Registry No. 1, 289-80-5; 2, 289-95-2; 3, 290-37-9; 4, 289-96-3; 5, 290-38-0; 6, 290-87-9; 7, 290-42-6; 8, 592-59-6; 9, 290-96-0; 12, 288-36-8; 13, 288-35-7; 14, 288-88-0; 15, 63598-71-0; 16, 288-94-8; 17, 288-95-9; **19a**, 69365-63-5; **19b**, 69365-64-6; **19c**, 50275-24-6; **21a**, 98858-73-2; **21b**, 98858-74-3; **21c**, 98858-75-4; **23a**, 98900-92-6; **23b**, 98900-91-5; **23c**, 98858-76-5; **24ab**, 98921-31-4; **24ac**, 61788-15-6; **24b**, 61788-17-8; **24c**, 98858-77-6.

Supplementary Material Available: MNDO equilibrium geometries for all the reported compounds and STO-3G equilibrium geometries for **5** and **16** (4 pages). Ordering information is given on any current masthead page.

The Photochemistry of Bis(2,2-diphenylvinyl) Ether: A Search for the 3-Oxa-di-π-methane Rearrangement

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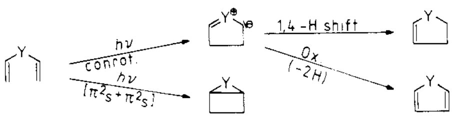
A convenient synthesis for bis(2,2-diphenylvinyl) ether (**1a**) from diglycolic acid via dehydration of 2,2′-oxybis(1,1-diphenylethanol) (**3a**) is described. The solution photochemistry of divinyl ether **1a** derives from its singlet π,π*-state and parallels that of the unsubstituted divinyl ether (**1d**) and that of furan in the gas phase. Formation of a singlet $D_{\sigma,\pi}$ vinyl–vinyloxy radical pair is the primary photoreaction (Φ_{-S} = 0.12–0.19). All photoproducts can be convincingly rationalized from this initial radical pair. For example, cage recombination affords 2,2,4,4-tetraphenyl-3-butenal (**13**) as the main product. The mechanistic interpretations are based on results from product studies, photo-CIDNP and crossover experiments. The triplet excited state of divinyl ether **1a** was found to be inert toward decomposition. *trans,trans*-Bis(2-phenylvinyl) ether (**1c**) could be prepared from *trans,trans*-1,4-diphenyl-1,3-butadiene via epoxidation of its Diels–Alder adduct with bis(2,2,2-trichloroethyl) azodicarboxylate and thermal denitrogenation of the corresponding azo compound. The divinyl ether **1c** readily cis–trans isomerizes upon triplet sensitization, thus implicating cis–trans isomerization as the deactivation mode of triplet divinyl ether **1a**. 3-Oxa-di-π-methane reactivity of divinyl ether **1a** could not be observed. This result is interpreted in terms of Zimmerman's formalism of bond-order control. Irradiation of the authentic vinyloxirane **7** resulted in the photoextrusion of diphenylcarbene affording 3,3-diphenylpropenal. The intermediacy of the corresponding carbonyl ylide **14** was established by low-temperature UV spectroscopy.

The di-π-methane rearrangement[1] (eq 1, X = CR_2) has been shown to be one of the most ubiquitous reactions in organic photochemistry. Substitution of carbon by heteroatoms in the 1,4-pentadiene chromophore gave rise to the analogous oxa-[1,2a] (eq 1, X = O) and aza-[3] (eq 1, X = NR) di-π-methane reactions. However, other reaction modes have been possible as well.[4,5] Replacement of the sp^3 carbon in the 3-position by heteroatoms such as O, S, N, Se,[6] or B[7,8] afforded so far only inactive di-π-methane systems. Ring closure to five-membered heterocycles or (2 + 2) cycloadditions to bicyclic products were documented as the most prominent reaction pathways (eq 2).

(1)



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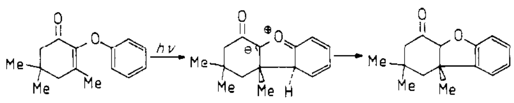

(3)

In most of the heterosystems of this type that have been investigated[6], aromatic rings provided at least one active π-bond of the 1,4-diene chromophore. An example is the photocyclization of 2-phenoxy-1,5,5-trimethylcyclohexene-3-one[9] (eq 3). To the best of our knowledge, no detailed examinations of the photolytic behavior of divinyl ethers in solution have been reported. Previous work was concerned with the gas-phase flash photolysis of the parent divinyl ether (**1d**).[10] Vinyl and vinyloxy radicals were formed in the primary step (eq 4). Tetraphenyldioxin (**2**) proved to be photochemically inert.[11]

Thus, we found it worthwhile to prepare the hitherto unknown bis(2,2-diphenylvinyl) ether (**1a**) and investigate

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[∥] Max-Planck-Institut für Festkörperforschung.

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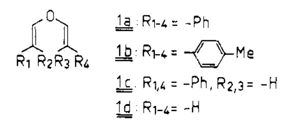

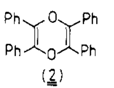
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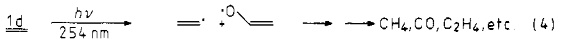
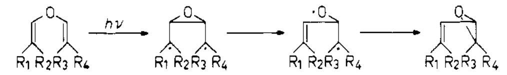


(4)

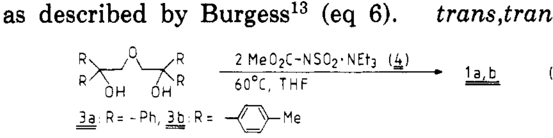
its photochemistry. Photolysis in solution was hoped to proceed more selectively in favor of the 3-oxa-di-π-methane[2b] rearrangement, leading to vinyloxiranes (eq 5).



(5)

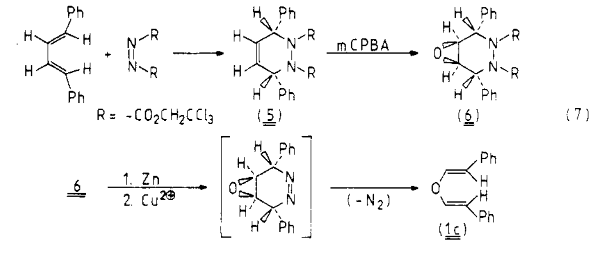
Results

Syntheses. The aryl-substituted divinyl ethers **1a** and **1b** were prepared by dehydration of the corresponding 2,2′-oxybis(1,1-diarylethanols) **3a**[12] and **3b** with the complex of methyl *N*-sulfonylcarbamate and triethylamine (**4**), as described by Burgess[13] (eq 6). *trans,trans*-Bis(2-



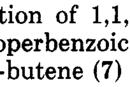
(6)

phenylvinyl) ether (**1c**) was synthesized in high yield according to the stereospecific reaction sequence shown in eq 7. Epoxidation of the Diels–Alder adduct **5** afforded *only* (90-MHz ^{1}H NMR) the *exo,exo*-2,5-diphenyl-7-oxa-3,4-diazabicyclo[4.1.0]heptane (**6**). Its stereochemistry was



(7)

rigorously proven by means of X-ray crystallography (cf. Experimental Section) (Figure 4). Reductive removal of the protecting groups and subsequent oxidation with copper(II) chloride did not lead to the expected copper complex of the azo compound but instead gave directly divinyl ether **1c** in quantitative yield. Again, 90-MHz ^{1}H NMR analysis did not indicate the presence of the known[14] cis–trans or cis–cis isomers of divinyl ether **1c**. Epoxidation of 1,1,4,4-tetraphenyl-1,3-butadiene with *m*-chloroperbenzoic acid led to 1,1,4,4-tetraphenyl-3,4-epoxy-1-butene (**7**) in high yield. The dimerization of di-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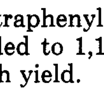
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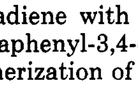
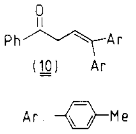

(9)

phenylacetaldehyde sodium enolate with iodine was reported[15] to yield 2,2,3,3-tetraphenylbutanedial (**8**). Instead, a crystalline product having the reported melting point was isolated, but spectral analysis proved its structure to be that of the head-to-tail dimer **9**. The enol ether moiety could readily be recognized by its C=C stretching vibration at 1630 cm^{-1} and the olefinic proton at δ 6.52. Addition of 2 mol of *p*-tolyllithium to ethyl β-benzoylpropionate, hydrolysis, and subsequent acid-catalyzed dehydration led to 1-phenyl-4-,4-di-*p*-tolyl-3-buten-1-one (**10**). Further reaction of enone **10** with 1 mol of phenyllithium, hydrolysis, and acid-catalyzed dehydration afforded 1,1-diphenyl-4,4-di-*p*-tolyl-1,3-butadiene (**11**).



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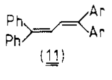
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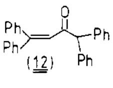
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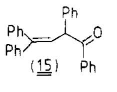
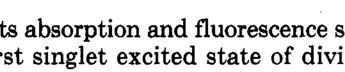

(15)

Product Studies. The product distributions obtained upon photolysis of the phenyl-substituted divinyl ether **1a** under various conditions are given in Table I. When the direct photolysis was carried out at 254 nm, secondary photoreactions of the primary products occurred, making their quantitative determination difficult. Laser irradiation at 333.6 nm did not cause significant alterations of the product distributions (Table I, entries 2,3 and 4,5). Neither the expected 3-oxa-di-π-methane product **7** nor enone **12**[16] could be detected under any of the irradiation conditions by means of HPLC coinjections of authentic materials and 400-MHz ^{1}H NMR. Diphenylacetaldehyde was found in significant amounts only when the irradiation of divinyl ether **1a** was carried out in diisopropyl ether (Table I, entry 6) or in methyl *tert*-butyl ether in the presence of tributyltin hydride. The unsatisfactory product balances in the photolyses of divinyl ether **1a** were due to the formation of undefined higher molecular weight products. Gravimetry of the noneluable zone in the preparative TLC of the photolysates showed in some cases up to 60% of such material. Minor amounts of benzophenone were found under each of the irradiation conditions (Table I, entries 1–7, 9, 10). When the solutions of divinyl ether **1a** were rigorously degassed and sealed, no benzophenone was formed. The assumption that the formation of benzophenone was caused by traces of oxygen penetrating the photolysis cell during irradiation was further supported by photolyzing divinyl ether **1a** in CFCl$_3$ under oxygen pressure. In this case, benzophenone was the only detectable (TLC) product.

Ketone-sensitized photolysis of divinyl ether **1a** led to very slow conversions without significant alteration of the product distributions (Table I, entries 3, 8; Table II, entries 5–7). Energy transfer from triplet benzophenone to the divinyl ether **1a** was shown to occur efficiently since the divinyl ether **1a** quenched the hydrogen abstraction reaction[17] of triplet benzophenone with benzhydrol. Also, on chemiexcitation (eq 8) with tetramethyl-1,2-dioxetane,[18] the divinyl ether **1a** was inert. In the case of the divinyl ether **1c**, benzophenone sensitization resulted in its conversion to the cis,trans and cis,cis isomers.



