than in the corresponding *trans* isomer (Figure 3). As an example, derivatives with one or two ortho substituents in the  $\beta$  ring, which are very different in photochemical behavior (see compounds **36–39**), will show large differences in the ratio between a + b and c + d in the *cis* isomer, but much less between the conformers of the *trans* isomer.

Such influences on the conformation equilibria seem to be reflected in the NMR data of the vinylic protons in 2-vinylstilbenes (Table III). The position of the lower field signal ( $\delta H_1$ ) is nearly equal in most of the isomer pairs and rather independent of the presence of substituents, indicating that  $H_1$  is rather outside the influence of the  $\beta$  ring in all compounds investigated. The position of  $H_2$ , at higher field, differs significantly for *cis*- and *trans*-**19** which may be ascribed to larger

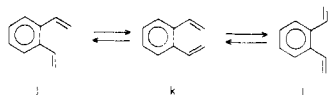


Figure 4.

shielding of this proton in the cis isomer when occurring in the conformations a and b. In the other compounds  $\Delta\delta H_2$  becomes smaller, approaching zero in **39**. This points to shifts of the conformation equilibria to those conformations (c and d) in which the vinyl group is at larger distance from the  $\beta$  ring.

On the ground of these considerations we suppose that the differences in photochemical behavior between the compounds **19**, **20**, and **35–39** must be explained by the supposition that their photoproducts mainly arise from the cis isomers of these compounds. This supposition is reasonable in view of the high quantum yield for trans–cis isomerization (0.39 for **19**) and the high cis–trans ratio (4:1) in the resulting photostationary states.

Among the four conformations represented in Figure 2, conformation a, having a more or less helical form, seems to be most apt for [2 + 2] cycloaddition; the olefinic bonds are nearly perpendicular and at a small distance; b and c seem to be more useful for [4 + 2] cycloaddition, and the absence of a related product in the irradiation mixture of **19** should then be caused by a lower reaction rate for the latter process. The conformation d seems only apt for cyclization into a 4a,4b-dihydrophenanthrene derivative.

Most of the results obtained can well be explained by these conformational considerations. In **20** the conformation a of the cis isomer is less suitable for [2 + 2] cycloaddition in comparison with **19** as the distance between the olefinic bonds will be increased by the additional methyl group. The reaction rate will be lower, and [4 + 2] cycloaddition will become more competitive. In **35** the 6-methyl substituent will similarly cause an increase of the distance between the olefinic bonds by enlargement of the torsion angle of the  $\alpha$ -phenyl ring.

The photochemistry of **36** and **37** should not be very different from that of **1** as the 2' substituents are mainly outside the crowded region. Indeed, the compounds yield only [2 + 2] cycloaddition products though with lower quantum yields.

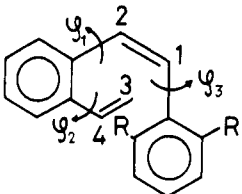
Finally, in **38** and **39** both phenyl rings will be rotated out of the plane of the central olefinic bond over a much larger angle than in **19**. The distance between the olefinic bonds will be increased in all four conformations a–d, thus prohibiting [2 + 2] as well as [4 + 2] cycloaddition.

It may be noted that the preference of *o*-divinylbenzene to give the [4 + 2] cycloaddition product, benzobicyclo[3.1.0]hex-2-ene, instead of the [2 + 2] cycloaddition product, benzobicyclo[2.1.1]hex-2-ene, may be ascribed in a similar way to a larger population of the conformation j than of the sterically less favorable conformation k (Figure 4).

**The [2 + 2] Cycloaddition.** The [2 + 2] cycloaddition of **19** has been described as a radical process because of the results of several quenching experiments. To this, it may now be added that the stereochemistry of the reaction, leading to *exo*-**21** as the main product, should be in conflict with the Woodward–Hoffmann rules for pericyclic reactions when the photoproduct was formed from the cis isomer of **19**, as now is supposed.

In order to establish whether there is an indication for positive or negative overlap between the atoms involved in the reaction, calculations of the Mulliken overlap populations<sup>39</sup> in the first excited state were carried out for two *cis*-2-vinylstilbenes, viz., **19** in the conformation in which all dihedral angles are 30° and 2',6'-dimethyl-2-vinylstilbene in a conformation with torsion angles of 50° for the phenyl–ethylenic bonds (the angles were found by calculations with the Warshel conformation program<sup>40</sup>). The calculated overlap populations (Table IV) show a positive sign for  $n_{2,3}$  in the former com-

Table IV. Mulliken Overlap Populations ( $n_{k,l}$ ) for Atoms Involved in the Photochemistry of *cis*-2-Vinylstilbenes



R	$\Phi_1$	$\Phi_2$	$\Phi_3$	$k,l$	$n_{k,l}$
H	30°	30°	30°	2,3	0.0027
				1,4	−0.0015
CH <sub>3</sub>	50°	30°	50°	2,3	−0.0049
				1,4	−0.0012

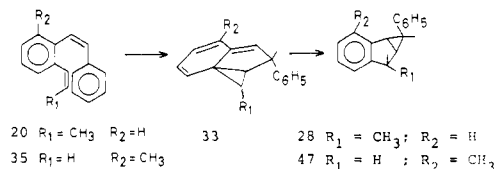
pound, but a negative sign in the latter. The negative sign for  $n_{1,4}$  may be an indication that no concerted reaction takes place.

For a radical process a solvent dependence of the quantum yield as mentioned previously for the [2 + 2] cycloaddition of **19** (0.024 in hexane, 0.01 in benzene, 0.009 in methanol) should not be expected. The effect cannot well be ascribed to viscosity effects as the solvents used have rather equal viscosities, nor to differences in the quantum yields of the trans  $\rightleftharpoons$  cis isomerization which precedes the cycloadditions, as these have never been found for stilbene derivatives without polar substituents.<sup>41</sup> An explanation may be that the population of the preferential conformation (a) for the cycloaddition is influenced by variation of the solvent used.

**The [4 + 2] Cycloaddition.** Several reaction mechanisms have been proposed for the photoconversions of 1,3,5-hexatrienes into bicyclo[3.1.0]hexenes. Dauben et al.<sup>42</sup> and Courtot et al.<sup>43</sup> proposed a [ $\pi 4_a + \pi 2_a$ ] cyclization, while Padwa et al.<sup>44</sup> proposed a [ $\pi 4_s + \pi 2_a$ ] process. Seeley<sup>45</sup> and Schmid<sup>46</sup> gave arguments for a nonconcerted reaction, and Salem<sup>47</sup> suggested that the excited hexatriene has rotated over its central double bond by ca. 90°.