(8)

From its absorption and fluorescence spectra the energy of the first singlet excited state of divinyl ether **1a** was estimated to be 82–85 kcal/mol. Its first oxidation potential in acetonitrile was found to be +1.22 V (vs. SCE); the reduction potential of 1,4-dicyanobenzene is reported

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Table I. Product Yields[a] of the Photolysis of Divinyl Ether 1a

solvent	conditions		convn, %	$Ph_2C{=}CH_2$	$(Ph_2C{=}CH)_2$	13	$Ph_2C{=}CHCHPh_2$	Ph_2CO	product balance, %	13 + $Ph_2C{=}CHCHPh_2$	ratio of $Ph_2C{=}CH_2$/$(Ph_2C{=}CH)_2$
	time, min	λ, nm									
(1) benzene[b,c]	10–12	300	55–59	3.7 ± 0.4	7.3 ± 0.5	57.3 ± 2.0	none	4.5 ± 0.7	72.8 ± 3.6	57.3 ± 2.0	0.5 ± 0.1
(2) methyl *tert*-butyl ether	10–11	300	63–68	15.1 ± 0.6	5.4 ± 0.32	41.4 ± 1.0	none	4.0 ± 0.4	65.9 ± 2.3	41.4 ± 1.0	2.8 ± 0.3
(3) methyl *tert*-butyl ether[b]	15–16	333.6	61–65	13.1 ± 1.8	5.0 ± 0.5	38.2 ± 3.2	none	6.2 ± 0.2	62.5 ± 5.7	38.2 ± 3.2	2.6 ± 0.6
(4) acetonitrile[b]	12–14	300	82–89	10.3 ± 0.3	4.4 ± 0.3	41.8 ± 0.1	trace	3.8 ± 0.3	60.3 ± 1.0	41.8 ± 0.1	2.3 ± 0.3
(5) acetonitrile[b]	10–12	333.6	62–75	11.3 ± 0.1	4.5 ± 0.5	43.3 ± 0.1	trace	4.9 ± 0.5	64.0 ± 1.2	43.3 ± 0.1	2.5 ± 0.3
(6) diisopropyl ether[g]	10–11	300	46–50	13.1 ± 0.8	3.5 ± 0.3	55.3 ± 4.2	none	3.9 ± 0.6	89.6 ± 6.4	55.3 ± 4.2	3.7 ± 0.3
(7) acetone	12	300	72–78	9.2 ± 0.3	2.2 ± 0.1	28.1 ± 0.2	trace	4.8 ± 1.9	44.3 ± 2.5	28.1 ± 0.2	4.2 ± 0.3
(8) methyl *tert*-butyl ether/benzophenone[d]	90	350	58–62	4.6 ± 0.3	1.9 ± 0.1	35.0 ± 0.9	4.84 ± 0.61		46.3 ± 1.9	39.8 ± 1.5	2.4 ± 0.3
(9) methyl *tert*-butyl ether/1,4-dicyanobenzene[e]	15–17	333.6	58–66	13.2 ± 0.4	5.4 ± 0.3	39.5 ± 0.6	none	7.2 ± 0.7	65.3 ± 2.0	39.5 ± 0.6	2.5 ± 0.2
(10) acetonitrile/1,4-dicyanobenzene[f]	12–14	333.6	68–74	13.2 ± 0.6	5.5 ± 0.7	45.0 ± 2.4	trace	3.9 ± 0.4	67.6 ± 4.1	45.0 ± 2.4	2.4 ± 0.5

[a] Weight %, normalized to 100% conversion of divinyl ether 1a. [b] Traces of diphenylmethane. [c] Traces of biphenyl. [d] Molar ratio of divinyl ether **1a** to benzophenone of 0.18 was used. [e] Molar ratio of divinyl ether **1a** to 1,4-dicyanobenzene of 0.42 was used. [f] Molar ratio of divinyl ether **1a** to 1,4-dicyanobenzene of 0.30 was used. [g] 13.8 ± 0.5 % (by weight) of diphenylacetaldehyde was also formed.

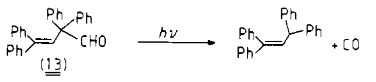
Table II. Quantum Yields (Φ_{-S}) for the Divinyl Ether 1a

solvent	λ, nm	quantum yields (Φ_{-S}): without radical scavenger	quantum yields (Φ_{-S}): with radical scavenger[a]
(1) benzene	300	0.12 ± 0.01	0.10 ± 0.01
(2) methyl *tert*-butyl ether	300	0.16 ± 0.02	0.11 ± 0.01
(3) acetonitrile	300	0.19 ± 0.03	0.14 ± 0.02
(4) diisopropyl ether	300	0.12 ± 0.02	0.12 ± 0.02
(5) acetone	300	0.08 ± 0.01	
(6) acetophenone	350	0.03 ± 0.01	
(7) benzene/benzophenone[b]	350	0.01 ± 0.01	

[a] 2,6-Di-*tert*-butyl-4-methylphenol was used as scavenger at a 10–11 molar ratio of scavenger to divinyl ether **1a**. [b] A sixfold molar ratio of benzophenone to divinyl ether **1a** was used.

to be −1.64 V (vs. SCE).[19] On the basis of these values, the Rehm–Weller equation[19] predicts electron transfer from excited divinyl ether **1a** to 1,4-dicyanobenzene to be exergonic by about −19 to −22 kcal/mol. However, addition of the electron acceptor did not affect the product distributions (Table I, entries 3,9 and 5,10).

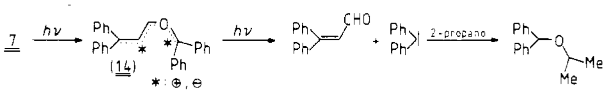
As control experiments, each of the observed and expected photoproducts of divinyl ether **1a** was checked for its photostability under the irradiation conditions. Only the 2,2,4,4-tetraphenyl-3-butanal[20] (**13**) underwent efficient secondary photolysis (eq 9) to yield 1,1,3,3-tetraphenylpropene. Enone **12**[16] was decomposed only very slowly



(9)

in the presence of divinyl ether **1a**. 1,1-Diphenylethene, 1,1,4,4-tetraphenyl-1,3-butadiene, diphenylacetaldehyde, and ene epoxide **7** did not decay as long as the starting material **1a** was still present. When diphenylacetaldehyde was photolyzed in 2-propanol, diphenylmethane and 1,1,2,2-tetraphenylethane were formed in a 9:1 molar ratio.

To estalish rigorously the absence of the 3-oxa-di-π-methane product **7** among the photoproducts of divinyl ether **1a**, the photolytic behavior of authentic ene epoxide **7** was checked independently. ¹H NMR analysis of its photoproducts at 300 nm in benzene indicated the formation of 3,3-diphenylpropenal. In 2-propanol, benzhydryl isopropyl ether could be identified (eq 10).



(10)

When ene epoxide **7** was photolyzed at 8 K in an argon matrix, a strong absorption at 560 nm could be detected. Presumably this absorption is due to the formation of the carbonyl ylide **14** as the primary photoproduct of the ene epoxide **7**. Attempts to trap the ylide **14** with norbornene or methyl acetylenedicarboxylate failed. In the latter case isomerization of the epoxide **7** to the enone **15**[21] was observed. As benzophenone sensitization had the same effect, energy transfer from triplet methyl acetylenedicarboxylate is thought to be the reason for this unexpected rearrangement.[22]

3,3-Diphenylpropenal was shown to be stable under the irradiation conditions used for the divinyl ether **1a**. None of the photoproducts of ene epoxide **7** could be detected

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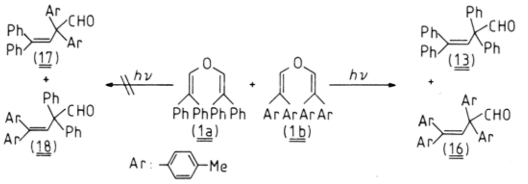
(22) For similar isomerizations of triplet ene epoxides, see: Paulson, D. R.; Korngold, G.; Jones, G. *Tetrahedron Lett.* **1972**, 1723.

in the photolysates of divinyl ether **1a**. Traces of the acid-catalyzed isomerization of ene epoxide **7** into 1,2,4,4-tetraphenyl-3-buten-1-one (**15**) were observed.[21]

The absence of enone **15**, tetraphenylfuran, aldehyde **9**, and 1,1,2,2-tetraphenylethane as photoproducts of divinyl ether **1a** was rigorously established by HPLC coinjection with authentic samples. Since the main photoproduct of enone **12**[16b] in the presence of methanol is methyl 3,3,4,4-tetraphenylbutanoate, its absence and that of methyl diphenylacetate in the photolysate of divinyl ether **1a** in methanol and catalytic amounts of acetic acid were established by HPLC coinjection with authentic material. The photolysis of enol aldehyde **9** gave 1,1,2,2-tetraphenylethane as the final photoproduct.

Quantum Yields. Quantum yields of substrate consumption (Φ_{-S}) and fluorescence (Φ_F) were determined for the divinyl ether **1a**. Φ_{-S} values and conditions are given in Table II. Essentially no solvent effects on Φ_{-S} (**1a**) could be observed. In a second set, the Φ_{-S} values of divinyl ether **1a** were measured in the presence of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (Table II, entries 1–4). No significant effects were detected. With anthracene as fluorescence standard (Φ_F = 0.27[23]), the fluorescence quantum yield of divinyl ether **1a** in methylene chloride was found to be ca. 0.001.

Crossover Experiment. A 1:1 mixture of the divinyl ethers **1a** and **1b** in methyl *tert*-butyl ether (~0.1 M) was irradiated at 300 nm. Careful examination of the photolysate by HPLC indicated the presence of the crossover butadiene **11** and the noncrossover aldehydes **13** and **16** but the absence of the corresponding crossover aldehydes **17** and **18** (eq 11).



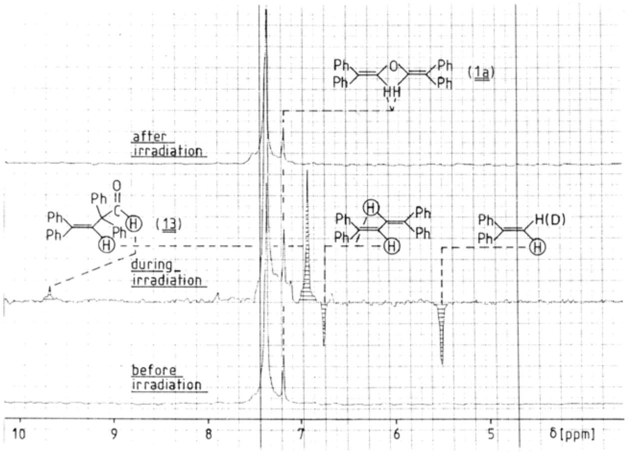
(11)

Photo-CIDNP Experiment. The photo-CIDNP ^{1}H NMR spectrum of divinyl ether **1a** in CD_3CN (Figure 1) showed four polarized signals, which could readily be assigned to the vinylic protons of 1,1-diphenylethene, 1,1,4,4-tetraphenyl-1,3-butadiene, and unsaturated aldehyde **13** and to the aldehydic proton of the latter one by means of authentic samples.

Discussion

For sake of clarity, the most important experimental results shall briefly be summarized here.

(i) Energy transfer from triplet-excited benzophenone to divinyl ether **1a** occurred efficiently, but the divinyl ether **1a** proved inert toward decomposition. The analogous *trans,trans*-bis(2-phenylvinyl) ether (**1c**) cis–trans isomerized on benzophenone sensitization. (ii) The direct irradiation of divinyl ether **1a** afforded 2,2,4,4-tetraphenyl-3-butenal (**13**) as the main product. This aldehyde is of intramolecular origin as shown by crossover experiments. (iii) Photo-CIDNP ^{1}H spectroscopy of divinyl ether **1a** revealed that the rearranged aldehyde **13** is a cage recombination product of an initially formed vinyl–vinyloxy radical pair, whereas the minor products 1,1-diphenylethene and 1,1,4,4-tetraphenyl-1,3-butadiene stem from statistically free radicals. (iv) The vinyl epoxide **7** and the enone **12** (the potential 3-oxa-di-π-methane products of divinyl ether **1a**) could not be detected among the photoproducts of divinyl ether **1a** and are also ruled out as possible transient primary photoproducts.



chemical shift, δ [ppm]	polarization	assignment
5.49	emission	1,1-diphenylethene-(H,D)
6.73	emission	1,1,4,4-tetraphenyl-1,3-butadiene
6.89	strongly enhanced absorption	2,2,4,4-tetraphenyl-3-butenal (13), vinyl-H
7.15	none	divinyl ether 1a, vinyl-H
9.55	enhanced absorption	2,2,4,4-tetraphenyl-3-butenal (13), -CHO

Figure 1. Photo-CIDNP ^{1}H NMR spectrum of divinyl ether **1a** in CD_3CN.

The triplet state of the divinyl ether **1a** appears to be inert. Taking into account that the analogous *trans,-trans*-bis(2-phenylvinyl) ether (**1c**) readily cis–trans isomerizes on triplet sensitization, the free rotor effect,[1] well-known for acyclic di-π-methane systems, is the most likely explanation for this behavior. The slow consumption of divinyl ether **1a** in the presence of benzophenone (Table I, entry 8) is due to some direct excitation, while in acetone as solvent (Table I, entry 7) singlet sensitization via the quite long-lived excited singlet state of acetone[23] seems to be responsible. For example, triplet acetone, generated by thermolysis of the tetramethyl-1,2-dioxetane[18] (eq 8), does not promote any reaction of the divinyl ether **1a**. The low quantum yields of divinyl ether **1a** consumption (Φ_{-S}) under triplet ketone sensitization also reflect the inefficiency of the triplet state of this substrate (Table II, entries 6 and 7).

Upon direct excitation, the divinyl ether **1a** is converted to the β,γ-unsaturated aldehyde **13** as the main product. The crossover experiment between the tetraphenyl- and the tetra-*p*-tolyl-substituted divinyl ethers **1a** and **1b**, respectively, clearly established that the aldehyde **13** was of *intramolecular* origin since the tetraphenyl- and tetra-*p*-tolyl-substituted aldehydes **13** and **16** were formed but not the crossover products **17** and **18**. In view of the fact that the crossover tetraaryl diene **11** was obtained, arising from coupling of statistically free 2,2-diarylvinyl radicals, the intramolecular origin of the aldehyde **13** is especially evident through this control experiment.

Such intramolecularity makes the 3-oxa-di-π-methane mechanism **1a** → A → B → C → **13** (path b, Scheme I) plausible. However, oxatrimethylene diradicals such as B are well-known[24] to cyclize into epoxides **7** or rearrange into enones **12**. Therefore, the absence of these expected products and their potential secondary photoproducts in the photolysates of divinyl ether **1a** render the 3-oxa-di-π-methane sequence (Scheme I, path b) unlikely. Fur-

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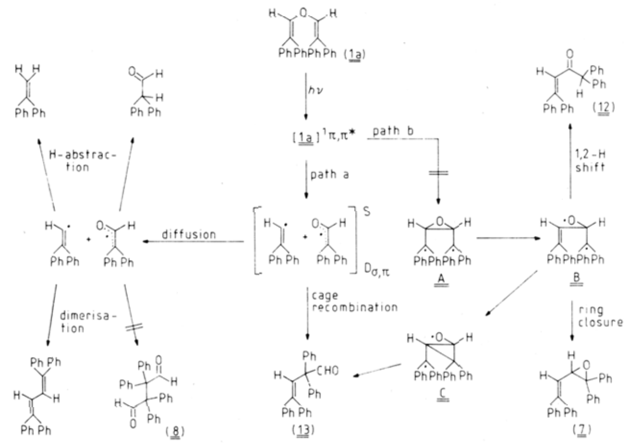
Scheme I. Mechanistic Interpretation of the Photochemistry of Divinyl Ether 1a

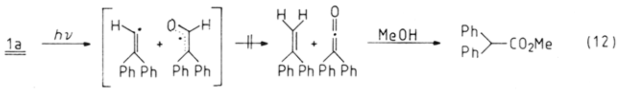


thermore, the photostability of authentic samples of these potential products of the 1,3-diradical B under the photolysis conditions of the divinyl ether **1a** established that they should have accumulated had they been formed.

The photo ^1H CIDNP experiment of the divinyl ether **1a** fortunately throws light on the mechanism of aldehyde **13** formation. Strongly enhanced absorption is observed for the vinylic proton and less enhanced absorption for the aldehydic proton of the aldehyde **13**. On the basis of the known g and $\alpha[H]$ values of the unsubstituted vinyl radical[25] and the reasonable assumption that the g value of a vinyloxy radical should be greater than that of a vinyl radical,[26] Kaptein's net polarization rule[28] reconciles the observed polarizations of the aldehyde **13** as resulting from cage recombination of singlet-state vinyl–vinyloxy radical pairs (Scheme I, path a). The relatively low enhanced absorption of the aldehydic proton of **13** might be explained by the fact that $\alpha[H_\beta]$ in the vinyloxy radical is small and negative.[26] It must be emphasized that CIDNP effects cannot rigorously exclude a competitive concerted 1,3-vinyl shift in the excited divinyl ether **1a** or alternative isomerizations[29] involving diradicals such as A–C (Scheme I). However, the strong polarization of the vinyl proton of the aldehyde **13** suggests that path a in Scheme I predominates.

The finding that the absolute yield of aldehyde **13** is relatively insensitive to the solvents used (Table I, entries 1–6) is also consistent with the proposed mechanism. It is known[30] that the ratio of cage recombination vs. escape and subsequent reactions is mainly a function of solvent viscosity. Since no pronounced variation of viscosity was obtained in the series of solvents used, i.e., diisopropyl ether ($\eta^{20} = 0.33$ cP[31]), acetonitrile ($\eta^{20} = 0.36$ cP[31]), and benzene ($\eta^{20} = 0.65$ cP[31]), only minor variation in the absolute yields of aldehyde **13** is expected, as experimentally observed.

Alternative cage recombinations of the vinyl–vinyloxy radical pairs are possible but do not take place. For example, recombination of the initial radical pairs to the starting divinyl ether **1a** cannot be important since the CIDNP spectrum does not show appreciable polarization for the ether vinyl protons. Also the disproportionation show in eq 12 can definitely be excluded, since no methyl diphenylacetate could be detected upon irradiation of divinyl ether **1a** in the presence of methanol and a catalytic amount of acetic acid.

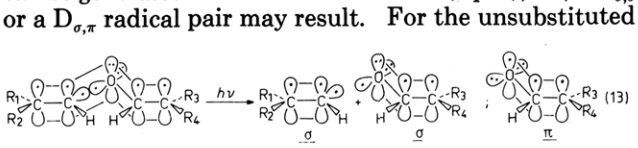


(12)

Besides the cage recombination, the initial radical pair can diffuse apart and undergo the typical free-radical reactions depicted in Scheme I. As established by the photo ^1H CIDNP experiment, the free diphenylvinyl radical can dimerize (strong emission by the vinylic protons of the 1,1,4,4-tetraphenyl-1,3-butadiene) or abstract hydrogen from the solvent (strong emission by the vinylic protons of 1,1-diphenylethene). Furthermore, the crossover experiment clearly showed that the 1,1,4,4-tetraphenyl-1,3-butadiene stems from free-radical combination. As expected, the ratio of H abstraction vs. dimerization is strongly dependent on the hydrogen-donating ability of the solvent (Table I, entries 1–6).

In the case of the free vinyloxy radical, hydrogen abstraction is only observed to a considerable extent in diisopropyl ether as solvent or when tributyltin hydride is added. ab initio SCF calculations on the unsubstituted acetaldehyde radical[32] show that the odd electron is mainly located at the carbon site. Consequently, also the free (diphenylvinyl)oxy radical should mainly exist as a highly resonance-stabilized carbon radical. Consequently, hydrogen abstraction from the solvent should be an energetically unfavored process. Besides electronic factors, its steric hindrance readily explains the absence of dimers such as the dialdehyde **8** or the vinyloxy aldehyde **9** among the photoproducts of divinyl ether **1a**. As an undesirable side reaction, both the vinyl and vinyloxy free radicals may attack the starting divinyl ether **1a** and induce its transformation to products of higher molecular weight. For example, addition of a radical scavenger slightly lowers the Φ_{-S} values of divinyl ether **1a** (Table II, entries 1–4). The product balance is best when diisopropyl ether is used as solvent (Table I, entry 6).

The principal question to be answered now is why the divinyl ether **1a** prefers carbon–oxygen bond cleavage to give a vinyl–vinyloxy radical pair (path a, Scheme I) instead of pursuing the 3-oxa-di-π-methane route (path b, Scheme I). For this purpose a detailed consideration of the primary photochemical event and the electronic nature of the radical pair must be made. In Salem's[33] terminology the homolytic C–O bond cleavage to the vinyl–vinyloxy radical pair is a tritopic process, since the vinyloxy radical can be generated as a σ- or as a π-radical (eq 13), i.e., a $D_{\sigma,\sigma}$ or a $D_{\sigma,\pi}$ radical pair may result. For the unsubstituted



(13)

vinyloxy radical it is known from both experimental data

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(25) (a) Fischer, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, p 435. $g = 2.002\,20$, $a[H_\alpha] = +13.39$ G. (b) As the vinyl radical is of the σ-type, β-substitution should not markedly affect its magnetic properties.

(26) Oxygen-centered radicals usually show higher g values than carbon-centered radicals, see, e.g., ref. 25a. Also for the acetaldehyde radical a g value of 2.0046 is reported:[27] $\alpha[H_\alpha] = 19.2, 18.7$ G; $\alpha[H_\beta] = 0.5$ G; no signs determined.