In the case of 1,2-divinylbenzenes or 2-vinylstilbenes such a rotation over the "central" double bond is rather improbable because of the incorporation in a benzene ring. However, in the case of 1,2-divinylbenzenes both radical and concerted reactions ([ $\pi 4_s + \pi 2_a$ ] or [ $\pi 4_a + \pi 2_s$ ]) have equally well been proposed for the formation of benzobicyclo[3.1.0]hexenes.

In our case (compounds **20** and **35**) the formation of the final product (**28** or **47**) proceeds with complete stereoselectivity and leads exclusively to the thermodynamically less favored 6-*endo*-phenyl isomer. As already mentioned formation in a concerted step via a supposed intermediate **33** presupposes that in **33** the cyclopropyl group and phenyl residue are at the same



side of the cyclopentane ring. Such an intermediate can be expected from *cis*-**20** or *cis*-**35** when the reaction occurs in the conformation b (Figure 2) via a concerted [ $\pi 4_a + \pi 2_s$ ] or [ $\pi 4_s + \pi 2_a$ ] process. A choice between these modes cannot be made, as it is unknown whether **20** reacts as a *cis*- or *trans*-propenyl derivative.

## Experimental Section

Spectrometer measurements were made with a Varian MAT SM2B mass spectrometer, a Cary 15 or a Beckman DK2A UV spectrophoto-



tometer, a Perkin-Elmer fluorescence spectrophotometer MPF-4, and a Perkin-Elmer 257 IR spectrophotometer. Nuclear magnetic resonance spectra (NMR) were obtained with either a Varian Model T-60 or HA-100 spectrometer with tetramethylsilane as an internal standard. The samples were ca. 5% solutions in carbon tetrachloride, except where noted otherwise. Frequencies of the absorptions were determined with the side band technique. Melting points were determined with a Leitz melting point microscope and are uncorrected.

Alumina (Woelm, activity 1, neutral) or silica gel (Merck, 0.05–0.2 mm) and preparative thin layer chromatography (TLC) were used for the chromatographic separations. Irradiations were performed in a Rayonet RPR-100 or RPR-208 reactor, fitted with 300- or 350-nm lamps.

**2-Methylstilbene.** A solution of sodium ethoxide (prepared by dissolving 1.38 g of sodium in 60 mL of absolute methanol) was added dropwise to a stirred solution of benzyltriphenylphosphonium bromide (13 g, 0.03 mol) and *o*-methylbenzaldehyde (3.6 g, 0.03 mol) in absolute ethanol (140 mL), and the resulting solution was stirred at room temperature overnight. After removal of the solvent under reduced pressure, the residue was worked up by adding water and then extracting with benzene. The combined benzene extracts were dried (MgSO<sub>4</sub>) and evaporated to dryness affording a semisolid residue which was purified by column chromatography on silica gel. 2-Methylstilbene was obtained in 80% yield<sup>48</sup> as a mixture of *cis* and *trans* isomers: NMR  $\delta$  2.16 (s, *cis* CH<sub>3</sub>), 2.28 (s, *trans* CH<sub>3</sub>).

**2-Vinylstilbene (19).** To a solution of 2-methylstilbene (3.88 g, 0.02 mol) in 50 mL of CCl<sub>4</sub> were added 5.34 g (0.03 mol) of freshly crystallized *N*-bromosuccinimide (NBS) and a few milligrams of benzoyl peroxide. The mixture was irradiated (Philips IR-1000W) and refluxed until the NBS was consumed (usually 6–7 h). The reaction mixture was cooled to room temperature, filtered to remove the succinimide, and concentrated under reduced pressure to give a yellow oil of *trans*-2-bromomethylstilbene in a 70% yield by NMR. The oil was dissolved in 120 mL of xylene and 5.24 g (0.02 mol) of triphenylphosphine was added. The solution was stirred overnight. The precipitated phosphonium salt (7.1 g, 95%) was filtered and subjected to a Wittig reaction with an alcoholic solution of formaldehyde<sup>49</sup> (5 mL, ca. 15% solution) in a similar manner as described above for 2-methylstilbene. After column chromatography on silica gel with hexane as the eluent, a 65% yield of *trans*-2-vinylstilbene (19) was obtained: mass spectrum *m/e* (rel intensity) 206 (M, 96.5), 91 (100); UV  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH) 200 nm (sh, log  $\epsilon$  4.29), 250 (4.31), 298 (4.38); NMR  $\delta$  6.7–7.5 (m, 12 H), 5.55 and 5.26 (2 d of d, =CH<sub>2</sub>,  $J_{\text{trans}} = 17.5$ ,  $J_{\text{cis}} = 11$ ,  $J_{\text{gem}} = 1.5$  Hz). By NMR integration the product was shown to be contaminated with ca. 1% of 2-methylstilbene which was removed by repeated chromatography over a silica gel column impregnated with 5% silver nitrate.<sup>50</sup> *cis*-2-Vinylstilbene (*cis*-19) was obtained by irradiation of the *trans* isomer in hexane (ca. 10<sup>−3</sup> M solution) for 0.5 h at 300 nm. The first fractions from column chromatography over alumina (Woelm, activity 1, neutral) gave *cis*-19 with the following spectral data: UV  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH) 220 nm (sh, log  $\epsilon$  4.34), 258 (4.26), 287 (sh, 3.93); NMR  $\delta$  6.5–7.5 (m, 12 H), 5.54 and 5.11 (2 d of d, =CH<sub>2</sub>,  $J_{\text{trans}} = 17.5$ ,  $J_{\text{cis}} = 11.0$ ,  $J_{\text{gem}} = 1.2$  Hz). Anal. Calcd for C<sub>16</sub>H<sub>14</sub>: C, 93.16; H, 6.84. Found: C, 92.9; H, 7.1.

**Benzy lindene.** Benzy lindene was obtained by the addition of benzyl bromide (34.2 g, 0.2 mol) to a solution of indenylsodium (0.2 mol) in liquid ammonia (200 mL) according to the literature procedure,<sup>51</sup> bp 145–152 °C (3 mm) (lit.<sup>51</sup> bp 116 °C (5 mm); lit.<sup>52</sup> bp 114–115 °C (0.3 mm)) in a 30% yield.