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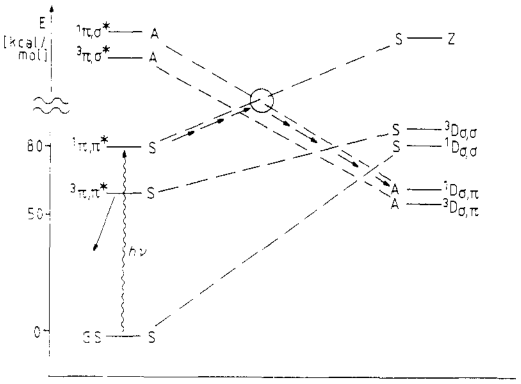
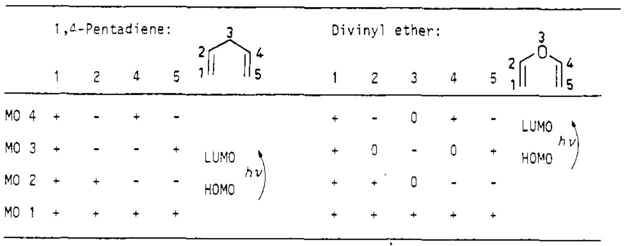


Figure 2. State correlation diagram for the photochemical homolysis of the parent divinyl ether (**1d**). [The higher energy n,π^* states were not included since they correlate with higher excited states of the products.[36]] (a) Excited state energies of 1,3-butadiene were used.[23] (b) $\Delta H_f°$ divinyl ether = −3 kcal/mol.[37] (c) The energies of these diradical states were estimated by taking the vinyl C–O bond energy of 85 kcal/mol[38] and 22 kcal/mol for the energy gap between the $D_{\sigma,\sigma}$ and the $D_{\sigma,\pi}$ states.[34]

and calculations[34] that the π-configuration (as mentioned earlier, with the odd electron mainly located at the carbon atom) is the electronic ground state and that the σ-configuration (with the odd electron in a highly localized p orbital on oxygen) is ca. 22 kcal/mol higher in energy. From the UV spectrum of divinyl ether **1a** and from the photoelectron spectrum of its methyl analogue, i.e., bis(2-methyl-1-propenyl) ether,[35] it can be concluded that the first electronic transition of divinyl ether **1a** is of the π,π^*- rather than n,π^*-type. These features closely resemble those of the primary process in the photorearrangement of furans to acylcyclopropenes via initial carbon–oxygen bond cleavage leading to a vinyl–vinyloxy diradical. In analogy to the state correlation diagram for the initial C–O bond cleavage of furan,[36] the corresponding qualitative diagram for the unsubstituted divinyl ether (**1d**) is depicted in Figure 2. The initially populated $^1\pi,\pi^*$-state of the divinyl ether correlates with a high-energy zwitterionic primary product (Z). However, as the C–O bond is elongated, the $^1\pi,\pi^*$-Z energy surface intersects the energy surface that correlates the higher excited $^1\pi,\sigma^*$-state with the ground state $^1D_{\sigma,\pi}$ radical pair. Thus, the $^1D_{\sigma,\pi}$ radical pair—the energetically most favorable primary product—becomes accessible from the initially populated $^1\pi,\pi^*$-state via surface jump (shaded area, Figure 2). Since this is an activated process, it also explains the low efficiency of this photochemical process. The corresponding triplet state circumvents this activated process by dissipating its energy via cis–trans isomerization.

The photochemical behavior of the divinyl ether **1a** discussed here markedly contrasts the di-π-methane photochemistry of all-carbon 1,4-pentadienes and requires some further consideration. Zimmerman's formalism of bond-order control[39] helps to explain the reluctance of the divinyl ether toward 3-oxa-di-π-methane rearrangement. Whereas the 1,4-pentadiene constitutes a four π-electron system, the divinyl ether represents a six π-electron system. The additional two π-electrons derive from the lone pairs of the central oxygen atom. Inspection of Figure 3 reveals that HOMO–LUMO excitation of the 1,4-pentadiene reduces the antibonding interaction between C-2 and C-4, whereas the same excitation in the case of the divinyl ether increases the antibonding interaction between C-2 and C-4. Thus, *this simplistic analysis complies with the experimental observations.* Once the π-vinyloxy radical is formed, the odd electron is mainly located at the carbon site.[32] Therewith it is well lined up for recombination with the vinyl radical to afford the rearranged β,γ-unsaturated aldehyde. As experimentally shown (CIDNP) for the tetraphenyl-substituted system **1a**, recombination to the starting material does not occur to a significant extent.

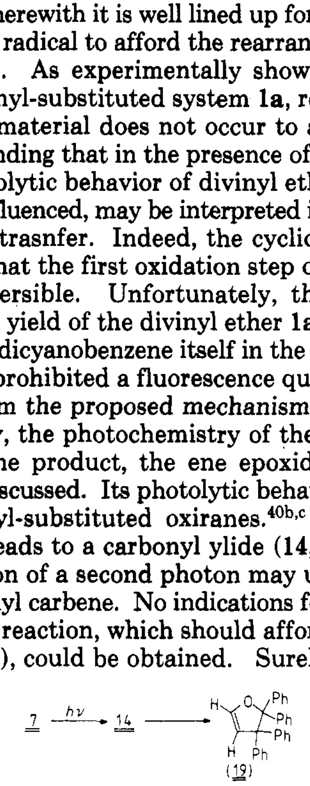


	1,4-Pentadiene: 1	2	4	5	Divinyl ether: 1	2	3	4	5
MO 4	+	-	+	-	+	-	0	+	-
MO 3	+	-	-	+	+	0	-	0	+
MO 2	+	+	-	-	+	+	0	-	-
MO 1	+	+	+	+	+	+	+	+	+

Figure 3. Orbital phases of the π-MO's for 1,4-pentadiene and 3-oxa-1,4-pentadiene (divinyl ether).

The finding that in the presence of 1,4-dicyanobenzene the photolytic behavior of divinyl ether **1a** is not significantly influenced, may be interpreted in terms of reversible electron trasnfer. Indeed, the cyclic voltammogram indicates that the first oxidation step of divinyl ether **1a** is fully reversible. Unfortunately, the low fluorescence quantum yield of the divinyl ether **1a** and some emission from 1,4-dicyanobenzene itself in the wavelength range of interest prohibited a fluorescence quenching experiment to confirm the proposed mechanism.

Finally, the photochemistry of the expected 3-oxa-di-π-methane product, the ene epoxide **7**, remains to be briefly discussed. Its photolytic behavior parallels that of other aryl-substituted oxiranes.[40b,c] Absorption of a photon leads to a carbonyl ylide (**14**, eq 10) which upon absorption of a second photon may undergo elimination of diphenyl carbene. No indications for an intramolecular trapping reaction, which should afford the dihydrofuran **19** (eq 14), could be obtained. Surely, steric congestion around the tetraphenyl-substituted carbon–carbon bond in dihydrofuran **19** should discourage such cyclization. Furthermore, that dipole **14** could not be trapped with norbornene or acetylenedicarboxylate is not surprising in view of earlier reports[40a] that *gem*-diphenyl-substituted carbonyl ylides derived from oxiranes on photolysis are persistent toward such dipolarophiles. Presumably again steric factors play a role.



(14)

Experimental Section

Melting points are uncorrected. Infrared spectra were taken on a Beckman Acculab 4 spectrometer and ^{1}H NMR spectra at 90 MHz on a Varian EM-390 spectrometer or at 400 MHz on a Bruker WM 400 spectrometer. Photo-CIDNP ^{1}H NMR spectra were obtained at 90 MHz on a Bruker WH 90 instrument, equipped with a Nicolet BNC 12 computer. The samples were

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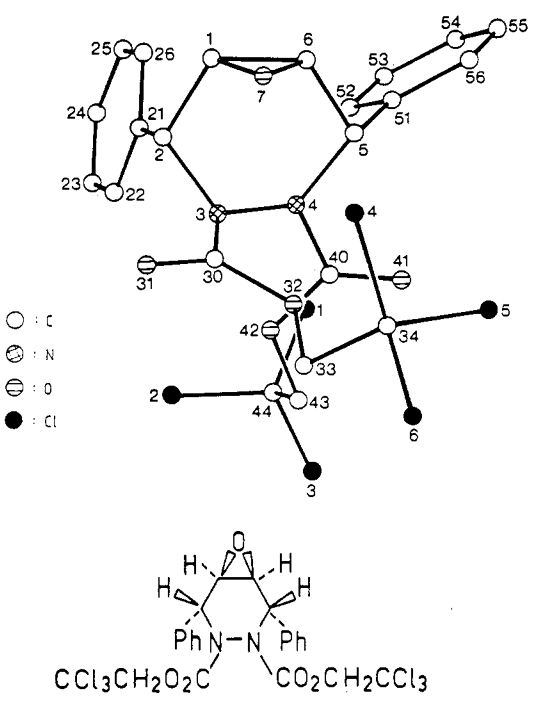

(6)

Figure 4. Perspective drawing of the crystal structure of epoxide **6**; the numbering of the atoms corresponds to Tables III–VI (supplementary material).

irradiated at 285–370 nm with a light flux of ca. 10^{-2} mEinstein/min. ^{13}C NMR spectra were measured at 22.6 MHz on a Bruker WH 90 spectrometer or at 100.61 MHz on the Bruker WM 400 spectrometer. Mass spectra were run on a Varian MAT CH 7 spectrometer, UV spectra on a Cary 17 instrument, and fluorescence spectra on a Perkin-Elmer MPF-44B spectrophotometer. The elemental analyses were kindly run for us by Professor G. Maier's staff of the Universität Giessen. Commercial reagents and solvents were purified according to the literature procedures to match the reported physical and spectral data. Known compounds used in this research were either purchased from standard suppliers or prepared according to the literature procedures and purified to match the reported physical and spectral data. Only the experimental details of hitherto unknown compounds are provided. Photolyses were carried out in a Rayonet Model RP-100 (Southern New England Ultraviolet Co.) photochemical reactor at 254 (quartz vessel) and 300 and 350 nm (Vycor vessel). The laser irradiations at 333.6 and 363.8 nm were done with a Coherent CR 18 supergraphite argon ion laser (Vycor vessel). For the determination of quantum yields, a 1000-W xenon high-pressure arc equipped with a Kratos monochromator served as light source. Analytical HPLC was carried out on a Waters apparatus (6000 A, U6K, M440); in all cases UV detection at 254 nm was employed. Capillary GC was done on a Fractovap 2000 (Carlo Erba Co.) instrument. The oxidation potential of divinyl ether **1a** was determined on a PAR T-170 instrument, employing a Pt electrode and a Ag/AgCl counter electrode (+150 mV).