**1-Benzylindan.** A suspension of 1-benzylindene (1.10 g, 5.4 mmol) and 5% Pd/C in 30 mL of ethanol was shaken at atmospheric pressure in a hydrogen atmosphere at room temperature until hydrogen uptake ceased (131 mL, 23 °C). The mixture was filtered and the solvent was evaporated. 1-Benzylindan<sup>53</sup> remained as a colorless oil: NMR  $\delta$  7.72–6.96 (m, 9 aromatic protons), 3.52–2.48 (m, 5 H), 2.24–1.5 (m, 2 H).

**1-Methylphenanthrene.** A solution of 776 mg of 2-methylstilbene and 10.2 mg (10<sup>−4</sup> mol/L) of iodine in 4 L of hexane was irradiated at 300 nm for 6 h.<sup>54</sup> The solvent was removed in vacuo and the resulting oil was chromatographed on a silica gel column. After recrystallization from methanol 388 mg (yield 50%) of 1-methylphenanthrene was obtained, mp 121–122 °C (lit.<sup>55</sup> mp 118–119 °C).

**1-Vinylphenanthrene (22).** A suspension of 384 mg (2 mmol) of 1-methylphenanthrene in carbon tetrachloride was brominated under the conditions described for 2-vinylstilbene. NBS had been consumed after 5 min. To the isolated 1-bromomethylphenanthrene a solution

of triphenylphosphine (524 mg, 2 mmol) in 50 mL of xylene was added. The yield of phosphonium salt was 55%. This phosphonium salt (587.4 mg) was dissolved in 50 mL of absolute ethanol, and 2.5 mL (ca. 15% solution) of alcoholic formaldehyde<sup>49</sup> was added together with sodium ethoxide. The usual workup gave 1-vinylphenanthrene (22)<sup>56</sup> in a 90% yield, mp 105–107 °C. The spectral data follow: UV  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH) 239 nm (log  $\epsilon$  4.37), 258 (4.59), 300 (4.15); NMR  $\delta$  8.4–8.6 (m, 2 H), 7.28–8.07 (m, 8 H), 5.40 and 5.67 (2 d of d, 2 H, methylene protons of vinyl group,  $J_{\text{trans}} = 17.2$ ,  $J_{\text{cis}} = 11$ ,  $J_{\text{gem}} = 1.5$  Hz).

**endo- and exo-6-Phenylbenzobicyclo[3.1.0]hex-2-en-4-ones (26).** The procedure described<sup>24</sup> for the preparation of *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-en-4-one (26) was followed. A mixture of *cis*- and *trans*-stilbene-2-carboxylic esters, obtained by a Wittig reaction from the phosphonium salt of the ethyl ester of 2-bromomethylbenzoic acid and benzaldehyde, was hydrolyzed to a mixture of *cis*- and *trans*-stilbene-2-carboxylic acids (24), mp 120–124 °C (lit.<sup>57</sup> 145–146 °C *cis*, 158–160 °C *trans* isomer). The acids were heated with an excess of thionyl chloride to give the acid chlorides.<sup>57</sup> A solution of the acid chlorides in ether was added to a stirred solution of diazomethane in ether at −5 °C to give *cis*- and *trans*-stilbenyl-2-diazomethyl ketone (25). Decomposition of the isolated crude diazo ketones in a dilute solution of boiling cyclohexane, in the presence of cuprous chloride, afforded a mixture (1:1) of *exo*- and *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-en-4-one (26) in a 64% yield. The *exo* isomer was crystallized from the mixture. Its spectral data correspond completely with those reported for this compound in the literature.<sup>24</sup> The concentrated filtrate was then chromatographed over alumina to give the *endo* isomer, mp 54–65 °C, with the following spectral data: *m/e* 220 (M<sup>+</sup>, 100%); UV  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH) 252 nm (log  $\epsilon$  4.01); NMR  $\delta$  6.5–7.5 (m, 9 H, aromatic), 3.04–3.36 (m, 2 H), 2.7 (q, 1 H).

**endo- and exo-6-Phenylbenzobicyclo[3.1.0]hex-2-enes (23).** Both *endo*- and *exo*-23 were obtained by the Wolff–Kishner reduction of the ketones just described. A solution of a mixture of the ketones (26) (1 mmol) in diethylene glycol (3.5 mL) to which 80% hydrazine hydrate (0.5 mL) and potassium hydroxide (276 mg) had been added was heated for 4 h at 170–180 °C and then for 2 h at 210–220 °C. The mixture was diluted with water and extracted with petroleum ether. After working up in the usual way there was obtained 54% of a mixture of *endo*- and *exo*-23 which were then separated.

**exo-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (23):** mp 72–73 °C (lit.<sup>24</sup> 73.5–74 °C); NMR  $\delta$  6.85–7.36 (m, 9 H, aromatic), 3.3 (d of d, H<sub>exo-4</sub>,  $J_{\text{exo-4,endo-4}} = 17$ ,  $J_{\text{exo-4,5}} = 6$  Hz), 3.05 (d, H<sub>endo-4</sub>,  $J_{\text{endo-4,5}} = 0$  Hz), 2.58 (d of d, H<sub>1</sub>,  $J_{\text{endo-6,1}} = J_{\text{endo-6,5}} = 3$  Hz), 2.10 (t of d, H<sub>5</sub>,  $J_{1,5} = 6$  Hz).

**endo-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (23):** *m/e* 206 (M<sup>+</sup>, 65), 91 (100); NMR  $\delta$  6.58–7.40 (m, 9 H, aromatic), 2.1–3.2 (m, 5 H).

*endo*-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (23) was also prepared (yield 3%) by the reaction of benzal bromide with butyllithium in the presence of indene, as described previously.<sup>58</sup> The photolysis of phenyldiazomethane in indene did not give the expected bicyclic product.

**Hydrogenation of exo-5-Phenylbenzobicyclo[2.1.1]hex-2-ene (21).** A solution of *exo*-21 (0.15 mmol) in ethanol (3 mL) was hydrogenated as described (5% palladium on charcoal). The resulting product was identified as 1-benzylindan by comparison with an authentic sample (see above).

**2-Propenylstilbene (20).** 2-Propenylstilbene (20) was prepared according to Scheme I. To a stirred solution of 5.35 g (0.01 mol) of the appropriate phosphonium salt (see above) and 0.9 g (0.02 mol) of acetaldehyde in 25 mL of methylene chloride at room temperature was added dropwise 5 mL of a 50% sodium hydroxide solution. The red-brown mixture was stirred for 15 min. The organic layer was separated, the water layer was extracted with ether, and the ether washings were combined with the methylene chloride layer, washed with water, and dried (MgSO<sub>4</sub>). Concentration afforded a dark oil which was purified by chromatography on a silica gel column by elution with hexane. The yield of a mixture of *cis*-2-propenyl-*trans*-stilbene (20) and of *trans*-2-propenyl-*trans*-stilbene (20) was 1.1 g (50%). By repeated separations on a silica gel column with hexane as eluent it was possible to separate the *cis*-propenyl- and *trans*-propenyl-*trans*-stilbenes.

**cis-2-Propenyl-*trans*-stilbene (20):** UV  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH) 222 nm (log  $\epsilon$  4.24), 232 (sh, 4.20), 245 (sh, 4.13), 299 (4.42); NMR  $\delta$  6.78–7.64 (m, 11 H, H<sub>st</sub> ethylenic 6.88 as d,  $J_{\text{H,H}} = 16$  Hz), 6.55 (d of q, H<sub>1</sub>,

$J_{H_1, H_2} = 11.25$ ,  $J_{H_1, CH_3} = 1.75$  Hz), 5.81 (d of q,  $H_2$ ,  $J_{H_2, CH_3} = 6.83$  Hz), and 1.68 (d of d, 3 H,  $CH_3$ ).

**trans-2-Propenyl-trans-stilbene (20):** UV  $\lambda_{max}$  ( $CH_3OH$ ) 223 nm (log  $\epsilon$  4.19), 240 (sh, 4.17), 254 (4.31), 300 (4.39); NMR  $\delta$  6.70–7.64 (m, 11 H,  $H_{st}$  ethylenic 6.83 as d,  $J_{H, H} = 16.0$  Hz), 6.00 (d of q,  $H_2$ ,  $J_{H_1, H_2} = 15.25$ ,  $J_{H_2, CH_3} = 6.5$  Hz), 6.67 (d of q,  $H_1$ ), and 1.93 (d of d, 3 H,  $CH_3$ ). Anal. Calcd for  $C_{17}H_{16}$ : C, 92.68; H, 7.32. Found: C, 91.1; H, 7.4.

**2,6-Dimethylstilbene.** 2,6-Dimethylstilbene was synthesized by the Wittig reaction of benzyltriphenylphosphonium bromide with 2,6-dimethylbenzaldehyde in a 40% yield as described for 2-vinylstilbene. The spectral data follow: trans isomer,  $m/e$  208 ( $M^+$ , 59%); UV  $\lambda_{max}$  ( $CH_3OH$ ) 215 nm (sh, log  $\epsilon$  4.31), 276 nm (4.27); NMR  $\delta$  6.37–7.47 (m, 10 H), 2.30 (s,  $CH_3$ ).

**6-Methyl-2-vinylstilbene (35).** 2,6-Dimethylstilbene (0.02 mol) was brominated with NBS (0.02 mol) in the way described for 2-vinylstilbene for ca. 1 h. The isolated, crude bromide, obtained in 80% yield according to the NMR spectrum, was dissolved in xylene (ca. 100 mL) and transformed into the phosphonium salt (60% yield) with triphenylphosphine (0.02 mol). The phosphonium salt (6.6 g) was subjected to a Wittig reaction with an alcoholic formaldehyde solution (5 mL, ca. 15% solution, 100% excess). The product, 6-methyl-2-vinylstilbene (47% yield), was contaminated with 2,6-dimethylstilbene which was separated by column chromatography with hexane on silica gel impregnated with 5% silver nitrate. The *trans*-35 obtained from the column with hexane–benzene was crystallized from methanol (mp 32–33 °C). The spectral data for *trans*-6-methyl-2-vinylstilbene follow:  $m/e$  (rel intensity) 220 ( $M^+$ , 16.4), 205 (14.3), 129 (50), 91 (100); UV  $\lambda_{max}$  ( $CH_3OH$ ) 252 nm (log  $\epsilon$  4.39), 286 (4.25); NMR  $\delta$  6.42–7.52 (m, 11 H), 5.57 and 5.17 (2 d of d,  $=CH_2$ ,  $J_{cis} = 10.25$ ,  $J_{trans} = 16.5$ ,  $J_{gem} = 1.5$  Hz), 2.31 (s, 3 H,  $CH_3$ ). Anal. Calcd for  $C_{17}H_{16}$ : C, 92.68; H, 7.32. Found: C, 89.9; H, 7.6.

**2'-Chloro-2-methylstilbene (41).** To a methanolic solution of 20.3 g (0.045 mol) of triphenyl-*o*-xylylphosphonium bromide and 7 g (0.05 mol) of *o*-chlorobenzaldehyde, sodium methoxide (3.6 g, 0.067 mol) was added and the brown-red solution was stirred overnight at room temperature. The solution was evaporated, extracted with benzene, washed with water, dried ( $MgSO_4$ ), and concentrated in vacuo to afford an oil which was chromatographed on a silica gel column. A mixture of *cis*- and *trans*-2'-chloro-2-methylstilbenes (41) was obtained in 78% yield. *trans*-41 was crystallized from methanol: mp 57–59 °C;  $m/e$  228, 230 ( $M^+$ , 100%, 36.3%); UV  $\lambda_{max}$  ( $CH_3OH$ ) 227 nm (log  $\epsilon$  4.19), 294 (4.35); NMR  $\delta$  6.90–7.66 (m, 10 H), 2.34 (s, 3 H,  $CH_3$ ).

**2'-Chloro-2-vinylstilbene (36).** A solution of 8 g (0.035 mol) of 41 in  $CCl_4$  was brominated with 6.9 g (0.039 mol) of NBS overnight. The bromide was not isolated but, after filtration from the formed succinimide and evaporation of the solvent, converted with triphenylphosphine into the corresponding phosphonium salt as described for 2-vinylstilbene. The salt was dissolved in methanol and supplied with an alcoholic solution of formaldehyde (ca. 15 mL of a 15% solution) together with 2.1 g (0.039 mol) of sodium methoxide. After the reaction mixture was worked up, as described above, *trans*-2'-chloro-2-vinylstilbene (36) was obtained in a 34% yield: mp 41–43 °C (from  $CH_3OH$ );  $m/e$  (rel intensity) 240, 242 ( $M^+$ , 19, 8), 127 (49), 125 (100), 115 (85); UV  $\lambda_{max}$  ( $CH_3OH$ ) 218 nm (log  $\epsilon$  4.26), 234 (sh, 4.24), 243 (sh, 4.26), 250 (4.27), 298 (4.36); NMR  $\delta$  6.85–7.75 (m, 11 H), 5.56 and 5.31 (2 d of d,  $=CH_2$ ,  $J_{trans} = 16.5$ ,  $J_{cis} = 10.5$ ,  $J_{gem} = 1.5$  Hz). Anal. Calcd for  $C_{16}H_{13}Cl$ : C, 79.83; H, 5.44. Found: C, 77.8; H, 5.5.