Syntheses. Bis(2,2-diphenylvinyl) Ether (1a). A 250-mL, round-bottomed flask was charged with a solution of 4.00 g (9.74 mmol) of 2,2′-oxybis(1,1-diphenylethanol) (**3a**)[12] and 6.00 g (25.2 mmol) of methyl *N*-sulfonylcarbamate/triethylamine complex (**4**)[13] in 100 mL of absolute THF. The flask was protected from external moisture by means of a $CaCl_2$ drying tube and the reaction mixture allowed to stir magnetically at 60 °C for 2 h. During the course of reaction a white solid precipitated. The solvent was roto-evaporated at 30 °C (15 torr) and the remaining slurry taken up in 100 mL of benzene. The benzene solution was extracted with water (3 × 50 mL), dried over anhydrous sodium sulfate, and roto-evaporated at 30 °C (15 torr). The remaining yellow oil crystallized upon stirring with 20 mL of absolute methanol at 0–10 °C. The crude product was washed with 5 mL of cold methanol and recrystallization from ethanol yielded 1.27 g (35%) of the pure divinyl ether **1a** as colorless needles, mp 110 °C. From the mother liquor another 400 mg (11%) of divinyl ether **1a**, mp 109 °C, were isolated by silica gel chromatography (adsorbant–substrate ratio 100:1), eluting with 9:1 hexane/methylene chloride mixture: IR (CCl_4) 3090, 3070, 3040, 1620, 1602, 1500, 1450, 1215, 1120, 1077, 1032 cm^{-1}; UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 297 (4.30); ^1H NMR (CCl_4, 90 MHz) δ 6.78 (s, 2 H, vinyl), 7.1–7.4 (m, 20 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 123.42 (s, vinyl), 126.92, 127.83, 128.32, 128.39, 129.88, 136.64, 139.33 (C_6H_5), 141.97 (d, vinyl CH); MS (70 eV), *m/e* (relative intensity) 374 (6, M^+), 195 (1, $M^+ - C_{14}H_{11}$), 180 (100, $C_{14}H_{12}^+$), 167 (16, $C_{13}H_{11}^+$), 77 (11, $C_6H_5^+$). Anal. Calcd for $C_{28}H_{22}O$ (374.5): C, 89.81; H, 5.92. Found: C, 90.09; H, 5.90.

Bis(2,2-di-*p*-tolylvinyl) Ether (1b). A sample of 3.55 g (7.61 mmol) of the crude hydroxy ether **3b** was dehydrated with 5.30 g (22.3 mmol) of methyl *N*-sulfonylcarbamate/triethylamine complex (**4**)[13] as described above for the divinyl ether **1a**, affording the divinyl ether **1b** as crude yellow oil after roto-evaporation of the benzene phase at 30 °C (15 torr). Silica gel chromatography (adsorbant–substrate ratio 90:1), eluting with 8:2 hexane/methylene chloride mixture, gave 800 mg (24%) colorless oil, which crystallized on standing at −20 °C after ca. 5 days. Recrystallization from ethanol yielded colorless plates: mp 126 °C; IR (CCl_4) 3040, 2935, 2880, 1665, 1622, 1520, 1415, 1229, 1212, 1190, 1115, 1028 cm^{-1}; UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 296 (4.35); ^1H NMR (CCl_4, 90 MHz) δ 2.32 (s, 6 H, methyl), 2.35 (s, 6 H, methyl), 6.66 (s, 2 H, vinyl), 6.9–7.3 (m, 16 H, C_6H_4); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 21.08 (q, methyl), 21.24 (q, methyl), 123.23 (s, vinyl), 128.42, 128.53, 129.04, 129.91, 134.06, 136.45, 136.64, 136.79 (C_6H_4), 141.44 (d, vinyl CH); MS (70 eV), *m/e* (relative intensity) 430 (32, M^+), 222 (8, $M^+ - C_{16}H_{16}$), 207 (19, $C_{16}H_{15}^+$), 195 (100, $C_{15}H_{15}^+$), 91 (17, $C_7H_7^+$). Anal. Calcd for $C_{32}H_{30}O$ (430.6): C, 89.26; H, 7.02. Found: C, 89.49; H, 6.86.

Bis(2,2,2-trichloroethyl) 3,6-Diphenyl-1,2,3,6-tetrahydropyridazine-1,2-dicarboxylate (5). A sample of 1.00 g (4.85 mmol) of *trans,trans*-1,4-diphenyl-1,3-butadiene and 2.10 g (5.51 mmol) of bis(2,2,2-trichloroethyl) azodicarboxylate were dissolved in 10 mL of toluene and stirred at 85 °C for 3 h. The solvent was then roto-evaporated at 30–40 °C (15 torr). The remaining yellow oil crystallized upon addition of ca. 6 mL of methanol. Filtration and washing with cold methanol afforded 2.60 g (91%) nearly colorless crystals, mp 139–140 °C. An analytically pure sample was obtained by recrystallization from ethanol; colorless prisms, mp 141 °C; IR (KBr) 3063, 3022, 2945, 1750, 1599, 1453, 1405, 1328, 1292, 1263, 1143, 813, 802, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 4.3–5.3 (m, 4 H, methylene), 5.4–6.5 (m, 4 H, methine, vinyl), 7.0–7.8 (m, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 58.01, 58.35, 60.06, 61.19 (d, methine), 75.44, 75.80, 76.01, 77.22 (t, methylene), 94.76 (s, CCl_3), 124.02, 124.73, 126.97, 127.67, 127.98, 128.08, 128.14, 128.57, 130.11, 130.59, 138.00, 139.46 (vinyl, C_6H_5), 155.04 (br s, CO); MS (70 eV), *m/e* (relative intensity) 586 (14, M^+, Cl_6 pattern), 206 (100, $C_{16}H_{14}^+$), 91 (54, $C_7H_7^+$). Anal. Calcd for $C_{22}H_{18}Cl_6N_2O_4$ (587.1): C, 45.01; H, 3.09; N, 4.77. Found: C, 45.26; H, 3.05; N, 5.01.

Bis(2,2,2-trichloroethyl) *exo,exo*-2,5-Diphenyl-7-oxa-3,4-diazabicyclo[4.1.0]heptane-3,4-dicarboxylate (6). A sample of 1.00 g (1.70 mmol) of the tetrahydropyridazine **5** was dissolved in 13 mL of absolute chloroform, ca. 50 mg of sodium bicarbonate added, and the mixture cooled to 0 °C. After addition of 538 mg (2.50 mmol) of 80% *m*-chloroperbenzoic acid, the reaction mixture was stirred for 2 h at 0 °C and for 3 days at ca. 20 °C. It was then extracted with 10% aqueous NaOH (2 × 15 mL) and with water (1 × 15 mL), dried over anhydrous sodium sulfate, and again stirred for 3 days at ca. 20 °C after addition of 50 mg of sodium bicarbonate and 200 mg (0.927 mmol) of 80% *m*-chloroperbenzoic acid. The reaction mixture was extracted again with NaOH (2 × 15 mL) and water (1 × 15 mL), dried, and roto-evaporated at 20–30 °C (15 torr). The remaining yellow oil was taken up in 5 mL of absolute methanol and allowed to crystallize by storing it overnight at +4 °C. The product was collected on a Büchner funnel, and washing with cold methanol afforded 600 mg (57%) of a colorless, crystalline powder, mp 135–136 °C. An analytically pure sample was obtained by recrystallization from hexane/ethyl acetate: colorless prisms, mp 136–137 °C; IR (KBr) 3070, 3035, 2955, 1745, 1500, 1390, 1331, 1272, 1174, 1139, 1052, 802, 723, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.2–3.5 (m, 1 H, oxirane CH), 3.8–4.0 (m; 1 H, oxirane CH), 4.3–5.2 (m, 4 H, methylene), 5.2–5.4

(m, 1 H, methine), 6.1–6.3 (m, 1 H, methine), 6.8–7.9 (m, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 49.84, 54.79, 55.75, 56.60, 56.84, 57,78, 58.00 (d, oxirane CH, methine), 75.43, 75.55, 76.10, 76.25 (t, methylene), 126.48, 127.11, 127.55, 127.66, 127.97, 128.50, 128.73, 128.82, 134.49, 134.67, 137.58, 137.84 (C_6H_5), 152.94, 153.57, 156.13, 156.33 (s, CO); MS (70 eV); *m/e* (relative intensity) 602 (7, M^+, Cl_6 pattern), 131 (30, $CH_2CCl_3^+$, Cl_3 pattern), 103 (100, $C_8H_7^+$), 91 (78, $C_7H_7^+$). Anal. Calcd for $C_{22}H_{18}Cl_6N_2O_5$ (603.1): C, 43.81; H, 3.01; N, 4.64. Found: C, 44.19; H, 3.23, N, 4.23.

***trans,trans*-Bis(2-phenylvinyl) Ether (1c).** In a 250-mL, three-necked, round-bottomed flask, equipped with nitrogen inlet and outlet, was placed 13.8 g (221 mmol) of zinc dust activated under nitrogen by first treating it with 5% aqueous HCl (3 ′ 18 mL, 1 min) and washing with distilled water (5 × 18 mL), absolute ethanol (4 × 18 mL), and absolute ether (5 × 18 mL). The activated zinc was then dried at ca. 20 °C (0.01 torr). A solution of 2.00 g (3.32 mmol) of the epoxide **6** in a mixture of 50 mL of glacial acetic acid and 50 mL of absolute THF was added and the reaction mixture ultrasonicated under nittrogen for 90 min at 0–20 °C. The flask was then cooled to 0 °C, and the solution was filtered under nitrogen into a 500-mL, round-bottomed flask, the excess zinc powder being washed with water (3 × 20 mL). The pH of the filtrate was adjusted to 7–8 by addition of concentrated aqueous NH_3, and 10 mL of 2 M aqueous $CuCl_2$ was added at 0 °C. A slightly yellow solid precipitated, which was extracted with methylene chloride (3 × 50 mL). The organic phase was washed with 5% KOH (2 × 50 mL) and with water (1 × 50 mL), dried over anhydrous sodium sulfate, and roto-evaporated at 20 °C (15 torr). Recrystallization of the pale yellow solid residue from ethanol afforded 500 mg (68%) of colorless prisms: mp 70–72 °C; IR (CCl_4) 3021.1641, 1451, 1333, 1299, 1234, 1161, 1074, 1033, 988, 930 cm^{-1}; UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 281 (4.16); ^1H NMR ($CDCl_3$, 90 MHz) δ 6.21 (d, J = 13 Hz, 2 H, vinyl), 7.09 (d, J = 13 Hz, 2 H, vinyloxy), 7.1–7.5 (m, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 111.93 (d, vinyl CH), 125.65 (d, C_6H_5, C ortho), 126.63 (d, C_6H_5, C para), 128.68 (d, C_6H_5, C meta), 134.96 (s, C_6H_5, C ipso), 144.36 (d; vinyloxy CH); MS (70 eV) *m/e* (relative intensity) 222 (47, M^+), 103 (61, $C_8H_7^+$), 91 (95, $C_7H_7^+$), 77 (100, $C_6H_5^+$). Anal. Calcd for $C_{16}H_{14}O$ (222.3): C, 86.45; H, 6.35. Found: C, 86.48; H, 6.31.