**2,2'-Dimethylstilbene (42).** *o*-Xylylphosphonium bromide, obtained from the reaction between equimolar amounts of *o*-xylyl bromide and triphenylphosphine (yield 85%), in xylene was subjected to a Wittig reaction with *o*-tolualdehyde. After purification on a silica gel column, 40% of a mixture of *cis*- and *trans*-2,2'-dimethylstilbenes (42) was obtained: mp of the mixture was 40–46 °C (lit.<sup>59</sup> mp 56.4 °C (*cis*), 81.5–82.5 °C (*trans*)).

**2,2'-Divinylstilbene (37).** 2,2'-Dimethylstilbene (42) was brominated with NBS as described for 2-vinylstilbene for 8 h. The isolated crude 2,2'-bis(bromomethyl)stilbene was immediately converted into the diphosphonium salt (50% yield) with triphenylphosphine in dimethylformamide as the solvent. The Wittig reaction with an alcoholic formaldehyde solution in dimethylformamide gave 55% of *trans*-2,2'-divinylstilbene (37), mp 53.5–54.5 °C. The spectral data follow:  $m/e$  (rel intensity), 232 ( $M^+$ , 39), 217 (49), 117 (100), 115 (35); UV  $\lambda_{max}$  ( $CH_3OH$ ) 245 nm (log  $\epsilon$  4.43), 300 nm (4.34); NMR  $\delta$  6.9–7.6

(m, 12 H), 5.6 and 5.30 (2 d of d,  $=CH_2$ ,  $J_{trans} = 17.3$ ,  $J_{cis} = 10.8$ ,  $J_{gem} = 1.5$  Hz). Anal. Calcd for  $C_{18}H_{16}$ : C, 93.06; H, 6.94. Found: C, 92.7; H, 7.1.

**2',6'-Dichloro-2-methylstilbene (44).** To a xylene solution of triphenylphosphine, an equimolar amount of 2,6-dichlorobenzyl chloride was added and the mixture was stirred at room temperature. After some hours the phosphonium salt (43) precipitated (69%). The salt (15.9 g, 0.035 mol) was subjected to a Wittig reaction with 4.2 g (0.035 mol) of *o*-tolualdehyde. After the usual workup and purification by column chromatography over silica gel 50% of a mixture of *cis*- and *trans*-2',6'-dichloro-2-methylstilbene (44) was obtained. The isomers were separated by chromatography. *trans*-44: mp 40–41 °C;  $m/e$  (rel intensity) 262, 264 ( $M^+$ , 15, 10), 192 (100), 115 (45); UV  $\lambda_{max}$  ( $CH_3OH$ ) 223 nm (sh, log  $\epsilon$  4.28), 283 (4.21); NMR  $\delta$  6.79–7.71 (m, 9 H), 2.38 (s,  $CH_3$ ). *cis*-44: mp 108–109 °C UV  $\lambda_{max}$  ( $CH_3OH$ ) 224 nm (sh, log  $\epsilon$  4.24), 258 (4.00); NMR  $\delta$  6.35–7.31 (m, 9 H), 2.31 (s, 3 H,  $CH_3$ ).

**2',6'-Dichloro-2-vinylstilbene (38).** Compound 44 (3.2 g, 0.012 mol) was brominated with 2.3 g (0.013 mol) of NBS for about 2 h. The isolated bromide was treated with 3.1 g (0.012 mol) of triphenylphosphine in xylene. The resulting triphenyl phosphonium salt was subjected to a Wittig reaction with 15 mL of an alcoholic formaldehyde solution (ca. 15%). After workup and purification on a column packed with silica gel 42% of *trans*-2',6'-dichloro-2-vinylstilbene was obtained. *trans*-38: mp 79–80 °C;  $m/e$  (rel intensity) 274, 276 ( $M^+$ , 13, 7), 159 (36), 161 (25), 115 (100); UV  $\lambda_{max}$  ( $CH_3OH$ ) 225 nm (log  $\epsilon$  4.38), 241 (sh, 4.32), 285 nm (4.26); NMR  $\delta$  6.78–7.66 (m, 10 H), 5.61 and 5.34 (2 d of d,  $=CH_2$ ,  $J_{trans} = 16.5$ ,  $J_{cis} = 10.5$ ,  $J_{gem} = 1.25$  Hz). Anal. Calcd for  $C_{16}H_{12}Cl_2$ : C, 69.84; H, 4.40. Found: C, 69.7; H, 4.5.

**2-Carboxy-2',4',6'-trimethylstilbene (45).** *o*-Methylbenzoic acid (40.8 g, 0.3 mol) was brominated with 58.7 g (0.33 mol) of NBS for ca. 3 h and transformed into the 2-carboxybenzyltriphenylphosphonium salt (53% yield). The salt (35.5 g, 0.074 mol) was dissolved in 500 mL of dimethylformamide (DMF), the solution was supplied with 10 g (0.0675 mol) of mesitaldehyde, and then, while stirring, a solution of 8 g (0.015 mol) of sodium methoxide was added. DMF was evaporated in vacuo, the residue was washed with ether, and aqueous hydrochloric acid (1:1) was added to the water layer to precipitate the acid (45). This was extracted with ether (yield 95%). After recrystallization from methanol 52% of *trans*-2-carboxy-2',4',6'-trimethylstilbene (45) was isolated: mp 162–164 °C (lit.<sup>60</sup> 155–156 °C);  $m/e$  266 ( $M^+$ , 100%); UV  $\lambda_{max}$  ( $CH_3OH$ ) 283 nm (log  $\epsilon$  4.21); IR  $\nu_{CO}$  1690  $cm^{-1}$ ; NMR  $\delta$  6.69–8.09 (m, 8 H), 2.29 (s, 6 H, *o*- $CH_3$ ), 2.24 (s, 3 H, *p*- $CH_3$ ).

**2-Hydroxymethyl-2',4',6'-trimethylstilbene.** To a solution of 45 (10 g, 0.038 mol) in 300 mL of dry ether, a slurry of  $LiAlH_4$  (1.6 g, 0.04 mol) in 50 mL of ether was added dropwise. After 3 h of reflux the reaction mixture was worked up in the usual way. After filtration and washing with ether, the solvent was removed in vacuo to afford 98% of the crystalline alcohol. The obtained *trans* product was crystallized from methanol (yield 75%): mp 114–115 °C;  $m/e$  252 ( $M^+$ , 56%); UV  $\lambda_{max}$  ( $CH_3OH$ ) 220 nm (sh, log  $\epsilon$  4.25), 280 nm (4.25); IR  $\nu_{OH}$  3260  $cm^{-1}$  (in Nujol); NMR  $\delta$  6.74–7.64 (m, 8 H), 4.58 (s, 2 H,  $-CH_2-$ ), 2.87 (s, 1 H,  $-OH$ ), 2.28 (s, 6 H, *o*- $CH_3$ ), 2.24 (s, 3 H, *p*- $CH_3$ ).

**2-Bromomethyl-2',4',6'-trimethylstilbene.** A stream of HBr was conducted at room temperature through a benzene solution of 4 g (0.0159 mol) of the above alcohol, to which  $MgSO_4$  had been added, until the characteristic frequency of the alcohol ( $\nu_{OH}$  3260  $cm^{-1}$ ) had disappeared (ca. 30 min). After evaporation, a brown-colored oil remained, which was purified by column chromatography on silica gel followed by crystallization from hexane (73% yield), mp 84–85 °C. The spectral data follow:  $m/e$  314, 316 ( $M^+$ , 44%, 42%); UV  $\lambda_{max}$  ( $CH_3OH$ ) 235 nm (sh, log  $\epsilon$  4.23), 290 (4.21); NMR  $\delta$  6.76–7.66 (m, 8 H), 4.46 (s,  $-CH_2-$ ), 2.34 (s, 6 H, *o*- $CH_3$ ), 2.24 (s, 3 H, *p*- $CH_3$ ).

**2',4',6'-Trimethyl-2-vinylstilbene (39).** The above bromide was transformed with triphenylphosphine, in xylene as solvent, into the corresponding phosphonium salt (92% yield). To a solution of 3 g (0.0052 mol) of this salt and formaldehyde (15% alcoholic solution, ca. 15 mL) in ethanol, an excess of sodium methoxide in methanol was added dropwise. After the usual workup and purification of the product by column chromatography on silica gel followed by crystallization from methanol *trans*-2',4',6'-trimethyl-2-vinylstilbene (39) was obtained in a 74% yield: mp 57–58 °C;  $m/e$  (rel intensity) 248 ( $M^+$ , 45), 233 (17), 133 (100); UV  $\lambda_{max}$  ( $CH_3OH$ ) 224 nm (log  $\epsilon$  4.33), 252 (4.27), 284 (4.26); NMR  $\delta$  6.73–7.63 (m, 9 H), 5.57 and 5.26 (2 d of

d,  $\text{=CH}_2$ ,  $J_{\text{trans}} = 16.25$ ,  $J_{\text{cis}} = 10.25$ ,  $J_{\text{gem}} = 1.5$  Hz), 2.30 (s, 6 H,  $\text{o-CH}_3$ ), 2.23 (s, 3 H,  $\text{p-CH}_3$ ). Anal. Calcd for  $\text{C}_{19}\text{H}_{20}$ : C, 91.88; H, 8.12. Found: C, 91.9 H, 8.3.

**Irradiations of 2-Vinylstilbene in the Absence of Oxygen.** A degassed solution of 370.8 mg of 2-vinylstilbene in 1500 mL of hexane ( $1.2 \times 10^{-3}$  M) under nitrogen was irradiated for 6 h at 300 nm. The hexane was removed in vacuo and the resulting yellow oil was chromatographed on a column packed with alumina (Woelm, activity 1, neutral) in hexane. Elution with hexane gave 70% of **exo-5-phenylbenzobicyclo[2.1.1]hex-2-ene (21)**: mp 32–33 °C;  $m/e$  (rel intensity) 206 ( $\text{M}^+$ , 69), 128 (22.3), 115 (23.2), 91 (100); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 254 nm (sh,  $\log \epsilon$  3.00), 260 (3.09), 267 (3.15), 274 (3.13); NMR  $\delta$  6.8–7.26 (m, 9 H, aromatic), 3.87 (d,  $\text{H}_{\text{endo-5}}$ ,  $J_{\text{endo-6,5}} = 7.5$ ,  $J_{\text{exo-6,5}} = J_{1,5} = J_{4,5} = 0$  Hz), 3.31 (d,  $\text{H}_1$  and  $\text{H}_4$ ,  $J_{\text{exo-6,1}} = J_{\text{exo-6,4}} = 2.5$ ,  $J_{1,5} = J_{4,5} = J_{\text{endo-6,1}} = J_{\text{endo-6,4}} = 0$  Hz), 3.07 (d of t,  $\text{H}_{\text{exo-6}}$ ,  $J_{\text{endo-6,exo-6}} = 6.25$  Hz), 2.32 (d of d,  $\text{H}_{\text{endo-6}}$ ).

**endo-5-Phenylbenzobicyclo[2.1.1]hex-2-ene (21)** was isolated from combined fractions of several irradiations in ca. 2% yield by column and thin layer chromatography: mp 88–90 °C;  $m/e$  (rel intensity) 206 ( $\text{M}^+$ , 54), 128 (29.6), 115 (22.7), 91 (100); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 256 nm (sh,  $\log \epsilon$  2.77), 262 (2.90), 269 (2.98), 275 (2.94); NMR  $\delta$  6.6–7.2 (m, 9 H, aromatic), 4.26 (t,  $\text{H}_{\text{exo-5}}$ ,  $J_{1,5} = J_{4,5} = 2.5$  Hz), 3.44 (t,  $\text{H}_1$  and  $\text{H}_4$ ,  $J_{1,\text{exo-6}} = J_{4,\text{endo-6}} = 2.5$  Hz), 2.66 (d of t,  $\text{H}_{\text{exo-6}}$ ,  $J_{\text{exo-6,endo-6}} = 5.5$  Hz), 2.35 (d,  $\text{H}_{\text{endo-6}}$ ).

Finally, elution with 5–10% benzene in hexane gave 1-vinylphenanthrene (**22**) in a 15% yield. The product was identical with that obtained by an independent synthesis (see above).