1,1,4,4-Tetraphenyl-3,4-epoxy-1-butene (7). A 100-mL, round-bottomed flask was charged with 50 mL of absolute chloroform, ca. 500 mg of sodium bicarbonate, and 1.00 g (2.79 mmol) of 1,1,4,4-tetraphenyl-1,3-butadiene and protected by means of a $CaCl_2$ drying tube. The mixture was cooled to 0 °C, and 600 mg (2.79 mmol) of 80% *m*-chloroperbenzoic acid was added while stirring magnetically for 6 h at 0 °C and for 20 h at ca. 20 °C. The chloroform solution was extracted with 10% aqueous sodium hydroxide (1 × 50 mL) and with water (2 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, the solvent roto-evaporated at 30 °C (15 torr), and the remaining white solid chromatographed on activity III basic alumina (adsorbant–substrate ratio 200:1) by eluting with 9:1 hexane/chloroform mixture. Final recrystallization from acetone yielded 800 mg (77%) of white needles: mp 174 °C; IR (KBr) 3030, 3015, 1605, 1500, 1450, 1081, 1035, 935, 889, 765, 756, 700 cm^{-1}; UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 266 (4.24); ^1H NMR ($CDCl_3$, 90 MHz) δ 3.87 (d, J = 9 Hz, 1 H, oxirane), 5.52 (d, J = 9 Hz, 1 H, vinyl), 7.0–7.6 (m, 20 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 64.21 (d, oxirane CH), 68.23 (s, oxirane), 124.09 (d, vinyl CH), 126.85, 127.67, 127.78, 127.91, 128.15, 128.26, 128.32, 130.14, 137.64, 138.88, 140.78, 141,49, 148.38 (vinyl, C_6H_5). MS (70 eV), *m/e* (relative intensity) 374 (3, M^+), 269 (100, $C_{21}H_{17}^+$), 105 (36, $C_7H_5O^+$). Anal. Calcd for $C_{28}H_{22}O$ (374.5): C, 89.81; H, 5.92. Found: C, 89.66; H, 5.82.

[(2,2-Diphenylethenyl)oxy]diphenylacetaldehyde (9). The reported[15] dimerization of diphenylacetaldehyde sodium enolate with iodine gave 20% of colorless plates: mp 127–128 °C (lit.[15] mp 127–128 °C); IR (KBr) 3022, 3008, 2917, 1730, 1630, 1592, 1490, 1445, 1223, 1195, 1118, 790 cm^{-1}. UV (methyl *tert*-butyl ether) λ_{max} (log ϵ) 262 (4.20); ^1H NMR ($CDCl_3$, 90 MHz) δ 6.52 (s, 1 H, vinyl), 6.9–7.7 (m, 20 H, C_6H_5), 10.00 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 90.84 (s, O–*C*($Ph)_2$), 123.21 (s, vinyl), 126.63, 126.82, 127.94, 128.21, 128.30, 128.36, 128.76, 130.21, 137.52, 137.67, 140.22 (C_6H_5), 139.48 (d, vinyl CH), 196.74 (d, CHO); MS (70 eV), *m/e* (relative intensity) 390 (3, M^+), 195 (66, $C_{14}H_{11}O^+$), 167 (100, $C_{13}H_{11}^+$). Anal. Calcd for $C_{28}H_{22}O_2$ (390.5): C, 86.13; H, 5.68. Found: C, 85.98; H, 5.57.

1-Phenyl-4,4-di-*p*-tolyl-3-buten-1-one (10). A 250-mL, three-necked, round-bottomed flask, equipped with a magnetic stirrer, nitrogen inlet and outlet, and rubber septum, was charged with a solution of 2.00 g (9.70 mmol) of ethyl β-benzoylpropionate in 60 mL of absolute ether. The flask was flushed with nitrogen and cooled to −20 °C, and 19.4 mL (21.3 mmol) of a 1.10 M solution of *p*-tolyllithium in ether was syringed into the reaction mixture within 20 min under magnetic stirring. The yellow reaction mixture was stirred for an additional 15 min at −20 °C and allowed to warm up within 15 min to ambient temperature, ca. 20 °C. The flask was then cooled to 0 °C, and 50 mL of water was added. The ether layer was separated, washed with water (2 × 30 mL), dried over anhydrous sodium sulfate, and roto-evaporated at 20 °C (15 torr). The residual yellow oil was taken up in 50 mL of absolute toluene, ca. 30 mg *p*-toluenesulfonic acid was added, and the solution was refluxed for 30 min. After cooling to ca. 20 °C, the toluene solution was washed with water (1 × 30 mL), with saturated, aqueous sodium bicarbonate (1 × 30 mL), and with water again (1 × 30 mL). Silica gel chromatography (adsorbant–substrate ratio 50:1), eluting with 1:1 hexane/methylene chloride mixture, and final recrystallization from hexane/methyl *tert*-butyl ether yielded 1.00 g (32%) of colorless plates: mp 146 °C; IR (KBr) 3020, 2910, 2870, 1690, 1600, 1512, 1451, 1338, 1213, 995, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.33 (s, 3 H, methyl), 2.40 (s, 3 H, methyl), 3.82 (d, J = 7 Hz, 2 H, methylene), 6.37 (t, J = 7 Hz, 1 H, vinyl), 6.9–8.1 (m, 13 H, aryl); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 21.05 (q, methyl), 21.23 (q, methyl), 39.92 (t, methylene), 120.08 (d, vinyl CH), 127.39, 128.25, 128.51, 128.79, 129.07, 129.67, 133.00, 136.79, 136.98, 137.04, 139.52, 144.52 (aryl, vinyl), 198.31 (s, CO); MS (70 eV) *m/e* (relative intensity) 326 (10, M^+), 221 (100, $M^+ - C_7H_5O$), 129 (56, $M^+ - C_7H_5O, C_7H_8$), 105 (53, $C_7H_5O^+$). Anal. Calcd for $C_{24}H_{22}O$ (326.4): C, 88.31; H, 6.79. Found: C, 88.27; H, 6.67.

1,1-Diphenyl-4,4-di-*p*-tolyl-1,3-butadiene (11). A solution of 100 mg (0.306 mmol) of 1-phenyl-4,4-di-*p*-tolyl-3-buten-1-one (**10**) in 5 mL of absolute ether was placed into a 20-mL, round-bottomed flask. The flask was capped with a rubber septum, provided with two syringe needles serving as nitrogen in- and outlets. After being flushed with nitrogen, the flask was cooled to 0 °C, 0.50 mL (0.50 mmol) of a 1.00 M solution of phenyllithium in ether syringed into the flask, and the reaction mixture stirred for an additional 15 min at ca. 20 °C. Then 10 mL of water was syringed into the reaction mixture within 5 min, and the organic layer was separated, washed with water (2 × 10 mL), and dried over anhydrous sodium sulfate and the solvent roto-evaporated at 20 °C (15 torr). The residual yellow oil was taken up in 10 mL of 9:1 glacial acetic acid/concentrated aqueous hydrochloric acid mixture and refluxed for 5 min. Upon cooling to ca. 20 °C, the butadiene 11 precipitated, which was collected, washed with 2 mL of glacial acetic acid, and recrystallized from ethanol/ethyl acetate to yield 30 mg (25%) of pale yellow needles: mp 199 °C; IR (KBr) 3055, 3022, 2920, 1595, 1510, 1492, 1442, 825, 768, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.27 (s, 3 H, methyl), 2.40 (s, 3 H, methyl) [AB system δ_A 6.71, δ_B 6.79 (J = 11 Hz, vinyl)], 7.0 – 7.5 (m, 18 H, aryl); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 21.08 (q, methyl), 21.30 (q, methyl), 125.18, 126.00, 126.12, 126.39, 127.21, 127.39, 127.72, 128.11, 128.21, 128.86, 128.93, 130.65, 130.74, 137.14, 140.04, 140.13, 142.71, 144.13 (aryl, vinyl); MS (70 eV); *m/e* (relative intensity) 386 (100, M^+), 294 (9, $M^+ - C_7H_8$), 202 (9, $M^+ - 2\,C_7H_8$), 181 (37, $C_{14}H_{13}^+$). Anal. Calcd for $C_{30}H_{26}$ (386.5): C, 93.22; H, 6.78. Found: C, 93.23; H, 6.64.

Photolyses. General. The solutions were flushed with nitrogen for 5–30 min before irradiation. In the case of preparative runs, nitrogen purging was continued during the photolysis. Analytical runs were carried out in airtight vessels after nitrogen purging. During the photolysis the solutions were stirred magnetically. Samples were taken out by means of a syringe, while operating under a stream of nitrogen to prevent air from entering the solutions.

Quantitative Photolyses. Divinyl Ether 1a. The concentrations of the solutions of divinyl ether **1a** were kept in the range 0.006 92–0.0105 M. Samples of 3 mL were irradiated, the consumption of the starting material and the product distribution monitored by HPLC, using a 25 cm × 4 mm column, packed with

LiChrosorb Si 60, 5 μm, and a 4 cm × 4 mm scrubber column, packed with Nucleosil 5 CN, 5 μm. Hexane/ethyl acetate (98:2) was employed as eluent at a flow rate of 1.5 mL/min. The quantitative determination of the volatile components diphenylmethane and biphenyl was achieved by capillary GC, using a 50-m OV 101 column, operated at column, injector, and detector temperatures all of 200 °C and carrier gas (N_2) flow of 1.1 mL/min. Absolute concentration values were obtained using independently recorded calibration lines. The results are given in Table I.

Benzophenone-Sensitized Photolysis of Divinyl Ether 1c. Samples of 30.0 mg (0.135 mmol) of divinyl ether **1c** and 58.0 mg (0.318 mmol) of benzophenone were dissolved in ca. 1 mL of C_6D_6. The solution was placed into a quartz NMR tube, flushed with nitrogen to 5 min, and irradiated at 363.8 nm for 40 min, and the 90-MHz ^{1}H NMR spectrum was taken. The isomeric distribution of bis(2-phenylvinyl) ethers was calculated from the average of three integrations to be 1.00:0.83:0.60 of *trans,trans-*, *trans,cis-*,[14] and *cis,cis-***1c**[14] isomers.

Preparative Photolysis of Divinyl Ether 1a. A sample of 560 mg (1.50 mmol) of divinyl ether **1a** in 100 mL of absolute methyl *tert*-butyl ether was photolyzed at 300 nm for 90 min. The solvent was roto-evaporated at 20 °C and (15 torr), and the remaining yellow oil was subjected to radial chromatography (Chromatotron) on silica gel (4 mm), eluting with a hexane and methylene chloride solvent gradient, starting with 9:1 mixture, respectively, and finishing with pure CH_2Cl_2. The products eluted in the following amount and order: 70.0 mg (13:) of 1,1-diphenylethene; 40.0 mg (7%) of 1,1,4,4-tetraphenyl-1,3-butadiene; 50.0 mg (9%) of divinyl ether **1a**; 210 mg (38%) of 2,2,4,4-tetraphenyl-3-butenal (**13**).

Simultaneous Irradiation (Crossover) of the Divinyl Ethers 1a and 1b. A solution of 13.3 mg (0.0355 mmol) of divinyl ether **1a** and 14.0 mg (0.0325 mmol) of divinyl ether **1b** (A) in 0.5 mL of methyl *tert*-butyl ether was degassed with nitrogen for 5 min, sealed in a glass tube, and irradiated at 300 nm for 150 min. Under the same conditions, solutions of 13.8 mg (0.0369 mmol) of **1a** in 0.5 mL of methyl *tert*-butyl ether (B) and of 14.5 mg (0.0337 mmol) of **1b** in 0.5 mL of methyl *tert*-butyl ether (C) were irradiated independently. Comparison of the three HPL chromatograms (for HPLC conditions, cf. quantitative photolyses of divinyl ether **1a**) did not give any sign as to the presence of the crossed-over aldehydes **17** and **18**. Coinjection of a sample of butadiene **11** with photolysate A (25 cm × 4 mm LiChrosorb Si 60, 5 μm, 99:1 hexane/ethyl acetate, 1 mL/min, and 25 cm × 4 mm Nucleosil 5 C_{18}, 5 μm, methanol, 2 mL/min) proved the presence of butadiene **11** in the photolysate A.