Thermolysis of **exo-21** for 60 min at 200 °C resulted in the formation of *cis*- and *trans*-2-vinylstilbene (**19**) as detected by UV spectroscopy and gas chromatography.

**Irradiation in the Presence of Oxygen.** 2-Vinylstilbene (**29**, 258.0 mg) was dissolved in 1500 mL of hexane ( $0.8 \times 10^{-3}$  M) and irradiated for 6 h at 300 nm. After evaporation of the solvent the yellow residue (insoluble in  $\text{CCl}_4$ , soluble in  $\text{CHCl}_3$  and benzene) was chromatographed over alumina. Elution with hexane and with 10% benzene in hexane gave 10% of a mixture of **exo-5-phenylbenzobicyclo[2.1.1]hex-2-ene (21)** and 1-vinylphenanthrene (**22**) (identified by NMR spectra). The polymerization and oxidation products remained on the column.

**Irradiation in the Absence of Oxygen with Iodine.** A degassed hexane solution of 309 mg (1.5 mmol/1500 mL) of **19** and 381 mg (1.5 mmol) of iodine was irradiated for 6 h at 300 nm. The hexane was evaporated and the resulting yellow oil was chromatographed over alumina. The first fractions obtained by elution with hexane contained 15% of 1-benzylindan (identified by comparison with an authentic sample). Further elution with a solution of 5–10% benzene in hexane gave a fraction consisting of 1-ethylphenanthrene (15% yield), identified with a sample independently synthesized by hydrogenation of **22**. About 70% of polar, probably polymeric products remained on the column.

**Irradiation of 2-Propenylstilbene.** A solution of 360 mg of **20** in hexane ( $1.1 \times 10^{-3}$  M) was degassed and irradiated for 25 h at 300 nm. The solvent was removed and the yellow residue chromatographed on alumina. The separation of the photoproducts was difficult owing to the presence of 20% of unreacted starting material. The photoproducts appeared in the chromatographic fractions in the following order: **exo-6-phenyl-endo-5-methylbenzobicyclo[2.1.1]hex-2-ene (27)**, 30%, **exo-4-methyl-endo-6-phenylbenzobicyclo[3.1.0]hex-2-ene (28)**, 10%, and *cis*- and *trans*-1-propenylphenanthrenes (**29**, 10%). Besides the mentioned products, the presence of other products of unknown structure was observed in the NMR spectrum but these products could not be isolated owing to their small quantity. On the alumina column there remained about 25% of high molecular weight products. The spectral data of the photoproducts follow.

**exo-6-Phenyl-endo-5-methylbenzobicyclo[2.1.1]hex-2-ene (27)**:  $m/e$  (rel intensity) 220 ( $\text{M}^+$ , 78.5), 205 (100), 129 (44); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 254 nm ( $\log \epsilon$  3.25), 261 (3.28), 267 (3.29), 274 (3.26); NMR  $\delta$  6.88–7.48 (m, 9 H, aromatic), 3.82 (s,  $\text{H}_{\text{endo-6}}$ ), 3.28 (d,  $\text{H}_1$  and  $\text{H}_4$ ,  $J_{\text{endo-6,1}} = J_{\text{endo-6,exo-5}} = 0$ ,  $J_{1,\text{exo-5}} = J_{4,\text{exo-5}} = 2.25$  Hz), 3.62 (q of t,  $\text{H}_{\text{exo-5}}$ ,  $J_{\text{exo-5,CH}_3} = 6.0$  Hz), 0.55 (d, 3 H,  $\text{CH}_3$ ).

**exo-4-Methyl-endo-6-phenylbenzobicyclo[3.1.0]hex-2-ene (28)**:  $m/e$  (rel intensity) 220 ( $\text{M}^+$ , 100), 205 (60.5), 129 (97.2), 91 (52); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 259 nm ( $\log \epsilon$  3.04), 266 (3.08), 271 (3.11), 278 nm (3.05); NMR  $\delta$  6.64–7.38 (m, 9 H, aromatic), 2.88 (m,  $\text{H}_1$  and  $\text{H}_{\text{endo-4}}$ ), 2.42 (t,  $\text{H}_{\text{exo-6}}$ ,  $J_{\text{exo-6,1}} = J_{\text{exo-6,5}} = 8.0$  Hz), 1.96 (d of d,  $\text{H}_5$ ,  $J_{1,5} = 6.0$ ,  $J_{\text{endo-4,5}} = 0$  Hz), 1.27 (d,  $\text{CH}_3$ ,  $J_{\text{endo-4,CH}_3} = 6.25$  Hz).

**Quenching and Sensitizing Experiments.** These experiments were carried out using quartz test tubes of 60-mL capacity in a “merry-go-round” at 300 and 350 nm. The tubes were irradiated simultaneously under the same conditions with and without quenchers or sensitizers. The benzene solution of **19** (ca. 40 mg) with benzophenone (ca. 1 g) was prepared so that at 350 nm the sensitizer absorbed more than 99% of the incident light. The irradiations with piperylene at 300 nm were performed with various concentrations of piperylene in hexane. Azulene (51.8 mg, 0.4 mmol) was dissolved in a benzene solution of 2-vinylstilbene (42.3 mg, 0.2 mmol) and irradiated at 350 nm. The irradiation of **19** in the presence of 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide (5–10 molar excess was used) was carried out in benzene at 300 nm. The experiment with DTBN (a twofold molar excess was used) was performed in hexane at 300 nm. After the irradiations the resulting solutions were evaporated and analyzed by NMR spectroscopy.

**Quantum Yields.** Irradiations ( $\lambda_{\text{max}}$  300 nm) for the determination of quantum yields of 2-vinylstilbene (**19**) were performed in a Rayonet reactor RPR-100 equipped with a “merry-go-round” and quartz test tubes of 60-mL capacity. The light intensity was determined by ferrioxalate actinometry in the modification described by Murov.<sup>27</sup> The quantum yield of **exo-5-phenylbenzobicyclo[2.1.1]hex-2-ene (21)** formation was determined by NMR spectroscopy of the crude mixtures.

The quantum yield of *trans*-*cis* isomerization of **19** was determined in a Black Box apparatus as described by Zimmerman.<sup>61</sup> The light intensity was determined by ferrioxalate actinometry. The filter solutions employed for the irradiations were: cell 1 of a triple compartment filter was filled with 1.7 M nickel sulfate in 10% sulfuric acid, cell 2 with 1.0 M cobalt sulfate in 10% sulfuric acid, and cell 3 with 0.0133 M stannous dichloride in 40% hydrochloric acid. This filter is opaque below 300 nm and above 350 nm; it shows a maximum transmission of 18% at 325 nm.