Control Experiments of Divinyl Ether 1a. Quantitative Determination of Polymeric Products. A sample of 100 mg (0.267 mmol) of divinyl ether **1a** in 42 mL of absolute benzene was irradiated at 300 nm for 32 min. HPLC monitoring showed 88% consumption of **1a**. The solvent was roto-evaporated at 30 °C (15 torr) and the remaining yellow oil chromatographed on a 20 × 20 cm silica gel preparative TLC plate, by eluting with methylene chloride. Eluting of the separated zones with ether and roto-evaporation of the solvent afforded 26 mg of a sticky, yellow material, representing the immobile fraction, which together with the mobile fraction amounted to a total of 92 mg. On normalization to 100% consumption of divinyl ether **1a**, the immobile fraction represented 32% by weight of polymers.

Photolyses of Divinyl Ether 1a in the Presence of Methanol and Acetic Acid. A sample of 5.00 mg (0.0134 mmol) of divinyl ether **1a** was dissolved in a mixture of 1.5 mL of absolute methanol, 1.5 mL of absolute methyl *tert*-butyl ether, and 0.1 mL of acetic acid, purged with nitrogen for 10 min, and irradiated at 300 nm. After 18 min, the HPLC analysis (25 cm × 4 mm Nucleosil 5 C_{18}, 5 μm, eluting with 9:1 methanol/water at a flow rate of 1.0 mL/min) of the photolysate indicated 96% consumption of the starting divinyl ether **1a** and the absence of methyl 3,3,4,4-tetraphenylbutanoate[16b] (coinjection with an authentic sample). In a second run, 20.0 mg (0.0534 mmol) of divinyl ether **1a** was dissolved in a mixture of 2 mL of absolute acetonitrile, 1 mL of absolute methanol, and 0.1 mL of acetic acid, purged with nitrogen for 10 min, and irradiated at 300 nm. After 30 min, 89% of the starting divinyl ether was consumed (HPLC). Capillary GC analysis of the photolysate on a 40-m OV 101 column, operated at column, injector, and detector temperatures of 165, 200, and 200 °C, respectively, and a carrier gas (N_2) flow of 0.9 mL/min, showed the absence of methyl diphenylacetate (coinjection with an authentic sample).

Photolysis of Divinyl Ether 1a under Oxygen Pressure. A solution of 210 mg (0.561 mmol) of divinyl ether **1a** in 30 mL of $CFCl_3$ was placed into a Griffin-Worden tube, cooled to −20 °C, and saturated with oxygen at a pressure of 9 atm. After 30 min of irradiation at 333.6 nm, TLC indicated the formation of one product and the absence of peroxidic material (KI/HOAc). The photolysate was roto-evaporated at 0 °C (15 torr) and the residual semisolid subjected to silica gel chromatography (adsorbant–substrate ratio 100:1), eluting with 1:1 hexane/methylene chloride, affording 90.0 mg (43%) of unchanged starting divinyl ether **1a** and 80.0 mg (38%) of benzophenone as the sole product.

Other Control Experiments. Photolysis of 2,2,4,4-Tetraphenyl-3-butenal (13).[20] A sample of 60.0 mg (0.160 mmol) of aldehyde **13** in 5 mL of absolute benzene was irradiated at 300 nm for 1 h. TLC control indicated that the starting material was consumed. Roto-evaporation of the solvent at 30 °C (15 torr) and silica gel chromatography (adsorbant–substrate ratio 100:1), eluting with 8:2 hexane/methylene chloride mixture, yielded 50.0 mg (90%) of colorless needles of 1,1,3,3-tetraphenylpropene, mp 128–129 °C (lit.[41] mp 127–128 °C).

Photolysis of Diphenylacetaldehyde. A sample of 500 mg (2.55 mmol) of diphenylacetaldehyde in 50 mL of absolute methyl *tert*-butyl ether was irradiated at 300 nm for 100 min. The solvent was roto-evaporated at 20 °C (15 torr) and the remaining semisolid subjected to Kugelrohr distillation at 130 °C (0.01 torr), yielding 308 mg (1.83 mmol) of diphenylmethane as a colorless liquid and 77.0 mg (0.230 mmol) of 1,1,2,2-tetraphenylethane, colorless needles, mp 206 °C (lit.[42] mp 209 °C).

In a second run, a solution of 100 mg (0.510 mmol) of diphenylacetaldehyde in 25 mL of absolute 2-propanol was irradiated at 300 nm for 40 min, and the solvent was roto-evaporated at 30 °C (15 torr). ^{1}H NMR analysis of the semisolid residue indicated that diphenylmethane and 1,1,2,2-tetraphenylethane were formed in a 9:1 molar ratio.

Photolysis of 1,1,4,4-Tetraphenyl-3,4-epoxy-1-butene (7). A sample of 100 mg (0.267 mmol) of epoxide **7** in 50 mL of absolute benzene was purged with nitrogen for 10 min and irradiated at 300 nm for 105 min. The solvent was roto-evaporated at 30 °C (15 torr). The presence of 3,3-diphenylpropenal in the residual yellow oil was established by comparing its ^{1}H NMR spectrum with that of an authentic sample and with decoupling. TLC analysis of the photolysate, using 9:1 hexane/chloroform as eluant (two elutions), showed the presence of traces of the ketone **15** by comparison with an authentic sample of enone **15**.[21]

Another sample of 50.0 mg (0.134 mmol) of epoxide **7** in 50 mL of absolute 2-propanol was purged with nitrogen for 10 min and irradiated at 300 nm for 3 h. The solvent was roto-evaporated at 30 °C (15 torr). The presence of benzhydryl isopropyl ether in the residual pale yellow oil was established by comparison of its ^{1}H NMR spectrum with that of the authentic sample.

Photolysis of Ene Epoxide 7 in the Presence of Norbornene and Dimethyl Acetylenedicarboxylate. A sample of 250 mg (0.668 mmol) of ene epoxide **7** and 2.00 g (21.2 mmol) of norbornene were dissolved in a mixture of 30 mL of absolute acetonitrile and 5 mL of absolute benzene. The solution was flushed with nitrogen for 15 min and irradiated under nitrogen at 300 nm for 2 h. The photolysate was then roto-evaporated at 20–30 °C (15 torr), and the residue was analyzed by ^{1}H NMR, which showed no incorporation of the norbornene moiety but indicated the presence of 3,3-diphenylpropenal as decomposition product of ene epoxide **7**.

In a second run, 150 mg (0.401 mmol) of ene epoxide **7** and 1.50 g (10.6 mmol) of dimethyl acetylenedicarboxylate were dissolved in 50 mL of absolute methyl *tert*-butyl ether. The solution was flushed with nitrogen for 15 min and irradiated under nitrogen at 300 nm for 2 h. After roto-evaporation at ca. 20 °C (15 torr), the excess acetylenedicarboxylate was distilled off at 20–50 °C (0.01 torr). The residue was analyzed by ^{1}H NMR, which showed no incorporation of the methyl ester but indicated the presence of enone **15**[21] as isomerization product of ene epoxide **7**. Radial

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chromatography (Chromatotron) of the residue on silica gel (2 mm), eluting with a hexane and methylene chloride solvent gradient, starting with 9:1 mixture, respectively, and finishing with pure CH_2Cl_2, afforded 110 mg (73%) of pure enone **15**[21] as a colorless oil.

Benzophenone-Sensitized Photolysis of Ene Epoxide 7. A sample of 40.0 mg (0.107 mmol) of ene epoxide **7** and 40.0 mg (0.220 mmol) of benzophenone were dissolved in 1 mL of C_6D_6. The solution was placed into a quartz NMR tube, flushed with nitrogen for 10 min, and irradiated at 363.8 nm. ^1H NMR monitoring of the photolysis showed that the starting ene epoxide **7** was nearly completely consumed after 38 min. Enone **15**[21] but no 3,3-diphenylpropenal could be detected as photoproduct.

Acid-Catalyzed Rearrangement of Ene Epoxide 7 to 1,2,4,4-Tetraphenyl-3-buten-1-one[21] (15). A sample of 20.0 mg (0.0534 mmol) of ene epoxide **7** was dissolved in 1 mL $CDCl_3$, and the ^1H NMR spectrum was taken. Ca. 2 mg of trifluoroacetic acid in ca. 0.05 mL of $CDCl_3$ was added and the spectrum retaken. The signals of ene epoxide **7** had completely vanished and were replaced by those of the enone **15**.[21]

Photolysis of [(2,2-Diphenylethenyl)oxy]diphenylacetaldehyde (9). A sample of 50.0 mg (0.128 mmol) of aldehyde **9** in ca. 0.5 mL of C_6D_6 was irradiated at 300 nm in a quartz NMR tube for 8 h. During the photolysis the consumption of aldehyde **9** and the formation of 1,1,2,2-tetraphenylethane was monitored by ^1H NMR. At the end of the irradiation, colorless crystals precipitated, which were collected, washed with ca. 0.5 mL of benzene, and dried at 40 °C (15 torr), mp 205 °C (lit.[42] mp 209 °C).

Photostability of 1,1-Diphenylethene and 1,1,4,4-Tetraphenyl-1,3-butadiene in the Photolysate of 1a. A sample of 40.0 mg (0.107 mmol) of divinyl ether **1a** in 10 mL of absolute methyl *tert*-butyl ether was irradiated at 300 nm for 90 min, the consumption of the starting material and the concentrations of the butadiene and the ethylene being monitored by HPLC (for HPLC conditions, cf. quantitative photolyses of divinyl ether **1a**). The consumption of divinyl ether **1a** was complete after 45 min; however, only a very slow decay of the concentrations of the butadiene and the ethene was observed during the following 45 min of irradiation.

Photostability of Diphenylacetaldehyde in the Photolysate of Divinyl Ether 1a. A sample of 25.0 mg (0.0668 mmol) of divinyl ether **1a** was dissolved in ca. 0.5 mL of C_6D_6 together with 25.0 mg (0.127 mmol) of diphenylacetaldehyde. The solution was irradiated at 300 nm in a quartz NMR tube for 3 h. ^1H NMR monitoring of the reaction showed that the divinyl ether **1a** was completely decomposed after 2 h, whereas only a slight decrease of the signal intensity of diphenylacetaldehyde could be observed during irradiation.

Photostability of 1,1,4,4-Tetraphenyl-3,4-epoxy-1-butene (7) in the Photolysate of Divinyl Ether 1a. A sample of 40.0 mg (0.107 mmol) of divinyl ether **1a** was dissolved in ca. 0.5 mL of C_6D_6 together with 40.0 mg (0.107 mmol) of the epoxide **7**. The solution was irradiated at 300 nm in a quartz NMR tube for 5 h. ^1H NMR monitoring of the reaction showed that the divinyl ether **1a** was completely decomposed after 3.5 h, whereas only a slight decrease of the signal intensity of epoxide **7** could be observed during irradiation.

In another run, 50.0 mg (0.134 mmol) of divinyl ether **1a** was dissolved in 20 mL of absolute acetonitrile and irradiated at 30 nm for 5 min. HPLC analysis (for conditions, cf. quantitative photolyses) showed 71% conversion of divinyl ether **1a**. A sample of 10.0 mg (0.0267 mmol) of epoxide **7** was added to the photolysate and irradiation was continued for 5 min. Whereas divinyl ether **1a** was completely decomposed after the second irradiation, no significant decrease in the concentration of epoxide **7** could be observed.

Photostability of 3,3-Diphenylpropenal. A sample of 50.0 mg (0.240 mmol) of 3,3-diphenylpropenal in ca. 0.5 mL of C_6D_6 was irradiated at 300 nm in a quartz NMR tube for 12 h. ^1H NMR monitoring did not indicate any consumption of the aldehyde during this period. In a second run, 40.0 mg (0.10 mmol) of divinyl ether **1a** was added to the spent solution of the aldehyde in C_6D_6 and the irradiation repeated. Again no aldehyde was consumed, whereas the divinyl ether **1a** was completely decomposed after 4 h.

Photostability of 1,1,4,4-Tetraphenyl-3-buten-2-one[16b] (12) in the Photolysate of Divinyl Ether 1a. A sample of 2.10 mg (0.005 61 mmol) of divinyl ether **1a** and 2.21 mg (0.005 90 mmol) of enone **12** were dissolved in 1.5 mL of absolute benzene. The solution was flushed with nitrogen for 5 min and irradiated at 300 nm for 10 min. HPLC analysis (for HPLC conditions, cf. quantitative photolyses of divinyl ether **1a**) of the photolysate showed that 82% of the starting divinyl ether **1a** and only 31% of the enone **12** were consumed.

Photostability of Methyl 3,3,4,4-Tetraphenylbutanoate in the Photolysate of Divinyl Ether 1a. A sample of 3.29 mg (0.008 79 mmol) of divinyl ether **1a** and 3.12 mg (0.007 68 mmol) of the butanoate were dissolved in a mixture of 1 mL of absolute methanol, 1 mL of absolute methyl *tert*-butyl ether, and 0.1 mL of acetic acid. The solution was flushed with nitrogen for 5 min and irradiated at 300 nm for 20 min. HPLC analysis (for HPLC conditions, cf. photolysis of divinyl ether **1a** in the presence of methanol and acetic acid) of the photolysate showed that the starting divinyl ether **1a** was quantitatively consumed, whereas the concentration of the butanoate remained unchanged.

Photostability of Methyl Diphenylacetate in the Photolysate of Divinyl Ether 1a. A sample of 30.0 mg (0.0801 mmol) of divinyl ether **1a** and 30.0 mg (0.133 mmol) of methyl diphenylacetate were dissolved in 1 mL of C_6D_6 and irradiated in a quartz NMR tube at 300 nm. ^1H NMR monitoring of the reaction showed that the divinyl ether **1a** was completely decomposed after 2 h, whereas no decrease of the signal intensity of the acetate could be observed during the irradiation.

Test for Energy Transfer in the Benzophenone-Sensitized Photolysis of Divinyl Ether 1a. A 10-mL aliquot of a solution of 0.256 M benzophenone and 0.003 53 M benzhydrol in benzene was irradiated at 350 nm, monitoring the consumption of benzhydrol by capillary GC on a 50-m Carbowax column, operated at column, injector, and detector temperatures of 210, 250, and 250 °C, respectively, and a carrier gas (N_2) flow of 1.5 mL/min. After 40 min of irradiation, 54% of the benzhydrol were consumed. In a second run, 10 mL of a solution of 0.256 M benzophenone, 0.003 53 M benzhydrol, and 0.003 30 M divinyl ether **1a** were irradiated at 350 nm for 40 min. Capillary GC showed that only 7% of the benzhydrol were consumed.

Chemiexcitation of Divinyl Ether 1a. A solution of 1.93 mg (0.005 15 mmol) of divinyl ether **1a** and 2.80 mg (0.0241 mmol) of tetramethyl-1,2-dioxetane[18] in 1 mL of absolute benzene was placed into a sealed tube and kept at 80 °C for 2 h under exclusion of light. After this period, the benzene solution showed negative peroxide test (KI/HOAc). HPLC analysis (for conditions, cf. quantitative photolyses) showed that the divinyl ether **1a** was not consumed under these conditions.

Quantum Yields of Substrate Consumptin (Φ_{-S}) of Divinyl Ether 1a. By those of the Hatchard-Parker actinometer,[23] the light flux of the UV source was determined to be 1.35×10^{-4} mEinstein/min at 300 nm and 1.46×10^{-4} mEinstein/min at 350 nm. The concentrations of the solutions of divinyl ether **1a** in the various solvents (Table II) were in the range 0.002 23–0.002 65 M (total absorption at 300 nm). Samples of 3 mL of these solutions were irradiated for a specified time, and the decay of the divinyl ether **1a** was monitored by HPLC (for conditions, cf. quantitative photolyses). In the direct photolyses the samples were irradiated for ca. 1 h, affording 15–35% consumption of divinyl ether **1a**. In a second run, 2,6-di-*tert*-butyl-4-methylphenol was added to the solutions of divinyl ether **1a** in a molar ratio of 10–11 for phenol. In the case of the ketone-sensitized photolyses only very low conversions (3–7%) of divinyl ether **1a** could be achieved even upon prolonged irradiation (up to 105 min). The quantum yields are given in Table II.

X-ray Analysis of the Epoxide 6. The orientation matrix and the cell parameters were determined from a clear colorless crystal of dimensions 0.35 × 0.45 × 0.15 mm on a Syntex-P3 four-circle diffractometer. Measurement of intensities were as follows ω-scan, 1° range, Mo Kα, 2θ maximum = 55°. The intensities of 4682 reflections were measured, 4233 of them with $F \geq 3\sigma(F)$ were applied for the structure determination. The structure was solved by direct phase determination. The phases of 425 strong reflections were determined and on the resulting E map approximate positions of all non-hydrogen atoms could be refined by anisotropic least-squares cycles, $R = 0.042$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

Epoxide **6** crystallizes triclinically in the space group $P\bar{1}$ (No. 2) with a = 996.2 (3) pm, b = 1533.1 (6) pm, c = 920.5 (4) pm, α = 94.04 (3)°, β = 102.40 (3)°, and γ = 108.50°. The unit cell contains Z = 2 formula units, and the density was calculated to be 1.556 g·cm^{-3}. For details see supplementary material paragraph at the end of this section.

Photo-CIDNP Experiment of Divinyl Ether 1a. A sample of 10.0 mg (0.0267 mmol) of divinyl ether **1a** was dissolved in 1 mL of CD_3CN. ^1H NMR spectra (30 scans) were taken before, during, and after irradiation. (cf., Figure 1). The vertical gain for the spectrum during irradiation is increased by a factor of 2 in comparison to the spectra before and after irradiation.

Cyclic Voltammetry of Divinyl Ether 1a. A sample of 15.0 mg (0.0401 mmol) of divinyl ether **1a** and 200 mg (0.607 mmol) of tetrabutylammonium tetrafluoroborate were dissolved in 20 mL of absolute acetonitrile. The solution was purged with nitrogen, and the cyclic voltammogram was taken at a scan speed of 200 mV/s, employing a Pt electrode and a Ag/AgCl reference counter electrode. A reversible oxidation of divinyl ether **1a** was observed at +1.22 V (vs. SCE). A second oxidation was detected at ca. +1.51 V (vs. SCE).

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Registry No. **1a**, 93620-51-0; **1b**, 98760-54-4; **1c**, 98760-55-5; **3a**, 23219-07-0; **3b**, 98760-56-6; **5**, 98760-57-7; **6**, 98760-58-8; **7**, 98760-59-9; **9**, 98760-60-2; **10**, 98760-61-3; 11, 98760-62-4; **13**, 41326-74-3; **15**, 2491-41-0; (E,E)-Ph(CH=CH)$_2$Ph, 538-81-8; $Cl_3CCH_2OCON{=}NCO_2CH_2CCl_3$, 38857-88-4; $Ph_2C{=}C{=}C{=}CPh_2$, 1450-63-1; $Ph_2C^-CHONa^+$, 55795-21-6; PhCO(CH$_2$)$_2$COOEt, 6270-17-3; 4-MeC$_6$H$_4$Li, 2417-95-0; PhLi, 591-51-5; **4**, 98760-63-5; $PH_2C{=}CH_2$, 530-48-3; $PH_2C{=}CHCHPh_2$, 4960-55-8; Ph_2CHCHO, 947-91-1; Ph_2CH_2, 101-81-5; $Ph_2CHCHPh_2$, 632-50-8; $Ph_2C{=}CCHO$, 1210-39-5; $Ph_2CHOCH(CH_3)_2$, 5670-79-1.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters (Table III), bond lengths (Table IV), bond angles (Table V), and anisotropic thermal parameters (Table VI) for the epoxide **6** (4 pages). Ordering information is given on any current masthead page.

Organic Chemistry of L-Tyrosine. 1. General Synthesis of Chiral Piperazines from Amino Acids

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A new method for the conversion of optically active diketopiperazines (*cyclo*-dipeptides) into optically pure piperazines is described. Due to poor solubility of certain *cyclo*-dityrosine derivatives, the usual method using lithium aluminum hydride reaction was problematic, giving racemization under forcing conditions. However, the use of borane/tetrahydrofuran for this diketopiperazine to piperazine reduction proceeded well, affording high yields of optically pure materials. In this manner several mixed *cyclo*-dityrosine derivatives **9a–d** were transformed into the piperazines **10a–d**, potentially useful intermediates for the synthesis of the antibiotic alkaloids, piperazinomycin (**1**) and herquline (**2**). Finally, the naturally occuring alkaloid isolated from *Zanthoxylum arborescens*, **7b**, was prepared by this route.

The use of optically pure starting materials to control absolute stereochemistry is a well-established strategy in organic synthesis. Chiral α-amino acids are particularly valuable in this regard due to their great diversity of side chain structures and (often) ready availability.

In planning the total synthesis of the antifungal agent piperazinomycin[3] (**1**) and the platelet-aggregation inhibitor herquline[4] (**2**), alkaloids presumed to arise biosynthetically from two molecules of tyrosine[5] (**5**), we conceived of a common strategy utilizing substituted L-tyrosine-derived (2S,5S)-bis[(p-hydroxyphenyl)methyl]piperazines (**3**) as key intermediates. If one could successfully prepare compounds such as **3** in optically pure form in high overall yield from simple tyrosine derivatives, then several potential routes to piperazinomycin (**1**) and herquline (**2**) could be tested. For example, an intramolecular Ullmann coupling to give diaryl ethers applied to **3** (R = Me, X = I or Br, R′ = X′ = H) would produce the methyl ether of **1**. Similarly a carbon–carbon bond formation between a reduced derivative of **3** (X = X′ = Br or I) would give an intermediate for the synthesis of herquline **2**. Thus it appeared important for the synthesis of **1** and **2** to test methods for the preparation of **3** in high optical purity.

There are several general methods in the literature[6-9] for preparing the corresponding sterically pure pipera-

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