**Irradiation of 6-Methyl-2-vinylstilbene (35).** A degassed solution of 260 mg of **35** in 1 L of hexane was irradiated at 300 nm for 24 h. Evaporation under reduced pressure gave a slightly yellow oil which was chromatographed on an alumina column.

The first fractions, eluted with hexane and 1% benzene in hexane, consisted of **7-methyl-endo-6-phenylbenzobicyclo[3.1.0]hex-2-ene (47)**: yield 17%;  $m/e$  (rel intensity) 220 ( $\text{M}^+$ , 100), 205 (19), 129 (42.9); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 253 nm ( $\log \epsilon$  2.69), 259 (2.76), 266 (2.81), 271 (2.81), 274 (sh, 2.76), 279 (2.69); NMR  $\delta$  6.42–7.12 (m, 8 H, aromatic), 2.10–3.24 (m, 5 H), 2.30 (s,  $\text{CH}_3$ ).

The next fractions, eluted with 2–5% benzene in hexane, consisted of **7-methyl-exo-5-phenylbenzobicyclo[2.1.1]hex-2-ene (46)**: yield 51%; NMR  $\delta$  6.70–7.44 (m, 8 H, aromatic), 3.88 (d,  $\text{H}_5$ ,  $J = 7$  Hz), 3.42 and 3.36 (2 d of d,  $\text{H}_1$  and  $\text{H}_4$ ,  $J = 2.5$ , 7 Hz), 3.12 (d of t,  $\text{H}_{6a}$ ,  $J = 2.5$ , 5.75 Hz), 2.22–2.46 (4 protons,  $\text{H}_{6b}$  and  $\text{CH}_3$ ).

The bicyclic product (**46**) was contaminated with unreacted **35** (10%) and 10% of unidentified products. Compound **46** was purified by repeated TLC on alumina. It appeared, however, that **46** underwent thermolysis at a rather low temperature. The presence of vinylic protons could then be detected in the NMR spectra.

**Irradiation of 2'-Chloro-2-vinylstilbene (36).** *trans*-2'-Chloro-2-vinylstilbene (**36**, 400 mg), dissolved in ca. 1500 mL of hexane, was irradiated under anaerobic conditions at 300 nm for 30 h. After evaporation of the solvent the remaining yellow oil was chromatographed on an alumina column. Only the main product, **exo-5-(2-chlorophenyl)benzobicyclo[2.1.1]hex-2-ene (48)**, was isolated (35% yield) and characterized spectroscopically: mp 82–84 °C;  $m/e$  (rel intensity) 240, 242 ( $\text{M}^+$ , 100, 37), 205 (58.3), 202 (34.5), 125 (66.5), 115 (52.4); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 252 nm ( $\log \epsilon$  2.85), 260 (2.96), 266 (3.08), and 274 (3.08); NMR  $\delta$  6.84–7.60 (m, 8 H, aromatic), 3.92 (d,  $\text{H}_5$ ,  $J_{5,\text{endo-6}} = 7$  Hz), 3.46 (d,  $\text{H}_1$  and  $\text{H}_4$ ,  $J_{1,\text{exo-6}} = J_{4,\text{exo-6}} = 2.5$  Hz), 3.03 (d of t,  $\text{H}_{\text{exo-6}}$ ,  $J_{\text{exo-6,endo-6}} = 6$  Hz), 2.34 (d of d,  $\text{H}_{\text{endo-6}}$ ).

**Irradiation of 2,2'-Divinylstilbene (37).** A degassed hexane solution of 2,2'-divinylstilbene (**37**) was irradiated under the same conditions as 2-vinylstilbene (**19**). The resulting mixture, obtained after irradiation for 24 h and evaporation of the solvent, was separated on a chromatographic column packed with alumina. From the first fractions, dibenzotricyclo[4.3.1.0<sup>3,7</sup>]deca-4,8-diene (**51**), mp 157–158 °C, was obtained in a 70% yield by elution with hexane. The spectral data follow:  $m/e$  232 ( $\text{M}^+$ , 100%); UV  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{OH}$ ) 239 nm (sh,  $\log \epsilon$  2.75), 246 (sh, 3.0), 251 (3.19), 258 (3.30), 264 (3.19); NMR  $\delta$  6.98–7.35 (symmetrical m, 8 H, aromatic), 3.72 (t,  $\text{H}_7$ ,  $J_{6,7} = J_{3,7}$

= 4.5 Hz), 3.14 (qi,  $H_1$ ,  $J_{1,2} = J_{1,2'} = J_{1,10} = J_{1,10'} = 2.9$  Hz), 2.82 (m,  $H_3$  and  $H_6$ ,  $J_{2,3} = J_{6,10} = 1.5$ ,  $J_{2',3} = J_{6,10'} = 9.0$  Hz), 1.95–1.40 (m,  $H_{2'}$ ,  $H_{10}$ ,  $H_{10'}$ ,  $J_{2,2'} = J_{10,10'} = 12$  Hz).

The next fractions (ca. 10%, as based on the NMR spectra) consisted of the cycloadduct (50), *exo*-5-(2-vinylphenyl)-benzobicyclo[2.1.1]hex-2-ene: NMR  $\delta$  6.54–7.58 (m, aromatic H), 3.97 (d,  $H_{endo-5}$ ,  $J_{endo-5,endo-6} = 7.0$ ,  $J_{exo-5,4} = J_{endo-5,1} = 0$  Hz), 3.36 (d,  $H_1$  and  $H_4$ ,  $J_{1,exo-6} = J_{4,exo-6} = 2.5$  Hz), 3.19 (d of t,  $H_{exo-6}$ ,  $J_{exo-6,endo-6} = 6.5$  Hz), 2.34 (d of d,  $H_{endo-6}$ ), 5.6 and 5.24 (2 d of d,  $=CH_2$ ,  $J_{trans} = 17.25$ ,  $J_{cis} = 11$ ,  $J_{gem} = 1.5$  Hz).

**Irradiation of 2',6'-Dichloro-2-vinylstilbene (38) and 2',4',6'-Trimethyl-2-vinylstilbene (39).** Degassed hexane solutions of 38 as well as of 39 were irradiated under anaerobic conditions analogously to 2-vinylstilbene (19) for 100 h. The NMR spectra of the products revealed only substantial *trans*-*cis* isomerization of the parent compound and an indication of the occurrence of traces of phenanthrene-like compounds.

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